for the unfiltered flash light gives $r_0 = 4.8 \times 10^{-8}$ cm., hence $\beta_0 = 1 - \phi = 5\beta/6$ and $\beta = 0.935$. It can be shown[23] further that $\sigma \cong [3a(1 - \beta)]/\beta$ for small values of σ, and therefore the mean diffusive displacement is ca. 0.4×10^{-8} cm. based on the above value for β.

The assumption that the liquid is a continuous medium is obviously quite severe in view of such a small calculated diffusive displacement. Required is that the diffusive process take place by a series of very small steps occurring at very high frequency and hence low activation energy. This is consistent with the constant-volume measurements on the diffusion of molecular iodine in carbon tetrachloride[24] and the self-diffusion of carbon tetrachloride,[25] whereby the temperature coefficients of diffusion are very nearly the temperature

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coefficient of kinetic energy. However, in view of the discrepancies between the measured and calculated parameters in the diffusion-controlled rate expression, Noyes[20] has concluded that a small but significant energy barrier exists for recombination and dissociation processes.

Electron Spin Relaxation in Pseudo-Tetrahedral Cobalt(II) and Nickel(II) Complexes in Solution[1a]

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It is shown that the well-resolved proton magnetic resonance spectra of the paramagnetic, pseudo-tetrahedral Ni(II) complexes with aminotroponeimines and salicylaldimines, and the Ni(II) and Co(II) complexes with triarylphosphines, are the result of very short electron relaxation times, of magnitude $\sim 10^{-13}$ sec. The possible mechanisms responsible for these short relaxation times are investigated, and it is concluded that: (1) dynamic interconversion between diamagnetic and paramagnetic forms in solution for the Ni(II) complexes is too slow to be the dominant relaxation mechanism; (2) coupling of the zero field splitting to the tumbling of the complex in solution dominates the relaxation time for both the Co and Ni systems of interest. For the Ni complexes, these conclusions are reached by systematic elimination of the other possible mechanisms and by demonstrating that the electronic structures for these complexes favor the appearance of large zero field splittings necessary for such rapid relaxation. For the Co complexes, it is demonstrated that the short relaxation times can be quantitatively accounted for by a zero field splitting constant well within the range of values observed for other tetrahedral Co systems. The differences in p.m.r. line width for some triarylphosphine and aminotroponeimine complexes in carbon disulfide and chloroform are shown to be consistent with this relaxation mechanism.

Introduction

The appearance of a well-resolved proton magnetic resonance (p.m.r.) signal for paramagnetic complexes is the result[2] of their unpaired electron(s) possessing a very short relaxation time, T_1, or exchange time, T_e. For a sufficiently short electronic relaxation time, the p.m.r. line width for the complex may be only imperceptibly broader than for the diamagnetic ligands.[3]

Recently, a number of paramagnetic systems containing tetrahedrally coordinated Ni(II)[4-6] and Co(II)[7] have been investigated, whose p.m.r. spectra are characterized[4,8-14] by very narrow line widths (as narrow as 4-5

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c.p.s.). These systems of interest are the Ni(II) complexes of the various substituted aminotroponeimines,[4,8] (ATI)$_2$Ni, salicylaldimines,[9–11] (SAI)$_2$Ni, and the Co(II) and Ni(II) complexes with triarylphosphines,[12–14] (TAP)$_2$MX$_2$ and (TAP)MX$_3^-$, where X is a halogen. To date, there has been very little attention given to the possible reasons[8] for the narrow p.m.r. lines, or more directly, for the extremely short electronic relaxation times in these systems. A recent calculation,[15] using the observed p.m.r. line widths, gave values of $\sim 10^{-13}$ sec. for T_1 in the case of the TAP complexes. The p.m.r. spectra for the ATI[4,8] and SAI[9–11] complexes have approximately the same line widths as the TAP systems,[15] so that T_1 values of about the same magnitude could be anticipated.

The factors determining electron spin relaxation and their effect on electron spin resonance have been treated by several authors.[16–20] There are several important relaxation mechanisms which may operate in dilute solution.[16] Interaction with low-lying orbital states *via* spin–orbit coupling[16,17] will limit the lifetime of a spin state. This mechanism is most important for ions which have orbitally degenerate ground states,[16] where small low-symmetry distortions result in low-lying orbital levels. Anisotropy in the *g*-tensor or hyperfine tensor will lead to spin relaxation.[18] The importance of this mechanism depends upon the extent of anisotropy and the tumbling time of the complex in solution. The coupling of the zero field splitting of the ground-state spin multiplet to the tumbling in solution[16,19,20] can greatly decrease the electron relaxation time. This mechanism can only operate in complexes possessing two or more unpaired spins. Carrington and Luckhurst[19] concluded that for complexes with $S \geq 1$, this constitutes the dominant factor determining the relaxation time. Magnetic dipolar relaxation and exchange interaction are negligible at the concentrations used for p.m.r. studies.[16]

Another possible relaxation mechanism could result from a rapid interconversion in solution between two forms of a complex which are characterized by different spin multiplicity.[4,5,8–11,21] This mechanism has been suggested[8] as the possible cause of the short T_1 values, and resulting narrow p.m.r. line widths, for the (ATI)$_2$-Ni complexes. The known presence[5] of such a dynamic interconversion in solution for some of the (SAI)$_2$Ni complexes has been related to the expectation[9] of well-resolved p.m.r. spectra for this system. It thus seems of interest to determine exactly which mechanism(s) are responsible for the short T_1 values in the system of interest.

Estimates of T_1

In order to assess the relative importance of the various mechanisms, it would be desirable to have

numerical estimates of the electron relaxation times for a typical ATI and SAI complex. T_1 values have been estimated[15] for (TAP)$_2$MX$_2$. The equation relating the observed p.m.r. line width to the electron correlation times is[15,20,22]

$$\Delta H_{1/2} = B\left[4\tau_c + \frac{3\tau_c}{1 + \omega_I^2\tau_c^2} + \frac{13\tau_c}{1 + \omega_S^2\tau_c^2}\right] + C\left[\tau_e + \frac{\tau_e}{1 + \omega_S^2\tau_e^2}\right] \quad (1)$$

where $B = S(S + 1)\gamma_I^2 g^2\beta^2/15r^6$, $C = S(S + 1)A^2/3h^2$, and the other symbols are defined as previously.[15,20] The first term results from a dipolar interaction and the second one from the contact interaction.[20] In order to estimate the electron correlation time from eq. 1, the line width, $\Delta H_{1/2}$, for a specific proton in a paramagnetic ATI and SAI is required. Since these systems exhibit temperature-dependent magnetic moments in solution,[4,5] only $\Delta H_{1/2}$ values for essentially fully paramagnetic complexes in solution can be used in eq. 1. For the ATI system,[4,8] such a complex is N,N-ditolylamino-troponeiminenickel(II), for which the α-proton has a $\Delta H_{1/2}$ of 24 c.p.s. in CHCl$_3$ solution.[23] It has been concluded that the relaxation at this position is primarily by the dipolar interaction.[23] For the SAI complexes,[5,9–11] we estimate $\Delta H_{1/2}$ for the methyl protons on the isopropyl group in bis(5-methyl-N-iso-propylsalicylaldimine)nickel(II) from its published spectrum,[10] obtaining ~ 20 c.p.s. However, this complex is only $\sim^2/_3$ paramagnetic[10] in CHCl$_3$ at 25°. As a crude correction for this, we assumed that $\Delta H_{1/2}$ is proportional to the fraction of paramagnetic molecules in solution, arriving at $\Delta H_{1/2} = \sim 30$ c.p.s. for the fully paramagnetic form of this complex. Using only the first term in eq. 1, with $\langle r^6 \rangle = 1.0 \times 10^{-44}$ cm.^{6} and 8.4×10^{-45} cm.^{6} for these two ATI and SAI complexes, respectively, we obtain the upper limits[15,22] to the electronic correlation time, $\tau_c < 3 \times 10^{-13}$ sec. for ATI complexes and $\tau_c < 2 \times 10^{-13}$ sec. for SAI complexes. Since these correlation times are too short to be associated with the tumbling time in solution,[15] they may be confidently attributed to the electron relaxation times (T_1), which *may* also be the times characteristic for the interconversion rates. The T_1 values for the TAP complexes, estimated previously,[15] are $< 2 \times 10^{-13}$ and $< 6 \times 10^{-13}$ sec. for the Ni and Co complexes, respectively.

The Interconversion Mechanism

It has been demonstrated[4,5,8–11,21] that all three Ni systems of interest undergo a dynamic interconversion in solution between a square-planar, diamagnetic and tetrahedral, paramagnetic form, which accounts for the observed temperature dependence of the magnetic moments in solution. The time which characterizes this interconversion, τ_i, is not known, but a lower limit to the lifetime can be derived[4] from the observation of separate absorption bands for the diamagnetic and paramagnetic forms in the optical spectrum. For the ATI complexes,[4] the diamagnetic and paramagnetic peaks appear at 8000 and 12,000 Å., while for the SAI[5] and TAP[21] complexes, they appear at 6000 and 9000 Å., respectively. To give separate peaks,[4] the interconversion time must be long compared to this energy separa-

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tion, so that we conclude that $\tau_i > 10^{-13}$ sec. However, the p.m.r. line widths led to relaxation times such that essentially $T_1 < 10^{-13}$ sec. We may thus conclude that in all probability, the possible rates of interconversion are all too slow to give rise to the "observed" electron relaxation times. This conclusion is confirmed[23,24] by p.m.r. studies on the Ni(II) chelates of pyrromethenes, whose p.m.r. spectra are characterized by resonances of approximately the same width as for the ATI, SAI, and TAP systems. This system, however, has given no evidence[23] of participating in any diamagnetic $\rightleftharpoons$ paramagnetic equilibrium in solution, so that this mechanism can be definitely eliminated. Electron spin relaxation through rapid interconversion between the tetrahedral and square-planar forms of these complexes can therefore be discarded as the dominant mechanism in all the Ni(II) systems concerned.

It should be pointed out, however, that for the Ni complexes, this paramagnetic $\rightleftharpoons$ diamagnetic equilibrium does lead to p.m.r. line narrowing by averaging the line widths for the diamagnetic and paramagnetic forms. It has been observed that the p.m.r. lines become narrower as the equilibrium shifts toward the diamagnetic form.[4,23] The conclusion reached above is that this interconversion does not significantly determine the line width for the paramagnetic form.

Interaction with Low-Lying Orbital States

Interaction with low-lying orbital states[17] is expected to be weak for ions which have an orbitally nondegenerate ground state, such as Co(II) in a tetrahedral ligand field,[16] with $^4A_2$ as ground state, so that this relaxation mechanism is in all probability quite insignificant in determining T_1 in the case of the Co complexes. Ni(II) in a tetrahedral field has a $^3T_2$ ground state, which could yield low-lying orbital levels in the presence of a small low-symmetry distortion. However, studies of the absorption spectra[25] for TAP complexes indicate that the low-symmetry distortions cause splittings of approximately 3000 cm.$^{-1}$ of the $^3T_2$ ground state, which is nearly as large a separation to the first excited orbital state as for the analogous Co complexes,[7,25] where $10Dq = \sim 4000$ cm.$^{-1}$. Therefore this mechanism would not be expected to be dominant for the NiL_2X_2 complexes.

The separation between the split components of the $^3T_2$ ground states for the ATI and SAI Ni complexes have not been estimated. The observed magnetic moments for fully paramagnetic ATI[4] and SAI[10,11] complexes are ~ 3.3 B.M., considerably below the 3.9–4.2 B.M. predicted[26] and usually found[27] for strictly tetrahedral Ni(II) complexes, indicating a fairly large splitting of the $^3T_2$ ground state.[6,25] Since the magnetic moments for the ATI and SAI complexes are essentially identical[4,10,11] with those observed[6] for the TAP complexes with Ni, it might be assumed that the low-symmetry splitting is of a magnitude similar to the TAP complexes (~ 2000–3000 cm.$^{-1}$). The effect of low-lying orbital levels may therefore be eliminated as

the dominant relaxation mechanism in all the systems concerned.

Anisotropy in g-Tensor or Hyperfine Interaction

This mechanism, first treated by McConnell,[18] involves the coupling of the g-tensor or hyperfine anisotropy to the rapid tumbling of the complex in solution. This mechanism has been shown to determine the electron relaxation time in several Cu(II) complexes.[16,18] This mechanism would not be expected to produce T_1 values as short as encountered in the systems of interest, unless the anisotropies were very large.[16] For the Ni(II) complexes, there is no hyperfine interaction[28] due to the low abundance (1.25%) of ^{61}Ni. It has been convincingly demonstrated[4,8–14] that the g-tensor anisotropies for these Ni complexes are usually negligible, so that this mechanism is eliminated for the case of Ni. For the Co system, although there exists hyperfine interaction, it would not be expected[28] to be very anisotropic because the ion possesses a $^4A_2$ ground state. These complexes exhibit some g-tensor anisotropy,[12,13] but it would also be expected[28] to be small, as observed in other tetrahedral Co(II) systems,[28,29] and thus not contribute significantly to the electron relaxation time.

Zero Field Splitting

The coupling of the splitting of the ground-state spin multiplet in the absence of an external magnetic field[30] with the random tumbling of the complex in solution has been demonstrated[16,19] to dominate the spin relaxation in various Cr(III) complexes. As indicated before, this mechanism has been postulated[19] to be dominant for complexes with two or more unpaired electrons. The effectiveness in reducing the relaxation time depends on the magnitude of this splitting and the tumbling time in solution.[16] Bloembergen and Morgan[20] have attributed the ineffectiveness on Ni(II) in reducing the proton relaxation time in aqueous solution to rapid electron relaxation *via* the zero splitting mechanism.

The $^4A_2$ ground state of tetrahedral Co(II) cannot be split by either spin–orbit coupling or low-symmetry fields, but the combined effects produce[31] a splitting into two doublets ($m_s = \pm 1/2$ and $m_s = \pm 3/2$) separated by $2D$, which can be as large as a few cm.$^{-1}$. Since the Co complexes of interest exhibit low-symmetry distortions[7,25] (C_{2v} for $(TAP)_2CoX_2$, C_{3v} for $(TAP)CoX_3^-$), the conditions for relaxation through this mechanism are present. The magnitude of the zero field splitting constant D has not been determined for these complexes, but it has been shown for other distorted tetrahedral Co(II) complexes that fairly large values for D can be expected,[31] having been observed[29–31] in the range 1–5 cm.$^{-1}$. The complex $(TAP)CoX_3^-$ has a T_1 essentially identical[11] with that of $(TAP)_2CoX_2$. For this axially distorted complex, the spin Hamiltonian will take the form[28,32]

$$\mathcal{H} = g\beta HS + ASI + D[S_z^2 - 1/3 S(S + 1)] \quad (2)$$

neglecting the small anisotropies in g and A. The contribution to T_1 from the last term in this spin Hamil-

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tonian has been given by McGarvey[16]

$$\frac{1}{T_1} = \frac{32\pi^2}{5}\left(\frac{D^2}{h^2}\right)\left[\frac{\tau}{1 + \omega_s^2\tau^2} + \frac{\tau}{1 + 4\omega_s^2\tau^2}\right] \quad (3)$$

where D is defined in eq. 2, τ is the tumbling time in solution, and ω_s is the electron Larmor frequency in angular units at 60 Mc./sec. Using eq. 3, it is possible to determine whether such a short relaxation time[11] can be accounted for by a reasonable value for D. A good estimate for τ can be obtained from the Debye equation, $\tau = 4\pi\eta r^3/3kT$, with $\eta = 0.543$ cp. for CHCl$_3$,[33] $r = 5$ Å.,[11] obtaining $\tau = \sim 7 \times 10^{-11}$ sec. Inserting this value for τ in eq. 3, we find that the calculated relaxation time[11] ($T_1 = 6 \times 10^{-13}$ sec.) could be accounted for by a zero field splitting constant of ~ 2.5 cm.$^{-1}$. This value is well within the range observed[29-31] for other tetrahedrally coordinated systems with low-symmetry distortions. For the (TAP)$_2$CoX$_2$ complexes, the spin Hamiltonian should include[28, 30] a term such as $E(S_z^2 - S_y^2)$. However, it has been shown[12, 34] that the axial distortion in this system is larger than the rhombic distortion, so that E can probably be neglected in comparison to D. It therefore appears that the expected zero field splittings and tumbling times in CHCl$_3$ solution can quantitatively account for the extremely short electron spin relaxation times for the Co(II) complexes of interest.

To evaluate this mechanism for the Ni(II) complexes is more difficult, since there has been no electron spin resonance work done for this ion with tetrahedral coordination, so that nothing is known about the possible magnitude of the zero field splitting constant. It will be shown, however, that the expected electronic structure for the Ni complexes of interest is consistent with a fairly large value for D. The form of the spin Hamiltonian will depend[30, 32, 35] on the relative sizes of the spin-orbit coupling constant λ and the magnitude of the splitting of the $^3T_2$ ground state by the low-symmetry distortion. Should this splitting be comparable to λ, we might expect[16, 17, 32] that interaction with the low-lying orbital level would dominate the relaxation time, so that zero field splitting would become negligible.[32] It has been estimated[25] that this splitting is ~ 3000 cm.$^{-1}$ for the (TAP)$_2$NiX$_2$ complexes and is postulated to be of similar magnitude for the ATI and SAI complexes, since the deviations of the observed magnetic moments for all three systems are approximately the same.[4, 6, 10] For Ni(II),[36] λ is -270 cm.$^{-1}$, so that the low-symmetry splitting of $^3T_2$ is large compared[35] to λ for the three systems.

The question of the orbital degeneracy of the ground states resulting from the axial distortion in both ATI and SAI complexes has received some attention.[11, 24, 35, 37] Though it was first postulated[35] that the ATI complexes have a ^3E ground state, it has now been shown[37] that temperature studies of unsymmetrically substituted ATI complexes are inconsistent with this result, and instead a $^3A_2$ ground state is more reasonable. The same conclusions[11] have been reached for the SAI complexes from similar studies. For the

(TAP)$_2$NiX$_2$ system, the ground state must be singly degenerate, since the C$_{2v}$ field completely splits $^3T_2$. Spin-orbit coupling will then result in interaction[30, 35, 38] between the orbitally nondegenerate ground state and the split component(s) of the $^3T_2$ state, resulting in the spin multiplicity of the ground state being lifted. For the axially distorted cases,[35, 38] it will result in a separation of the $m_s = \pm 1$ and $m_s = 0$ components, while the former level will again split[30] for the (TAP)$_2$NiX$_2$ case. The magnitude of this zero field splitting will depend[30, 38, 39] very much on the separation between the split orbital components and could be expected to be quite large. Such a situation has been observed[39] for the V^{+3} ion in octahedral coordination with a trigonal distortion. The ligand field levels for V(III) in O$_h$ are identical with Ni(II) in T$_d$. The trigonal field for V-(III) produces a $^3A_2$ ground state, which has its spin multiplicity removed[38, 39] by spin-orbit interaction, resulting in a large zero field splitting (~ 8 cm.$^{-1}$). Though it cannot be quantitatively established that the resulting zero field splitting for the Ni complexes of interest is indeed large enough to produce electron relaxation times as short as $\sim 10^{-13}$ sec., it is shown that such a situation might well be expected.[38, 39]

There exist some data on a few systems of interest which verify the dominance of this mechanism. It has been observed[40] that for some of the TAP complexes, the p.m.r. peaks are slightly narrower in CS$_2$ than in CHCl$_3$ solution. This effect has also been observed[23] for the N,N-ditolylaminotroponeiminenickel complex. This difference in line widths indicates[15, 20] that the electron relaxation is more efficient for the complexes dissolved in CS$_2$ than in CHCl$_3$. Such an effect could not readily be interpreted by the other relaxation mechanisms, but a simple explanation can be offered if coupling of the zero field splitting to the tumbling determines the relaxation times.

Since the viscosity[33] of CS$_2$ is only about 65% of that of CHCl$_3$, the Debye equation predicts that the tumbling rate of the complex would be faster in CS$_2$ than in CHCl$_3$. Inspection of eq. 3 reveals that the variation of $1/T_1$ with the tumbling time τ depends on the magnitude of the term $\omega_s^2\tau^2$. For the magnetic fields used in the p.m.r. studies,[4, 8, 13] and estimating $\tau = \sim 7 \times 10^{-11}$ sec., $\omega_s^2\tau^2 = \sim 20$, so that $1/T_1$ is approximately proportional to $1/\tau$. As τ is shorter in CS$_2$, we can conclude that electron relaxation will be more efficient in that solvent, hence narrower p.m.r. lines, as observed.[23, 40]

The significance of this correlation for the TAP complexes is somewhat obscured by the fact that facile ligand exchange[14, 15] will affect the line widths, and the possibility that varying ligand-exchange rates in the two solvents could be responsible for this line width change cannot be definitely eliminated. For the ATI complex the position for the diamagnetic paramagnetic equilibrium could complicate the above interpretation, since it is known[4] that the effective magnetic moment is dependent upon the solvent. However, it has been determined[4] that this ATI complex is *more* paramagnetic in CS$_2$ than in CHCl$_3$, so that the narrower p.m.r.

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lines in CS_2 definitely indicate a shorter relaxation time than in $CHCl_3$.

Conclusions

The dominant factor determining the short electronic relaxation times in the Co(II) complexes of interest is concluded to arise from the coupling of the zero field splitting of the tumbling of the complex in solution. For the TAP complex of Co, a calculation showed that a zero field splitting well in the range observed[29-31] for tetrahedral Co can quantitatively account for the electron relaxation time. The other possible mechanisms are demonstrated to be expected to make only insignificant contributions.

For the Ni(II) systems, the previously suggested[8,9] relaxation mechanism through interconversion[4,5,21] between the square-planar, diamagnetic and the tetrahedral, paramagnetic forms in solution is eliminated as being dominant. This was based on the observation that the upper limit to this interconversion rate, as determined from the peak separation in the absorption spectrum,[4,5,17] appears to be too slow to result in relaxation times[15] of $\sim<10^{-13}$ sec., and on the fact that narrow p.m.r. lines are also observed[24] for similar Ni systems where there exists no evidence[23,24] for such an interconversion in solution. It is postulated that zero field splitting also accounts for the short Ni relaxation times, based on the fact that the electronic structures of all the systems of interest favor[35,36,38,39] a large zero field splitting, and that the other possible mechanisms are expected to be quite ineffective for such electronic structures.

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A Double-Scale Equation for Correlating Enthalpies of Lewis Acid–Base Interactions

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In this article a double-scale enthalpy equation is proposed to correlate the enthalpy of adduct formation in poorly solvating media for several acid–base systems. Two constants are assigned to an acid, E_A and C_A, and two constants are assigned to a base, E_B and C_B, such that substitution into the following equation produces the enthalpy of interaction: $-\Delta H = E_A E_B + C_A C_B$. This equation is found to correlate systems where reversals in donor strength are observed. The constants obtained for the acids and bases are interpreted in terms of the electrostatic and covalent nature of the interaction. The magnitude of the constants are found to agree with qualitative chemical intuition regarding acid or base properties. The amounts of covalency or ionicity in an acid–base adduct, indicated by these constants, agree with semiquantitative estimates that have been reported. Limitations of the correlation are discussed.

Introduction

The reversals that occur in donor strength for a series of donors with change in the reference Lewis acid have interested many chemists. Ahrland, Chatt, and Davies[2] recognized, rather early, that metals and metal ions could be divided into two general categories. Those metal ions which interacted most effectively with donor atoms of first row elements rather than donor atoms in succeeding rows were put in class A, and those metals that interacted more effectively with the highly polarized second, third, etc., row donor atoms than with the first row donor atoms were placed in class B. Acids whose charge clouds are easily distorted (second and third row metal ions) interact most strongly with distortable bases, while acids that are not easily distorted (first row metal ions) interact most strongly with polar bases. Unfortunately, the criteria used for stability were not thermodynamic (free energy or enthalpy) and thus the inferences could be subject to criticism.

Thermodynamic data obtained in CCl_4, a poorly solvating solvent, manifest reversals of this type.[3] Toward the reference acid phenol, it has been found that the magnitude of the interaction, as measured by the enthalpy of formation of a donor–acceptor adduct in the solvent CCl_4, is greater with an oxygen donor than with the analogous sulfur donor; e.g., $Et_2O > Et_2S$ and $CH_3C(O)N(CH_3)_2 > CH_3C(S)N(CH_3)_2$. Toward the Lewis acid iodine, the enthalpy of adduct formation is greater for the sulfur donor than the analogous oxygen donor. Acids which are large and whose charge clouds are easily distorted interact most strongly with bases that are large and whose charge clouds are easily distorted. Smaller acids which are polar and not easily distorted interact most strongly with polar bases.

Variations in the relative importance of polarity and distortability were proposed to explain the donor properties of ammonia and a series of amines[4] and also to

(1) Abstracted in part from the Ph.D. Thesis of B. Wayland, N.S.F. Graduate Fellow, University of Illinois, 1964.

(2) S. Ahrland, J. Chatt, and N. Davies, *Quart. Rev.* (London), 12, 265 (1958).

(3) R. S. Niedzielski, R. S. Drago, and R. L. Middaugh, *J. Am. Chem. Soc.*, 86, 1694 (1964), and papers referenced therein.

(4) R. S. Drago, D. W. Meek, R. Longhi, and M. D. Joesten, *Inorg. Chem.*, 2, 1056 (1963).