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INORGANIC SEMINAR ABSTRACTS

1969-1970

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ENERGY-TRANSFER PROCESSES IN RARE EARTH CHELATES[1]

Mary Ellen Phelan September 23, 1969

Introduction

In 1942 Weissman[2] discovered that Eu(III) line emissions occur when the tris salicylaldehyde complex is irradiated anywhere in the absorption band of salicylaldehyde. $EuCl_3$ gives these emissions only when irradiated at the specific wavelengths 3200 and 3920 A; also no absorbance characteristic of europic ion is observed in the spectrum of the chelate. Hence, Weissman attributes this effect to an intramolecular energy transfer.

It will be the purpose of this seminar to examine the nature of the energy-transfer processes in rare earth chelates and the experimental methods used to study them.

The Role of the Triplet State: Semiquantitative Studies

Absorption spectra of rare earth chelates depend on the ligand, not on the central ion. Emission spectra, by contrast, vary appreciably with the central ion. Whan and Crosby[3] found the following luminescence characteristics for various tris benzoylacetonates (B) irradiated in the first absorption band of the ligand:

1. GdB_3, LaB_3, LuB_3 and NaB all are characterized by high yields of total luminescence, well-defined molecular fluorescence and phosphorescence characteristic of the ligand and no line emission. The ratio of phosphorescence to fluorescence is very high.

2. PrB_3, NdB_3, HoB_3, ErB_3, TmB_3 and YbB_3 all have low yields of total luminescence, low ratios of phosphorescence to fluorescence, and weak line emission characteristic of the central ion.

3. The remaining chelates (SmB_3, EuB_3, TbB_3, DyB_3) show primarily the bright line emissions characteristic of the central ion. Similar trends exist for the tris dibenzoylmethides, except that no line emission occurs from the Dy(III) complex. With these compounds, with other β-diketones[4,5,6] and with bipyridyl and terpyridyl complexes;[7,8] no ion emission is observed unless the lowest triplet of the ligand lies nearly equal to or above the resonance (emissive) level of the ion.

Crosby et al.[6] interpret these data in terms of mechanism I. However, mechanism II explains the correlation with the ligand triplet, and so does mechanism III with the added postulate of possible quenching of the rare earth resonance level by the ligand triplet:

I. $S_0 \rightarrow S_1 \rightsquigarrow T_1 \rightsquigarrow RE \rightarrow$ emission

II. $S_0 \rightarrow S_1 \rightsquigarrow$ RE levels higher than $T_1 \rightsquigarrow T_1 \rightsquigarrow$ RE resonance
levels $\rightarrow$ emission[9]

III. $S_0 \rightarrow S_1 \rightsquigarrow$ RE levels higher than resonance $\rightsquigarrow$ RE
resonance levels $\rightarrow$ emission[10]

The Mechanism of the Intramolecular Energy Transfer

One question remains: What is the mechanism of energy transfer in the rare earth chelates? Crosby and coworkers[6,11] and Filipescu et al.[12] postulate energy transfer to the metal ion by an exchange mechanism involving vibronic coupling of the ligand triplet and the ion levels. At present, it is not possible to distinguish among the following three possibilities:

1. The resonance level of the ion is definitely below the triplet state and transfer can occur from the zeroth vibrational level of the latter to some vibronic state of the metal ion.

2. Crossing between the triplet and ion resonance levels comes at upper vibrational levels.

3. The resonance level is slightly above the triplet state.

McAvoy et al.[13] propose an alternate mechanism, a slight electronic mixing of the ligand triplet with the ion levels. The molecular triplet is associated with a biradical structure involving two unpaired spins formed by rupture of a bond. These spins arrange themselves for minimum overlap and at least one of them will increase the electron density at the oxygen-rare earth (or nitrogen-rare earth) bond.

Weak Ion Emitters: Vibronic Coupling to Surroundings

On the basis of these relatively qualitative studies, it is still possible to explain the occurrence of weak ion emitters. (These also have low yields of total luminescence.) The chemical similarities throughout a series of chelates suggests that the extent of the energy transfer is also similar.[6] The high yields of bright line emission in Eu(III) and Tb(III) chelates suggest efficient transfer to the ions. It has therefore been postulated that most of the quenching of rare earth ion emission occurs after transfer to the ion. The ions which have low yields of emission are those which have a number of closely packed ion excited states in which excess energy can readily be dissipated non-radiatively. For the efficient ion emitters, large gaps exist between these levels.

Whan and Crosby[3] suggest that the principal mechanism for quenching luminescence in the rare earth ion levels is through vibronic coupling to the ligands and thence to the surrounding solvent. Satellite lines attributable to vibronic progressions are observed on the more intense peaks.

Quantitative studies of quantum yield as a function of temperature and selective excitation of various levels give further insight into the quenching process; these will be discussed later.

Intermolecular Transfer and Quenching Studies

The studies of Heller and Wasserman[14] establish that the triplet of the organic species takes part in the intermolecular transfer reaction with rare earth chelates. Bhaumik and El-Sayed[15] rule out the possibility of direct transfer to the rare earth ion and establish the path of intermolecular transfer as $T^*_{donor} \rightsquigarrow T^*_{ligand} \rightsquigarrow RE \rightarrow$ emission.

The idea that intramolecular transfer involves the ligand triplet is put on a firmer basis by Bhaumik and El-Sayed's study[9,15] of the reaction of rare earth chelates with a series of organic quenchers. Cis-piperylene does not react with singlet states but does quench rare earth ion emission when the triplet of the ligand lies higher in energy than the quencher's triplet. The authors demonstrate that intermolecular quenching does not depend on the rare earth levels and set an upper limit of 10% for the extent of intramolecular transfer directly from the ligand singlet to the rare earth levels. From these studies, the authors obtained 10^{10} sec^{-1} for the intersystem crossing rate.

Preparative Problems

Rare earth chelates exist in both a tris and a tetrakis form with different spectra, lifetimes and decay curves.[16,17] Adduct formation[18-2 and partial dissociation[22,23] in solution and different crystalline forms[24] have been found. Many preparations are sensitive to changes in pH or order of mixing. The piperidinium salt of the ligand is a common impurity in early preparations. Hence, particularly in evaluating quantitative studies, one must be careful to consider only adequately characterized chelates.

Spectra and Energy Levels

Spectral transitions and ordering of ion energy levels in rare earth compounds are essentially independent of the ligand. For the rare earths e^2/r_{ij} is about 20,000 cm^{-1}, the spin-orbit interaction about 1000 cm^{-1} and the ligand field interaction about 100 cm^{-1}.[21] Hence, complete characterization of the compound is not so essential when one is assigning energy levels.

Studies Using More Elaborate Methods

Bhaumik and Telk[25,26] used the quantum counter technique to measure the absolute quantum yields of a series of rare earth chelates as a function of temperature. Results indicate rapid transfer to the ion levels. But two observations suggest that some quenching occurs in the ligand prior to transfer: different chelates have slightly different fluorescence decay times at liquid-nitrogen temperature; as the temperature increases, the quantum yield falls more quickly than the fluorescence decay time. The facts that the compounds with the highest yields are also those with the longest lifetimes and that the rise time of $^5D_0 \rightarrow {}^7F_2$ fluorescence equals the decay time of the $^5D_1 \rightarrow {}^7F$ transitions[27,28] are further evidence for radiationless deactivation of rare earth levels via a cascade mechanism.

The most cogent evidence for this type of radiationless deactivation is provided by Kropp and Dawson,[29,30] who selectively excited upper levels of ammonium or pyperidinium tetrakis β-diketone chelates and measured the quantum yield for the radiative transition characteristic of the ion. Their results indicate that the quantum yield is lower the higher the energy level excited. The extent of quenching in the ligand is about comparable to that in the ion.

Summary

We have seen then that the energy is absorbed by the ligand singlet and transferred to a triplet level at a rate of about 10^{11} sec^{-1}. Transfer to the rare earth manifold occurs with a rate constant of 10^{10} sec^{-1}.[9,31] Both the transfer of energy from the ligand to the ion and the radiationless transitions within the ion manifold appear to occur by a vibronic coupling mechanism.

References

1. G. A. Crosby, *Molecular Crystals*, *1*, 37 (1966).
2. S. L. Weissman, *J. Chem. Phys.*, *10*, 214 (1942).
3. R. E. Whan and G. A. Crosby, *J. Mol. Spectry.*, *8*, 315 (1962).
4. G. A. Crosby and R. E. Whan, *Naturwiss.*, *47*, 276 (1960).
5. G. A. Crosby and R. E. Whan, *J. Chem. Phys.*, *32*, 614 (1960).
6. G. A. Crosby *et al.*, *J. Chem. Phys.*, *34*, 743 (1961).
7. S. P. Sinha, *Z. Naturforsch.*, *20a*, 164 (1965).
8. S. P. Sinha, *Z. Naturforsch.*, *20a*, 835 (1965).
9. M. L. Bhaumik and M. A. El-Sayed, *J. Chem. Phys.*, *42*, 787 (1965).
10. M. Kleinerman, *Bull. Am. Phys. Soc.*, *9*, 265 (1964).
11. G. A. Crosby and M. Kasha, *Spectrochim. Acta*, *10*, 377 (1958).
12. N. Filipescu *et al.*, *J. Phys. Chem.*, *68*, 3324 (1964).
13. N. McAvoy *et al.*, *J. Phys. Chem. Solids*, *25*, 461 (1964).
14. A. Heller and E. Wasserman, *J. Chem. Phys.*, *42*, 949 (1965).
15. M. L. Bhaumik and M. A. El-Sayed, *J. Phys. Chem.*, *69*, 275 (1965).
16. M. L. Bhaumik and I. R. Tannenbaum, *J. Phys. Chem.*, *67*, 2500 (1963).
17. M. Metlay, *J. Chem. Phys.*, *39*, 491 (1963).
18. R. C. Ohlmann and R. G. Charles, *J. Chem. Phys.*, *40*, 3131 (1964).
19. M. Kleinerman *et al.*, *J. Chem. Phys.*, *41*, 4009 (1964).
20. S. M. Lee and L. J. Nugent, *J. Inorg. Nucl. Chem.*, *26*, 2304 (1964).
21. L. J. Nugent *et al.*, *J. Chem. Phys.*, *41*, 1305 (1964).
22. C. Brecher *et al.*, *J. Chem. Phys.*, *42*, 1081 (1965).
23. M. L. Bhaumik, *J. Inorg. Nucl. Chem.*, *27*, 243 (1965).
24. H. Bauer *et al.*, *J. Am. Chem. Soc.*, *86*, 5125 (1964).
25. M. L. Bhaumik and C. L. Telk, *J. Opt. Soc. Am.*, *54*, 1211 (1964).
26. M. L. Bhaumik, *J. Chem. Phys.*, *40*, 3711 (1964).
27. M. L. Bhaumik and L. J. Nugent, *J. Chem. Phys.*, *43*, 1680 (1965).
28. M. L. Bhaumik, *J. Chem. Phys.*, *41*, 574 (1964).
29. W. R. Dawson *et al.*, *J. Chem. Phys.*, *45*, 2410 (1966).
30. W. R. Dawson and J. L. Kropp, *J. Opt. Soc. Am.*, *55*, 822 (1965).
31. D. L. Ross and J. Blanc, *Adv. Chem. Ser.*, *71*, 155 (1967).

CHEMICALLY INDUCED DYNAMIC NUCLEAR POLARIZATION

Cheryl Johnson September 30, 1969

Introduction

Dynamic nuclear polarization was first predicted by Overhauser in 1953,[1] and was experimentally confirmed, using metallic lithium, by Carver and Slichter.[2] The Overhauser effect, enhanced NMR absorption, was predicted to occur in paramagnetic metals if the NMR sample was simultaneously exposed to microwave resonance radiation. The effect applies only to metals and is the result of hyperfine interactions in unfilled conduction bands which involve nuclear spin flip.

Chemically induced dynamic nuclear polarization (CIDNP) is a similar absorption and emission enhancement which may occur when radicals are produced in a chemically reacting system. CIDNP was first observed independently by two teams of investigators, J. Bargon and H. Fischer,[3] using peroxide and azo compounds, and H. R. Ward and R. G. Lawler,[4] using organometallic compounds.

Discussion

A tentative explanation of the spectra characteristic of CIDNP[5-10] is based on three assumptions.

1. At t=0 (mixing of reagents), the radicals formed populate the two electron spin Zeeman levels equally.
2. In the reaction

$$R\cdot + L \rightarrow R + L\cdot$$

the proton spin orientation of R· relative to the magnetic field, H_o, is held fixed and is transferred to R.

3. The electron spin and proton spins of R couple.

By the first assumption, at t=0 the population difference is given by

$$P_e = \frac{e_+ - e_-}{e_+ + e_-} = 0$$

The electrons undergo spin-lattice relaxation and approach the Boltzman equilibrium distribution, where

$$P_e = \gamma_e \hbar H_o / 2kT$$

The nuclear spin population difference, p_n, which at t=0 equalled P_n^o, becomes much larger than the equilibrium value as a result of the coupling with the electron spin. After the electron spins approach p_e^o, the nuclear spins will relax through nuclear spin-lattice interactions and will again approach p_n^o. This relaxation occurs much more rapidly in radicals than in diamagnetic species. Hence, if the radical formed has a fairly long lifetime ($>10^{-4}$ sec), the nuclear spins relax rapidly and the abnormal distribution will disappear. If, however, the radicals react in a time short relative to nuclear relaxation (10^{-8} - 10^{-4} sec) to form a diamagnetic species, nuclear relaxation occurs slowly and the abnormal population distribution of nuclear spins may be observed in NMR spectra as emission and enhanced absorption.

The above explanation proposed by Ward, Lawler, Fischer, Bargon, and others[7,8,14] is disputed by Kaptein[6] and Closs.[16] These investigators propose a mechanism that is essentially the reverse. The radicals are produced with an equilibrium population. Because the reaction of radicals to form a diamagnetic species requires equal numbers of each spin orientation, a portion of the electrons must flip after formation of the radicals in order to fulfill this requirement. Due to coupling an equal number of nuclei must also flip and polarization occurs.

An interesting feature of CIDNP is its effect on multiplets.[17,20,3] In many systems, both emission and enhanced absorption occur in the same spin-spin multiplet. This effect is not predicted by the general theory and can be explained only by assuming that there is some dependence of the rates of population of the radical electron spin states on the associated nuclear spin states.

Another peculiar effect occurs in alkyllithium systems. The peaks due to the organolithium species do not show the effects of CIDNP, and in several cases, the normal pmr signal of the alkyl group coordinated to the lithium atom is completely lost a short time after the reaction begins.[6,19,20] One proposed explanation for the absence of CIDNP effects is that the radicals form a weak cage complex with the R_nLi_n species[6,14,18,19,20,21] and through a charge transfer-radical trapping sequence lengthen the lifetime of the free radical, thereby allowing time for normal relaxation. The disappearance of the signal is attributed to exchange broadening.[6]

The presence of paramagnetic impurities[3,8] in the reacting solution results in a decrease in the amplitude of the emission and a shift of the maximum emission to shorter times. It is postulated that this is a result of relaxation of the free radical electron spins caused by the ions.

The amplitude of the emission is also a function of the applied magnetic field.[3,11] The amplitude is inversely proportional to the applied field and maximumamplitude shifts slightly to longer times with increasing field.

From preliminary studies, it appears that solvent effects can significantly affect the spectra.[12,13]

Conclusions

Most research in CIDNP thus far has been in the study of pmr spectra in order to confirm the presence of a radical intermediate, to clarify the mechanism of a reaction, or, as Closs and Trifunac[22] have suggested, to determine the spin multiplicity of the radical-pair precursor. Recently, however, Bragon and Fischer began studies of CIDNP using ^{19}F spectra.[23]

Although as yet we cannot fully assess the potential of CIDNP, it appears that it will become a valuable tool in the study of mechanisms and kinetics of radical reactions.

References

1. A. W. Overhauser, Phys. Rev., 92, 411 (1953).
2. T. R. Carver and C. P. Slichter, Phys. Rev., 102, 975 (1956).
3. H. Fischer and J. Bargon, Accts. Chem. Res., 2, 110 (1969).
4. H. R. Ward and R. G. Lawler, J. Am. Chem. Soc., 89, 5518 (1967).
5. J. Bargon, H. Fischer, and U. Johnsen, Z. Naturforschg., 22a, 1551 (1967).
6. T. L. Brown, to be published.
7. R. G. Lawler, J. Am. Chem. Soc., 89, 5519 (1967).
8. J. Bargon, H. Fischer, and U. Johnsen, Z. Naturforschg., 22a, 1556 (1967).
9. R. Kaptein, Chem. Phys. Ltrs., 2, 261 (1968).
10. D. Stehlik and K. H. Hausser, Z. Naturforschg., 22a, 914 (1967).
11. K. H. Hausser, Z. fur Physik, 183, 265 (1965).
12. Anon., Chem. and Eng. News, 46, 40 (Jan. 15, 1968).
13. G. A. Russell and D. W. Lamson, J. Am. Chem. Soc., 91, 3967 (1969).
14. H. R. Ward, R. G. Lawler, H. Y. Loken, J. Am. Chem. Soc., 90, 7359 (1968).
15. A. R. Lepley, J. Am. Chem. Soc., 90, 2710 (1968).
16. G. L. Closs, J. Am. Chem. Soc., 91, 4552 (1969).
17. A. R. Lepley, J. Am. Chem. Soc., 91, 749 (1969).
18. F. S. D'yachkovskii and A. E. Shilov, Russ. Chem. Revs. (English Transl.), 35, 300 (1966).
19. A. R. Lepley and R. L. Landau, J. Am. Chem. Soc., 91, 748 (1969).
20. A. R. Lepley, Chem. Comm., 64 (1969).
21. H. R. Ward, R. G. Lawler, R. A. Cooper, J. Am. Chem. Soc., 91, 746 (1968).
22. G. L. Closs and A. D. Trifunac, J. Am. Chem. Soc., 91, 4554 (1969).
23. H. Fischer and J. Bargon, Z. Naturforschg., 23a, 2109 (1968).
24. C. G. Screttas and J. F. Eastham, J. Am. Chem. Soc., 88, 5668 (1966).
25. D. E. Applequist and D. F. O'Brien, J. Am. Chem. Soc., 85, 743 (1963).
26. G. L. Closs and L. E. Closs, J. Am. Chem. Soc., 91, 4549 (1969).
27. G. L. Closs and L. E. Closs, J. Am. Chem. Soc., 91, 4550 (1969).
28. H. R. Ward, R. G. Lawler, H. Y. Loken, and R. A. Cooper, J. Am. Chem. Soc., 91, 4928 (1969).
29. J. Bargon and H. Fischer, Z. Naturforschg., 23a, 2109 (1968).
30. H. R. Ward, R. G. Lawler, and R. A. Cooper, Tetrahedron Letters, 7, 527 (1969).

THE THEORY OF ELECTRON TRANSFER REACTIONS: THE MARCUS APPROACH

John K. Orrell October 14, 1969

Introduction

Although Marcus has discussed and developed equations[1-6] for treating both homogeneous electron transfer reactions in solution and reactions at electrodes, this seminar will be confined to a discussion of the former. It is also pointed out that his theoretical development applies to direct electron transfer reactions which proceed via an outer-sphere mechanism and in which the inner coordination shells remain intact.

Theory

One can describe the course of an electron transfer reaction by making use of potential energy surfaces. The potential energy at each point on the surface represents the sum of the electronic kinetic and potential energies and the nuclear potential energy.[7] The full display is usually represented as a contour map, but the form more familiar in the literature is a two-dimensional profile of the variation in the potential energy of the reacting species with a change in the reaction coordinate for the most probable path.[7]

In the case of zero electronic interaction between reacting species, as depicted in Fig. 1a, such a two-dimensional representation consists of two curves, one for the reactants (R), another for the products (P). The abscissa,marked "nuclear configuration" represents any concerted motion of all the atoms in the system leading from an arrangement suited to the electronic configuration of the reactants to one of the products.[6] However, if electronic interaction takes place when the reactants are at the intersection region, then the curves are split as depicted in Fig. 1b. In this case, electron transfer may take place.

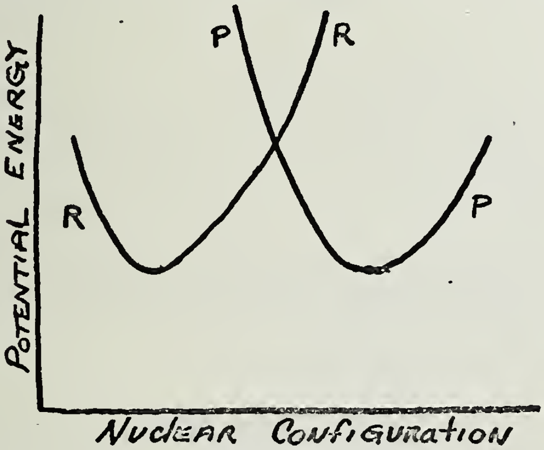


Fig. 1a

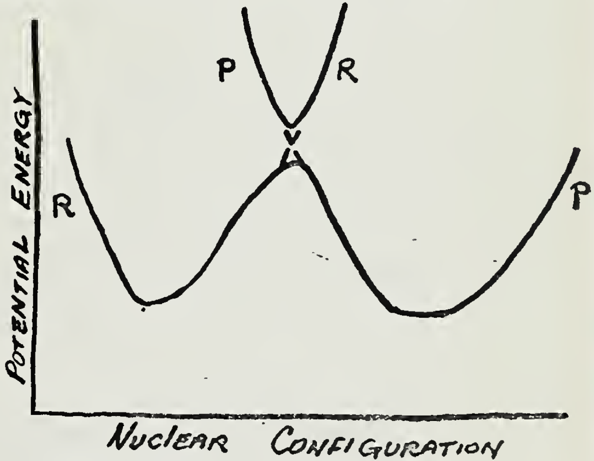


Fig. 1b

Marcus assumed a weak-interaction activated complex in which the electronic interaction is strong enough to cause the probability of electron transfer to be unity, but not large enough to make a contribution to the activation energy. He noted that the activated complex has the nuclear configuration of the intersection region and its electronic configuration should be some intermediate between that of the reactants and that of the products.[1] He also pointed out that so long as the interaction is small, for computational purposes, one could consider the activated complex as composed of two hypothetical states, X* and X. These states have the electronic configurations of the reactants and products, respectively, but the nuclear configuration of the activated complex.[1] To satisfy the law of conservation of energy, these states must have the same total energies.

This energy condition imposes a restraint upon the solvation of the activated complex. The degree of solvent orientation in any state depends to a large extent on whether the reacting species have the charges of the reactants or the products. Now the solvent arrangement in the activated complex and therefore in X* and X is intermediate between that for the reactants and that for the products. Therefore, states X* and X possess a non-equilibrium solvent orientation.

To obtain an expression for the rate constant for comparison with experimental values, Marcus assumed the following reaction scheme:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} X^* \qquad (1)$$

$$X^* \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} X \qquad (2)$$

$$X \overset{k_3}{\rightarrow} \text{products} \qquad (3)$$

where by use of a steady state treatment

$$k_{bi} = k_1/[1 + (1 + k_{-2}/k_3)(k_{-1}/k_2)].$$

If $k_{-1} \cong k_2$ and $k_{-2} \cong k_3$ then $k_{bi} \cong k_1$ where k_1 is obtained from the equilibrium constant for eq. (1), namely

$$k_1 = Z\exp\,(-\Delta F^*/kT)$$

where Z is the collision number and ΔF^* the electrostatic activation free energy.[1] The latter term is simply

$$\Delta F^* = F^* - W_{iso}^{s*}$$

where F^* is the electrostatic free energy of X* and W_{iso}^{s*} is the work done to "charge up" the reactants in the medium at infinite separation.

Marcus pointed out that since the atomic configuration of all the atoms is fixed in the states X^* and X, not only do the total energies have to be the same but the configurational entropies must also be the same. Hence, with the exception of a negligible entropy difference, ΔSe, due to electron degeneracy differences, the free energies of X^* and X must be the same.[1] This is summarized in the expression for the overall free energy change:

$$\Delta F^o = (F^* - \mathrm{Wi}_{so}^{s^*}) - T\Delta Se - (F - \mathrm{Wi}_{so}^{s})$$

where F^* and F are the electrostatic free energies of X^* and X, $\mathrm{Wi}_{so}^{s^*}$ the work to "charge up" the reactants at infinite separation in the medium and Wi_{so}^{s} the corresponding term for the reactants.

To calculate ΔF^*, Marcus assumed the following model of the system. The reactants were treated as spheres of fixed radii which included both the ion and its inner coordination shell. The medium outside these reacting spheres was treated as a continuous dielectric of orientationally and electronically polarizable material.[1,11] The polarization of the medium by the reacting species is composed of three kinds: electronic (E-type), atomic (U-type) and orientational (U-type).[10] Due to differences in the times required for each kind of solvent polarization to adjust to a rapid charge change, only the E-type remains in electrostatic equilibrium with the charges in X^* and X. Consequently, X^* and X are states of "non-equilibrium solvent polarization" and as such ΔF^* cannot be calculated in the usual way.[1,10,17]

Marcus calculated F^* by computing the work done to "charge up" the reacting spheres in the medium at the separation distance in X^*.[1] The calculation consisted of a two step process and the final expression was obtained in terms of the polarization of state X^* and electric field strength (in vacuo).

Now to obtain the most probable activated complex this expression was minimized subject to the restraint that the atomic and orientational polarization must be the same in X^* and X. When this calculation was performed and conversion to more accessible parameters such as the ionic radii and charges was made, Marcus obtained the following:[1]

$$\Delta F^* = \frac{e_1^* e_2^*}{D_s R} + m^2\lambda \tag{4}$$

where $$2m + 1 = -(\Delta F^o + W_p - W_R)/\lambda \tag{5}$$

and $$\lambda = \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)(\Delta e)^2 \tag{6}$$

where the first term on the right hand side of (4) is the electrostatic work done to bring the reactants together expressed in terms of the charges on the reactants, e_1^* and e_2^*, the state dielectric constant, Ds, and the separation distance in X^*, R. The second

term represents the solvent reorganization energy which is obtained from equations (5) and (6) where W_p and W_R are the work done to bring the products and reactants together, respectively, a_1 and a_2 the radii of the reactants, D_{op} the optical dielectric constant of the solvent and Δe the charge change on either reactant.

Applications

Some early comparisons[2,13] showed the need to include the contribution to the activation free energy from the reorganization of the inner coordination shell. However, accurate values are difficult to obtain.

A more rewarding area has been the study of "cross-reactions" for which suitable expressions have been derived by Marcus.[5] For the reaction

$$Ox_1 + Red_2 \overset{k_{12}}{\rightleftarrows} Red_1 + Ox_2 \quad , \qquad (7)$$

Marcus showed that the forward rate constant can be expressed as follows:

$$k_{12} = (k_{11}\ k_{22}\ k_{12}f)^{1/2} \qquad (8)$$

where k_{11}, k_{22} are the rate constants for the corresponding exchange reactions, K_{12} the equilibrium constant for the cross-reaction and f is defined so as to satisfy eq. (8), namely,

$$\log f = \frac{(\log K_{12})^2}{4\ \log\left(\frac{k_{11}k_{22}}{Z^2}\right)}$$

Sutin has employed eq. (8) to verify theoretical predictions.[13-17]

References

1. R. A. Marcus, J. Chem. Phys., 24, 966 (1956).
2. R. A. Marcus, J. Chem. Phys., 26, 867 (1957).
3. R. A. Marcus, J. Chem. Phys., 26, 872 (1957).
4. R. A. Marcus, Disc. Farad. Soc., 29, 21 (1960).
5. R. A. Marcus, J. Phys. Chem., 67, 853 (1963).
6. R. A. Marcus, J. Chem. Phys., 43, 679 (1965).
7. W. L. Reynolds and R. W. Lumry, *Mechanisms of Electron Transfer Reactions*, The Ronald Press Co., New York (1966), p. 74.
8. Ref. 7, p. 117.
9. Ref. 7, p. 134.
10. R. A. Marcus, J. Chem. Phys., 24, 979 (1956).
11. R. A. Marcus, J. Chem. Phys., 38, 1858 (1963).
12. B. M. Gordon, L. L. Williams, and N. Sutin, J. A. C. S., 83, 2061 (1961).

13. M. H. Ford-Smith and N. Sutin, J. A. C. S., 83, 1830 (1961).
14. G. Dulz and N. Sutin, Inorg. Chem., 2, 917 (1963).
15. H. Diebler and N. Sutin, J. Phys. Chem., 68, 174 (1964).
16. R. J. Campion, N. Purdie and N. Sutin, Inorg. Chem., 3, 1091 (1964).
17. R. A. Marcus, Ann. Rev. Phys. Chem., 15, 155 (1964).
18. R. Marcus, B. J. Zwolinsky, and H. Eyring, J. Phys. Chem., 58, 432 (1954).
19. R. A. Marcus, Can. J. Chem., 37, 155 (1959).

LIGAND FIELD THEORY FOR PENTACOORDINATE COMPLEXES OF FIRST ROW TRANSITION METALS

Yu Wang October 23, 1969

Introduction

The five-coordinate complexes of transition metals have not been studied as thoroughly as six- and four-coordinate compounds primarily because of uncertainty in the coordination number (especially in solution) and lack of X-ray data.

After the first high-spin cobalt(II) and nickel(II) pentacoordinate complexes had been described in 1965 (2,3), it became necessary to study the influence of the nature of the ligand on the magnetic and spectroscopic properties of the complexes. It has been shown (4,5) that low-spin complexes are formed by ligands with donor atoms of low electronegativity such as P and As (6,7); while high-spin complexes are formed by ligands having donor atoms of high electronegativity, in particular, O and N (8,9,10). Sulfur ligands form both types of complexes (11,12).

According to Zemann (13), the relative stabilities of the different geometric forms are: trigonal bipyramid > distorted square pyramid with ∠LML = 104° > square pyramid. In fact, most of the five-coordinate complexes are trigonal bipyramid.

Ligand Field Interpretation of Electronic Spectra

Define two parameters (14)

$$Ds = \frac{1}{14}\left(\frac{4Z_A}{b^3} - \frac{3Z_E}{a^3}\right)\overline{r^2}$$

$$Dt = \frac{1}{168}\left(\frac{16Z_A}{b^5} - \frac{9Z_E}{a^5}\right)\overline{r^4}$$

where Z_A, Z_E are the axial and equitorial charges lacated at distances b and a respectively. $\overline{r^2}$, $\overline{r^4}$ are the expectation values.

A. One electron splitting scheme: The orbital energy of the d-manifold in D_{3h} has been calculated as follows (14):

state (M_l)	d-orbital	symm. representation	orbital energy
$\vert 0 >$	z^2	a_1'	$2Ds + 6Dt$
$\vert \pm1 >$	(xz, yz)	e''	$Ds - 4Dt$
$\vert \pm2 >$	(xy, x^2-y^2)	e'	$-2Ds + Dt$

This energy splitting gives fairly good agreement with the spectra of d^1 (15), d^9; high spin d^4, d^6 (16,17) and low spin d^6, d^7, d^8 (6); for example, $[Fe(Me_6tren)Br]Br$ and $[Ni(QAS)Br]^+$. ($Me_6tren = N[CH_2CH_2N(CH_2)_2]_3$ QAS = $As(o\text{-}ph_2\text{-}As\text{-}C_6H_4)_3$).

B. Many electron splitting scheme. The total Hamiltonian is

$$H = -\frac{h^2}{2m}\sum_i \nabla_i^2 - \sum_i \frac{Ze^2}{r_i} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{r_{ij}} + \sum_i \xi_i(r)\, l_i \cdot s_i + V_{c.F.}$$

In first row transition elements $\xi(r) l \cdot s < V_{c.F.} < \frac{e^2}{r_{ij}}$

We therefore first consider the interelectronic repulsion term, i.e., $\sum_{i\neq j}\frac{e^2}{r_{ij}}$ and express the coulomb integral J(a,b) and exchange integral K(a,b) in terms of parameters F_0, F_2, F_4 or Racah parameters B and C. Secondly, we consider the splitting of energy levels in the crystal field; i.e., the $V_{c.F.}$ term. So far, the spin orbit coupling has been neglected. However, the absorption spectra show very good agreement with the calculation.

Condon and Shortley (18) calculated the interelectronic repulsion energy terms for all d^n configurations. The energy level diagrams for Ni(II) and Co(II) complexes with five equivalent dipoles of strength μ in the D_{3h} configuration have been calculated (19,20). Even the changes of energy levels which depend upon changes in β (∠LML) and Dq(ax)/Dq(base) have been estimated (21). From the spectra, all the parameters can be determined.

Even though $[Co(Et_4dien)X_2]$ and $[Co(Me_6tren)X]X$ are quite different in symmetry, they show similar spectral and magnetic properties. It can be concluded that, for high spin pentacoordinate complexes containing similar ligands, the key electronic structural properties do not depend critically on the exact geometry of the molecules (22). Therefore the ligand field model can be assumed to be D_{3h}.

Magnetic Properties

A. With E ground term (23), the d^1, d^3, d^6 and d^8 configurations have $^2E''$, $^4E'$, $^5E''$ and $^3E'$ as the ground states in D_{3h} respectively. The perturbation Hamiltonian is

$$H' = V_{c.F.} + \lambda \vec{L}\cdot\vec{S} + \beta \vec{H}\cdot(k\vec{L} + 2\vec{S})$$

Using crystal field eigenfunctions as basis functions, the first order perturbation of L-S coupling gives 2S + 1 levels separated by equal spacing. Then, the magnetic susceptibility can be evaluated by the Zeeman operators and Van Vleck's formula (24,1)

$$\mu_{\parallel} = \beta(kL_z + 2S_z)\ ;\ \mu_{\perp} = \beta(kL_x + 2S_x)$$

$$\chi_i = N\frac{\sum_{n,m}\left(\frac{E^{(1)}_{n,m}}{kT} - 2E^{(2)}_{n,m}\right)e^{-E^0_n/kT}}{\sum_n e^{-E^0_n/kT}} \quad (i=x,y,z)$$

where N = Avogadro's number
E_n^o = energy after L-S coupling
$E_{n,m}^{(1)}$ = 1st order Zeeman energy
$E_{n,m}^{(2)}$ = 2nd order Zeeman energy.

From the variation of μ_{eff} with respect to temperature, the orbital reduction factor "k" must be considered at high temperature and the presence of low symmetry is taken into account at low temperature.

B. With A ground term (2f), the d^2, d^4, d^7 and d^9 configurations have $^3A_2'$, $^5A_1'$, $^4A_2'$ and $^2A_1'$ symmetries as ground states. In a weak field, the true wave function for A symmetry includes mixing of A symmetry from both P and F (terms from inter-electronic repulsion force). Again, with spin-orbit coupling, the 1st order perturbation gives no correction to the energy of the ground state. However, the 2nd order perturbation will split it into Kramer's doublet. In this model, temperature independent paramagnetism (TIP) arises from mixing the high energy orbitally degenerate state with the singlet ground state. Apart from this TIP term, the susceptibilities of this type of compound might be expected to follow Curie's law down to very low temperature ($\Delta \cong kT$). Sometimes the magnetic data may be taken as a support for the assignment of the electronic spectra.

Conclusion

At present, the experimental knowledge of pentacoordinate complexes is still rather scattered and far from complete. The exact structures of such complexes are known only in a few cases. Therefore, there is still an attempt being made to ascertain whether the ligand field theory leads to acceptable results for pentacoordinate complexes.

References

1. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Company, Inc., 1962.
2. L. Sacconi, P. Nannelli, N. Nardi and U. Campigli, Inorg. Chem., 4, 943 (1965).
3. L. Sacconi, M. Ciampolini and G. P. Speroni, J. Am. Chem. Soc., 87, 3102 (1965).
4. L. Sacconi and I. Bertini, J. Am. Chem. Soc., 90, 5443 (1968).
5. C. Furlani, Coord. Chem. Rev., 3, 141 (1968).
6. M. J. Norgett and J. H. M. Thornley, J. Chem. Soc. (A), 540 (1967).
7. G. Dyer and Devon W. Meek, Inorg. Chem., 6, 149 (1967).
8. M. Ciampolini and G. P. Speroni, Inorg. Chem., 5, 45 (1966).
9. M. Ciampolini and N. Nardi, Inorg. Chem., 6, 445 (1967).
10. M. Ciampolini and N. Nardi, Inorg. Chem., 5, 41 (1966).
11. M. Ciampolini and J. Gelsomini, Inorg. Chem., 6, 1821 (1967).

12. G. Dyer and D. W. Meek, Inorg. Chem., 4, 1398 (1965).
13. J. Zemann, Z. Anorg. Allg. Chem., 324, 241 (1963).
14. J. S. Wood, Inorg. Chem., 7, 855 (1968).
15. G. W. A. Fowles and R. A. Hoodless, J. Chem. Soc., 33 (1963).
16. M. Ciampolini, Chem. Comm., 47 (1966).
17. M. Ciampolini and N. Nardi, Inorg. Chem., 5, 1150 (1966).
18. Condon and Shortley, "Theory of Atomic Spectra," Cambridge University Press, 1951.
19. M. Ciampolini, Inorg. Chem., 5, 35 (1966).
20. M. Ciampolini, N. Nardi and G. P. Speroni, Coord. Chem. Rev., 1, 222 (1966).
21. M. Ciampolini and I. Bertini, J. Chem. Soc. (A), 2241 (1968).
22. Zvi Dori and Harry B. Gray, Inorg. Chem., 7, 889 (1968).
23. J. S. Wood and Peter T. Greene, Inorg. Chem., 8, 491 (1969).
24. J. H. Van Vleck, "Theory of Electronic and Magnetic Susceptibility," Oxford University Press, London, 1932.
25. J. S. Wood, J. Chem. Soc. (A), 1582 (1969).

STRUCTURAL STUDIES OF SOME PHOSPHORUS PENTACHLORIDE-METAL TRI- AND TETRACHLORIDE ADDUCTS

Thomas J. Kistenmacher October 28, 1969

Introduction

The syntheses of several adducts of phosphorus pentachloride and transition metal chlorides have been reported by Groeneveld.[1] In most cases where previous work has been carried out in this area, the final products have been postulated to arise by the donation of a Cl^- from PCl_5 to the metal chloride to give PCl_4^+ and the corresponding chlorometallate anion. In many of these reactions, the resulting chlorometallate is of chemical, spectroscopic, and structural interest, e.g., $PCl_5 \cdot CrCl_3$, $PCl_4^+CrCl_4^-$; $PCl_5 \cdot FeCl_3$, $PCl_4^+FeCl_4^-$; $PCl_5 \cdot TiCl_4$, $PCl_4^+TiCl_5^-$; $PCl_5 \cdot SnCl_4$, $PCl_4^+SnCl_5^-$, and many others. In this seminar, the results of an investigation of the solid state structures of the adducts with $FeCl_3$, $CrCl_3$ and $TiCl_4$ will be discussed.

Results

(1) Tetrachlorphosphonium Tetrachloroferrate(III), $[PCl_4][FeCl_4]$

Reaction of PCl_3, $SOCl_2$, and $FeCl_3$ yielded a product of empirical formula $PFeCl_8$. The reaction product has been shown by single-crystal X-ray techniques to be $[PCl_4][FeCl_4]$. Both the anion and cation were found to be nearly tetrahedral.

(2) Bis-tetrachlorophosphonium Di-μ-chlorooctachloro-dititanate(IV), $[PCl_4]_2[Ti_2Cl_{10}]$

Addition of $PCl_5(s)$ to a solution of $TiCl_4$ in $POCl_3$ yields a crystalline product of empirical formula $PTiCl_9$. An X-ray structural determination has led to the formulation of the product as PCl_4^+ and the edge-shared, dimeric ion $[Ti_2Cl_{10}]^{2-}$. A similar geometric configuration is known for Ti^{4+} in the complex $[POCl_3 \cdot TiCl_4]_2$.[2]

(3) Tetrachlorophosphonium Tri-μ-chlorohexachloro-dititanate(IV), $[PCl_4][Ti_2Cl_9]$

The adduct $PCl_5 \cdot 2TiCl_4$ has been prepared by two methods: (a) reaction of PCl_3, $SOCl_2$, and $TiCl_4$, and (b) addition of $PCl_5(s)$ to $TiCl_4$ in thionyl chloride solution. The product has been shown by X-ray analysis to be PCl_4^+ and the unusual, face-shared bioctahedron $[Ti_2Cl_9]^-$. This is the first known example of a first row transition metal ion in the +4 formal oxidation state to assume this geometry.

(4) $PCl_5 \cdot CrCl_3$

A study of the magnetic properties of the adduct $PCl_5 \cdot CrCl_3$ led to its formulation as $PCl_4^+CrCl_4^-$.[3] However, on the basis of the electronic spectrum of this complex, it is proposed that the Cr^{3+} is in an octahedral environment. A model consistent with the electronic

spectrum and the magnetic results is that of an infinite chain of $[CrCl_6]^{3-}$ units sharing two edges. The infrared spectrum is in accord with this proposal. Two bands are found in the Cr-Cl stretching region (370 cm^{-1} and 340 cm^{-1}), and may be assigned to the terminal and bridging Cr-Cl stretches.

The three X-ray structural studies described above have allowed the observation of the PCl_4^+ ion in a variety of crystal lattices. The PCl_4^+ in each case exhibits nearly tetrahedral symmetry. The average of 18 independent Cl-P-Cl angles is 109.4 ± 0.3°. An analysis of the thermal corrections to the P-Cl distance[4] has yielded some very interesting results. The average of 12 independent, thermally-corrected P-Cl distances is 1.944 ± 0.006 Å.

The study of the $TiCl_4$ adducts has shown that Ti^{4+} can satisfy its known preference for octahedral geometry by edge-sharing or face-sharing of octahedra. The role of the non-aqueous solvent in the choice of anion stoichiometry and geometry will also be discussed.

References

1. W. L. Groeneveld, Rec. Trav. Chim., 71, 1152 (1952).

2. C.-I. Branden and I. Lindquist, Acta Chem. Scand., 14, 726 (1960).

3. D. J. Machin, D. F. C. Morris, and E. L. Short, J. Chem. Soc., 4658 (1964).

4. W. R. Busing and H. A. Levy, Acta Cryst., 22, 451 (1967).

THE PREPARATION AND OPTICAL AND ELECTRON SPIN RESONANCE SPECTRA OF SOME HEXACHLORO AND PENTACHLOROALKOXO VANADATES(IV)

Robert D. Bereman November 13, 1969

Introduction

Much recent interest has centered on the investigation of d^1 transition elements involving oxyions of the type Mo^{n+} where $M^{(n+2)+}$ is Cr^{+5}, Mo^{+5}, W^{+5}, or V^{+4}. The halide complexes of these ions have been studied and it is well established that there is substantial π-bonding between the metal and oxygen atoms.[1-7] The relatively simple optical and magnetic properties which arise from a single unpaired electron and C_{4v} symmetry have made these systems particularly appealing. The bonding and molecular orbitals of interest in the vanadyl (VO^{++}) system have been discussed in detail by Ballhausen and Gray.[8] The bonding in the other systems has been discussed by various authors.[1-7]

Alcohol solutions are among the few solvent systems in which one can work with d^1 transition element halides and avoid the formation of oxyions. Due to the recent success in preparing d^1 transition element alkoxides and complexes containing alkoxides as ligands,[9-16] it was decided that vanadium(IV) chloro-alkoxide complexes might be stable. The pentachloroalkoxovanadate(IV) ion should be six coordinate and the metal to oxygen bond would formally be a single bond. A study of a series of these complexes in which the alkoxide group is changed would show the effect on the bonding parameters of changing the donating strength of the oxygen. The effect on the molecular orbital parameters of changing the donating strength of the halide by changing from F^- to Cl^- to Br^- has been shown in the case of the pentahalo(oxo)molybdate(IV) ion.[1]

Discussion

A new class of crystalline vanadium(IV) compounds, the pentachloroalkoxovanadates(IV), has been prepared and characterized. The alkoxo group was methoxo, ethoxo, _n_-propoxo, or _n_-butoxo, while the cation was tetramethylammonium, tetraethylammonium, or pyridinium. The relative stability of the complexes is dependent on the cation. The color of the complexes is golden. Two new salts of the hexachlorovanadate(IV) ion were also prepared and characterized.

The pentachloroalkoxovanadates(IV) were prepared by the addition of one equivalent of the appropriate alcohol to a slurry of the tetraalkylammonium or pyridinium hexachlorovanadate(IV) in an acetonitrile-ethyl ether mixture. The alkoxo complexes could be converted to the appropriate hexachloro complex by the addition of HCl which indicates the absences of a vanadyl species.

Magnetic studies indicated Curie-Weiss paramagnetism and verified the presence of the vanadium(IV) ion with $3d^1$ configuration. The infrared spectra of the complexes were in agreement with the formulation $V(OR)Cl_5^{-2}$. The ultraviolet-visible spectra of the

alkoxides consisted of two peaks around 14,000 cm^{-1} while the hexachlorovanadates(IV) had an asymmetric peak around 15,500 cm^{-1}. The reflectance spectrum of each of the complexes agreed with the solution spectrum.

Attempts to prepare a tetrachlorodialkoxovanadate(IV) species were unsuccessful.

No esr signal was observed for the hexachlorovanadates(IV) in the solid or in $SOCl_2$ at 297°K or 77°K. Electron spin resonance spectra were obtained for the alkoxides as pure powders at 297°K and as solutions at 297°K and 100°K (glasses). The V metal hyperfine was observed and the spectra of the glasses could be resolved into parallel and perpendicular components.

The observed g and A values were used to calculate the coefficients in a simple molecular orbital scheme. The gound state for the $V(OR)Cl_5^{-2}$ ion is a $^2B_2$ and the molecular orbitals which are necessary for discussion are those which are the basis of the b_1, b_2, and e representations:

$$B_2 > * = N_{\pi_2}(dxy - \lambda_{\pi_2} \varnothing b_2)$$

$$B_1 > * = N_{\sigma_2}(dx^2 - y^2 - \lambda_{\sigma_2} \varnothing b_1)$$

$$E > * = N_{\pi_1}(dxz \text{ or } dyz - \lambda^e_{\pi_1} \varnothing^e_e - \lambda^a_{\pi_1} \varnothing^a_e)$$

where the metal orbitals are d functions and $\lambda^a_{\pi_1}$ and $\lambda^e_{\pi_1}$ are the xz (yz) molecular orbital coefficients for the equatorial and axial ligands respectively.

In going through the series from the methoxo to the n-butoxo complex, the $B_2>*$ and $B_1>*$ molecular orbitals become more covalent and the $E>*$ molecular orbital becomes more ionic.

The unpaired electron density in each of the four equatorial halide $3p_\pi$ orbitals was calculated for the complexes and the density increased along the series (methoxo to n-butoxo) as was expected.

References

1. L. A. Dalton, R. D. Bereman, and C. H. Brubaker, Jr., Inorg. Chem., 8 (1969) in press.
2. P. T. Monoharan and Max T. Rogers, J. Chem. Phys., 49, 5510 (1968).
3. K. DeArmond, B. B. Garrett and H. S. Gutowsky, ibid., 42, 1019 (1965).
4. B. R. McGarvey, J. Phys. Chem., 71, 51 (1967).
5. H. A. Kuska and M. T. Rogers, "Radical Ions," E. T. Kaiser and L. Devans, Ed., New York: Interscience Publishers, Inc., 1968. Chapter 13.
6. P. T. Monoharan and M. T. Rogers, J. Chem. Phys., 49, 3912 (1968).
7. H. Kon and N. Sharpless, J. Phys. Chem., 70, 105 (1966).
8. C. J. Ballhausen and H. B. Gray, Inorg. Chem., 1, 111 (1962).

9. R. A. D. Wentworth and C. H. Brubaker, Jr., *ibid.*, *2*, 551 (1963).
10. R. A. D. Wentworth and C. H. Brubaker, Jr., *ibid.*, *3*, 47 (1964).
11. P. G. Rasmussen, H. A. Kuska and C. H. Brubaker, Jr., *ibid.*, *4*, 343 (1965).
12. D. A. McClung, L. R. Dalton and C. H. Brubaker, Jr., *ibid.*, *5*, 1985 (1966).
13. W. Giggenbach and C. H. Brubaker, Jr., *ibid.*, *7* (1968).
14. W. Reagan, D. P. Rillema and C. H. Brubaker, Jr., *ibid.*, *8*, 581 (1969).
15. D. P. Rillema and C. H. Brubaker, Jr., *ibid.*, *8*, 1645 (1969).
16. W. Giggenbach and C. H. Brubaker, Jr., *ibid.*, *8*, 1141 (1969).

A STUDY OF INFRARED BAND SHAPES OF SOME METAL CARBONYLS IN CONDENSED PHASES - CORRELATION FUNCTION ANALYSIS OF MOLECULAR REORIENTATION

Richard Lauver January 13, 1970

Studies of the dynamics of molecular motion in condensed phases have become more detailed as well as more numerous during the past two decades. The fundamental interest evolves from the quest for a better understanding of the liquid state and the intermolecular potentials which dominate all internal dynamical processes. A problem of this scope, of course, cannot be treated in any single experiment and awaits the compilation and correlation of the rapidly increasing store of experimental data into a comprehensive theory. A remarkable variety of physical studies have been brought to bear on the various aspects of the problem. Traditionally, macroscopic transport properties like viscosity, diffusion and conductivity were considered. Debye's classic work[1] in the field of dielectric relaxation marked a most significant step towards the formulation of a molecular model for such processes. More recently, spin relaxation, light scattering, and infrared and Raman line shape studies have been employed in the study of molecular reorientation in condensed phases.

The use of time correlation functions to analytically relate time dependent fluctuations of molecular motion to observable transport coefficients and spectral line shapes has, perhaps, been the most cohesive development in these studies. Fundamentally, the correlation function provides a mathematically tenable approach to nonequilibrium processes comparable to the partition functions used for systems in equilibrium. Recent reviews by Gordon[2] and by Zwanzig[3] give an enlightening account of the extent that correlation functions are now used. The contributions of Gordon have been particularly instrumental in illucidating the correlation function analysis of spectral line shapes.

In this seminar, we consider a band shape study of some metal carbonyls. The infrared band shapes (CO stretch) were numerically analyzed to determine the correlation function and spectral moments as described by Gordon.[4,5] The results are discussed in terms of relative rates of rotational reorientation and qualitative aspects of the intermolecular potential.

The dependence of the correlation function, $\phi(t)$, and second moment, $\mu(2)$, on experimental variable was examined for some hexacarbonyls. A systematic variation with slit width and range of integration was found, but no concentration dependence was detected. The solvent dependence of $\phi(t)$ and $\mu(2)$ for $Cr(CO)_6$ was considered in detail. The changes seen were related to polarizability or dielectric constant of the solvent rather than to bulk viscosity. Anisotropy of reorientation was observed for axially symmetric carbonyls ($Fe(CO)_5$, $Hg[Co(CO)_4]_2$, $LMn(CO)_5$, L = H, CH_3, CF_3, $Mn(CO)_5$). Internal rotation was evident for $CH_3Mn(CO)_5$, $CF_3Mn(CO)_5$ and $Hg[Co(CO)_4]_2$, but not for $Mn_2(CO)_{10}$. Diffusion constants and correlation times were calculated for comparison with related data

available in the literature. The reorientation process is best described as slightly hindered rotation at short times (< 1 picosec) followed by collision controlled diffusion. The results are compared to several models which predict $\rho(t)$ for limiting cases.

Bibliography

1. P. Debye, Polar Molecules, Dover Pub. Inc., New York (1929).
2. R. G. Gordon, Advan. Magnetic Resonance, 3, 1 (1968).
3. R. Zwanzig, Ann. Rev. Phys. Chem., 16, 67 (1965).
4. R. G. Gordon, J. Chem. Phys., 39, 2788 (1963).
5. Ibid., 43, 1307 (1965).

Additional references of interest:

a) Application of correlation functions,
H. Shimizu, J. Chem. Phys., 43, 2453 (1965).
Ibid., 48, 2494 (1968.
W. A. Steele, J. Chem. Phys., 38, 2411 (1963).

b) Reorientational anisotropy,
J. Jones and T. M. DiGennaro, J. Chem. Phys., 50, 6 (1969).
R. A. Assink and J. Jonas, J. Phys. Chem., 73, 2445 (1969).
D. E. Woessner, B. S. Snowden, Jr., and E. T. Strom,
Molec. Phys., 14, 265 (1968).

THE COORDINATION CHEMISTRY OF THE AZO GROUP

John Thatcher March 17, 1970

The process by which metallo-enzymes "fix" atmospheric nitrogen and convert it into nitrogenous-cell constituents is efficient and occurs under mild conditions. Ammonia is the key intermediate before assimilation of "fixed" nitrogen into carbon skeletons occurs. A reductive pathway possibly via diimide (H-N=N-H) and hydrazine is preferred. The mechanism for fixation involves two active metal sites on the enzyme, but it is not known whether a dinuclear metal site is necessary for binding the nitrogen molecule prior to reduction.[1] Diimide is the simplest azo compound. Since azo compounds are weakly basic and decompose readily liberating N_2, metal-azo complexes may be useful as models for and a possible route to molecular nitrogen complexes.

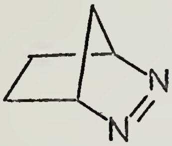
Metal azo complexes are well known.[2,3] However, most of these complexes involve aromatic azo compounds in which the azo group bonds to the metal as part of a chelate ring.

For these reasons, a study of the coordination properties of 2,3,Diazobicyclo(2.2.1)Heptene-2 DBH(I) was undertaken.

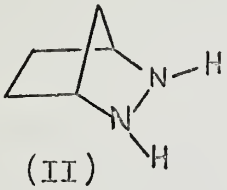
Platinum(II)-(DBH)·complexes have been synthesized by (a) addition of DBH to K_2PtCl_4 in aqueous solution;[4] (b) addition of $[DBHz\text{-}H]_2SO_4$ (DBHz(II)) to H_2PtCl_6 in aqueous solution; (c) oxidation of (DBHz)-Pt(II) complexes with cupric chloride in methanol; (d) reduction of $(DBH)_2PtCl_4$ with sodium iodide in methanol.

The chloro complexes characterized have stoichiometries:

$M[(DBH)\ Pt_2Cl_5]$, $[(DBH)PtCl_2]_2$, $(DBH)_2PtCl_2$ and $[(DBH)_3PtCl]ClO_4$.



(I)



(II)

Nuclear magnetic resonance spectroscopy and an x-ray crystal structure determination showed that coordination to platinum occurs through a single nitrogen of the azo group to form monocoordinated complexes or through both nitrogens of the azo group, one nitrogen to each platinum atom, to form bridged complexes. Both types of coordination have been found to occur in molecular nitrogen complexes.[1,5]

Four types of reactions have been observed for monocoordinated (DBH)-Pt(II) complexes. (a) Replacement of DBH by entering ligand; (b) replacement of ligand other than (DBH) by entering ligand; (c) oxidative addition by Cl_2; (d) coordination of DBH to a second metal by bridging. From the reactivity of the azo complexes, it is deduced that the monocoordinated azo group has a higher trans effect than chloride in substitution reactions and that the Pt-N bond is weaker when the azo group is bridging than when it is monocoordinated.

The intense charge transfer bands in the U.V-visible absorption spectrum of these compounds and their chemical reactivity indicate that back donation of electron density from platinum to the π^* orbital on the nitrogen of the azo group occurs.

Infrared data show that for monocoordinated azo complexes, σ bonding increases while π bonding decreases the frequency of the (N=N) stretching vibration. This behavior is similar to that found for CO[6] and CN^- [7] and proposed for N_2.[8]

Two compounds III(A and B) with stoichiometry $[(DBH)PtCl_2]_2$ were isolated. Their physical and chemical properties were practically identical. The crystal structure of IIIA showed the molecule was boat shaped with two azo bridges. The coordination about each platinum is square planar with the nitrogens cis to each other. The five carbon skeletons of the DBH ligands in this type of molecule may assume either of two possible orientations. Only one orientation is found in IIIA. This suggests that the other orientation is found in IIIB.

The kinetics and mechanism of the reaction:

$$[(DBH)PtCl_2]_2 + Ø_4AsCl \qquad Ø_4As[(DBH)Pt_2Cl_5] + DBH$$

were investigated. The reaction rates were calculated from spectrophotometric data. A two step mechanism is proposed. The first step involves attack by chloride ion to form the intermediate $(DBH)_2Pt_2Cl_5^-$. In the second step DBH is displaced and a chloride ion bridges between the two platinums.

DBH complexes with Pt(IV), Pd(II), Cu(II), and Co(II) have been isolated as well as Pt(II) complexes with the hydrazo derivative DBHz(II). Both monocoordinated and bridged DBHz complexes were isolated.

The compound $(azobenzene)_2PtCl_4$ reported by Kharash and Ashford[9] was reinvestigated and it was found that the compound was incorrectly formulated.[10] It is in fact $[azobenzene\text{-}H]_2PtCl_6$ a salt with no coordination of the azobenzene to platinum. However, preliminary studies indicate that azobenzene can form Pt(IV) complexes.

It is concluded that the coordination chemistry of the azo group closely parallels that of N_2. Thus, diimide is a likely intermediate in N_2-fixation. Since N≡N, N=N, and N-N can form monocoordinate or bridging complexes, either a mononuclear or a dinuclear metal site may be utilized in the enzymatic fixation of nitrogen.

References

1. R. Murrey, D. C. Smith, Coordin. Chem. Rev., 3 (1968), 429-470.
2. H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, New York, N. Y. (1961).
3. A. C. Cope and R. W. Siekman, J. Am. Chem. Soc., 87, 3273 (1965).
4. R. G. Denning and J. Thatcher, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 5, 1968, No. M199.

5. I. M. Treitel, M. T. Flood, R. E. Marsh, H. B. Gray, J. Am. Chem. Soc., 91, 6512 (1969).
6. D. J. Darensbourg, Ph.D. Thesis, University of Illinois, 1967.
7. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.
8. K. G. Caulton, R. L. Dekock, and R. F. Fenske, J. Am. Chem. Soc., 92, 515 (1970).
9. M. S. Kharash and T. A. Ashford, ibid., 58, 1733 (1936).
10. R. G. Denning and J. Thatcher, ibid., 90, 5917 (1968).

THE PSEUDO-JAHN-TELLER EFFECT

John W. Boettcher March 24, 1970

Introduction

Approximately ten years ago, Bader[1] proposed a symmetry rule with which he could correctly predict the sign of the interaction force constants frequently introduced in normal coordinate analyses. Just as the Jahn-Teller effect deals with the mixing of degenerate electronic ground states upon nuclear displacement, so the pseudo-Jahn-Teller effect deals with the mixing of the ground state with low-lying excited states. This mixing tends to stabilize the ground state, leading to a smaller increase of energy upon distortion than if this mixing did not occur.

This seminar will be concerned with an examination of the foundations of this rule and some of its more recent applications.

Theory

Suppose we place a molecule in a given geometry and designate the electronic Hamiltonian by H^0. If one then displaces the nuclei along some normal coordinate, Q_i, the new Hamiltonian can be written to second order in Q_i as

$$\mathcal{H} = H^0 + H^i Q_i + \frac{1}{2} H^{ii} Q_i^2$$

where

$$H^i = \left(\partial H^0 / \partial Q_i\right)_0 \qquad H^{ii} = \left(\partial^2 H^0 / \partial Q_i^2\right)_0$$

Through use of perturbation theory, the energy of the ground electronic state to second order in Q_i is

$$\mathcal{E}_0 = \mathcal{E}_0^0 + Q_i \langle 0|H^i|0\rangle + \frac{1}{2} Q_i^2 \left[\langle 0|H^{ii}|0\rangle - 2 \sum_k{}' \frac{|\langle 0|H^i|k\rangle|^2}{\varepsilon_k^0 - \varepsilon_0^0} \right]$$

Under certain conditions, the linear term may be ignored, and we need only concern ourselves with the quadratic or force constant term. The first term in brackets is the force constant for the normal coordinate if the electronic distribution were to remain static. The second term in brackets is then a correction due to the mixing of the ground with excited electronic states.

The crucial assumption of the rule is that the summation may be replaced by one or at most a few important terms where $\varepsilon_k^0 - \varepsilon_0^0$ is small. Also assumed is that $\langle 0|H^i|k\rangle$, when non-zero, decreases or at worst remains constant as $|k\rangle$ increases in energy.

Symmetry is introduced by recognizing that the integral $\langle o|H^i|k\rangle$ is non-zero only when the direct product of $\Gamma|o\rangle$ with $\Gamma|k\rangle$ contains $\Gamma(H^i)$. The above direct product is simply taken to be $\Gamma(\phi_i)\times\Gamma(\phi_j)$ where ϕ_i is the molecular orbital occupied in the ground state and ϕ_j the molecular orbital occupied instead of ϕ_i in the excited state. The symmetry species of $\Gamma(H^i)$ is the same as $\Gamma(Q_i)$. Therefore, only certain normal coordinate displacements will allow coupling of the ground with low-lying excited states and bring about the resulting stabilization upon distortion.

Applications

In a second paper,[2] Bader applied this rule to a determination of the reaction coordinate in unimolecular and bimolecular decomposition reactions.

Recently, Bartell[3,4] and Pearson[5,6] have used this rule to correctly predict the structures of various molecules of formulas AX_n where n = 2 to 6.

Future

It has been suggested[6] that this rule may be useful as a test for calculated or assumed schemes of molecular orbitals to see whether they are compatible with known structures.

References

1. R. F. W. Bader, Mol. Phys., 3, 137 (1960).
2. R. F. W. Bader, Can. J. Chem., 40, 1164 (1962).
3. L. S. Bartell and R. M. Gavin, Jr., J. Chem. Phys., 48, 2466 (1968).
4. L. S. Bartell, J. Chem. Educ., 45, 754 (1968).
5. R. G. Pearson, J. Am. Chem. Soc., 91, 1252 (1969).
6. R. G. Pearson, *ibid.*, 91, 4947 (1969).

STERIC EFFECTS IN COORDINATION OF 1,1,1-TRIS(DIMETHYLAMINOMETHYL)ETHANE AND OF 1,1,1-TRIS(MONOMETHYLAMINOMETHYL)ETHANE

Walter Kasowski April 9, 1970

Zinc Complexes

Part I.

Steric effects in coordination of the new tripod ligand 1,1,1-tris(dimethylaminomethyl)ethane(TTN) and of 1,1,1-tris(monomethylaminomethyl)ethane(TSN) have been investigated by the preparation and characterization of their zinc chloride and zinc bromide complexes.[1] The stereochemistry of the complexes has been established on the basis of data from ^1H nuclear magnetic resonance (nmr) spectroscopy, infrared spectroscopy, and complementary physical-chemical studies. The complexes of TSN have a cage-like structure consisting of three fused six-membered chelate rings and a pentacoordinated zinc atom due to the sterically unhindered tridentate behavior of TSN. In contrast, the complexes of TTN have only one six-membered chelate ring and a tetracoordinated zinc atom due to the sterically controlled bidentate behavior of TTN. The chelate ring is in a frozen pseudo-chair conformation and yields strikingly similar ^1H nmr data to purely organic structurally analogous nitrogen-containing heterocycles. This indicates that the zinc(II) nucleus, though chemically different from the carbon atom, does not produce any conformational change in these systems.

Part II.

The stereochemistry of the chelate ring in the TTN complexes, and hence the controlling steric factor, has been elucidated by comparative studies of the model complexes $LZnX_2$ where L is the bidentate analog of TTN, N,N,N',N',2,2-hexamethyl-1,3-propanediamine (BTN). Only that conformer in which the free (dimethylaminomethyl) group is equatorially orientated at C_5 is formed. Furthermore, the iodo members of both TSN and TTN have been prepared and shown to possess structures similar to those described for their chloro and bromo counterparts. This indicates that the progressive increase in size of the halo group does not perturb the stereochemistry of these systems.

References:

1. Walter J. Kasowski and John C. Bailar, Jr., J. Am. Chem. Soc., 91, 3212 (1969).

THE CONSERVATION OF ORBITAL SYMMETRY

W. Karl Olander April 14, 1970

Introduction

In the six years since R. B. Woodward and R. Hoffmann initially formulated the rules which bear their names pertaining to the conservation of orbital symmetry in concerted reactions, the organic branch of chemistry in particular has experienced a wealth of publications verifying and expanding their treatment in examining a host of highly stereospecific reactions.[1-8] More recently, the conservation of orbital symmetry has found application in the realm of inorganic chemistry.[9-10]

Basically, they set the ground work for a theoretical treatment of all concerted reactions at a strictly qualitative level while simultaneously observing pertinent quantum mechanical restrictions. The fundamental principle enacted is that highly stereospecific reactions occur readily when there is congruence between orbital symmetry characteristics of reactants and products.

The purpose of this seminar is to review several general reaction types to which the Woodward-Hoffmann rules have been applied and examine several instances where they have been extended to inorganic systems.

Electrocyclic Reactions

By definition, an electrocyclic reaction entails the formation of a σ bond between the termini of a linear system containing $k\pi$ electrons or the converse process. The intramolecular conversion of the allyl cation to the cyclopropyl cation affords a simple system on which to examine the Woodward-Hoffmann approach. A priori, there are two rotational pathways, i.e., conrotary or disrotary, which will translate the π molecular orbitals of the allyl cation (X_1, X_2, X_3) into σ molecular orbitals of the cyclopropyl cation (σ, π, σ^*). Coincident with the conrotary and disrotary mechanisms are preserved two symmetry elements, a C_2 axis and a mirror plane respectively, with respect to which all molecular orbitals can be classified as symmetric (S) or antisymmetric (A). X_1(A) and X_3(A) translate via the conrotary mechanism into fragments of either π(A) or σ^*(A) while X_2(S) translates as σ(S). A correlation diagram, constructed by placing reactant and product molecular orbitals on either side at their respective energy levels and then connecting levels of like symmetry, reveals that the conrotary mode leads to an excited state product. This process is termed a symmetry forbidden reaction for the ground state. Examination of an analogous treatment for the disrotary mode shows a ground state--ground state correlation diagram for the conversion and is symmetry allowed. The behavior of the highest occupied molecular orbital, X_1, provides the answer. For the conrotary process, it is no longer bonding in the transition state, while the opposite is true for the disrotary mode. Also, the process is just reversed for the first excited state. Photochemical excitation of a X_1^2 electron to give the X_1X_2 species leads to a symmetry

allowed conversion for the conrotary mode, but is symmetry forbidden in the disrotary mode. An alternate method of correlating reactant and product molecular orbitals via electronic state diagrams yields an identical result.[11]

Based on the nodal properties of polyenes, Woodward-Hoffmann have derived a selection rule for electrocyclic reactions of $k\pi$ electrons. For $k = 4q$, a conrotary mode is predicted, but when $k = 4q+2$, a disrotary mechanism is foreseen ($q = 0,1,2...$). In the first excited state, the modes are reversed.

Correlation Diagrams

Symmetry elements are of no use when all of the orbitals are either symmetric or antisymmetric with respect to it and can only lead to the trivial solution where all reactions are symmetry allowed.

A symmetry element should bisect bonds formed or broken during a reaction course, otherwise one is often led to the erroneous conclusion that a reaction is symmetry allowed.

Symmetry is used primarily as a tool to observe the behavior of bonding m.o.'s in the transition state and determine if they are still bonding. Since the symmetry class of a particular orbital is invariant, the principle of the conservation of orbital symmetry affords a convenient method of predicting the "allowedness" of a particular reaction on the basis of whether bonding reactant m.o.'s remain bonding in the transition state.[12]

Cycloaddition Reactions

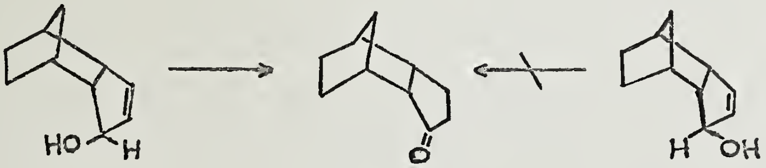
Two exemplary reactions are the concerted combination of two ethylene molecules to form cyclobutane and the Diels Alder combination of butadiene and ethylene to form cyclohexene. Examination of the latter shows that the molecular orbitals for the butadiene (X_1, X_2, X_3, X_4) and ethylene (π, π^*) molecules together with those for the cyclohexene product (σ_1, σ_2, π, π^*, σ_2^*, σ_1^*) can be classified as symmetric (S) or antisymmetric (A) with respect to a mirror plane preserved throughout the addition reaction. The resulting correlation diagram shows that all the reactant bonding m.o.'s translate as bonding m.o.'s of the product and hence the reaction is symmetry allowed in the ground state. Just the reverse is found for the addition of two ethylene molecules to form cyclobutane as bonding m.o.'s of the product are derivable from antibonding m.o.'s of the reactant making the reaction symmetry forbidden. For the two reaction processes described above, the "symmetry allowedness" of each is reversed in the first excited state reaction. A general rule which will distinguish the allowed cycloaddition reactions from the many various possibilities has been proposed.[8]

Inorganic Applications

Pettit and co-workers investigated certain symmetry forbidden polyolefin isomerization reactions which proceed rapidly in the presence of certain metal ions.[9] For example, the 1,3 hydrogen

migration via a suprafacial shift is a symmetry forbidden process. Nevertheless, it is apparent that the two accepted mechanisms for metal catalyzed 1,3 hydrogen atom shifts do not effectively explain all the observed cases, e.g., the 3-phenylpropene to 1-phenylpropene isomerization carried out in the presence of $DCo(CO)_4$. The expected high incorporation of deuterium atoms in the 1-phenylpropene product for the metal hydride addition mechanism or the involvement of an allyl intermediate was not observed by Orchin.[13] Pettit suggests a mechanism in which the presence of the metal now makes the 1,3 suprafacial hydrogen atom migration operative and questions if there is a favored spacial orientation of the coordinated metal with respect to the migrating hydrogen atom.

The $Fe(CO)_5$ catalyzed isomerization of the alcohol below to the corresponding ketone provides a possible explanation. While one epimer readily undergoes a 1,3 shift which ultimately tautomerizes to the ketone, the other remains unaffected. The transition state proposed is one in which the migrating hydrogen is on the same side as the Fe atom.



Eaton has combined orbital symmetry with crystal field theory and applied it to certain isomerization reactions involving d^8 transition metal complexes.[10] Using the set of d orbitals as his basis set, various ligand geometries are interconverted and the corresponding crystal field energies noted. Correlation diagram considerations concur that tetrahedral-square planar isomerization demonstrated by bis(N,N-disubstituted aminotroponeimineates) and bis(N-sec-alkylsalicylaldimines) of Ni(II) are symmetry allowed.[14,15] Similarly cis-trans isomerizations as for $Pt(PEt_3)_2Cl_2$ are thermally symmetry forbidden, but photochemically allowed. By analogous reasoning, axial-equatorial isomerizations for trigonal bipyramidal molecules through a square pyramidal intermediate are symmetry allowed in the ground state for d^8 systems, but symmetry forbidden for spin free d^2 and spin paired d^3 and d^4 complexes.

Future

While the most extensive use of the Woodward-Hoffmann rules will likely remain with organic chemistry, the door is open for the inorganic chemist. In view of the vast number of stereospecific reactions satisfactorily explained by organic chemists employing the Woodward-Hoffmann rules, one is dismayed at the meager output of their inorganic neighbors in this respect. The more complex nature of transition metal chemistry may inherently have slowed widespread inorganic application of the Woodward-Hoffmann rules; nevertheless, one must wonder when and if a real genesis will occur.

References

1. R. B. Woodward and R. Hoffmann, J. Am. Chem. Soc., 87, 395 (1965).
2. R. Hoffmann and R. B. Woodward, Ibid, 87, 2046 (1965).
3. R. B. Woodward and R. Hoffmann, Ibid, 87, 2511 (1965).
4. R. Hoffmann and R. B. Woodward, Ibid, 87, 4388 (1965).
5. R. Hoffmann and R. B. Woodward, Ibid, 87, 4389 (1965).
6. R. Hoffmann and R. B. Woodward, Accts. Chem. Res., 1, 17 (1968).
7. R. Hoffmann and R. B. Woodward, Science, 167, 825 (1970).
8. R. B. Woodward and R. Hoffmann, Angew. Chem. Int. Ed., 8, 781 (1969).
9. R. Pettit, H. Sugahara, J. Wristers and W. Merk, Disc. Faraday Soc., No. 47 (1969).
10. D. R. Eaton, J. Am. Chem. Soc., 90, 4272 (1968).
11. H. C. Longuet-Higgins and E. W. Abrahamson, Ibid, 87, 2045 (1965).
12. J. J. Vollmer and K. L. Servis, J. Chem. Ed., 45, 214 (1968).
13. R. W. Goetz and M. Orchin, J. Am. Chem. Soc., 85, 1549 (1963).
14. R. H. Holm, A. Chakravorty, and G. O. Dudek, Ibid, 86, 379 (1964).
15. D. R. Eaton, W. D. Phillips and D. J. Caldwell, Ibid, 85, 397 (1963).

METHODS OF DISTINGUISHING INNER AND OUTER SPHERE MECHANISMS IN ELECTRON TRANSFER REACTIONS

Dennis Mahoney April 21, 1970

Electron transfer reactions between transition metal complexes have been a popular topic in inorganic kinetics. Numerous reviews have been published.[1-4]

Early work by Taube showed that reactions may occur by one of two mechanisms: a simple transfer of the electron during which the ligand shells remain intact (outer sphere mechanism) or a displacement of a ligand on one complex by a ligand on the other to form a bridged intermediate (inner sphere mechanism).

Theoretical treatments[5,6] of outer sphere type reactions have been made, especially by Marcus. The relations derived allow predictions of rate constants for a related series of reactants to be made with quite good accuracy. This topic was discussed previously.[7] Little theoretical work on inner sphere mechanisms has been attempted, chiefly because of their greater complexity.[8,9]

Inner and outer sphere mechanisms are not always easy to distinguish even though the rate law may be readily obtained. For even though the mechanisms may be completely different identical bimolecular rate laws may result. Taube has stated the conditions which must be present in order that the two mechanisms may be differentiated. They are:[10]

i) a reaction is inner sphere if it can be shown that a ligand attached to one reactant before electron transfer is attached to the other immediately after reaction.

ii) a reaction is outer sphere if the transfer takes place at a rate greater than the rate of substitution of the ligands or if none of the ligands are capable of acting as a bridge.

Because many reactions do not satisfy the above conditions, a number of indirect tests have been proposed. The main methods are:

i) Entropies of activation
ii) Volumes of activation
iii) Comparison of reaction rates
iv) Azide-thiocyanate test
v) Effect of non-bridging ligands
vi) Effect of changing solvent from H_2O to D_2O

i) The main factors in determining the change in the entropies of activation in going from an outer sphere activated complex to an inner sphere one are an increasing

electrostriction of solvent and the setting free of the displaced ligand in an inner sphere case. The two factors work against each other and no clear cut pattern emerges.[3,11,12,13,14a,b,15]

ii) Volumes of activation should be positive for inner sphere reactions.[16] Little work has been done and it appears that conflicting effects, such as those in i) may make interpretation difficult.

iii) The Marcus theory predicts that rates of reactions in a series should vary in a simple fashion[17] provided the mechanisms are similar. For example, Zwickel and Taube[11] found the relative rate constants for $[Co(NH_3)_5X]^{2+}$ + Red to be

Oxidant	$k_{V^{2+}}$ *	$k_{Cr(bipy)_3^{2+}}$ **
$R-NH_3$ *‡	1	1
$R-OH_2$	135	91
R-OH	$<10^7$	50
R-Cl	1.6×10^3	1.5×10^3

* reductant is V^{2+}; ** reductant is $Cr(bipy)_3^{2+}$;
*‡ $R = [Co^{III}(NH_3)_5-]$

iv) If an oxidant R-X ($X = N_3^-$, SCN^-) forms an inner sphere activated complex and if the reductant bonds to the N and of the SCN^- better than the S end, then the rate constant for N_3^- is expected to be much greater than that for SCN^-.[18,20]

v) Studies by Haim and coworkers[19,20] have shown that a no-bridging ligand may have a significant effect on the rate of an inner sphere reaction. The usefulness of this observation as a test for mechanism is weakened, however, by the observations of Patel and Endicott,[21] who observe similar effects in reactions which are definitely outer sphere.

vi) Solvent effects on the rate are small and their significance, if any, with respect to the pathway is not understood.[3,11]

The method of Haim[22] is also discussed. In this procedure, one calculates an hypothetical equilibrium constant for the reaction:

$$[Co(NH_3)_5 - F - Red]^{\ddagger} + I^- \rightleftharpoons [Co(NH_3)_5 - I - Red]^{\ddagger} + F^- .$$

It is found that for inner sphere reactions, the value obtained is less than one, and for outer sphere reactions, it is greater than one.

Conclusions. The method of Haim and the azide-thiocyanate tests may be used with confidence. The azide-thiocyanate test does give intermediate values in some cases which are of questionable significance. The comparison of rates is also useful; entropies and volumes of activation are poorly understood and appear to be of little value. The effects of non-bridging ligands are also variable and must be used with caution.

Review Articles:

1) J. Halpern, Quart. Revs., 15, 207 (1960).
2) R. A. Marcus, Ann. Revs. Phys. Chem., 15, 155 (1964).
3) N. Sutin, ibid., 17, 119 (1966).
4) A. Sykes, Adv. Inorg. Chem. Radiochem., 10, 153 (1967).

Theoretical Discussions:

5) R. J. Marcus, B. Zwolinski and H. Eyring, Chem. Revs., 55, 157 (1955).
6) R. A. Marcus, J. Chem. Phys., 43, 679 (1965) and references therein.
7) J. Orrell, Chemistry 405, October 14, 1969, and references therein.
8) R. A. Marcus, J. Phys. Chem., 72, 891 (1968).
9) P. Schmidt, Aust. J. Chem., 12, 673 (1969).

Experimental Work:

10) F. Basolo and R. Pearson, Mechanisms of Inorganic Reactions (Wiley, 1968), p. 479ff.
11) A. Zwickel and H. Taube, J. Am. Chem. Soc., 83, 793 (1961).
12) J. Caudlin, J. Halpern and D. Trium, ibid., 86, 1019 (1964).
13) J. Endicott and H. Taube, ibid., 86, 1686 (1964).
14a) W. Higginson et al., Disc. Fara. Soc., 29, 49 (1960).
14b) W. Higginson et al., ibid., 29, p. 123ff (1960).
15) J. Stritar and H. Taube, Inorg. Chem., 8, 2281 (1969).
16) J. Caudlin and J. Halpern, ibid., 4, 1086 (1965).
17) R. A. Marcus, J. Phys. Chem., 67, 853 (1963).
18) J. Espenson, Inorg. Chem., 4, 121 (1965).
19) P. Benson and A. Haim, J. Am. Chem. Soc., 87, 3826 (1965).
20) N. Sutin and A. Haim, ibid., 88, 434 (1966).
21) R. Patel and J. Endicott, ibid., 90, 6364 (1968).
22) A. Haim, Inorg. Chem., 7, 1475 (1968).

APPLICATIONS OF TEMPERATURE-JUMP RELAXATION METHODS TO THE STUDY OF FACTORS INFLUENCING THE RATE OF WATER REPLACEMENT IN TRANSITION-METAL COMPLEXES

Nicholas K. Kildahl April 28, 1970

Introduction

The development during the past 15 years of methods for studying chemical relaxation phenomena[1] has greatly extended the time range available to the kineticist. Using such methods as temperature-jump (T-jump), pressure-jump (P-jump), and electric field-jump (E-jump) relaxation, he is now able to measure reaction rates falling in the formerly inaccessible time range from 10^{-3} to 10^{-9} seconds. This seminar will be restricted to a review of the T-jump method and its uses in studying the rate of displacement of water by other ligands in complexes of the transition metals.

Theory

The principle of relaxation methods is quite simple. A chemical system is first allowed to come to equilibrium under conditions of constant temperature, pressure, etc. This equilibrium is then destroyed by a sudden change in some chosen external parameter, and the approach to equilibrium under the new set of conditions is followed by an appropriate detection technique. The perturbing parameter used in the T-jump method is, of course, the temperature. However, in order for a temperature change to affect the equilibrium of a given chemical reaction, it is necessary that the heat of reaction be nonzero. Since not all reactions meet this criterion, it would appear that this condition is somewhat restrictive. Nevertheless, in some cases, it is possible to couple the reaction of interest with an indicator reaction which does have a finite heat. This enables the experimentalist to study most interesting reaction types.

The observable associated with the relaxation experiment is the relaxation time, τ. For a one-step reaction, as will be shown, τ can be easily related to the rate constants and equilibrium concentrations of the reactants involved. However, for a multiple relaxation process, there will be as many relaxation times as there are independent reaction steps. Further, the single relaxation times do not usually correspond to the single reaction steps, due to coupling among these steps. Thus the observed relaxation times correspond to normal modes of reaction.

Applications

The study of the exchange kinetics of transition-metal complexes during the past decade has been intensive. One of

the major areas of interest has been the study of factors influencing the rate of water replacement in these complexes. It has been recognized for quite some time that for reactions of the type

$$ML_x(H_2O)_{6-x} + L' \underset{k_r}{\overset{k_f}{\rightleftharpoons}} ML_x(H_2O)_{5-x}\,L' + H_2O$$

the rate-determining step, following the initial formation of an ion-pair, is the release of a water molecule from the inner coordination sphere of the metal ion. However, the actual rate of release of the water molecule can vary, depending upon the nature of both L and L'.

In 1962, Hammes and Steinfeld[2] studied the rates of formation and dissociation of Ni(II) and Co(II) complexes with one, two, and three glycine, diglycine, triglycine, and imidazole molecules using the temperature-jump technique. They found that the rate of dissociation of water is faster for Co(II) than for Ni(II) and that, for the ligand glycine, this rate tends to increase in reactions involving the higher complexes. They took this as an indication for the loosening of the hydration shell due to bonding through the negative carboxyl group of glycine; and they concluded further that if bonding takes place through uncharged groups, the rate of water loss is independent of the number of bound ligands.

Hammes and Morrell[3] extended the above work in 1963 when they measured the rate constants for the formation of the Ni(II) and Co(II) complexes of pyrophosphate and tripolyphosphate using T-jump methods. They determined that the rate of water loss from the metal ion is the rate-determining step but that the highly-charged ligands accelerate this rate for Co(II).

Perhaps the most interesting study of the type with which this seminar is concerned was the one performed by Rorabacher in 1966.[4] He measured the kinetics of formation and dissociation for the monoammine complexes of Co(II), Ni(II), and Zn(II) in aqueous solution in order to compare these rates with those for the formation of previously-studied polyamine complexes, which were found to be abnormally fast. To account for the difference in rates, he proposed an internal conjugate base mechanism which explained increases in K_0, the equilibrium constant for ion-pair formation, and k_0, the rate constant for water loss.

Other important work was carried out in 1966 by Kustin et al.,[5,6] when they used T-jump techniques to measure rate constants for the formation of complexes of α- and β-alanine and α- and β-aminobutyric acids with Co(II) and Ni(II). They found that with α-alanine, Co(II) substitution is faster than Ni(II) substitution; but with β-alanine, Co(II) substitution is slowed considerably, whereas that of Ni(II) remains about the same. In the case of the aminobutyric

acids, both Ni(II) and Co(II) react more slowly with the β- than with the α-ligand. They interpret these results as being indicative of a rate-limiting ring-closure mechanism in the case of the β-compounds.

Finally, Margerum and his group have done quite significant work on this problem. In 1966, Margerum and Rosen[7] observed the rates of displacement of water by ammonia to be dependent upon the nature of multidentate ligands already coordinated to Ni(II). Contrary to the results of Hammes et al., they found that the charge of the complex is not of much importance in determining this rate; instead they contend that the electron-donating ability of the coordinated groups and the structure of the complex are the important factors. In 1969, Margerum and Jones[8] found that formation of $Ni(en)_3^{2+}$ (en=ethylenediamine) from $Ni(en)_2(H_2O)_2^{2+}$ and en is very fast compared to formation of either of the two lower complexes. Further, they found that ring closure contributes to the limiting rate in the formation of $Ni(en)_3^{2+}$.

Conclusion

Although it appears that many of the factors influencing the rate of water loss from transition-metal complexes have been identified, they have yet to be combined into a unified theory. Temperature-jump relaxation techniques have so far proved to be quite valuable in the elucidation of this interesting problem. Undoubtedly, they will prove just as useful in future work.

References

1. M. Eigen and L. DeMaeyer in "Technique of Organic Chemistry," A. Weissberger, Ed., Vol. VIII, Part II, 2nd ed., Interscience Publishers, New York, N. Y., 1963.
2. G. Hammes and J. Steinfeld, J. Am. Chem. Soc., 84, 4639 (1962).
3. G. Hammes and M. Morrell, J. Am. Chem. Soc., 86, 1497 (1964).
4. D. B. Rorabacher, Inorg. Chem., 5, 1891 (1966).
5. K. Kustin, R. Pasternack, and E. Weinstock, J. Am. Chem. Soc., 88, 4610 (1966).
6. A. Kowalak, K. Kustin, R. Pasternack, S. Petrucci, J. Am. Chem. Soc., 89, 3126 (1967).
7. D. Margerum and H. Rosen, J. Am. Chem. Soc., 89, 1088 (1967).
8. J. Jones and D. Mergerum, J. Am. Chem. Soc., 92, 470 (1970).

KINETIC STUDIES ON SOLID STATE REACTIONS OF CHROMIUM COMPLEXES

J. E. House, Jr. May 5, 1970

Part I.

Although there has been a recent increase in interest in solid state reactions involving coordination compounds, the deamination of solid tris(ethylenediamine)- and tris(propylenediamine)chromium(III) salts has been the subject of several studies over many years. Pfeiffer reported that $[Cr(en)_3](NCS)_3$ and $[Cr(en)_3]Cl_3$ each lose a molecule of ethylenediamine when heated at 130° and 160°, respectively, to produce trans-$[Cr(en)_2(NCS)_2]NCS$ and cis-$[Cr(en)_2Cl_2]Cl$.[1] Rollinson and Bailar found that $[Cr(en)_3](NCS)_3$ prepared by Pfeiffer's method (treating a solution of the sulfate with ammonium thiocyanate) could be deaminated but $[Cr(en)_3]Cl_3$ prepared directly from anhydrous $CrCl_3$ and ethylenediamine could not.[2] They found that the deamination was catalyzed by the corresponding ammonium salt and that $[Cr(en)_3](NCS)_3$, which was highly pure, could not be deaminated easily. O'Brien and Bailar found that, of the compounds $[Cr(AA)_3]X_3$ (where AA = en or pn and X = Cl^-, Br^-, I^-, etc.), only the chloride and thiocyanate are easily deaminated to give a diacido product.[3]

Bear and Wendlandt studied these reactions using DTA and TGA and reported activation energies for the deaminations in the presence and absence of catalysts.[4] Ammonium thiocyanate was found to lower the activation energy by about 15 kcal/mole.

The work described in this seminar was undertaken to study the deamination of $[Cr(en)_3](NCS)_3$ and $[Cr(pn)_3](NCS)_3$ in more detail, and the reactions were followed by isothermal thermogravimetric measurements. The fraction of the complex deaminated was found to vary linearly with time up to about 50% completion, although no rate law was found which would describe the data for reactions proceeding 70-80% toward completion. Amine hydrothiocyanates were found to be as effective as catalysts as ammonium thiocyanate and the reaction shows a first order dependence on catalyst concentration over a wide range of catalyst/complex ratios. The deamination reactions are acid catalyzed reactions with the protonated amine functioning as the acid.[5] Other results obtained using differential scanning calorimetry (DSC) will be presented and discussed.

A proposed mechanism for the deamination is characterized by a rate determining step in which one end of a coordinated en molecule is detached from the chromium ion by electrophilic attack by the acidic species. An entering thiocyanate ion, exerting a strong trans influence, may labilize

the position trans to it with the breaking loose of an end of a second ethylenediamine molecule. A second thiocyanate ion attaches itself at this vacated position. The loosening of the attached end of one of the monocoordinated en molecules, followed by the attachment of the other, completes the process. In the case of $[Cr(en)_3]Cl_3$, either the chloride ion may not exert a strong enough trans effect or may exert a cis effect, the results being indistinguishable.

Part II.

Many examples of linkage isomerism are known involving CN^-, SCN^-, $SeCN^-$, and NO_2^- as ligands. Several compounds containing these ligands are known to undergo transformations from one form to another. Shriver, et al., predicted that the most stable form of $KFeCr(CN)_6$ would contain Fe^{2+} surrounded in an octahedral arrangement by the carbon ends of the cyanides and the Cr^{3+} would be surrounded in a similar arrangement by the nitrogen ends.[6] These workers found spectral evidence to show that if $Cr(CN)_6^{3-}$ is treated with Fe^{2+}, the resulting complex exhibits linkage isomerization in the solid state. The C≡N stretching band is found at 2168 cm^{-1} in Cr^{3+}-C≡N-Fe^{2+} and at 2092 cm^{-1} in Cr^{3+}-N≡C-Fe^{2+} linkages. In a subsequent report, this system was studied in greater detail using IR, x-ray diffraction, magnetic susceptibility, and Mössbauer spectroscopy.[7] The product containing iron(II) hexacyanochromate(III) was reported to have a variable composition and the linkage isomerization was accompanied by some oxidation. The reaction was reported to follow approximately first order kinetics and gave a fairly linear Arrhenius plot corresponding to an activation energy of 17 kcal/mole.

In the work carried out on this reaction, it was found that the linkage isomerization in a compound containing Fe^{2+} and Cr^{3+} in about a 1:1 ratio followed a second order rate law with a good linear fit of the data. The reaction was followed by the relative intensity of the peaks at 2168 and 2092 cm^{-1}. An activation energy of 24.1 kcal/mole was obtained.[8] The second order rate law implies that the cyanide ions change bonding modes in pairs, probably by a process involving a cis or trans effect depending on whether a cis or trans pair flips.

References:

1. P. Pfeiffer, P. Koch, G. Lando, and A Trieschmann, Ber., 37, 4269, 4277 (1904).

2. C. L. Rollinson and J. C. Bailar, Jr., J. Am. Chem. Soc., 66, 641 (1944).

3. T. D. O'Brien and J. C. Bailar, Jr., J. Am. Chem. Soc., 67, 1856 (1945).

4. J. L. Bear and W. W. Wendlandt, J. Inorg. Nucl. Chem., 17, 286 (1961).

5. J. E. House, Jr., and J. C. Bailar, Jr., J. Am. Chem. Soc., 91, 67 (1969).

6. D. F. Shriver, S. A. Shriver, and S. E. Anderson, Inorg. Chem., 4, 725 (1965).

7. D. B. Brown, D. F. Shriver, and L. H. Schwartz, Inorg. Chem., 7, 77 (1968).

8. J. E. House, Jr., and J. C. Bailar, Jr., Inorg. Chem., 8, 672 (1969).

NMR OF SOLUTES CONTAINING SPIN 1/2 NUCLEI IN NEMATIC LIQUID CRYSTAL SOLVENTS

Joel H. Elias May 12, 1970

Introduction:

The study of nuclear magnetic resonance spectroscopy of solutes dissolved in liquid crystal solvents began in 1963 with the publication by Saupe and Englert[1] of the spectrum of benzene dissolved in a nematic solution. They interpreted the complex spectrum observed in terms of the direct magnetic dipole-dipole interraction between magnetic nuclei. The theory of such interractions in molecules oriented in strong electric fields was first outlined by Buckingham and Pople.[2] The spin Hamiltonian for solute molecules ordered in nematic liquid crystals has been derived by Saupe[3,4] in terms of an order matrix S, and by Snyder[5] in terms of an expansion of the angular probability of the applied magnetic field orientations in a molecular fixed coordinate system. Both formulations have been shown to be related.[5] Snyder and Anderson[5,6] have applied computer techniques to both the experimental and analytical aspects of this method. By using the computer of average transients method, they obtained highly resolved spectra. Computer simulated spectra were employed in the analysis of experimental spectra.

Interpretation of the NMR spectra obtained by this method can yield much useful chemical information. Structural information such as bond lengths and angles,[4-7,9,10] absolute signs of indirect spin-spin coupling constants,[4-7,9,10] chemical shift anisotropies,[4,11] and quadrupolar coupling constants have been obtained.

This seminar will examine the theory of NMR spectra of solutes in nematic liquid crystal solvents and its application to the determination of molecular structures, chemical shift anisotropies, and absolute signs of indirect spin-spin coupling constants.

Theory:

The general spin Hamiltonian for magnetic nuclei is given by:

$$H = -\frac{h}{2\pi}\,\vec{H}_0 \cdot \sum_p \gamma_p\left(\overleftrightarrow{1} - \overleftrightarrow{\sigma}_p\right) \cdot \overleftarrow{I}_p + h\sum_{p>q} \vec{I}_p \cdot \overleftrightarrow{A}_{pq} \cdot \overleftarrow{I}_q \qquad (1)$$

where γ is the magnetogyric ratio, H_0 is the applied field, $\overleftrightarrow{\sigma}$ is the shielding tensor, $\overleftrightarrow{A}$ is a general spin coupling tensor which includes indirect, direct, inter-, and intramolecular interractions, and I is the nuclear spin angular momentum operator.

The general Hamiltonian can be reduced to the following form:[4]

$$H = -\frac{h}{2\pi} H_z \sum_p \gamma_p (1 - \sigma_p - \delta_p) I_{zp} + h \sum_{p>q} J_{pq} \vec{I}_p \cdot \overleftarrow{I}_q$$

$$+ h \sum_{p>q} B_{pq} (3 I_{zp} I_{zq} - \vec{I}_p \cdot \overleftarrow{I}_q) \qquad (2)$$

if terms coupling stationary states having different eigen values of the operator $F_z = \sum_p I_{zp}$ are neglected.[5] σ_p is the scalar shielding constant, δ_p is the orientation dependent shielding anisotropy, J_{pq} is the scalar indirect spin-spin coupling constant, B_{pq} is a spin-spin coupling constant which contains the anisotropic part of the indirect spin-spin coupling constant, and the direct magnetic dipole-dipole interraction.

The direct spin-spin coupling constant is given by:[4]

$$B^{dir}_{pq} = -\frac{h}{4\pi^2} \gamma_p \gamma_q \left\langle \frac{1}{r^3_{pq}} \right\rangle \frac{1}{2} \left\langle 3 \cos^2 \theta_{pq} - 1 \right\rangle \qquad (3)$$

$$= -\frac{h}{4\pi^2} \gamma_p \gamma_q \left\langle \frac{1}{r^3_{pq}} \right\rangle S_{pq}$$

$$\text{where} \quad S_{pq} = \frac{1}{2} \left\langle 3 \cos^2 \theta_{pq} - 1 \right\rangle \qquad (4)$$

r_{pq} is the internuclear distance, θ_{pq} is the angle between the internuclear axis and the applied field, and the brackets indicate averages over the molecular motion. The indirect contribution to B_{pq} appears to be negligible for proton-proton spin-spin couplings.[6] In isotropic liquids, the expectation values S_{pq} vanish and direct dipolar coupling is not observed.

Nematic liquid crystal solvents can be more or less completely homogeneously oriented by magnetic fields of the order of a few thousand gauss. Solute molecules dissolved in such oriented solvents are ordered to some degree by the anisotropic environment. Intramolecular dipolar interactions no longer average to zero and dipolar splittings are observed in the NMR spectrum of the solute. The solute molecules, while ordered, translate and rotate rapidly with respect to the solvent, and intermolecular dipolar coupling vanishes.

The degree of order of the solute is described[3] by an S matrix which may have up to five independent elements of the form:

$$S_{ij} = \frac{1}{2}\left\langle 3\cos\theta_i \cos\theta_j - \delta_{ij} \right\rangle \quad i,j = \xi, \eta, \zeta \qquad (5)$$

ξ, η, and ζ are the axes of a molecular fixed coordinate system, θ_i are the angles between the given axis and the optical axis of the aligned solvent and δ_{ij} is the Kroenecker delta function. The observed splittings are shown in equation (3) to depend on the values of S_{pq}, which are related to the S_{ij} by a cosine transformation, and $\left\langle 1/r^3_{pq} \right\rangle$. The amount of structural and motional information which can be derived from the spectrum depends on the number of direct dipolar interractions.

Applications:

Structural studies in nematic crystal solvents are presently limited to molecules containing no more than nine magnetic nuclei.[7] The spectra of molecules containing more than nine magnetic nuclei may not be sufficiently resolved and analysis by computer simulation becomes prohibitively costly. It should be noted that this method measures the average values over molecular vibrations $\left\langle 1/r^3_{pq} \right\rangle$ and not equilibrium internuclear distances.

In the analysis of chemical shielding anisotropies, contributions to δ due to volume susceptibility changes in the solvent, and anisotropic solvent effects must be considered.

Future:

The method of NMR in liquid crystals has proven to be useful for the determination of structural parameters for small molecules in solution. Selective deuteration and spin decoupling[7] may be used in the future to extend its application to larger molecules.

Absolute signs of indirect spin-spin coupling constants will be useful in the evaluation of theoretical calculations.[8]

References:

1. A. Saupe and G. Englert, Phys. Rev. Letters, 11, 462 (1963).

2. A. D. Buckingham and J. A. Pople, Trans. Faraday Soc., 59, 2421 (1963).

3. A. Saupe, Z. Naturforsch, 19a, 161 (1964).

4. A. Saupe, G. Englert, and A. Pouh, Adv. in Chemistry Series, 63, 51 (1967).

5. L. C. Snyder, J. Chem. Phys., 43, 4041 (1965); 47, 1480 (1967).

6. L. C. Snyder and E. W. Anderson, J. Am. Chem. Soc., 86, 5023 (1964); J. Chem. Phys., 42, 3336 (1965).

7. S. Meiboom and L. C. Snyder, Science, 162, 1337 (1968).

8. R. A. Bernheim and B. J. Lavery, J. Am. Chem. Soc., 89, 1279 (1967).

9. C. S. Yannoni, G. P. Ceasar, and B. P. Dailey, J. Am. Chem. Soc., 89, 2833 (1967).

10. G. Englert and A. Saupe, Mol. Cryst., 1, 503 (1966); 8, 233 (1969).

11. G. P. Ceaser, C. S. Yannoni, and R. P. Dailey, J. Chem. Phys., 50, 373 (1969); 51, 655 (1969).

APPLICATIONS OF ELECTRON DIFFRACTION TO INORGANIC COMPOUNDS

Ramsey H. Gitany May 21, 1970

Introduction:

It is now 32 years since Davisson and Germer first demonstrated the phenomenon of electron diffraction. Since then the electron diffraction method has been widely applied in the study of the structure of matter. It is the purpose of this seminar to review electron diffraction techniques and to show how they can be used to solve problems in inorganic chemistry. There seems to be no recent text or review which covers all topics of interest in electron diffraction, and each year new theories and techniques are developing.

Theory:

An electron diffraction experiment[1] consists primarily of the determination of the total (t) diffracted intensity, $I_t(s)$, as a function of the angle of diffraction (2θ). In the case of molecular (m) scattering, the diffracted intensity becomes $I_m(s)$ and is given by

$$I_m(s) = (K/s^4) \sum_{i \neq j}\sum (Z_i - f_i)(Z_j - f_j) \exp\left[-(1/2)(U_{ij}^2 s^2)\right]\left[(\sin R_{ij}^e s/(R_{ij}^e s)\right] \qquad (1)$$

$$\mu(r) = \text{Radial distribution} = (2/\pi)\int_0^\infty s^5 I_m(s)\phi(s) \sin r s \, ds \qquad (2)$$

Instead of the diffraction angle 2θ, it is convenient to write the dependence on $s = (4\pi/\lambda)\sin\theta$, where λ is the wave length and θ the Bragg angle (one half the diffraction angle). K is an instrumental constant at constant electron velocity, Z_i is the atomic number of the i th atom, f_i is the scattering amplitude of the i th atom, and R_{ij}^e is the equilibrium distance (Å) between the i th and the j th atom in the molecule. The root-mean-square deviation distance is U_{ij}, usually called "mean amplitude of vibration." $\mu(r)$, the radial distribution function (RD), gives the probability that a nucleus $\underline{j}$ will be found at a distance $\underline{r}$ from a nucleus $\underline{i}$ in the molecule. $\phi(s)$ is a modification function to simplify the RD curve. Thus $\mu(r)$ will have a maximum for each value of $\underline{r}$ corresponding to an internuclear distance in the molecule. Bond angles in a molecule can also be computed if sufficient neighboring internuclear distances are known. In short, the theoretical curve contains molecular structural information, namely the interatomic distances and U values. The validity of eqn. (1) is limited by the following assumptions: (1) small harmonic oscillations of the atoms occur, (2) no phase shift occurs in the scattering process.

In the actual experiment two things are particularly important. The $1/s^4$ factor in the expression for $I_m(s)$ is responsible for the steep fall off in the total intensity curve with diffraction angle. This effect is minimized by using a rotating sector to enhance the higher angle data. Also, the electron diffraction diagrams depend critically upon the gas nozzle which spreads out the gas in the apparatus.

Applications:

Some topics of current interest in electron diffraction are listed below.

I. Molecular structure

II. Molecular force fields, which give information about:

    A. Internal rotation
    B. Quadratic force constants from amplitudes of vibration
    C. Cubic force constants from effect on intermolecular distances of

        *(1) temperature[2]
        (2) isotopic substitution

III. Charge distributions in atoms and molecules

    A. In ground state:

        (1) $D_i(r)$ distribution of electrons about nuclei
        **(2) $P_{ij}(r)$ distribution of electrons about other electrons
        (3) $P_{mn}(r)$ distribution of nuclei about other nuclei

    B. In excited states: Information about geometry of excited state orbitals[3]

IV. Intermolecular forces in gases
    From nonuniform distribution of molecules[4]

V. Surfaces of solids
    Low energy electron diffraction (LEED)

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* Experiments to data rather rough
** Only a gleam in eyes of electron diffractionists

The main features of the molecular structure of ferrocene and ruthenocene have been firmly established[5,6] by X-ray diffraction in the crystal. However, the position of the hydrogen atoms and the shape and height of the barrier to internal rotation of the ligand in the isolated molecule remained unknown. In X-ray investigations, in the absence of contradictory evidence, the hydrogen atoms have been assumed to lie in the plane of the cyclopentadienyl ring (D_{5h} symmetry). Recent electron-diffraction experiments[7,8] by Haaland et. al. show that in the case of hydrogen atoms in ferrocene in the gas phase this assumption is invalid. The hydrogen atoms are bent about 5° out of the plane towards the metal atom. These workers also measured the barrier to internal rotation and concluded that the eclipsed model

of ferrocene seems the most probable in the gas phase although a freely rotating one cannot be excluded. The barriers to internal rotation in ferrocene and ruthenocene are, respectively, 0.91 ± 0.32 and 26±49 kcal mole^{-1} (ruthenocene value unsatisfactory). The origin of the barrier has been ascribed to ligand-to-metal-to-ligand bonding, or to Van der Waals' attraction between the rings.

We now address ourselves to the problem of calculating electron densities from gas-phase electron diffraction experiments.[9] A few experimental measurements[10,11] have been made which indicate that charge distributions can be obtained to an accuracy that is chemically meaningful. If r is the internuclear distance, then, according to the first Born approximation, the total intensity of scattered electrons depends on the sine transforms of (a) the nuclear charge distribution, i.e., the position of the nuclei in the scatterer, (b) the electron density $\rho(r)$ (related to $D_i(r)$ and $\sigma_{ne}(s)$ below) relative to the nuclear framework, and (c) the electron-electron function $\rho_c(r)$ (related to $P_{ij}(r)$ and $\sigma_{ee}(s)$ below) describing the density of electrons relative to the other electrons. The intensities must be averaged over all orientations of the scatterer. For a homonuclear diatomic molecule if one of the nuclei is chosen as the origin of the coordinate system and if the position of the other nucleus is given by the vector r_{aB}, the total scattered intensity for electrons can be expressed as

$$\sigma_{tot}(s) \doteqdot f_1[\rho(r)] + f_2[\rho_c(r)] \qquad (3)$$

$$\sigma_{tot} = S^4 I_{tot} = f_3[D_i(r)] + f_4[P_{ij}(r)] \qquad (4)$$

$$\sigma_{tot} = \sigma_{ne}(s) + \sigma_{ee}(s) \qquad (5)$$

where $D_i(r)$ and $P_{ij}(r)$ have been defined previously, and $\sigma_{ne}(s)$ and $\sigma_{ee}(s)$ are, respectively, the electron-nuclear and electron-electron contribution to the total scattered intensity. In principle $\rho(r)$ could be determined from the above expressions but this is quite difficult to do. It is easier to calculate differential cross sections. The sensitivity of the diffraction approach will be gauged from a comparison of results for molecules following Hartree-Fock theory with results for hypothetical molecules built up of independent Hartree-Fock atoms. The difference functions which are used are of the form $\Delta\sigma(s) = \sigma(s) - \sigma(s)$, where $\sigma^{iam}(s)$ is a reference function. Of special interest is the Roux function[12] $\Delta\rho(r) = \rho(r) - \rho_{atom}(r)$, the function corresponding to the difference between molecular electron density and the sum of the densities of the free atoms separated by a distance r_{AB}. There is the problem of uniqueness in the transformation from $\sigma_{ne}(s)$ to $\rho(r)$. On the other hand there is no problem as to the uniqueness in the transformation from $\rho(r)$ to $\sigma_{ne}(s)$, and the scattered intensity may prove to be more suitable as a test of computed electron densities than as a means for determining densities directly (the analogy here with X-ray crystallography is helpful). Since the potential energy difference, $\Delta\overline{U}$, between the actual molecule and the independent-atom molecule can be calculated rather well by electron diffraction, the method may prove to be one of the best observables in addition to the total energy for determining the quality of computed wavefunctions.

In the last few years low energy diffraction (LEED), where electrons are mainly reflected from atoms at the surface, has been developed to provide information on the two dimensional structure and constitution of surfaces. The method is best applied to surfaces which are well defined on the atomic scale. The particular usefulness of LEED for studying adsorption processes arises from the fact that adsorption usually results in some degree of order so that distinct diffraction patterns will appear and any new periodicity parallel to the substrate surface is easily established. Various applications of LEED are physical adsorption,[14] adsorption of metal atoms,[15] chemisorption[16] and heterogeneous catalysis.[17] Surface structures have been found for the adsorption of CO, n_2, C_2H_4, C_2H_2, O_2 on Pt(100) and Pt(111) surfaces. Other molecules (C_2H_6, H_2) gave no evidence for ordered structures. The results are interpreted as indicating sp^2 hybridization of the carbon atoms in the adsorbed state.

Conclusion:

Electron diffraction has had a rather varied history of triumphs and failures. Although it is thought of as a tool for measuring molecular structure in the gas phase, recently we have begun to be aware of its potential power for probing more deeply into the quantum chemistry of molecules. The development of LEED is revolutionizing the study of surface chemistry and catalysis. The electron diffraction method is blossoming into a number of promising directions and it is contributing significantly to the progress of chemistry.

References:

1. O. Bastiansen and P. N. Skancke, Advan. Chem. Phys., 3, 323 (1961).
2. K. Hedberg and M. Iwasaki, J. Chem. Phys. 36, 589 (1962).
3. J. Karle, J. Chem. Phys. 35, 963 (1961).
4. Y. Morino, K. Kuchitsu, and R. A. Bonham, Bull. Chem. Soc. Japan 38, 1796 (1965).
5. J. D. Dunitz, L. E. Orgel, A. Rich, Acta Cryst. 9, 373 (1956).
6. G. L. Hardgrave and D. H. Templeton, Acta Cryst. 12, 28 (1959).
7. R. K. Bohn and A. J. Haaland, J. Organomet. Chem. 5, 470 (1966).
8. A. Haaland and J. E. Nilsson, Acta. Chem. Scand. 22, 2653 (1968).
9. D. A. Kohl and L. S. Bartell, J. Chem. Phys. 51, 2891-2904 (1969).
10. D. A. Kohl and R. Bonham, J. Chem. Phys. 47, 1634 (1967).
11. M. Fink and J. Kessler, J. Chem. Phys. 47, 1780 (1967).
12. M. Roux, S. Besnainou and R. Daudel, J. Chim. Phys. 54, 218 (1956); M. Roux, M. Cornille, and L. Burnelle, J. Chem. Phys. 37, 933 (1962); C. W. Kern and M. Karplus, J. Chem. Phys. 40, 1374 (1964).
13. D. H. Templeton and G. A. Somorjai, eds., Trans. Amer. Crystallogr. Assoc. 2 (1968).
14. J. Morrison and J. J. Lander, Surf. Sci. 5, 163 (1966).
15. P. W. Palmberg and W. T. Peria, Surf. Sci. 6, 57 (1967).
16. P. J. Estrup and J. R. Anderson, J. Chem. Phys. 45, 2254 (1966).
17. A. E. Morgan and G. A. Somorjai, Trans. Amer. Crystallogr. Assoc. 2, 59 (1968).

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INORGANIC SEMINAR ABSTRACTS

1969-1970

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ENERGY-TRANSFER PROCESSES IN RARE EARTH CHELATES[1]

Mary Ellen Phelan September 23, 1969

Introduction

In 1942 Weissman[2] discovered that Eu(III) line emissions occur when the tris salicylaldehyde complex is irradiated anywhere in the absorption band of salicylaldehyde. $EuCl_3$ gives these emissions only when irradiated at the specific wavelengths 3200 and 3920 A; also no absorbance characteristic of europic ion is observed in the spectrum of the chelate. Hence, Weissman attributes this effect to an intramolecular energy transfer.

It will be the purpose of this seminar to examine the nature of the energy-transfer processes in rare earth chelates and the experimental methods used to study them.

The Role of the Triplet State: Semiquantitative Studies

Absorption spectra of rare earth chelates depend on the ligand, not on the central ion. Emission spectra, by contrast, vary appreciably with the central ion. Whan and Crosby[3] found the following luminescence characteristics for various tris benzoylacetonates (B) irradiated in the first absorption band of the ligand:

1. GdB_3, LaB_3, LuB_3 and NaB all are characterized by high yields of total luminescence, well-defined molecular fluorescence and phosphorescence characteristic of the ligand and no line emission. The ratio of phosphorescence to fluorescence is very high.

2. PrB_3, NdB_3, HoB_3, ErB_3, TmB_3 and YbB_3 all have low yields of total luminescence, low ratios of phosphorescence to fluorescence, and weak line emission characteristic of the central ion.

3. The remaining chelates (SmB_3, EuB_3, TbB_3, DyB_3) show primarily the bright line emissions characteristic of the central ion. Similar trends exist for the tris dibenzoylmethides, except that no line emission occurs from the Dy(III) complex. With these compounds, with other β-diketones[4,5,6] and with bipyridyl and terpyridyl complexes;[7,8] no ion emission is observed unless the lowest triplet of the ligand lies nearly equal to or above the resonance (emissive) level of the ion.

Crosby et al.[6] interpret these data in terms of mechanism I. However, mechanism II explains the correlation with the ligand triplet, and so does mechanism III with the added postulate of possible quenching of the rare earth resonance level by the ligand triplet:

I. $S_0 \rightarrow S_1 \rightsquigarrow T_1 \rightsquigarrow$ RE $\rightarrow$ emission

II. $S_0 \rightarrow S_1 \rightsquigarrow$ RE levels higher than $T_1 \rightsquigarrow T_1 \rightsquigarrow$ RE resonance levels $\rightarrow$ emission[9]

III. $S_0 \rightarrow S_1 \rightsquigarrow$ RE levels higher than resonance $\rightsquigarrow$ RE resonance levels $\rightarrow$ emission[10]

The Mechanism of the Intramolecular Energy Transfer

One question remains: What is the mechanism of energy transfer in the rare earth chelates? Crosby and coworkers[6,11] and Filipescu et al.[12] postulate energy transfer to the metal ion by an exchange mechanism involving vibronic coupling of the ligand triplet and the ion levels. At present, it is not possible to distinguish among the following three possibilities:

1. The resonance level of the ion is definitely below the triplet state and transfer can occur from the zeroth vibrational level of the latter to some vibronic state of the metal ion.

2. Crossing between the triplet and ion resonance levels comes at upper vibrational levels.

3. The resonance level is slightly above the triplet state.

McAvoy et al.[13] propose an alternate mechanism, a slight electronic mixing of the ligand triplet with the ion levels. The molecular triplet is associated with a biradical structure involving two unpaired spins formed by rupture of a bond. These spins arrange themselves for minimum overlap and at least one of them will increase the electron density at the oxygen-rare earth (or nitrogen-rare earth) bond.

Weak Ion Emitters: Vibronic Coupling to Surroundings

On the basis of these relatively qualitative studies, it is still possible to explain the occurrence of weak ion emitters. (These also have low yields of total luminescence.) The chemical similarities throughout a series of chelates suggests that the extent of the energy transfer is also similar.[6] The high yields of bright line emission in Eu(III) and Tb(III) chelates suggest efficient transfer to the ions. It has therefore been postulated that most of the quenching of rare earth ion emission occurs after transfer to the ion. The ions which have low yields of emission are those which have a number of closely packed ion excited states in which excess energy can readily be dissipated non-radiatively. For the efficient ion emitters, large gaps exist between these levels.

Whan and Crosby[3] suggest that the principal mechanism for quenching luminescence in the rare earth ion levels is through vibronic coupling to the ligands and thence to the surrounding solvent. Satellite lines attributable to vibronic progressions are observed on the more intense peaks.

Quantitative studies of quantum yield as a function of temperature and selective excitation of various levels give further insight into the quenching process; these will be discussed later.

Intermolecular Transfer and Quenching Studies

The studies of Heller and Wasserman[14] establish that the triplet of the organic species takes part in the intermolecular transfer reaction with rare earth chelates. Bhaumik and El-Sayed[15] rule out the possibility of direct transfer to the rare earth ion and establish the path of intermolecular transfer as $T^*_{\text{donor}} \rightsquigarrow T^*_{\text{ligand}} \rightsquigarrow \text{RE} \rightarrow$ emission.

The idea that intramolecular transfer involves the ligand triplet is put on a firmer basis by Bhaumik and El-Sayed's study[9,15] of the reaction of rare earth chelates with a series of organic quenchers. Cis-piperylene does not react with singlet states but does quench rare earth ion emission when the triplet of the ligand lies higher in energy than the quencher's triplet. The authors demonstrate that intermolecular quenching does not depend on the rare earth levels and set an upper limit of 10% for the extent of intramolecular transfer directly from the ligand singlet to the rare earth levels. From these studies, the authors obtained 10^{10} sec^{-1} for the intersystem crossing rate.

Preparative Problems

Rare earth chelates exist in both a tris and a tetrakis form with different spectra, lifetimes and decay curves.[16,17] Adduct formation[18-21] and partial dissociation[22,23] in solution and different crystalline forms[24] have been found. Many preparations are sensitive to changes in pH or order of mixing. The piperidinium salt of the ligand is a common impurity in early preparations. Hence, particularly in evaluating quantitative studies, one must be careful to consider only adequately characterized chelates.

Spectra and Energy Levels

Spectral transitions and ordering of ion energy levels in rare earth compounds are essentially independent of the ligand. For the rare earths e^2/r_{ij} is about 20,000 cm^{-1}, the spin-orbit interaction about 1000 cm^{-1} and the ligand field interaction about 100 cm^{-1}.[21] Hence, complete characterization of the compound is not so essential when one is assigning energy levels.

Studies Using More Elaborate Methods

Bhaumik and Telk[25,26] used the quantum counter technique to measure the absolute quantum yields of a series of rare earth chelates as a function of temperature. Results indicate rapid transfer to the ion levels. But two observations suggest that some quenching occurs in the ligand prior to transfer: different chelates have slightly different fluorescence decay times at liquid-nitrogen temperature; as the temperature increases, the quantum yield falls more quickly than the fluorescence decay time. The facts that the compounds with the highest yields are also those with the longest lifetimes and that the rise time of $^5D_0 \rightarrow {}^7F_2$ fluorescence equals the decay time of the $^5D_1 \rightarrow {}^7F$ transitions[27,28] are further evidence for radiationless deactivation of rare earth levels via a cascade mechanism.

The most cogent evidence for this type of radiationless deactivation is provided by Kropp and Dawson,[29,30] who selectively excited upper levels of ammonium or pyperidinium tetrakis β-diketone chelates and measured the quantum yield for the radiative transition characteristic of the ion. Their results indicate that the quantum yield is lower the higher the energy level excited. The extent of quenching in the ligand is about comparable to that in the ion.

Summary

We have seen then that the energy is absorbed by the ligand singlet and transferred to a triplet level at a rate of about 10^{11} sec^{-1}. Transfer to the rare earth manifold occurs with a rate constant of 10^{10} sec^{-1}.[9,31] Both the transfer of energy from the ligand to the ion and the radiationless transitions within the ion manifold appear to occur by a vibronic coupling mechanism.

References

1. G. A. Crosby, *Molecular Crystals*, *1*, 37 (1966).
2. S. L. Weissman, *J. Chem. Phys.*, *10*, 214 (1942).
3. R. E. Whan and G. A. Crosby, *J. Mol. Spectry.*, *8*, 315 (1962).
4. G. A. Crosby and R. E. Whan, *Naturwiss.*, *47*, 276 (1960).
5. G. A. Crosby and R. E. Whan, *J. Chem. Phys.*, *32*, 614 (1960).
6. G. A. Crosby *et al.*, *J. Chem. Phys.*, *34*, 743 (1961).
7. S. P. Sinha, *Z. Naturforsch.*, *20a*, 164 (1965).
8. S. P. Sinha, *Z. Naturforsch.*, *20a*, 835 (1965).
9. M. L. Bhaumik and M. A. El-Sayed, *J. Chem. Phys.*, *42*, 787 (1965).
10. M. Kleinerman, *Bull. Am. Phys. Soc.*, *9*, 265 (1964).
11. G. A. Crosby and M. Kasha, *Spectrochim. Acta*, *10*, 377 (1958).
12. N. Filipescu *et al.*, *J. Phys. Chem.*, *68*, 3324 (1964).
13. N. McAvoy *et al.*, *J. Phys. Chem. Solids*, *25*, 461 (1964).
14. A. Heller and E. Wasserman, *J. Chem. Phys.*, *42*, 949 (1965).
15. M. L. Bhaumik and M. A. El-Sayed, *J. Phys. Chem.*, *69*, 275 (1965).
16. M. L. Bhaumik and I. R. Tannenbaum, *J. Phys. Chem.*, *67*, 2500 (1963).
17. M. Metlay, *J. Chem. Phys.*, *39*, 491 (1963).
18. R. C. Ohlmann and R. G. Charles, *J. Chem. Phys.*, *40*, 3131 (1964).
19. M. Kleinerman *et al.*, *J. Chem. Phys.*, *41*, 4009 (1964).
20. S. M. Lee and L. J. Nugent, *J. Inorg. Nucl. Chem.*, *26*, 2304 (1964).
21. L. J. Nugent *et al.*, *J. Chem. Phys.*, *41*, 1305 (1964).
22. C. Brecher *et al.*, *J. Chem. Phys.*, *42*, 1081 (1965).
23. M. L. Bhaumik, *J. Inorg. Nucl. Chem.*, *27*, 243 (1965).
24. H. Bauer *et al.*, *J. Am. Chem. Soc.*, *86*, 5125 (1964).
25. M. L. Bhaumik and C. L. Telk, *J. Opt. Soc. Am.*, *54*, 1211 (1964).
26. M. L. Bhaumik, *J. Chem. Phys.*, *40*, 3711 (1964).
27. M. L. Bhaumik and L. J. Nugent, *J. Chem. Phys.*, *43*, 1680 (1965).
28. M. L. Bhaumik, *J. Chem. Phys.*, *41*, 574 (1964).
29. W. R. Dawson *et al.*, *J. Chem. Phys.*, *45*, 2410 (1966).
30. W. R. Dawson and J. L. Kropp, *J. Opt. Soc. Am.*, *55*, 822 (1965).
31. D. L. Ross and J. Blanc, *Adv. Chem. Ser.*, *71*, 155 (1967).

CHEMICALLY INDUCED DYNAMIC NUCLEAR POLARIZATION

Cheryl Johnson September 30, 1969

Introduction

Dynamic nuclear polarization was first predicted by Overhauser in 1953,[1] and was experimentally confirmed, using metallic lithium, by Carver and Slichter.[2] The Overhauser effect, enhanced NMR absorption, was predicted to occur in paramagnetic metals if the NMR sample was simultaneously exposed to microwave resonance radiation. The effect applies only to metals and is the result of hyperfine interactions in unfilled conduction bands which involve nuclear spin flip.

Chemically induced dynamic nuclear polarization (CIDNP) is a similar absorption and emission enhancement which may occur when radicals are produced in a chemically reacting system. CIDNP was first observed independently by two teams of investigators, J. Bargon and H. Fischer,[3] using peroxide and azo compounds, and H. R. Ward and R. G. Lawler,[4] using organometallic compounds.

Discussion

A tentative explanation of the spectra characteristic of CIDNP[5-10] is based on three assumptions.

1. At t=0 (mixing of reagents), the radicals formed populate the two electron spin Zeeman levels equally.
2. In the reaction

$$R\cdot + L \rightarrow R + L\cdot$$

the proton spin orientation of R· relative to the magnetic field, H_o, is held fixed and is transferred to R.

3. The electron spin and proton spins of R couple.

By the first assumption, at t=0 the population difference is given by

$$P_e = \frac{e_+ - e_-}{e_+ + e_-} = 0$$

The electrons undergo spin-lattice relaxation and approach the Boltzman equilibrium distribution, where

$$P_e = \gamma_e \hbar H_o/2kT$$

The nuclear spin population difference, p_n, which at t=0 equalled P_n^o, becomes much larger than the equilibrium value as a result of the coupling with the electron spin. After the electron spins approach p_e^o, the nuclear spins will relax through nuclear spin-lattice interactions and will again approach p_n^o. This relaxation occurs much more rapidly in radicals than in diamagnetic species. Hence, if the radical formed has a fairly long lifetime ($>10^{-4}$ sec), the nuclear spins relax rapidly and the abnormal distribution will disappear. If, however, the radicals react in a time short relative to nuclear relaxation (10^{-8} -10^{-4} sec) to form a diamagnetic species, nuclear relaxation occurs slowly and the abnormal population distribution of nuclear spins may be observed in NMR spectra as emission and enhanced absorption.

The above explanation proposed by Ward, Lawler, Fischer, Bargon, and others[7,8,14] is disputed by Kaptein[6] and Closs.[16] These investigators propose a mechanism that is essentially the reverse. The radicals are produced with an equilibrium population. Because the reaction of radicals to form a diamagnetic species requires equal numbers of each spin orientation, a portion of the electrons must flip after formation of the radicals in order to fulfill this requirement. Due to coupling an equal number of nuclei must also flip and polarization occurs.

An interesting feature of CIDNP is its effect on multiplets.[17,20,3] In many systems, both emission and enhanced absorption occur in the same spin-spin multiplet. This effect is not predicted by the general theory and can be explained only by assuming that there is some dependence of the rates of population of the radical electron spin states on the associated nuclear spin states.

Another peculiar effect occurs in alkyllithium systems. The peaks due to the organolithium species do not show the effects of CIDNP, and in several cases, the normal pmr signal of the alkyl group coordinated to the lithium atom is completely lost a short time after the reaction begins.[6,19,20] One proposed explanation for the absence of CIDNP effects is that the radicals form a weak cage complex with the R_nLi_n species[6,14,18,19,20,21] and through a charge transfer-radical trapping sequence lengthen the lifetime of the free radical, thereby allowing time for normal relaxation. The disappearance of the signal is attributed to exchange broadening.[6]

The presence of paramagnetic impurities[3,8] in the reacting solution results in a decrease in the amplitude of the emission and a shift of the maximum emission to shorter times. It is postulated that this is a result of relaxation of the free radical electron spins caused by the ions.

The amplitude of the emission is also a function of the applied magnetic field.[3,11] The amplitude is inversely proportional to the applied field and maximum amplitude shifts slightly to longer times with increasing field.

From preliminary studies, it appears that solvent effects can significantly affect the spectra.[12,13]

Conclusions

Most research in CIDNP thus far has been in the study of pmr spectra in order to confirm the presence of a radical intermediate, to clarify the mechanism of a reaction, or, as Closs and Trifunac[22] have suggested, to determine the spin multiplicity of the radical-pair precursor. Recently, however, Bragon and Fischer began studies of CIDNP using ^{19}F spectra.[23]

Although as yet we cannot fully assess the potential of CIDNP, it appears that it will become a valuable tool in the study of mechanisms and kinetics of radical reactions.

References

1. A. W. Overhauser, Phys. Rev., 92, 411 (1953).
2. T. R. Carver and C. P. Slichter, Phys. Rev., 102, 975 (1956).
3. H. Fischer and J. Bargon, Accts. Chem. Res., 2, 110 (1969).
4. H. R. Ward and R. G. Lawler, J. Am. Chem. Soc., 89, 5518 (1967).
5. J. Bargon, H. Fischer, and U. Johnsen, Z. Naturforschg., 22a, 1551 (1967).
6. T. L. Brown, to be published.
7. R. G. Lawler, J. Am. Chem. Soc., 89, 5519 (1967).
8. J. Bargon, H. Fischer, and U. Johnsen, Z. Naturforschg., 22a, 1556 (1967).
9. R. Kaptein, Chem. Phys. Ltrs., 2, 261 (1968).
10. D. Stehlik and K. H. Hausser, Z. Naturforschg., 22a, 914 (1967).
11. K. H. Hausser, Z. fur Physik, 183, 265 (1965).
12. Anon., Chem. and Eng. News, 46, 40 (Jan. 15, 1968).
13. G. A. Russell and D. W. Lamson, J. Am. Chem. Soc., 91, 3967 (1969).
14. H. R. Ward, R. G. Lawler, H. Y. Loken, J. Am. Chem. Soc., 90, 7359 (1968).
15. A. R. Lepley, J. Am. Chem. Soc., 90, 2710 (1968).
16. G. L. Closs, J. Am. Chem. Soc., 91, 4552 (1969).
17. A. R. Lepley, J. Am. Chem. Soc., 91, 749 (1969).
18. F. S. D'yachkovskii and A. E. Shilov, Russ. Chem. Revs. (English Transl.), 35, 300 (1966).
19. A. R. Lepley and R. L. Landau, J. Am. Chem. Soc., 91, 748 (1969).
20. A. R. Lepley, Chem. Comm., 64 (1969).
21. H. R. Ward, R. G. Lawler, R. A. Cooper, J. Am. Chem. Soc., 91, 746 (1968).
22. G. L. Closs and A. D. Trifunac, J. Am. Chem. Soc., 91, 4554 (1969).
23. H. Fischer and J. Bargon, Z. Naturforschg., 23a, 2109 (1968).
24. C. G. Screttas and J. F. Eastham, J. Am. Chem. Soc., 88, 5668 (1966).
25. D. E. Applequist and D. F. O'Brien, J. Am. Chem. Soc., 85, 743 (1963).
26. G. L. Closs and L. E. Closs, J. Am. Chem. Soc., 91, 4549 (1969).
27. G. L. Closs and L. E. Closs, J. Am. Chem. Soc., 91, 4550 (1969).
28. H. R. Ward, R. G. Lawler, H. Y. Loken, and R. A. Cooper, J. Am. Chem. Soc., 91, 4928 (1969).
29. J. Bargon and H. Fischer, Z. Naturforschg., 23a, 2109 (1968).
30. H. R. Ward, R. G. Lawler, and R. A. Cooper, Tetrahedron Letters, 7, 527 (1969).

THE THEORY OF ELECTRON TRANSFER REACTIONS: THE MARCUS APPROACH

John K. Orrell October 14, 1969

Introduction

Although Marcus has discussed and developed equations[1-6] for treating both homogeneous electron transfer reactions in solution and reactions at electrodes, this seminar will be confined to a discussion of the former. It is also pointed out that his theoretical development applies to direct electron transfer reactions which proceed via an outer-sphere mechanism and in which the inner coordination shells remain intact.

Theory

One can describe the course of an electron transfer reaction by making use of potential energy surfaces. The potential energy at each point on the surface represents the sum of the electronic kinetic and potential energies and the nuclear potential energy.[7] The full display is usually represented as a contour map, but the form more familiar in the literature is a two-dimensional profile of the variation in the potential energy of the reacting species with a change in the reaction coordinate for the most probable path.[7]

In the case of zero electronic interaction between reacting species, as depicted in Fig. 1a, such a two-dimensional representation consists of two curves, one for the reactants (R), another for the products (P). The abscissa, marked "nuclear configuration" represents any concerted motion of all the atoms in the system leading from an arrangement suited to the electronic configuration of the reactants to one of the products.[6] However, if electronic interaction takes place when the reactants are at the intersection region, then the curves are split as depicted in Fig. 1b. In this case, electron transfer may take place.

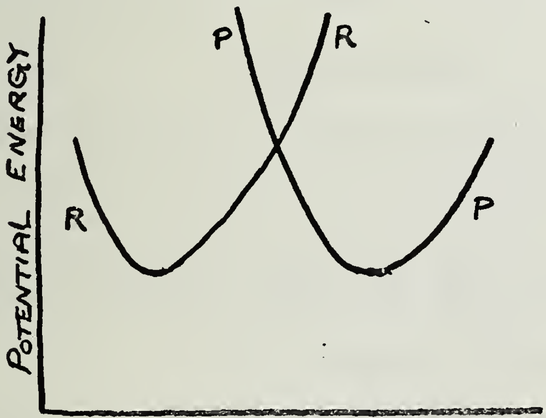

Fig. 1a

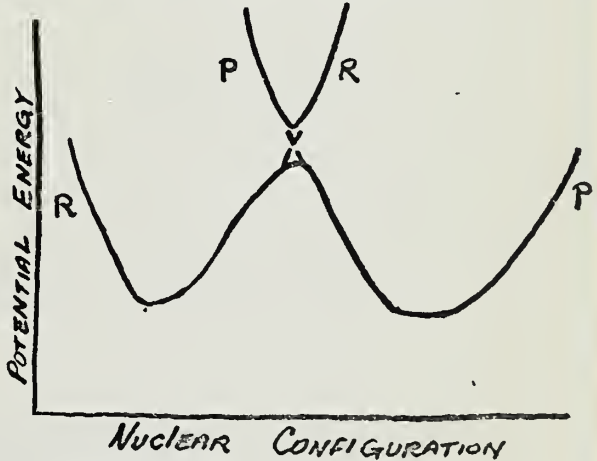

Fig. 1b

Marcus assumed a weak-interaction activated complex in which the electronic interaction is strong enough to cause the probability of electron transfer to be unity, but not large enough to make a contribution to the activation energy. He noted that the activated complex has the nuclear configuration of the intersection region and its electronic configuration should be some intermediate between that of the reactants and that of the products.[1] He also pointed out that so long as the interaction is small, for computational purposes, one could consider the activated complex as composed of two hypothetical states, X* and X. These states have the electronic configurations of the reactants and products, respectively, but the nuclear configuration of the activated complex.[1] To satisfy the law of conservation of energy, these states must have the same total energies.

This energy condition imposes a restraint upon the solvation of the activated complex. The degree of solvent orientation in any state depends to a large extent on whether the reacting species have the charges of the reactants or the products. Now the solvent arrangement in the activated complex and therefore in X* and X is intermediate between that for the reactants and that for the products. Therefore, states X* and X possess a non-equilibrium solvent orientation.

To obtain an expression for the rate constant for comparison with experimental values, Marcus assumed the following reaction scheme:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} X^* \qquad (1)$$

$$X^* \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} X \qquad (2)$$

$$X \xrightarrow{k_3} \text{products} \qquad (3)$$

where by use of a steady state treatment

$$k_{bi} = k_1/[1 + (1 + k_{-2}/k_3)(k_{-1}/k_2)].$$

If $k_{-1} \cong k_2$ and $k_{-2} \cong k_3$ then $k_{bi} \cong k_1$ where k_1 is obtained from the equilibrium constant for eq. (1), namely

$$k_1 = Z\exp(-\Delta F^*/kT)$$

where Z is the collision number and ΔF^* the electrostatic activation free energy.[1] The latter term is simply

$$\Delta F^* = F^* - \mathrm{Wiso}^{s*}$$

where F^* is the electrostatic free energy of X* and Wiso^{s*} is the work done to "charge up" the reactants in the medium at infinite separation.

Marcus pointed out that since the atomic configuration of all the atoms is fixed in the states X* and X, not only do the total energies have to be the same but the configurational entropies must also be the same. Hence, with the exception of a negligible entropy difference, ΔSe, due to electron degeneracy differences, the free energies of X* and X must be the same.[1] This is summarized in the expression for the overall free energy change:

$$\Delta F^{o} = (F^{*} - \mathrm{Wi}_{So}^{S*}) - T\Delta Se - (F - \mathrm{Wi}_{So}^{S})$$

where F* and F are the electrostatic free energies of X* and X, Wi_{So}^{S*} the work to "charge up" the reactants at infinite separation in the medium and Wi_{So}^{S} the corresponding term for the reactants.

To calculate ΔF*, Marcus assumed the following model of the system. The reactants were treated as spheres of fixed radii which included both the ion and its inner coordination shell. The medium outside these reacting spheres was treated as a continuous dielectric of orientationally and electronically polarizable material.[1,11] The polarization of the medium by the reacting species is composed of three kinds: electronic (E-type), atomic (U-type) and orientational (U-type).[10] Due to differences in the times required for each kind of solvent polarization to adjust to a rapid charge change, only the E-type remains in electrostatic equilibrium with the charges in X* and X. Consequently, X* and X are states of "non-equilibrium solvent polarization" and as such ΔF* cannot be calculated in the usual way.[1,10,17]

Marcus calculated F* by computing the work done to "charge up" the reacting spheres in the medium at the separation distance in X*.[1] The calculation consisted of a two step process and the final expression was obtained in terms of the polarization of state X* and electric field strength (in vacuo).

Now to obtain the most probable activated complex this expression was minimized subject to the restraint that the atomic and orientational polarization must be the same in X* and X. When this calculation was performed and conversion to more accessible parameters such as the ionic radii and charges was made, Marcus obtained the following:[1]

$$\Delta F^{*} = \frac{e_1^{*}\, e_2^{*}}{D_s R} + m^2\lambda \qquad (4)$$

where $2m + 1 = -(\Delta F^{o} + W_P - W_R)/\lambda$ (5)

and $$\lambda = \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)(\Delta e)^2 \qquad (6)$$

where the first term on the right hand side of (4) is the electrostatic work done to bring the reactants together expressed in terms of the charges on the reactants, e_1^* and e_2^*, the state dielectric constant, Ds, and the separation distance in X*, R. The second

term represents the solvent reorganization energy which is obtained from equations (5) and (6) where W_p and W_R are the work done to bring the products and reactants together, respectively, a_1 and a_2 the radii of the reactants, D_{op} the optical dielectric constant of the solvent and Δe the charge change on either reactant.

Applications

Some early comparisons[2,13] showed the need to include the contribution to the activation free energy from the reorganization of the inner coordination shell. However, accurate values are difficult to obtain.

A more rewarding area has been the study of "cross-reactions" for which suitable expressions have been derived by Marcus.[5] For the reaction

$$Ox_1 + Red_2 \overset{k_{12}}{\rightleftarrows} Red_1 + Ox_2 \quad , \qquad (7)$$

Marcus showed that the forward rate constant can be expressed as follows:

$$k_{12} = (k_{11}\ k_{22}\ k_{12}f)^{1/2} \qquad (8)$$

where k_{11}, k_{22} are the rate constants for the corresponding exchange reactions, K_{12} the equilibrium constant for the cross-reaction and f is defined so as to satisfy eq. (8), namely,

$$\log f = \frac{(\log K_{12})^2}{4 \log \left(\frac{k_{11}k_{22}}{z^2}\right)}$$

Sutin has employed eq. (8) to verify theoretical predictions.[13-17]

References

1. R. A. Marcus, J. Chem. Phys., 24, 966 (1956).
2. R. A. Marcus, J. Chem. Phys., 26, 867 (1957).
3. R. A. Marcus, J. Chem. Phys., 26, 872 (1957).
4. R. A. Marcus, Disc. Farad. Soc., 29, 21 (1960).
5. R. A. Marcus, J. Phys. Chem., 67, 853 (1963).
6. R. A. Marcus, J. Chem. Phys., 43, 679 (1965).
7. W. L. Reynolds and R. W. Lumry, Mechanisms of Electron Transfer Reactions, The Ronald Press Co., New York (1966), p. 74.
8. Ref. 7, p. 117.
9. Ref. 7, p. 134.
10. R. A. Marcus, J. Chem. Phys., 24, 979 (1956).
11. R. A. Marcus, J. Chem. Phys., 38, 1858 (1963).
12. B. M. Gordon, L. L. Williams, and N. Sutin, J. A. C. S., 83, 2061 (1961).

13. M. H. Ford-Smith and N. Sutin, J. A. C. S., 83, 1830 (1961).
14. G. Dulz and N. Sutin, Inorg. Chem., 2, 917 (1963).
15. H. Diebler and N. Sutin, J. Phys. Chem., 68, 174 (1964).
16. R. J. Campion, N. Purdie and N. Sutin, Inorg. Chem., 3, 1091 (1964).
17. R. A. Marcus, Ann. Rev. Phys. Chem., 15, 155 (1964).
18. R. Marcus, B. J. Zwolinsky, and H. Eyring, J. Phys. Chem., 58, 432 (1954).
19. R. A. Marcus, Can. J. Chem., 37, 155 (1959).

LIGAND FIELD THEORY FOR PENTACOORDINATE COMPLEXES OF FIRST ROW TRANSITION METALS

Yu Wang   October 23, 1969

Introduction

The five-coordinate complexes of transition metals have not been studied as thoroughly as six- and four-coordinate compounds primarily because of uncertainty in the coordination number (especially in solution) and lack of X-ray data.

After the first high-spin cobalt(II) and nickel(II) pentacoordinate complexes had been described in 1965 (2,3), it became necessary to study the influence of the nature of the ligand on the magnetic and spectroscopic properties of the complexes. It has been shown (4,5) that low-spin complexes are formed by ligands with donor atoms of low electronegativity such as P and As (6,7); while high-spin complexes are formed by ligands having donor atoms of high electronegativity, in particular, O and N (8,9,10). Sulfur ligands form both types of complexes (11,12).

According to Zemann (13), the relative stabilities of the different geometric forms are: trigonal bipyramid > distorted square pyramid with $\angle$ LML = 104° > square pyramid. In fact, most of the five-coordinate complexes are trigonal bipyramid.

Ligand Field Interpretation of Electronic Spectra

Define two parameters (14)

$$Ds = \frac{1}{14}\left(\frac{4Z_A}{b^3} - \frac{3Z_E}{a^3}\right)\overline{r^2}$$

$$Dt = \frac{1}{168}\left(\frac{16Z_A}{b^5} - \frac{9Z_E}{a^5}\right)\overline{r^4}$$

where Z_A, Z_E are the axial and equitorial charges lacated at distances b and a respectively. $\overline{r^2}$, $\overline{r^4}$ are the expectation values.

A. One electron splitting scheme: The orbital energy of the d-manifold in D_{3h} has been calculated as follows (14):

state (M_l)	d-orbital	symm. representation	orbital energy
$\vert 0 >$	z^2	a_1'	2Ds + 6Dt
$\vert \pm 1 >$	(xz, yz)	e''	Ds - 4Dt
$\vert \pm 2 >$	(xy, x^2-y^2)	e'	-2Ds + Dt

This energy splitting gives fairly good agreement with the spectra of d^1 (15), d^9; high spin d^4, d^6 (16,17) and low spin d^6, d^7, d^8 (6); for example, $[Fe(Me_6tren)Br]Br$ and $[Ni(QAS)Br]^+$. (Me_6tren = $N[CH_2CH_2N(CH_2)_2]_3$ QAS = $As(o\text{-}ph_2\text{-}As\text{-}C_6H_4)_3$).

B. Many electron splitting scheme. The total Hamiltonian is

$$H = -\frac{h^2}{2m}\sum_i \nabla_i^2 - \sum_i \frac{Ze^2}{r_i} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{r_{ij}} + \sum_i \xi_i(r)\, l_i \cdot S_i + V_{c.F.}$$

In first row transition elements $\xi(r) l \cdot S < V_{c.F.} < \frac{e^2}{r_{ij}}$

We therefore first consider the interelectronic repulsion term, i.e., $\sum_{i\neq j} \frac{e^2}{r_{ij}}$ and express the coulomb integral J(a,b) and exchange integral K(a,b) in terms of parameters F_0, F_2, F_4 or Racah parameters B and C. Secondly, we consider the splitting of energy levels in the crystal field; i.e., the $V_{c.F.}$ term. So far, the spin orbit coupling has been neglected. However, the absorption spectra show very good agreement with the calculation.

Condon and Shortley (18) calculated the interelectronic repulsion energy terms for all d^n configurations. The energy level diagrams for Ni(II) and Co(II) complexes with five equivalent dipoles of strength μ in the D_{3h} configuration have been calculated (19,20). Even the changes of energy levels which depend upon changes in β (∠LML) and Dq(ax)/Dq(base) have been estimated (21). From the spectra, all the parameters can be determined.

Even though $[Co(Et_4dien)X_2]$ and $[Co(Me_6tren)X]X$ are quite different in symmetry, they show similar spectral and magnetic properties. It can be concluded that, for high spin pentacoordinate complexes containing similar ligands, the key electronic structural properties do not depend critically on the exact geometry of the molecules (22). Therefore the ligand field model can be assumed to be D_{3h}.

Magnetic Properties

A. With E ground term (23), the d^1, d^3, d^6 and d^8 configurations have ${}^2E''$, ${}^4E'$, ${}^5E''$ and ${}^3E'$ as the ground states in D_{3h} respectively. The perturbation Hamiltonian is

$$H' = V_{c.F.} + \lambda \vec{L} \cdot \vec{S} + \beta \vec{H} \cdot (k \vec{L} + 2 \vec{S})$$

Using crystal field eigenfunctions as basis functions, the first order perturbation of L-S coupling gives 2S + 1 levels separated by equal spacing. Then, the magnetic susceptibility can be evaluated by the Zeeman operators and Van Vleck's formula (24,1)

$$\mu_{\parallel} = \beta(kL_z + 2S_z) \; ; \; \mu_{\perp} = \beta(kL_x + 2S_x)$$

$$\chi_i = N \frac{\sum_{n,m}\left(\frac{E^{(1)}_{n,m}}{kT} - 2E^{(2)}_{n,m}\right) e^{-E^o_n/kT}}{\sum_n e^{-E^o_n/kT}} \quad (i=x,y,z)$$

where N = Avogadro's number
E_n^o = energy after L-S coupling
$E_{n,m}^{(1)}$ = 1st order Zeeman energy
$E_{n,m}^{(2)}$ = 2nd order Zeeman energy.

From the variation of μ_{eff} with respect to temperature, the orbital reduction factor "k" must be considered at high temperature and the presence of low symmetry is taken into account at low temperature.

B. With A ground term (2f), the d^2, d^4, d^7 and d^9 configurations have $^3A_2'$, $^5A_1'$, $^4A_2'$ and $^2A_1'$ symmetries as ground states. In a weak field, the true wave function for A symmetry includes mixing of A symmetry from both P and F (terms from inter-electronic repulsion force). Again, with spin-orbit coupling, the 1st order perturbation gives no correction to the energy of the ground state. However, the 2nd order perturbation will split it into Kramer's doublet. In this model, temperature independent paramagnetism (TIP) arises from mixing the high energy orbitally degenerate state with the singlet ground state. Apart from this TIP term, the susceptibilities of this type of compound might be expected to follow Curie's law down to very low temperature ($\Delta \cong kT$). Sometimes the magnetic data may be taken as a support for the assignment of the electronic spectra.

Conclusion

At present, the experimental knowledge of pentacoordinate complexes is still rather scattered and far from complete. The exact structures of such complexes are known only in a few cases. Therefore, there is still an attempt being made to ascertain whether the ligand field theory leads to acceptable results for pentacoordinate complexes.

References

1. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Company, Inc., 1962.
2. L. Sacconi, P. Nannelli, N. Nardi and U. Campigli, Inorg. Chem., 4, 943 (1965).
3. L. Sacconi, M. Ciampolini and G. P. Speroni, J. Am. Chem. Soc., 87, 3102 (1965).
4. L. Sacconi and I. Bertini, J. Am. Chem. Soc., 90, 5443 (1968).
5. C. Furlani, Coord. Chem. Rev., 3, 141 (1968).
6. M. J. Norgett and J. H. M. Thornley, J. Chem. Soc. (A), 540 (1967).
7. G. Dyer and Devon W. Meek, Inorg. Chem., 6, 149 (1967).
8. M. Ciampolini and G. P. Speroni, Inorg. Chem., 5, 45 (1966).
9. M. Ciampolini and N. Nardi, Inorg. Chem., 6, 445 (1967).
10. M. Ciampolini and N. Nardi, Inorg. Chem., 5, 41 (1966).
11. M. Ciampolini and J. Gelsomini, Inorg. Chem., 6, 1821 (1967).

12. G. Dyer and D. W. Meek, Inorg. Chem., 4, 1398 (1965).
13. J. Zemann, Z. Anorg. Allg. Chem., 324, 241 (1963).
14. J. S. Wood, Inorg. Chem., 7, 855 (1968).
15. G. W. A. Fowles and R. A. Hoodless, J. Chem. Soc., 33 (1963).
16. M. Ciampolini, Chem. Comm., 47 (1966).
17. M. Ciampolini and N. Nardi, Inorg. Chem., 5, 1150 (1966).
18. Condon and Shortley, "Theory of Atomic Spectra," Cambridge University Press, 1951.
19. M. Ciampolini, Inorg. Chem., 5, 35 (1966).
20. M. Ciampolini, N. Nardi and G. P. Speroni, Coord. Chem. Rev., 1, 222 (1966).
21. M. Ciampolini and I. Bertini, J. Chem. Soc. (A), 2241 (1968).
22. Zvi Dori and Harry B. Gray, Inorg. Chem., 7, 889 (1968).
23. J. S. Wood and Peter T. Greene, Inorg. Chem., 8, 491 (1969).
24. J. H. Van Vleck, "Theory of Electronic and Magnetic Susceptibility," Oxford University Press, London, 1932.
25. J. S. Wood, J. Chem. Soc. (A), 1582 (1969).

STRUCTURAL STUDIES OF SOME PHOSPHORUS PENTACHLORIDE-METAL TRI- AND TETRACHLORIDE ADDUCTS

Thomas J. Kistenmacher October 28, 1969

Introduction

The syntheses of several adducts of phosphorus pentachloride and transition metal chlorides have been reported by Groeneveld.[1] In most cases where previous work has been carried out in this area, the final products have been postulated to arise by the donation of a Cl^- from PCl_5 to the metal chloride to give PCl_4^+ and the corresponding chlorometallate anion. In many of these reactions, the resulting chlorometallate is of chemical, spectroscopic, and structural interest, e.g., $PCl_5 \cdot CrCl_3$, $PCl_4^+CrCl_4^-$; $PCl_5 \cdot FeCl_3$, $PCl_4^+FeCl_4^-$; $PCl_5 \cdot TiCl_4$, $PCl_4^+TiCl_5^-$; $PCl_5 \cdot SnCl_4$, $PCl_4^+SnCl_5^-$, and many others. In this seminar, the results of an investigation of the solid state structures of the adducts with $FeCl_3$, $CrCl_3$ and $TiCl_4$ will be discussed.

Results

(1) Tetrachlorphosphonium Tetrachloroferrate(III), $[PCl_4][FeCl_4]$

Reaction of PCl_3, $SOCl_2$, and $FeCl_3$ yielded a product of empirical formula $PFeCl_8$. The reaction product has been shown by single-crystal X-ray techniques to be $[PCl_4][FeCl_4]$. Both the anion and cation were found to be nearly tetrahedral.

(2) Bis-tetrachlorophosphonium Di-μ-chlorooctachlorodititanate(IV), $[PCl_4]_2[Ti_2Cl_{10}]$

Addition of $PCl_5(s)$ to a solution of $TiCl_4$ in $POCl_3$ yields a crystalline product of empirical formula $PTiCl_9$. An X-ray structural determination has led to the formulation of the product as PCl_4^+ and the edge-shared, dimeric ion $[Ti_2Cl_{10}]^{2-}$. A similar geometric configuration is known for Ti^{4+} in the complex $[POCl_3 \cdot TiCl_4]_2$.[2]

(3) Tetrachlorophosphonium Tri-μ-chlorohexachlorodititanate(IV), $[PCl_4][Ti_2Cl_9]$

The adduct $PCl_5 \cdot 2TiCl_4$ has been prepared by two methods: (a) reaction of PCl_3, $SOCl_2$, and $TiCl_4$, and (b) addition of $PCl_5(s)$ to $TiCl_4$ in thionyl chloride solution. The product has been shown by X-ray analysis to be PCl_4^+ and the unusual, face-shared bioctahedron $[Ti_2Cl_9]^-$. This is the first known example of a first row transition metal ion in the +4 formal oxidation state to assume this geometry.

(4) $PCl_5 \cdot CrCl_3$

A study of the magnetic properties of the adduct $PCl_5 \cdot CrCl_3$ led to its formulation as $PCl_4^+CrCl_4^-$.[3] However, on the basis of the electronic spectrum of this complex, it is proposed that the Cr^{3+} is in an octahedral environment. A model consistent with the electronic

spectrum and the magnetic results is that of an infinite chain of $[CrCl_6]^{3-}$ units sharing two edges. The infrared spectrum is in accord with this proposal. Two bands are found in the Cr-Cl stretching region (370 cm^{-1} and 340 cm^{-1}), and may be assigned to the terminal and bridging Cr-Cl stretches.

The three X-ray structural studies described above have allowed the observation of the PCl_4^+ ion in a variety of crystal lattices. The PCl_4^+ in each case exhibits nearly tetrahedral symmetry. The average of 18 independent Cl-P-Cl angles is 109.4 ± 0.3°. An analysis of the thermal corrections to the P-Cl distance[4] has yielded some very interesting results. The average of 12 independent, thermally-corrected P-Cl distances is 1.944 ± 0.006 Å.

The study of the $TiCl_4$ adducts has shown that Ti^{4+} can satisfy its known preference for octahedral geometry by edge-sharing or face-sharing of octahedra. The role of the non-aqueous solvent in the choice of anion stoichiometry and geometry will also be discussed.

References

1. W. L. Groeneveld, Rec. Trav. Chim., 71, 1152 (1952).
2. C.-I. Branden and I. Lindquist, Acta Chem. Scand., 14, 726 (1960).
3. D. J. Machin, D. F. C. Morris, and E. L. Short, J. Chem. Soc., 4658 (1964).
4. W. R. Busing and H. A. Levy, Acta Cryst., 22, 451 (1967).

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References

1. W. L. Groeneveld, Rec. Trav. Chim., 71, 1152 (1952).
2. C.-I. Branden and I. Lindquist, Acta Chem. Scand., 14, 726 (1960).
3. D. J. Machin, D. F. C. Morris, and E. L. Short, J. Chem. Soc., 4658 (1964).
4. W. R. Busing and H. A. Levy, Acta Cryst., 22, 451 (1967).

THE PREPARATION AND OPTICAL AND ELECTRON SPIN RESONANCE SPECTRA OF SOME HEXACHLORO AND PENTACHLOROALKOXO VANADATES(IV)

Robert D. Bereman November 13, 1969

Introduction

Much recent interest has centered on the investigation of d^1 transition elements involving oxyions of the type Mo^{n+} where $M^{(n+2)+}$ is Cr^{+5}, Mo^{+5}, W^{+5}, or V^{+4}. The halide complexes of these ions have been studied and it is well established that there is substantial π-bonding between the metal and oxygen atoms.[1-7] The relatively simple optical and magnetic properties which arise from a single unpaired electron and C_{4v} symmetry have made these systems particularly appealing. The bonding and molecular orbitals of interest in the vanadyl (VO^{++}) system have been discussed in detail by Ballhausen and Gray.[8] The bonding in the other systems has been discussed by various authors.[1-7]

Alcohol solutions are among the few solvent systems in which one can work with d^1 transition element halides and avoid the formation of oxyions. Due to the recent success in preparing d^1 transition element alkoxides and complexes containing alkoxides as ligands,[9-16] it was decided that vanadium(IV) chloro-alkoxide complexes might be stable. The pentachloroalkoxovanadate(IV) ion should be six coordinate and the metal to oxygen bond would formally be a single bond. A study of a series of these complexes in which the alkoxide group is changed would show the effect on the bonding parameters of changing the donating strength of the oxygen. The effect on the molecular orbital parameters of changing the donating strength of the halide by changing from F^- to Cl^- to Br^- has been shown in the case of the pentahalo(oxo)molybdate(IV) ion.[1]

Discussion

A new class of crystalline vanadium(IV) compounds, the pentachloroalkoxovanadates(IV), has been prepared and characterized. The alkoxo group was methoxo, ethoxo, *n*-propoxo, or *n*-butoxo, while the cation was tetramethylammonium, tetraethylammonium, or pyridinium. The relative stability of the complexes is dependent on the cation. The color of the complexes is golden. Two new salts of the hexachlorovanadate(IV) ion were also prepared and characterized.

The pentachloroalkoxovanadates(IV) were prepared by the addition of one equivalent of the appropriate alcohol to a slurry of the tetraalkylammonium or pyridinium hexachlorovanadate(IV) in an acetonitrile-ethyl ether mixture. The alkoxo complexes could be converted to the appropriate hexachloro complex by the addition of HCl which indicates the absences of a vanadyl species.

Magnetic studies indicated Curie-Weiss paramagnetism and verified the presence of the vanadium(IV) ion with $3d^1$ configuration. The infrared spectra of the complexes were in agreement with the formulation $V(OR)Cl_5^{-2}$. The ultraviolet-visible spectra of the

alkoxides consisted of two peaks around 14,000 cm^{-1} while the hexachlorovanadates(IV) had an asymmetric peak around 15,500 cm^{-1}. The reflectance spectrum of each of the complexes agreed with the solution spectrum.

Attempts to prepare a tetrachlorodialkoxovanadate(IV) species were unsuccessful.

No esr signal was observed for the hexachlorovanadates(IV) in the solid or in $SOCl_2$ at 297°K or 77°K. Electron spin resonance spectra were obtained for the alkoxides as pure powders at 297°K and as solutions at 297°K and 100°K (glasses). The V metal hyperfine was observed and the spectra of the glasses could be resolved into parallel and perpendicular components.

The observed g and A values were used to calculate the coefficients in a simple molecular orbital scheme. The gound state for the $V(OR)Cl_5^{-2}$ ion is a $^2B_2$ and the molecular orbitals which are necessary for discussion are those which are the basis of the b_1, b_2, and e representations:

$$B_2 > * = N_{\pi 2}(dxy - \lambda_{\pi 2}\emptyset b_2)$$

$$B_1 > * = N_{\sigma 2}(dx^2 - y^2 - \lambda_{\sigma 2}\emptyset b_1)$$

$$E > * = N_{\pi 1}(dxz \text{ or } dyz - \lambda^{e}_{\pi 1}\emptyset^{e}_{e} - \lambda^{a}_{\pi 1}\emptyset^{a}_{e})$$

where the metal orbitals are d functions and $\lambda^{a}_{\pi 1}$ and $\lambda^{e}_{\pi 1}$ are the xz (yz) molecular orbital coefficients for the equatorial and axial ligands respectively.

In going through the series from the methoxo to the n-butoxo complex, the $B_2>^*$ and $B_1>^*$ molecular orbitals become more covalent and the $E>^*$ molecular orbital becomes more ionic.

The unpaired electron density in each of the four equatorial halide $3p_{\pi}$ orbitals was calculated for the complexes and the density increased along the series (methoxo to n-butoxo) as was expected.

References

1. L. A. Dalton, R. D. Bereman, and C. H. Brubaker, Jr., Inorg. Chem., 8 (1969) in press.
2. P. T. Monoharan and Max T. Rogers, J. Chem. Phys., 49, 5510 (1968).
3. K. DeArmond, B. B. Garrett and H. S. Gutowsky, ibid., 42, 1019 (1965).
4. B. R. McGarvey, J. Phys. Chem., 71, 51 (1967).
5. H. A. Kuska and M. T. Rogers, "Radical Ions," E. T. Kaiser and L. Devans, Ed., New York: Interscience Publishers, Inc., 1968. Chapter 13.
6. P. T. Monoharan and M. T. Rogers, J. Chem. Phys., 49, 3912 (1968).
7. H. Kon and N. Sharpless, J. Phys. Chem., 70, 105 (1966).
8. C. J. Ballhausen and H. B. Gray, Inorg. Chem., 1, 111 (1962).

9. R. A. D. Wentworth and C. H. Brubaker, Jr., <u>ibid</u>., <u>2</u>, 551 (1963).
10. R. A. D. Wentworth and C. H. Brubaker, Jr., <u>ibid</u>., <u>3</u>, 47 (1964).
11. P. G. Rasmussen, H. A. Kuska and C. H. Brubaker, Jr., <u>ibid</u>., <u>4</u>, 343 (1965).
12. D. A. McClung, L. R. Dalton and C. H. Brubaker, Jr., <u>ibid</u>., <u>5</u>, 1985 (1966).
13. W. Giggenbach and C. H. Brubaker, Jr., <u>ibid</u>., <u>7</u> (1968).
14. W. Reagan, D. P. Rillema and C. H. Brubaker, Jr., <u>ibid</u>., <u>8</u>, 581 (1969).
15. D. P. Rillema and C. H. Brubaker, Jr., <u>ibid</u>., <u>8</u>, 1645 (1969).
16. W. Giggenbach and C. H. Brubaker, Jr., <u>ibid</u>., <u>8</u>, 1141 (1969).

A STUDY OF INFRARED BAND SHAPES OF SOME METAL CARBONYLS IN CONDENSED PHASES - CORRELATION FUNCTION ANALYSIS OF MOLECULAR REORIENTATION

Richard Lauver January 13, 1970

Studies of the dynamics of molecular motion in condensed phases have become more detailed as well as more numerous during the past two decades. The fundamental interest evolves from the quest for a better understanding of the liquid state and the intermolecular potentials which dominate all internal dynamical processes. A problem of this scope, of course, cannot be treated in any single experiment and awaits the compilation and correlation of the rapidly increasing store of experimental data into a comprehensive theory. A remarkable variety of physical studies have been brought to bear on the various aspects of the problem. Traditionally, macroscopic transport properties like viscosity, diffusion and conductivity were considered. Debye's classic work[1] in the field of dielectric relaxation marked a most significant step towards the formulation of a molecular model for such processes. More recently, spin relaxation, light scattering, and infrared and Raman line shape studies have been employed in the study of molecular reorientation in condensed phases.

The use of time correlation functions to analytically relate time dependent fluctuations of molecular motion to observable transport coefficients and spectral line shapes has, perhaps, been the most cohesive development in these studies. Fundamentally, the correlation function provides a mathematically tenable approach to nonequilibrium processes comparable to the partition functions used for systems in equilibrium. Recent reviews by Gordon[2] and by Zwanzig[3] give an enlightening account of the extent that correlation functions are now used. The contributions of Gordon have been particularly instrumental in illucidating the correlation function analysis of spectral line shapes.

In this seminar, we consider a band shape study of some metal carbonyls. The infrared band shapes (CO stretch) were numerically analyzed to determine the correlation function and spectral moments as described by Gordon.[4,5] The results are discussed in terms of relative rates of rotational reorientation and qualitative aspects of the intermolecular potential.

The dependence of the correlation function, $\varphi(t)$, and second moment, $\mu(2)$, on experimental variable was examined for some hexacarbonyls. A systematic variation with slit width and range of integration was found, but no concentration dependence was detected. The solvent dependence of $\varphi(t)$ and $\mu(2)$ for $Cr(CO)_6$ was considered in detail. The changes seen were related to polarizability or dielectric constant of the solvent rather than to bulk viscosity. Anisotropy of reorientation was observed for axially symmetric carbonyls ($Fe(CO)_5$, $Hg[Co(CO)_4]_2$, $LMn(CO)_5$, L = H, CH_3, CF_3, $Mn(CO)_5$). Internal rotation was evident for $CH_3Mn(CO)_5$, $CF_3Mn(CO)_5$ and $Hg[Co(CO)_4]_2$, but not for $Mn_2(CO)_{10}$. Diffusion constants and correlation times were calculated for comparison with related data

available in the literature. The reorientation process is best described as slightly hindered rotation at short times (< 1 picosec) followed by collision controlled diffusion. The results are compared to several models which predict $\omega(t)$ for limiting cases.

Bibliography

1. P. Debye, Polar Molecules, Dover Pub. Inc., New York (1929).
2. R. G. Gordon, Advan. Magnetic Resonance, 3, 1 (1968).
3. R. Zwanzig, Ann. Rev. Phys. Chem., 16, 67 (1965).
4. R. G. Gordon, J. Chem. Phys., 39, 2788 (1963).
5. Ibid., 43, 1307 (1965).

Additional references of interest:

a) Application of correlation functions,
H. Shimizu, J. Chem. Phys., 43, 2453 (1965).
Ibid., 48, 2494 (1968.
W. A. Steele, J. Chem. Phys., 38, 2411 (1963).

b) Reorientational anisotropy,
J. Jones and T. M. DiGennaro, J. Chem. Phys., 50, 6 (1969).
R. A. Assink and J. Jonas, J. Phys. Chem., 73, 2445 (1969).
D. E. Woessner, B. S. Snowden, Jr., and E. T. Strom,
Molec. Phys., 14, 265 (1968).

THE COORDINATION CHEMISTRY OF THE AZO GROUP

John Thatcher March 17, 1970

The process by which metallo-enzymes "fix" atmospheric nitrogen and convert it into nitrogenous-cell constituents is efficient and occurs under mild conditions. Ammonia is the key intermediate before assimilation of "fixed" nitrogen into carbon skeletons occurs. A reductive pathway possibly via diimide (H-N=N-H) and hydrazine is preferred. The mechanism for fixation involves two active metal sites on the enzyme, but it is not known whether a dinuclear metal site is necessary for binding the nitrogen molecule prior to reduction.[1] Diimide is the simplest azo compound. Since azo compounds are weakly basic and decompose readily liberating N_2, metal-azo complexes may be useful as models for and a possible route to molecular nitrogen complexes.

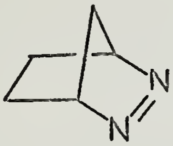
Metal azo complexes are well known.[2,3] However, most of these complexes involve aromatic azo compounds in which the azo group bonds to the metal as part of a chelate ring.

For these reasons, a study of the coordination properties of 2,3,Diazobicyclo(2.2.1)Heptene-2 DBH(I) was undertaken.

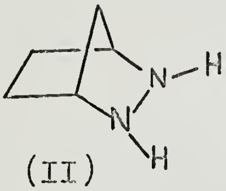
Platinum(II)-(DBH)·complexes have been synthesized by (a) addition of DBH to K_2PtCl_4 in aqueous solution;[4] (b) addition of $[DBHz-H]_2SO_4$ (DBHz(II)) to H_2PtCl_6 in aqueous solution; (c) oxidation of (DBHz)-Pt(II) complexes with cupric chloride in methanol; (d) reduction of $(DBH)_2PtCl_4$ with sodium iodide in methanol.

The chloro complexes characterized have stoichiometries:

$M[(DBH)\,Pt_2Cl_5]$, $[(DBH)PtCl_2]_2$, $(DBH)_2PtCl_2$ and $[(DBH)_3PtCl]ClO_4$.



(I)



(II)

Nuclear magnetic resonance spectroscopy and an x-ray crystal structure determination showed that coordination to platinum occurs through a single nitrogen of the azo group to form monocoordinated complexes or through both nitrogens of the azo group, one nitrogen to each platinum atom, to form bridged complexes. Both types of coordination have been found to occur in molecular nitrogen complexes.[1,5]

Four types of reactions have been observed for monocoordinated (DBH)-Pt(II) complexes. (a) Replacement of DBH by entering ligand; (b) replacement of ligand other than (DBH) by entering ligand; (c) oxidative addition by Cl_2; (d) coordination of DBH to a second metal by bridging. From the reactivity of the azo complexes, it is deduced that the monocoordinated azo group has a higher trans effect than chloride in substitution reactions and that the Pt-N bond is weaker when the azo group is bridging than when it is monocoordinated.

The intense charge transfer bands in the U.V-visible absorption spectrum of these compounds and their chemical reactivity indicate that back donation of electron density from platinum to the π^* orbital on the nitrogen of the azo group occurs.

Infrared data show that for monocoordinated azo complexes, σ bonding increases while π bonding decreases the frequency of the (N=N)stretching vibration. This behavior is similar to that found for CO[6] and CN^- [7] and proposed for N_2.[8]

Two compounds III(A and B) with stoichiometry $[(DBH)PtCl_2]_2$ were isolated. Their physical and chemical properties were practically identical. The crystal structure of IIIA showed the molecule was boat shaped with two azo bridges. The coordination about each platinum is square planar with the nitrogens cis to each other. The five carbon skeletons of the DBH ligands in this type of molecule may assume either of two possible orientations. Only one orientation is found in IIIA. This suggests that the other orientation is found in IIIB.

The kinetics and mechanism of the reaction:

$$[(DBH)PtCl_2]_2 + \varnothing_4AsCl \qquad \varnothing_4As[(DBH)Pt_2Cl_5] + DBH$$

were investigated. The reaction rates were calculated from spectrophotometric data. A two step mechanism is proposed. The first step involves attack by chloride ion to form the intermediate $(DBH)_2Pt_2Cl_5^-$. In the second step DBH is displaced and a chloride ion bridges between the two platinums.

DBH complexes with Pt(IV), Pd(II), Cu(II), and Co(II) have been isolated as well as Pt(II) complexes with the hydrazo derivative DBHz(II). Both monocoordinated and bridged DBHz complexes were isolated.

The compound $(azobenzene)_2PtCl_4$ reported by Kharash and Ashford[9] was reinvestigated and it was found that the compound was incorrectly formulated.[10] It is in fact $[azobenzene\text{-}H]_2PtCl_6$ a salt with no coordination of the azobenzene to platinum. However, preliminary studies indicate that azobenzene can form Pt(IV) complexes.

It is concluded that the coordination chemistry of the azo group closely parallels that of N_2. Thus, diimide is a likely intermediate in N_2-fixation. Since N≡N, N=N, and N-N can form monocoordinate or bridging complexes, either a mononuclear or a dinuclear metal site may be utilized in the enzymatic fixation of nitrogen.

References

1. R. Murrey, D. C. Smith, Coordin. Chem. Rev., 3 (1968), 429-470.
2. H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, New York, N. Y. (1961).
3. A. C. Cope and R. W. Siekman, J. Am. Chem. Soc., 87, 3273 (1965).
4. R. G. Denning and J. Thatcher, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 5, 1968, No. M199.

5. I. M. Treitel, M. T. Flood, R. E. Marsh, H. B. Gray, J. Am. Chem. Soc., 91, 6512 (1969).
6. D. J. Darensbourg, Ph.D. Thesis, University of Illinois, 1967.
7. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.
8. K. G. Caulton, R. L. Dekock, and R. F. Fenske, J. Am. Chem. Soc., 92, 515 (1970).
9. M. S. Kharash and T. A. Ashford, ibid., 58, 1733 (1936).
10. R. G. Denning and J. Thatcher, ibid., 90, 5917 (1968).

THE PSEUDO-JAHN-TELLER EFFECT

John W. Boettcher

March 24, 1970

Introduction

Approximately ten years ago, Bader[1] proposed a symmetry rule with which he could correctly predict the sign of the interaction force constants frequently introduced in normal coordinate analyses. Just as the Jahn-Teller effect deals with the mixing of degenerate electronic ground states upon nuclear displacement, so the pseudo-Jahn-Teller effect deals with the mixing of the ground state with low-lying excited states. This mixing tends to stabilize the ground state, leading to a smaller increase of energy upon distortion than if this mixing did not occur.

This seminar will be concerned with an examination of the foundations of this rule and some of its more recent applications.

Theory

Suppose we place a molecule in a given geometry and designate the electronic Hamiltonian by H^o. If one then displaces the nuclei along some normal coordinate, Q_i, the new Hamiltonian can be written to second order in Q_i as

$$\mathcal{H} = H^o + H^i Q_i + \tfrac{1}{2} H^{ii} Q_i^2$$

where

$$H^i = \left(\partial H^o / \partial Q_i\right)_o \qquad H^{ii} = \left(\partial^2 H^o / \partial Q_i^2\right)_o$$

Through use of perturbation theory, the energy of the ground electronic state to second order in Q_i is

$$\mathcal{E}_o = \mathcal{E}_o^o + Q_i \langle o|H^i|o\rangle + \tfrac{1}{2} Q_i^2 \left[\langle o|H^{ii}|o\rangle - 2 \sum_k{}' \frac{|\langle o|H^i|k\rangle|^2}{\mathcal{E}_k^o - \mathcal{E}_o^o} \right]$$

Under certain conditions, the linear term may be ignored, and we need only concern ourselves with the quadratic or force constant term. The first term in brackets is the force constant for the normal coordinate if the electronic distribution were to remain static. The second term in brackets is then a correction due to the mixing of the ground with excited electronic states.

The crucial assumption of the rule is that the summation may be replaced by one or at most a few important terms where $\mathcal{E}_k^o - \mathcal{E}_o^o$ is small. Also assumed is that $\langle o|H^i|k\rangle$, when non-zero, decreases or at worst remains constant as $|k\rangle$ increases in energy.

Symmetry is introduced by recognizing that the integral $\langle 0|H^i|k\rangle$ is non-zero only when the direct product of $\Gamma|0\rangle$ with $\Gamma|k\rangle$ contains $\Gamma(H^i)$. The above direct product is simply taken to be $\Gamma(\phi_i)\times\Gamma(\phi_j)$ where ϕ_i is the molecular orbital occupied in the ground state and ϕ_j the molecular orbital occupied instead of ϕ_i in the excited state. The symmetry species of $\Gamma(H^i)$ is the same as $\Gamma(Q_i)$. Therefore, only certain normal coordinate displacements will allow coupling of the ground with low-lying excited states and bring about the resulting stabilization upon distortion.

Applications

In a second paper,[2] Bader applied this rule to a determination of the reaction coordinate in unimolecular and bimolecular decomposition reactions.

Recently, Bartell[3,4] and Pearson[5,6] have used this rule to correctly predict the structures of various molecules of formulas AX_n where n = 2 to 6.

Future

It has been suggested[6] that this rule may be useful as a test for calculated or assumed schemes of molecular orbitals to see whether they are compatible with known structures.

References

1. R. F. W. Bader, Mol. Phys., 3, 137 (1960).
2. R. F. W. Bader, Can. J. Chem., 40, 1164 (1962).
3. L. S. Bartell and R. M. Gavin, Jr., J. Chem. Phys., 48, 2466 (1968).
4. L. S. Bartell, J. Chem. Educ., 45, 754 (1968).
5. R. G. Pearson, J. Am. Chem. Soc., 91, 1252 (1969).
6. R. G. Pearson, *ibid.*, 91, 4947 (1969).

STERIC EFFECTS IN COORDINATION OF 1,1,1-TRIS(DIMETHYLAMINOMETHYL)ETHANE AND OF 1,1,1-TRIS(MONOMETHYLAMINOMETHYL)ETHANE

Walter Kasowski April 9, 1970

Zinc Complexes

Part I.

Steric effects in coordination of the new tripod ligand 1,1,1-tris(dimethylaminomethyl)ethane(TTN) and of 1,1,1-tris(monomethylaminomethyl)ethane(TSN) have been investigated by the preparation and characterization of their zinc chloride and zinc bromide complexes.^{1} The stereochemistry of the complexes has been established on the basis of data from ^{1}H nuclear magnetic resonance (nmr) spectroscopy, infrared spectroscopy, and complementary physical-chemical studies. The complexes of TSN have a cage-like structure consisting of three fused six-membered chelate rings and a penta-coordinated zinc atom due to the sterically unhindered tridentate behavior of TSN. In contrast, the complexes of TTN have only one six-membered chelate ring and a tetracoordinated zinc atom due to the sterically controlled bidentate behavior of TTN. The chelate ring is in a frozen pseudo-chair conformation and yields strikingly similar ^{1}H nmr data to purely organic structurally analogous nitrogen-containing heterocycles. This indicates that the zinc(II) nucleus, though chemically different from the carbon atom, does not produce any conformational change in these systems.

Part II.

The stereochemistry of the chelate ring in the TTN complexes, and hence the controlling steric factor, has been elucidated by comparative studies of the model complexes $LZnX_2$ where L is the bidentate analog of TTN, N,N,N',N',2,2-hexamethyl-1,3-propanediamine (BTN). Only that conformer in which the free (dimethylaminomethyl) group is equatorially orientated at C_5 is formed. Furthermore, the iodo members of both TSN and TTN have been prepared and shown to possess structures similar to those described for their chloro and bromo counterparts. This indicates that the progressive increase in size of the halo group does not perturb the stereochemistry of these systems.

References:

1. Walter J. Kasowski and John C. Bailar, Jr., J. Am. Chem. Soc., 91, 3212 (1969).

THE CONSERVATION OF ORBITAL SYMMETRY

W. Karl Olander April 14, 1970

Introduction

In the six years since R. B. Woodward and R. Hoffmann initially formulated the rules which bear their names pertaining to the conservation of orbital symmetry in concerted reactions, the organic branch of chemistry in particular has experienced a wealth of publications verifying and expanding their treatment in examining a host of highly stereospecific reactions.[1-8] More recently, the conservation of orbital symmetry has found application in the realm of inorganic chemistry.[9-10]

Basically, they set the ground work for a theoretical treatment of all concerted reactions at a strictly qualitative level while simultaneously observing pertinent quantum mechanical restrictions. The fundamental principle enacted is that highly stereospecific reactions occur readily when there is congruence between orbital symmetry characteristics of reactants and products.

The purpose of this seminar is to review several general reaction types to which the Woodward-Hoffmann rules have been applied and examine several instances where they have been extended to inorganic systems.

Electrocyclic Reactions

By definition, an electrocyclic reaction entails the formation of a σ bond between the termini of a linear system containing $k\pi$ electrons or the converse process. The intramolecular conversion of the allyl cation to the cyclopropyl cation affords a simple system on which to examine the Woodward-Hoffmann approach. A priori, there are two rotational pathways, i.e., conrotary or disrotary, which will translate the π molecular orbitals of the allyl cation (X_1, X_2, X_3) into σ molecular orbitals of the cyclopropyl cation (σ, π, σ^*). Coincident with the conrotary and disrotary mechanisms are preserved two symmetry elements, a C_2 axis and a mirror plane respectively, with respect to which all molecular orbitals can be classified as symmetric (S) or antisymmetric (A). X_1(A) and X_3(A) translate via the conrotary mechanism into fragments of either π(A) or σ^*(A) while X_2(S) translates as σ(S). A correlation diagram, constructed by placing reactant and product molecular orbitals on either side at their respective energy levels and then connecting levels of like symmetry, reveals that the conrotary mode leads to an excited state product. This process is termed a symmetry forbidden reaction for the ground state. Examination of an analogous treatment for the disrotary mode shows a ground state--ground state correlation diagram for the conversion and is symmetry allowed. The behavior of the highest occupied molecular orbital, X_1, provides the answer. For the conrotary process, it is no longer bonding in the transition state, while the opposite is true for the disrotary mode. Also, the process is just reversed for the first excited state. Photochemical excitation of a X_1^2 electron to give the X_1X_2 species leads to a symmetry

allowed conversion for the conrotary mode, but is symmetry forbidden in the disrotary mode. An alternate method of correlating reactant and product molecular orbitals via electronic state diagrams yields an identical result.[11]

Based on the nodal properties of polyenes, Woodward-Hoffmann have derived a selection rule for electrocyclic reactions of $k\pi$ electrons. For $k = 4q$, a conrotary mode is predicted, but when $k = 4q+2$, a disrotary mechanism is foreseen ($q = 0,1,2...$). In the first excited state, the modes are reversed.

Correlation Diagrams

Symmetry elements are of no use when all of the orbitals are either symmetric or antisymmetric with respect to it and can only lead to the trivial solution where all reactions are symmetry allowed.

A symmetry element should bisect bonds formed or broken during a reaction course, otherwise one is often led to the erroneous conclusion that a reaction is symmetry allowed.

Symmetry is used primarily as a tool to observe the behavior of bonding m.o.'s in the transition state and determine if they are still bonding. Since the symmetry class of a particular orbital is invariant, the principle of the conservation of orbital symmetry affords a convenient method of predicting the "allowedness" of a particular reaction on the basis of whether bonding reactant m.o.'s remain bonding in the transition state.[12]

Cycloaddition Reactions

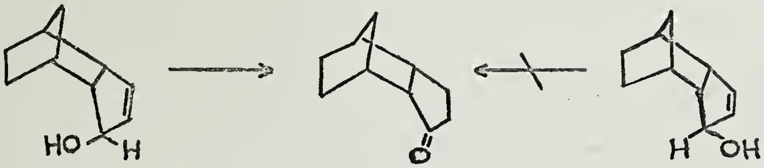
Two exemplary reactions are the concerted combination of two ethylene molecules to form cyclobutane and the Diels Alder combination of butadiene and ethylene to form cyclohexene. Examination of the latter shows that the molecular orbitals for the butadiene (X_1, X_2, X_3, X_4) and ethylene (π, π^*) molecules together with those for the cyclohexene product (σ_1, σ_2, π, π^*, $\sigma_2{}^*$, σ_1^*) can be classified as symmetric (S) or antisymmetric (A) with respect to a mirror plane preserved throughout the addition reaction. The resulting correlation diagram shows that all the reactant bonding m.o.'s translate as bonding m.o.'s of the product and hence the reaction is symmetry allowed in the ground state. Just the reverse is found for the addition of two ethylene molecules to form cyclobutane as bonding m.o.'s of the product are derivable from antibonding m.o.'s of the reactant making the reaction symmetry forbidden. For the two reaction processes described above, the "symmetry allowedness" of each is reversed in the first excited state reaction. A general rule which will distinguish the allowed cycloaddition reactions from the many various possibilities has been proposed.[8]

Inorganic Applications

Pettit and co-workers investigated certain symmetry forbidden polyolefin isomerization reactions which proceed rapidly in the presence of certain metal ions.[9] For example, the 1,3 hydrogen

migration via a supraficial shift is a symmetry forbidden process. Nevertheless, it is apparent that the two accepted mechanisms for metal catalyzed 1,3 hydrogen atom shifts do not effectively explain all the observed cases, e.g., the 3-phenylpropene to 1-phenylpropene isomerization carried out in the presence of $DCo(CO)_4$. The expected high incorporation of deuterium atoms in the 1-phenylpropene product for the metal hydride addition mechanism or the involvement of an allyl intermediate was not observed by Orchin.[13] Pettit suggests a mechanism in which the presence of the metal now makes the 1,3 suprafacial hydrogen atom migration operative and questions if there is a favored spacial orientation of the coordinated metal with respect to the migrating hydrogen atom.

The $Fe(CO)_5$ catalyzed isomerization of the alcohol below to the corresponding ketone provides a possible explanation. While one epimer readily undergoes a 1,3 shift which ultimately tautomerizes to the ketone, the other remains unaffected. The transition state proposed is one in which the migrating hydrogen is on the same side as the Fe atom.



Eaton has combined orbital symmetry with crystal field theory and applied it to certain isomerization reactions involving d^8 transition metal complexes.[10] Using the set of d orbitals as his basis set, various ligand geometries are interconverted and the corresponding crystal field energies noted. Correlation diagram considerations concur that tetrahedral-square planar isomerization demonstrated by bis(N,N-disubstituted aminotroponeimineates) and bis(N-sec-alkylsalicylaldimines) of Ni(II) are symmetry allowed.[14,15] Similarly cis-trans isomerizations as for $Pt(PEt_3)_2Cl_2$ are thermally symmetry forbidden, but photochemically allowed. By analogous reasoning, axial-equatorial isomerizations for trigonal bipyramidal molecules through a square pyramidal intermediate are symmetry allowed in the ground state for d^8 systems, but symmetry forbidden for spin free d^2 and spin paired d^3 and d^4 complexes.

Future

While the most extensive use of the Woodward-Hoffmann rules will likely remain with organic chemistry, the door is open for the inorganic chemist. In view of the vast number of stereospecific reactions satisfactorily explained by organic chemists employing the Woodward-Hoffmann rules, one is dismayed at the meager output of their inorganic neighbors in this respect. The more complex nature of transition metal chemistry may inherently have slowed widespread inorganic application of the Woodward-Hoffmann rules; nevertheless, one must wonder when and if a real genesis will occur.

References

1. R. B. Woodward and R. Hoffmann, J. Am. Chem. Soc., 87, 395 (1965).
2. R. Hoffmann and R. B. Woodward, Ibid, 87, 2046 (1965).
3. R. B. Woodward and R. Hoffmann, Ibid, 87, 2511 (1965).
4. R. Hoffmann and R. B. Woodward, Ibid, 87, 4388 (1965).
5. R. Hoffmann and R. B. Woodward, Ibid, 87, 4389 (1965).
6. R. Hoffmann and R. B. Woodward, Accts. Chem. Res., 1, 17 (1968).
7. R. Hoffmann and R. B. Woodward, Science, 167, 825 (1970).
8. R. B. Woodward and R. Hoffmann, Angew. Chem. Int. Ed., 8, 781 (1969).
9. R. Pettit, H. Sugahara, J. Wristers and W. Merk, Disc. Faraday Soc., No. 47 (1969).
10. D. R. Eaton, J. Am. Chem. Soc., 90, 4272 (1968).
11. H. C. Longuet-Higgins and E. W. Abrahamson, Ibid, 87, 2045 (1965).
12. J. J. Vollmer and K. L. Servis, J. Chem. Ed., 45, 214 (1968).
13. R. W. Goetz and M. Orchin, J. Am. Chem. Soc., 85, 1549 (1963).
14. R. H. Holm, A. Chakravorty, and G. O. Dudek, Ibid, 86, 379 (1964).
15. D. R. Eaton, W. D. Phillips and D. J. Caldwell, Ibid, 85, 397 (1963).

METHODS OF DISTINGUISHING INNER AND OUTER SPHERE MECHANISMS IN ELECTRON TRANSFER REACTIONS

Dennis Mahoney April 21, 1970

Electron transfer reactions between transition metal complexes have been a popular topic in inorganic kinetics. Numerous reviews have been published.[1-4]

Early work by Taube showed that reactions may occur by one of two mechanisms: a simple transfer of the electron during which the ligand shells remain intact (outer sphere mechanism) or a displacement of a ligand on one complex by a ligand on the other to form a bridged intermediate (inner sphere mechanism).

Theoretical treatments[5,6] of outer sphere type reactions have been made, especially by Marcus. The relations derived allow predictions of rate constants for a related series of reactants to be made with quite good accuracy. This topic was discussed previously.[7] Little theoretical work on inner sphere mechanisms has been attempted, chiefly because of their greater complexity.[8,9]

Inner and outer sphere mechanisms are not always easy to distinguish even though the rate law may be readily obtained. For even though the mechanisms may be completely different identical bimolecular rate laws may result. Taube has stated the conditions which must be present in order that the two mechanisms may be differentiated. They are:[10]

i) a reaction is inner sphere if it can be shown that a ligand attached to one reactant before electron transfer is attached to the other immediately after reaction.

ii) a reaction is outer sphere if the transfer takes place at a rate greater than the rate of substitution of the ligands or if none of the ligands are capable of acting as a bridge.

Because many reactions do not satisfy the above conditions, a number of indirect tests have been proposed. The main methods are:

i) Entropies of activation
ii) Volumes of activation
iii) Comparison of reaction rates
iv) Azide-thiocyanate test
v) Effect of non-bridging ligands
vi) Effect of changing solvent from H_2O to D_2O

i) The main factors in determining the change in the entropies of activation in going from an outer sphere activated complex to an inner sphere one are an increasing

electrostriction of solvent and the setting free of the displaced ligand in an inner sphere case. The two factors work against each other and no clear cut pattern emerges.[3,11,12,13,14a,b,15]

ii) Volumes of activation should be positive for inner sphere reactions.[16] Little work has been done and it appears that conflicting effects, such as those in i) may make interpretation difficult.

iii) The Marcus theory predicts that rates of reactions in a series should vary in a simple fashion[17] provided the mechanisms are similar. For example, Zwickel and Taube[11] found the relative rate constants for $[Co(NH_3)_5X]^{2+}$ + Red to be

Oxidant	$k_{V^{2+}}{}^{*}$	$k_{Cr(bipy)_3^{2+}}{}^{**}$
$R-NH_3{}^{*‡}$	1	1
$R-OH_2$	135	91
$R-OH$	$<10^7$	50
$R-Cl$	1.6×10^3	1.5×10^3

* reductant is V^{2+}; ** reductant is $Cr(bipy)_3{}^{2+}$;
*‡ $R = [Co^{III}(NH_3)_5{}^-]$

iv) If an oxidant R-X ($X = N_3^-$, SCN^-) forms an inner sphere activated complex and if the reductant bonds to the N and of the SCN^- better than the S end, then the rate constant for N_3^- is expected to be much greater than that for SCN^-.[18,20]

v) Studies by Haim and coworkers[19,20] have shown that a no-bridging ligand may have a significant effect on the rate of an inner sphere reaction. The usefulness of this observation as a test for mechanism is weakened, however, by the observations of Patel and Endicott,[21] who observe similar effects in reactions which are definitely outer sphere.

vi) Solvent effects on the rate are small and their significance, if any, with respect to the pathway is not understood.[3,11]

The method of Haim[22] is also discussed. In this procedure, one calculates an hypothetical equilibrium constant for the reaction:

$$[Co(NH_3)_5 - F - Red]^{‡} + I^- \rightleftharpoons [Co(NH_3)_5 - I - Red]^{‡} + F^- .$$

It is found that for inner sphere reactions, the value obtained is less than one, and for outer sphere reactions, it is greater than one.

Conclusions. The method of Haim and the azide-thiocyanate tests may be used with confidence. The azide-thiocyanate test does give intermediate values in some cases which are of questionable significance. The comparison of rates is also useful; entropies and volumes of activation are poorly understood and appear to be of little value. The effects of non-bridging ligands are also variable and must be used with caution.

Review Articles:

1) J. Halpern, Quart. Revs., 15, 207 (1960).
2) R. A. Marcus, Ann. Revs. Phys. Chem., 15, 155 (1964).
3) N. Sutin, ibid., 17, 119 (1966).
4) A. Sykes, Adv. Inorg. Chem. Radiochem., 10, 153 (1967).

Theoretical Discussions:

5) R. J. Marcus, B. Zwolinski and H. Eyring, Chem. Revs., 55, 157 (1955).
6) R. A. Marcus, J. Chem. Phys., 43, 679 (1965) and references therein.
7) J. Orrell, Chemistry 405, October 14, 1969, and references therein.
8) R. A. Marcus, J. Phys. Chem., 72, 891 (1968).
9) P. Schmidt, Aust. J. Chem., 12, 673 (1969).

Experimental Work:

10) F. Basolo and R. Pearson, Mechanisms of Inorganic Reactions (Wiley, 1968), p. 479ff.
11) A. Zwickel and H. Taube, J. Am. Chem. Soc., 83, 793 (1961).
12) J. Caudlin, J. Halpern and D. Trium, ibid., 86, 1019 (1964).
13) J. Endicott and H. Taube, ibid., 86, 1686 (1964).
14a) W. Higginson et al., Disc. Fara. Soc., 29, 49 (1960).
14b) W. Higginson et al., ibid., 29, p. 123ff (1960).
15) J. Stritar and H. Taube, Inorg. Chem., 8, 2281 (1969).
16) J. Caudlin and J. Halpern, ibid., 4, 1086 (1965).
17) R. A. Marcus, J. Phys. Chem., 67, 853 (1963).
18) J. Espenson, Inorg. Chem., 4, 121 (1965).
19) P. Benson and A. Haim, J. Am. Chem. Soc., 87, 3826 (1965).
20) N. Sutin and A. Haim, ibid., 88, 434 (1966).
21) R. Patel and J. Endicott, ibid., 90, 6364 (1968).
22) A. Haim, Inorg. Chem., 7, 1475 (1968).

APPLICATIONS OF TEMPERATURE-JUMP RELAXATION METHODS TO THE STUDY OF FACTORS INFLUENCING THE RATE OF WATER REPLACEMENT IN TRANSITION-METAL COMPLEXES

Nicholas K. Kildahl April 28, 1970

Introduction

The development during the past 15 years of methods for studying chemical relaxation phenomena[1] has greatly extended the time range available to the kineticist. Using such methods as temperature-jump (T-jump), pressure-jump (P-jump), and electric field-jump (E-jump) relaxation, he is now able to measure reaction rates falling in the formerly inaccessible time range from 10^{-3} to 10^{-9} seconds. This seminar will be restricted to a review of the T-jump method and its uses in studying the rate of displacement of water by other ligands in complexes of the transition metals.

Theory

The principle of relaxation methods is quite simple. A chemical system is first allowed to come to equilibrium under conditions of constant temperature, pressure, etc. This equilibrium is then destroyed by a sudden change in some chosen external parameter, and the approach to equilibrium under the new set of conditions is followed by an appropriate detection technique. The perturbing parameter used in the T-jump method is, of course, the temperature. However, in order for a temperature change to affect the equilibrium of a given chemical reaction, it is necessary that the heat of reaction be nonzero. Since not all reactions meet this criterion, it would appear that this condition is somewhat restrictive. Nevertheless, in some cases, it is possible to couple the reaction of interest with an indicator reaction which does have a finite heat. This enables the experimentalist to study most interesting reaction types.

The observable associated with the relaxation experiment is the relaxation time, τ. For a one-step reaction, as will be shown, τ can be easily related to the rate constants and equilibrium concentrations of the reactants involved. However, for a multiple relaxation process, there will be as many relaxation times as there are independent reaction steps. Further, the single relaxation times do not usually correspond to the single reaction steps, due to coupling among these steps. Thus the observed relaxation times correspond to normal modes of reaction.

Applications

The study of the exchange kinetics of transition-metal complexes during the past decade has been intensive. One of

the major areas of interest has been the study of factors influencing the rate of water replacement in these complexes. It has been recognized for quite some time that for reactions of the type

$$ML_x(H_2O)_{6-x} + L' \underset{k_r}{\overset{k_f}{\rightleftharpoons}} ML_x(H_2O)_{5-x}\,L' + H_2O$$

the rate-determining step, following the initial formation of an ion-pair, is the release of a water molecule from the inner coordination sphere of the metal ion. However, the actual rate of release of the water molecule can vary, depending upon the nature of both L and L'.

In 1962, Hammes and Steinfeld[2] studied the rates of formation and dissociation of Ni(II) and Co(II) complexes with one, two, and three glycine, diglycine, triglycine, and imidazole molecules using the temperature-jump technique. They found that the rate of dissociation of water is faster for Co(II) than for Ni(II) and that, for the ligand glycine, this rate tends to increase in reactions involving the higher complexes. They took this as an indication for the loosening of the hydration shell due to bonding through the negative carboxyl group of glycine; and they concluded further that if bonding takes place through uncharged groups, the rate of water loss is independent of the number of bound ligands.

Hammes and Morrell[3] extended the above work in 1963 when they measured the rate constants for the formation of the Ni(II) and Co(II) complexes of pyrophosphate and tripolyphosphate using T-jump methods. They determined that the rate of water loss from the metal ion is the rate-determining step but that the highly-charged ligands accelerate this rate for Co(II).

Perhaps the most interesting study of the type with which this seminar is concerned was the one performed by Rorabacher in 1966.[4] He measured the kinetics of formation and dissociation for the monoammine complexes of Co(II), Ni(II), and Zn(II) in aqueous solution in order to compare these rates with those for the formation of previously-studied polyamine complexes, which were found to be abnormally fast. To account for the difference in rates, he proposed an internal conjugate base mechanism which explained increases in K_O, the equilibrium constant for ion-pair formation, and k_O, the rate constant for water loss.

Other important work was carried out in 1966 by Kustin et al.,[5,6] when they used T-jump techniques to measure rate constants for the formation of complexes of α- and β-alanine and α- and β-aminobutyric acids with Co(II) and Ni(II). They found that with α-alanine, Co(II) substitution is faster than Ni(II) substitution; but with β-alanine, Co(II) substitution is slowed considerably, whereas that of Ni(II) remains about the same. In the case of the aminobutyric

acids, both Ni(II) and Co(II) react more slowly with the β- than with the α-ligand. They interpret these results as being indicative of a rate-limiting ring-closure mechanism in the case of the β-compounds.

Finally, Margerum and his group have done quite significant work on this problem. In 1966, Margerum and Rosen[7] observed the rates of displacement of water by ammonia to be dependent upon the nature of multidentate ligands already coordinated to Ni(II). Contrary to the results of Hammes et al., they found that the charge of the complex is not of much importance in determining this rate; instead they contend that the electron-donating ability of the coordinated groups and the structure of the complex are the important factors. In 1969, Margerum and Jones[8] found that formation of $Ni(en)_3^{2+}$ (en=ethylenediamine) from $Ni(en)_2(H_2O)_2^{2+}$ and en is very fast compared to formation of either of the two lower complexes. Further, they found that ring closure contributes to the limiting rate in the formation of $Ni(en)_3^{2+}$.

Conclusion

Although it appears that many of the factors influencing the rate of water loss from transition-metal complexes have been identified, they have yet to be combined into a unified theory. Temperature-jump relaxation techniques have so far proved to be quite valuable in the elucidation of this interesting problem. Undoubtedly, they will prove just as useful in future work.

References

1. M. Eigen and L. DeMaeyer in "Technique of Organic Chemistry," A. Weissberger, Ed., Vol. VIII, Part II, 2nd ed., Interscience Publishers, New York, N. Y., 1963.
2. G. Hammes and J. Steinfeld, J. Am. Chem. Soc., 84, 4639 (1962).
3. G. Hammes and M. Morrell, J. Am. Chem. Soc., 86, 1497 (1964).
4. D. B. Rorabacher, Inorg. Chem., 5, 1891 (1966).
5. K. Kustin, R. Pasternack, and E. Weinstock, J. Am. Chem. Soc., 88, 4610 (1966).
6. A. Kowalak, K. Kustin, R. Pasternack, S. Petrucci, J. Am. Chem. Soc., 89, 3126 (1967).
7. D. Margerum and H. Rosen, J. Am. Chem. Soc., 89, 1088 (1967).
8. J. Jones and D. Mergerum, J. Am. Chem. Soc., 92, 470 (1970).

KINETIC STUDIES ON SOLID STATE REACTIONS OF CHROMIUM COMPLEXES

J. E. House, Jr. May 5, 1970

Part I.

Although there has been a recent increase in interest in solid state reactions involving coordination compounds, the deamination of solid tris(ethylenediamine)- and tris(propylenediamine)chromium(III) salts has been the subject of several studies over many years. Pfeiffer reported that $[Cr(en)_3](NCS)_3$ and $[Cr(en)_3]Cl_3$ each lose a molecule of ethylenediamine when heated at 130° and 160°, respectively, to produce trans-$[Cr(en)_2(NCS)_2]NCS$ and cis-$[Cr(en)_2Cl_2]Cl$.[1] Rollinson and Bailar found that $[Cr(en)_3](NCS)_3$ prepared by Pfeiffer's method (treating a solution of the sulfate with ammonium thiocyanate) could be deaminated but $[Cr(en)_3]Cl_3$ prepared directly from anhydrous $CrCl_3$ and ethylenediamine could not.[2] They found that the deamination was catalyzed by the corresponding ammonium salt and that $[Cr(en)_3](NCS)_3$, which was highly pure, could not be deaminated easily. O'Brien and Bailar found that, of the compounds $[Cr(AA)_3]X_3$ (where AA = en or pn and X = Cl^-, Br^-, I^-, etc.), only the chloride and thiocyanate are easily deaminated to give a diacido product.[3]

Bear and Wendlandt studied these reactions using DTA and TGA and reported activation energies for the deaminations in the presence and absence of catalysts.[4] Ammonium thiocyanate was found to lower the activation energy by about 15 kcal/mole.

The work described in this seminar was undertaken to study the deamination of $[Cr(en)_3](NCS)_3$ and $[Cr(pn)_3](NCS)_3$ in more detail, and the reactions were followed by isothermal thermogravimetric measurements. The fraction of the complex deaminated was found to vary linearly with time up to about 50% completion, although no rate law was found which would describe the data for reactions proceeding 70-80% toward completion. Amine hydrothiocyanates were found to be as effective as catalysts as ammonium thiocyanate and the reaction shows a first order dependence on catalyst concentration over a wide range of catalyst/complex ratios. The deamination reactions are acid catalyzed reactions with the protonated amine functioning as the acid.[5] Other results obtained using differential scanning calorimetry (DSC) will be presented and discussed.

A proposed mechanism for the deamination is characterized by a rate determining step in which one end of a coordinated en molecule is detached from the chromium ion by electrophilic attack by the acidic species. An entering thiocyanate ion, exerting a strong trans influence, may labilize

the position trans to it with the breaking loose of an end of a second ethylenediamine molecule. A second thiocyanate ion attaches itself at this vacated position. The loosening of the attached end of one of the monocoordinated en molecules, followed by the attachment of the other, completes the process. In the case of $[Cr(en)_3]Cl_3$, either the chloride ion may not exert a strong enough trans effect or may exert a cis effect, the results being indistinguishable.

Part II.

Many examples of linkage isomerism are known involving CN^-, SCN^-, $SeCN^-$, and NO_2^- as ligands. Several compounds containing these ligands are known to undergo transformations from one form to another. Shriver, et al., predicted that the most stable form of $KFeCr(CN)_6$ would contain Fe^{2+} surrounded in an octahedral arrangement by the carbon ends of the cyanides and the Cr^{3+} would be surrounded in a similar arrangement by the nitrogen ends.[6] These workers found spectral evidence to show that if $Cr(CN)_6^{3-}$ is treated with Fe^{2+}, the resulting complex exhibits linkage isomerization in the solid state. The C≡N stretching band is found at 2168 cm^{-1} in $Cr^{3+}-C{\equiv}N-Fe^{2+}$ and at 2092 cm^{-1} in $Cr^{3+}-N{\equiv}C-Fe^{2+}$ linkages. In a subsequent report, this system was studied in greater detail using IR, x-ray diffraction, magnetic susceptibility, and Mössbauer spectroscopy.[7] The product containing iron(II) hexacyanochromate(III) was reported to have a variable composition and the linkage isomerization was accompanied by some oxidation. The reaction was reported to follow approximately first order kinetics and gave a fairly linear Arrhenius plot corresponding to an activation energy of 17 kcal/mole.

In the work carried out on this reaction, it was found that the linkage isomerization in a compound containing Fe^{2+} and Cr^{3+} in about a 1:1 ratio followed a second order rate law with a good linear fit of the data. The reaction was followed by the relative intensity of the peaks at 2168 and 2092 cm^{-1}. An activation energy of 24.1 kcal/mole was obtained.[8] The second order rate law implies that the cyanide ions change bonding modes in pairs, probably by a process involving a cis or trans effect depending on whether a cis or trans pair flips.

References:

1. P. Pfeiffer, P. Koch, G. Lando, and A Trieschmann, Ber., 37, 4269, 4277 (1904).

2. C. L. Rollinson and J. C. Bailar, Jr., J. Am. Chem. Soc., 66, 641 (1944).

3. T. D. O'Brien and J. C. Bailar, Jr., J. Am. Chem. Soc., 67, 1856 (1945).

4. J. L. Bear and W. W. Wendlandt, J. Inorg. Nucl. Chem., 17, 286 (1961).

5. J. E. House, Jr., and J. C. Bailar, Jr., J. Am. Chem. Soc., 91, 67 (1969).

6. D. F. Shriver, S. A. Shriver, and S. E. Anderson, Inorg. Chem., 4, 725 (1965).

7. D. B. Brown, D. F. Shriver, and L. H. Schwartz, Inorg. Chem., 7, 77 (1968).

8. J. E. House, Jr., and J. C. Bailar, Jr., Inorg. Chem., 8, 672 (1969).

NMR OF SOLUTES CONTAINING SPIN 1/2 NUCLEI IN NEMATIC LIQUID CRYSTAL SOLVENTS

Joel H. Elias May 12, 1970

Introduction:

The study of nuclear magnetic resonance spectroscopy of solutes dissolved in liquid crystal solvents began in 1963 with the publication by Saupe and Englert[1] of the spectrum of benzene dissolved in a nematic solution. They interpreted the complex spectrum observed in terms of the direct magnetic dipole-dipole interraction between magnetic nuclei. The theory of such interractions in molecules oriented in strong electric fields was first outlined by Buckingham and Pople.[2] The spin Hamiltonian for solute molecules ordered in nematic liquid crystals has been derived by Saupe[3,4] in terms of an order matrix S, and by Snyder[5] in terms of an expansion of the angular probability of the applied magnetic field orientations in a molecular fixed coordinate system. Both formulations have been shown to be related.[5] Snyder and Anderson[5,6] have applied computer techniques to both the experimental and analytical aspects of this method. By using the computer of average transients method, they obtained highly resolved spectra. Computer simulated spectra were employed in the analysis of experimental spectra.

Interpretation of the NMR spectra obtained by this method can yield much useful chemical information. Structural information such as bond lengths and angles,[4-7,9,10] absolute signs of indirect spin-spin coupling constants,[4-7,9,10] chemical shift anisotropies,[4,11] and quadrupolar coupling constants have been obtained.

This seminar will examine the theory of NMR spectra of solutes in nematic liquid crystal solvents and its application to the determination of molecular structures, chemical shift anisotropies, and absolute signs of indirect spin-spin coupling constants.

Theory:

The general spin Hamiltonian for magnetic nuclei is given by:

$$H = -\frac{h}{2\pi}\overrightarrow{H_0}\cdot\sum_p\gamma_p(\overleftrightarrow{1}-\overleftrightarrow{\sigma}_p)\cdot\overleftarrow{I}_p + h\sum_{p>q}\overrightarrow{I}_p\cdot\overleftrightarrow{A}_{pq}\cdot\overleftarrow{I}_q \qquad (1)$$

where γ is the magnetogyric ratio, H_0 is the applied field, $\overleftrightarrow{\sigma}$ is the shielding tensor, $\overleftrightarrow{A}$ is a general spin coupling tensor which includes indirect, direct, inter-, and intramolecular interractions, and I is the nuclear spin angular momentum operator.

The general Hamiltonian can be reduced to the following form:[4]

$$H = -\frac{h}{2\pi} H_z \sum_p \gamma_p (1 - \sigma_p - \delta_p) I_{zp} + h \sum_{p>q} J_{pq} \vec{I}_p \cdot \overleftarrow{I}_q$$

$$+ h \sum_{p>q} B_{pq} (3 I_{zp} I_{zq} - \vec{I}_p \cdot \overleftarrow{I}_q) \qquad (2)$$

if terms coupling stationary states having different eigen values of the operator $F_z = \sum_p I_{zp}$ are neglected.[5] σ_p is the scalar shielding constant, δ_p is the orientation dependent shielding anisotropy, J_{pq} is the scalar indirect spin-spin coupling constant, B_{pq} is a spin-spin coupling constant which contains the anisotropic part of the indirect spin-spin coupling constant, and the direct magnetic dipole-dipole interraction.

The direct spin-spin coupling constant is given by:[4]

$$B_{pq}^{dir} = -\frac{h}{4\pi^2} \gamma_p \gamma_q \left\langle \frac{1}{r_{pq}^3} \right\rangle \frac{1}{2} \left\langle 3 \cos^2\theta_{pq} - 1 \right\rangle \qquad (3)$$

$$= -\frac{h}{4\pi^2} \gamma_p \gamma_q \left\langle \frac{1}{r_{pq}^3} \right\rangle S_{pq}$$

$$\text{where} \quad S_{pq} = \frac{1}{2} \left\langle 3 \cos^2\theta_{pq} - 1 \right\rangle \qquad (4)$$

r_{pq} is the internuclear distance, θ_{pq} is the angle between the internuclear axis and the applied field, and the brackets indicate averages over the molecular motion. The indirect contribution to B_{pq} appears to be negligible for proton-proton spin-spin couplings.[6] In isotropic liquids, the expectation values S_{pq} vanish and direct dipolar coupling is not observed.

Nematic liquid crystal solvents can be more or less completely homogeneously oriented by magnetic fields of the order of a few thousand gauss. Solute molecules dissolved in such oriented solvents are ordered to some degree by the anisotropic environment. Intramolecular dipolar interactions no longer average to zero and dipolar splittings are observed in the NMR spectrum of the solute. The solute molecules, while ordered, translate and rotate rapidly with respect to the solvent, and intermolecular dipolar coupling vanishes.

The degree of order of the solute is described[3] by an S matrix which may have up to five independent elements of the form:

$$S_{ij} = \frac{1}{2}\left\langle 3\cos\theta_i \cos\theta_j - \delta_{ij}\right\rangle \quad i,j = \xi, n, \zeta \qquad (5)$$

ξ , n, and ζ are the axes of a molecular fixed coordinate system, θ_i are the angles between the given axis and the optical axis of the aligned solvent and δ_{ij} is the Kroenecker delta function. The observed splittings are shown in equation (3) to depend on the values of S_{pq}, which are related to the S_{ij} by a cosine transformation, and $\langle 1/r^3_{pq}\rangle$. The amount of structural and motional information which can be derived from the spectrum depends on the number of direct dipolar interractions.

Applications:

Structural studies in nematic crystal solvents are presently limited to molecules containing no more than nine magnetic nuclei.[7] The spectra of molecules containing more than nine magnetic nuclei may not be sufficiently resolved and analysis by computer simulation becomes prohibitively costly. It should be noted that this method measures the average values over molecular vibrations $\langle 1/r^3_{pq}\rangle$ and not equilibrium internuclear distances.

In the analysis of chemical shielding anisotropies, contributions to δ due to volume susceptibility changes in the solvent, and anisotropic solvent effects must be considered.

Future:

The method of NMR in liquid crystals has proven to be useful for the determination of structural parameters for small molecules in solution. Selective deuteration and spin decoupling[7] may be used in the future to extend its application to larger molecules.

Absolute signs of indirect spin-spin coupling constants will be useful in the evaluation of theoretical calculations.[8]

References:

1. A. Saupe and G. Englert, Phys. Rev. Letters, 11, 462 (1963).
2. A. D. Buckingham and J. A. Pople, Trans. Faraday Soc., 59, 2421 (1963).
3. A. Saupe, Z. Naturforsch, 19a, 161 (1964).
4. A. Saupe, G. Englert, and A. Pouh, Adv. in Chemistry Series, 63, 51 (1967).
5. L. C. Snyder, J. Chem. Phys., 43, 4041 (1965); 47, 1480 (1967).
6. L. C. Snyder and E. W. Anderson, J. Am. Chem. Soc., 86, 5023 (1964); J. Chem. Phys., 42, 3336 (1965).
7. S. Meiboom and L. C. Snyder, Science, 162, 1337 (1968).
8. R. A. Bernheim and B. J. Lavery, J. Am. Chem. Soc., 89, 1279 (1967).
9. C. S. Yannoni, G. P. Ceasar, and B. P. Dailey, J. Am. Chem. Soc., 89, 2833 (1967).
10. G. Englert and A. Saupe, Mol. Cryst., 1, 503 (1966); 8, 233 (1969).
11. G. P. Ceaser, C. S. Yannoni, and R. P. Dailey, J. Chem. Phys., 50, 373 (1969); 51, 655 (1969).

APPLICATIONS OF ELECTRON DIFFRACTION TO INORGANIC COMPOUNDS

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Introduction:

It is now 32 years since Davisson and Germer first demonstrated the phenomenon of electron diffraction. Since then the electron diffraction method has been widely applied in the study of the structure of matter. It is the purpose of this seminar to review electron diffraction techniques and to show how they can be used to solve problems in inorganic chemistry. There seems to be no recent text or review which covers all topics of interest in electron diffraction, and each year new theories and techniques are developing.

Theory:

An electron diffraction experiment[1] consists primarily of the determination of the total (t) diffracted intensity, $I_t(s)$, as a function of the angle of diffraction (2θ). In the case of molecular (m) scattering, the diffracted intensity becomes $I_m(s)$ and is given by

$$I_m(s) = (K/s^4) \sum_{i \neq j}\sum (Z_i - f_i)(Z_j - f_j) \exp[-(1/2)(U_{ij}^2 s^2)][(\sin R_{ij}^e s/(R_{ij}^e s)] \tag{1}$$

$$\mu(r) = \text{Radial distribution} = (2/\pi)\int_0^\infty s^5 I_m(s)\phi(s) \sin r\, s\, ds \tag{2}$$

Instead of the diffraction angle 2θ, it is convenient to write the dependence on $s = (4\pi/\lambda)\sin\theta$, where λ is the wave length and θ the Bragg angle (one half the diffraction angle). K is an instrumental constant at constant electron velocity, Z_i is the atomic number of the i^{th} atom, f_i is the scattering amplitude of the i^{th} atom, and R_{ij}^e is the equilibrium distance (Å) between the i^{th} and the j^{th} atom in the molecule. The root-mean-square deviation distance is U_{ij}, usually called "mean amplitude of vibration." μ(r), the radial distribution function (RD), gives the probability that a nucleus j will be found at a distance r from a nucleus i in the molecule. ϕ(s) is a modification function to simplify the RD curve. Thus μ(r) will have a maximum for each value of r corresponding to an internuclear distance in the molecule. Bond angles in a molecule can also be computed if sufficient neighboring internuclear distances are known. In short, the theoretical curve contains molecular structural information, namely the interatomic distances and U values. The validity of eqn. (1) is limited by the following assumptions: (1) small harmonic oscillations of the atoms occur, (2) no phase shift occurs in the scattering process.

In the actual experiment two things are particularly important. The $1/s^4$ factor in the expression for $I_m(s)$ is responsible for the steep fall off in the total intensity curve with diffraction angle. This effect is minimized by using a rotating sector to enhance the higher angle data. Also, the electron diffraction diagrams depend critically upon the gas nozzle which spreads out the gas in the apparatus.

Applications:

Some topics of current interest in electron diffraction are listed below.

I. Molecular structure

II. Molecular force fields, which give information about:

  A. Internal rotation
  B. Quadratic force constants from amplitudes of vibration
  C. Cubic force constants from effect on intermolecular distances of

    *(1) temperature[2]
    (2) isotopic substitution

III. Charge distributions in atoms and molecules

  A. In ground state:

    (1) $D_i(r)$ distribution of electrons about nuclei
    **(2) $P_{ij}(r)$ distribution of electrons about other electrons
    (3) $P_{mn}(r)$ distribution of nuclei about other nuclei

  B. In excited states: Information about geometry of excited state orbitals[3]

IV. Intermolecular forces in gases
  From nonuniform distribution of molecules[4]

V. Surfaces of solids
  Low energy electron diffraction (LEED)

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* Experiments to data rather rough
** Only a gleam in eyes of electron diffractionists

The main features of the molecular structure of ferrocene and ruthenocene have been firmly established[5,6] by X-ray diffraction in the crystal. However, the position of the hydrogen atoms and the shape and height of the barrier to internal rotation of the ligand in the isolated molecule remained unknown. In X-ray investigations, in the absence of contradictory evidence, the hydrogen atoms have been assumed to lie in the plane of the cyclopentadienyl ring (D_{5h} symmetry). Recent electron-diffraction experiments[7,8] by Haaland _et. al._ show that in the case of hydrogen atoms in ferrocene in the gas phase this assumption is invalid. The hydrogen atoms are bent about 5° out of the plane towards the metal atom. These workers also measured the barrier to internal rotation and concluded that the eclipsed model

of ferrocene seems the most probable in the gas phase although a freely rotating one cannot be excluded. The barriers to internal rotation in ferrocene and ruthenocene are, respectively, 0.91 ± 0.32 and 26±49 kcal mole^{-1} (ruthenocene value unsatisfactory). The origin of the barrier has been ascribed to ligand-to-metal-to-ligand bonding, or to Van der Waals' attraction between the rings.

We now address ourselves to the problem of calculating electron densities from gas-phase electron diffraction experiments.[9] A few experimental measurements[10,11] have been made which indicate that charge distributions can be obtained to an accuracy that is chemically meaningful. If r is the internuclear distance, then, according to the first Born approximation, the total intensity of scattered electrons depends on the sine transforms of (a) the nuclear charge distribution, i.e., the position of the nuclei in the scatterer, (b) the electron density $\rho(r)$ (related to $D_i(r)$ and $\sigma_{ne}(s)$ below) relative to the nuclear framework, and (c) the electron-electron function $\rho_c(r)$ (related to $P_{ij}(r)$ and $\sigma_{ee}(s)$ below) describing the density of electrons relative to the other electrons. The intensities must be averaged over all orientations of the scatterer. For a homonuclear diatomic molecule if one of the nuclei is chosen as the origin of the coordinate system and if the position of the other nucleus is given by the vector r_{aB}, the total scattered intensity for electrons can be expressed as

$$\sigma_{tot}(s) = f_1[\rho(r)] + f_2[\rho_c(r)] \tag{3}$$

$$\sigma_{tot} = S^4 I_{tot} = f_3[D_i(r)] + f_4[P_{ij}(r)] \tag{4}$$

$$\sigma_{tot} = \sigma_{ne}(s) + \sigma_{ee}(s) \tag{5}$$

where $D_i(r)$ and $P_{ij}(r)$ have been defined previously, and $\sigma_{ne}(s)$ and $\sigma_{ee}(s)$ are, respectively, the electron-nuclear and electron-electron contribution to the total scattered intensity. In principle $\rho(r)$ could be determined from the above expressions but this is quite difficult to do. It is easier to calculate differential cross sections. The sensitivity of the diffraction approach will be gauged from a comparison of results for molecules following Hartree-Fock theory with results for hypothetical molecules built up of independent Hartree-Fock atoms. The difference functions which are used are of the form $\Delta\sigma(s) = \sigma(s) - \sigma(s)$, where $\sigma^{iam}(s)$ is a reference function. Of special interest is the Roux function[12] $\Delta\rho(r) = \rho(r) - \rho_{atom}(r)$, the function corresponding to the difference between molecular electron density and the sum of the densities of the free atoms separated by a distance r_{AB}. There is the problem of uniqueness in the transformation from $\sigma_{ne}(s)$ to $\rho(r)$. On the other hand there is no problem as to the uniqueness in the transformation from $\rho(r)$ to $\sigma_{ne}(s)$, and the scattered intensity may prove to be more suitable as a test of computed electron densities than as a means for determining densities directly (the analogy here with X-ray crystallography is helpful). Since the potential energy difference, $\Delta\overline{U}$, between the actual molecule and the independent-atom molecule can be calculated rather well by electron diffraction, the method may prove to be one of the best observables in addition to the total energy for determining the quality of computed wavefunctions.

In the last few years low energy diffraction (LEED), where electrons are mainly reflected from atoms at the surface, has been developed to provide information on the two dimensional structure and constitution of surfaces. The method is best applied to surfaces which are well defined on the atomic scale. The particular usefulness of LEED for studying adsorption processes arises from the fact that adsorption usually results in some degree of order so that distinct diffraction patterns will appear and any new periodicity parallel to the substrate surface is easily established. Various applications of LEED are physical adsorption,[14] adsorption of metal atoms,[15] chemisorption[16] and heterogeneous catalysis.[17] Surface structures have been found for the adsorption of CO, n_2, C_2H_4, C_2H_2, O_2 on Pt(100) and Pt(111) surfaces. Other molecules (C_2H_6, H_2) gave no evidence for ordered structures. The results are interpreted as indicating sp^2 hybridization of the carbon atoms in the adsorbed state.

Conclusion:

Electron diffraction has had a rather varied history of triumphs and failures. Although it is thought of as a tool for measuring molecular structure in the gas phase, recently we have begun to be aware of its potential power for probing more deeply into the quantum chemistry of molecules. The development of LEED is revolutionizing the study of surface chemistry and catalysis. The electron diffraction method is blossoming into a number of promising directions and it is contributing significantly to the progress of chemistry.

References:

1. O. Bastiansen and P. N. Skancke, Advan. Chem. Phys., 3, 323 (1961).
2. K. Hedberg and M. Iwasaki, J. Chem. Phys. 36, 589 (1962).
3. J. Karle, J. Chem. Phys. 35, 963 (1961).
4. Y. Morino, K. Kuchitsu, and R. A. Bonham, Bull. Chem. Soc. Japan 38, 1796 (1965).
5. J. D. Dunitz, L. E. Orgel, A. Rich, Acta Cryst. 9, 373 (1956).
6. G. L. Hardgrave and D. H. Templeton, Acta Cryst. 12, 28 (1959).
7. R. K. Bohn and A. J. Haaland, J. Organomet. Chem. 5, 470 (1966).
8. A. Haaland and J. E. Nilsson, Acta. Chem. Scand. 22, 2653 (1968).
9. D. A. Kohl and L. S. Bartell, J. Chem. Phys. 51, 2891-2904 (1969).
10. D. A. Kohl and R. Bonham, J. Chem. Phys. 47, 1634 (1967).
11. M. Fink and J. Kessler, J. Chem. Phys. 47, 1780 (1967).
12. M. Roux, S. Besnainou and R. Daudel, J. Chim. Phys. 54, 218 (1956); M. Roux, M. Cornille, and L. Burnelle, J. Chem. Phys. 37, 933 (1962); C. W. Kern and M. Karplus, J. Chem. Phys. 40, 1374 (1964).
13. D. H. Templeton and G. A. Somorjai, eds., Trans. Amer. Crystallogr. Assoc. 2 (1968).
14. J. Morrison and J. J. Lander, Surf. Sci. 5, 163 (1966).
15. P. W. Palmberg and W. T. Peria, Surf. Sci. 6, 57 (1967).
16. P. J. Estrup and J. R. Anderson, J. Chem. Phys. 45, 2254 (1966).
17. A. E. Morgan and G. A. Somorjai, Trans. Amer. Crystallogr. Assoc. 2, 59 (1968).