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Acceptor Strengths of Some Group IV Lewis Acids by Electron Paramagnetic Resonance Studies of Their Complexes with Aliphatic Nitroxides

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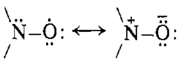
Molecular complexes have been formed between two aliphatic nitroxides, di-*tert*-butyl nitroxide and 2,2,6,6-tetramethylpiperidine-*N*-oxyl, and group IV Lewis acids. Analysis of the epr spectra shows that in all cases 1:1 complexes are formed. The π-electron spin density of a nitroxide complex can be analyzed from its epr spectrum and changes in the nitroxide ^{14}N hfs upon complexation are a measure of the acceptor strength of the Lewis acid. For the acids studied here the order of acceptor strength is $TiCl_4 > SnCl_4 > SnBr_4 > SiF_4 \gtrsim Sn(t\text{-}Bu)_2Cr(CO)_5 \approx SiCl_4 \gtrsim GeCl_4 \approx Ti(OPh)_4$. In some cases epr spectra show the nitroxide and its complex to be in equilibrium and thermodynamic constants for complex formation are obtained.

Inquiries into the nature of the dative bond formed by interaction of a Lewis acid and base complement studies of the acidity as judged by the stability of a complex with respect to its components. Formation constants and the thermodynamic variables obtained from them usually cannot provide specific information about the donor–acceptor bond because other bonds may be altered upon complex formation. More specific information about the bonding within a complex is available from the measurement of physical properties, such as the donor–acceptor bond distance and vibrational force constant, or, less directly, from infrared absorption frequencies and nmr chemical shifts.[3]

Recently epr has been used to study the properties of the dative bond in complexes in which aliphatic nitroxides (R_2NO) behave as Lewis bases.[4,5] Complexation involves the partial donation of a pair of oxygen nonbonding electrons without change in oxidation states or intramolecular rearrangement. The nitroxide unpaired π electron does not directly participate in the dative bond but serves as a probe of the electronic structure of the adduct.[4]

In terms of valence bond theory complexation can be viewed as favoring resonance structure over structure I,



I II

causing a redistribution in the N–O π-electron system, with a shift of charge density toward oxygen but of spin density toward nitrogen.

A similar picture is obtained by consideration of a simple MO scheme in which the three electrons of the nitroxide bond are in orbitals derived from linear combinations of the nitrogen and oxygen 2pπ orbitals. The effective electronegativity of oxygen is enhanced by the σ interaction with an electron-withdrawing agent, increasing the oxygen character of the paired electrons in the π orbital but increasing the nitrogen character of the unpaired electron in the π^* orbital. The resulting changes of $\rho_N{}^\pi$ and $\rho_O{}^\pi$, the nitrogen and oxygen π-spin densities, are equal and opposite in magnitude ($\Delta\rho_N{}^\pi = -\Delta\rho_O{}^\pi \equiv \Delta\rho^\pi$) and monotonically increase with the strength of the interaction.[6]

The π-electron spin density distribution of a nitroxide molecular complex can be analyzed from its epr spectrum since nitroxide ^{14}N hyperfine splittings (hfs) and ^{17}O hfs are linearly related to the π-spin densities.[6] The redistribution of spin density upon complexation thus gives changes in hfs which are proportional to $\Delta\rho^\pi$: the ^{14}N hfs increase and ^{17}O hfs decrease with increasing $\Delta\rho^\pi$ and thus with increasing strength of interaction. We may therefore use the measured ^{14}N (^{17}O) hfs to measure $\Delta\rho^\pi$ and thus the acceptor strength of a Lewis acid. From a knowledge of $\Delta\rho^\pi$ and use of the simplest Huckel M-O scheme for the nitroxide π system, a change in effective electronegativity of oxygen upon complexation may be calculated and also used as a measure of the donor–acceptor interactions.

Molecular complex formation may also change the isotropic *g* value (g_{iso}) of a nitroxide. In favorable cases, this change can be analyzed to give estimates of the spin density delocalization onto the Lewis acid.[4b] Similar information is derivable from studies of solution line widths and frozen-solution spectra when hfs are observed from the central metal of the Lewis acid.

Previous studies of nitroxide complexes have concentrated upon the group III trihalides and have given results which are consistent with other measures of acceptor strength.[3] In the present work, we report epr studies of a series of free-radical molecular complexes in which the nitroxide Lewis base is 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TMPN) or the equivalent di-*tert*-butyl nitroxide (DTBN) and the Lewis acid contains a central metal atom from group IVa or b: SiF_4, $SiCl_4$, $GeCl_4$, $SnCl_4$, $SnBr_4$, $TiCl_4$, $Ti(OPh)_4$, and $(t\text{-}Bu)_2SnCr(CO)_5$. There is little information previously available about the relative acceptor strengths of the group IV tetrahalides. Current concepts are based on limited thermodynamic data and inferences from catalytic activity[7,8] but only one extensive spectroscopic study, a measurement of the carbonyl stretching frequency shifts in ethyl acetate complexes.[9]

In some cases reported here, epr spectra show the nitroxide and its Lewis acid adduct to be in equilibrium. From the temperature dependence of this equilibrium, we obtain thermodynamic constants for complex formation. Thus, in

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these instances, epr gives both of the complementary types of information about Lewis acid-base interactions.

Experimental Section

DTBN was synthesized by the method of Hoffmann[10] or purchased (Eastman Kodak Co.) and purified by vacuum distillation. TMPN was prepared by the method of Briere[11] and purified by vacuum sublimation. TMPN 11% enriched in ^{17}O (TMPN(^{17}O)) was prepared in the form of a reaction mixture, *ca.* 5×10^{-3} *M* in total TMPN(^{17}O ~11%), in parent amine in the presence of α,α'-azobis(isobutylnitrile) as previously described[6] and was used without purification.

Except when expressly noted, the two substituted nitroxides used in this work, TMPN and DTBN, are essentially equivalent in their behavior with respect to complexation to a Lewis acid. The choice of one over the other in certain cases, such as the synthesis of the ^{17}O-enriched nitroxide, was primarily a question of convenience.

Toluene, used as the solvent for molecular complexes, was distilled in a nitrogen atmosphere from calcium hydride onto sodium and degassed. Other organic liquids were purified by fractional trap-to-trap distillation under vacuum.

Lewis acids (MX_n) were obtained in the purest form available from Ventron Corp. or from Research Organic/Inorganic Chemical Corp. unless specifically noted otherwise. Those which were liquid or were sublimable were transferred in a glove bag under dry nitrogen to a storage bulb and then purified by trap-to-trap fractionation under vacuum. An additional fraction was distilled off and discarded before each sample preparation. SiF_4, a gas, was initially transferred to a storage bulb on a vacuum line and then similarly purified. The solid Lewis acids, not transferable on a vacuum line [$Ti(OPh)_4$, $(t\text{-}Bu)_2SnCr(CO)_5\cdot THF$, and $[(t\text{-}Bu)_2SnFe(CO)_4]_2$], were transferred from their original containers directly into quartz epr sample tubes in a glove bag under dry nitrogen.

Samples were prepared in a preparative high-vacuum system.[12] Molecular complex formation in toluene solution with volatile Lewis acids involved condensing a minimum of a fivefold excess of the Lewis acid onto a frozen toluene–nitroxide solution (*ca.* 5×10^{-3} *M*) in a quartz epr sample tube. This solution had been prepared by first transferring a measured volume of the nitroxide vapor in equilibrium with condensed nitroxide at a known temperature into a quartz epr sample tube and then distilling in toluene under vacuum. When a Lewis acid was used as solvent, for example $SiCl_4$ and $GeCl_4$, the nitroxide solution tended to be unstable at room temperature, and the samples were prepared as were the toluene solutions, except that the quartz tube was kept at −78° while transferring the Lewis acid and then immediately transferred to liquid nitrogen.

With nonvolatile Lewis acids, the solid in the epr tube was vacuum-dried, and then solvent was distilled in and the resulting solution degassed and frozen. Next, more solvent was distilled in and frozen and finally nitroxide was added as above.

Samples with TMPN enriched in ^{17}O were prepared as above, but with the TMPN(^{17}O) reaction mixture replacing the pure TMPN.

In all cases, mixing and complexation took place in the epr cavity, at a temperature just above the melting point of the solvent (−90° for toluene).

Epr spectra were recorded as previously described.[6b] Unless explicitly indicated errors are ±0.04 G for the isotropic hfs, ±0.1 G for the anisotropic hfs, and ±0.00003 for g_{iso}.

Generally, isotropic hfs values were measured directly. In the case of DTBN in $SiCl_4$ or $GeCl_4$ the spectra were superpositions of overlapping spectra from free nitroxide and complex, and therefore computer simulations were used to obtain sufficiently accurate coupling constants. The ratio of complexed to free nitroxide in equilibrium systems was taken to be the ratio of the half-width squared times the half-height for the respective partially overlapping high-field lines. Selected computer simulations showed that the error introduced by this method was always less than 10%.

Simulations were also used to obtain accurate line widths of the partially overlapping $^{14}N^{117-119}Sn$ lines in the solution isotropic spectrum of nitroxide–$SnCl_4$ system. Using measured values of the ^{14}N and $^{117-119}Sn$ hfs, the values of the individual line widths were independently varied until a best fit was obtained. The only restriction was that complexes with ^{117}Sn and ^{119}Sn have identical line widths. The unresolved nitroxide alkyl group proton hfs values were not considered explicitly but were accounted for in the line width.

The anisotropic $^{117-119}Sn$ hfs values for the DTBN·$SnCl_4$ were estimated from the appropriate features of the powder spectrum as well as by using a computer simulation program coupled with a direct-search minimization subroutine.

Results

The fluid-solution epr spectrum of TMPN or DTBN (Figure 1A) in relatively inert solvents such as hexane or toluene consists of three main lines due to the interaction between the unpaired electron and the ^{14}N nucleus ($I = 1$, 99.6% natural abundance). The separation between the lines is the ^{14}N isotropic hfs, a_N. In addition, splitting can usually be observed from the α and/or β ^{13}C ($I = {}^1/_2$, 1.1% natural abundance), from ^{15}N ($I = {}^1/_2$, 0.37% natural abundance), and occasionally under ideal conditions from ^{17}O ($I = {}^5/_2$, 0.037% natural abundance).[13] ^{17}O hfs values are easily observed in solution spectra of TMPN enriched in ^{17}O to 11 atom % (TMPN(^{17}O)). Complexes between nitroxides and a Lewis acid (MX_n) may exhibit additional splitting from the metal (M) nucleus (for example, see Figure 1B) and from ^{17}O in TMPN(^{17}O) (Figure 2).

In some cases even with an excess of Lewis acid the solution spectrum is a superposition of overlapping spectra from complex and free nitroxide (Figure 3). The ratio of these two species varies with temperature in a reversible fashion indicating a true equilibrium.

In frozen nitroxide solutions the epr spectrum is usually dominated by anisotropic ^{14}N hfs (Figure 4A). To a good approximation, nitroxides have axial hfs and the powder spectra can be interpreted on the basis of the spin Hamiltonian[14]

$$\mathcal{H} = \mathbf{S}\cdot\mathbf{g}\cdot\mathbf{H} + A_N S_z I_z + B_N(S_x I_x + S_y I_y) \qquad (1)$$

using appropriate spectral features and computer simulations.

The large central line results from the unresolved perpendicular component of the anisotropic ^{14}N hfs (B_N) while the breadth of the spectrum results from the parallel component of the anisotropic hfs (A_N). The TMPN(^{17}O) coupling with ^{17}O may also be important[6b] while for the molecular complexes where M = B, Al,[4] Ga,[5] or Sn (Figure 2B) both A_M and B_M may be observed. In such cases, a term for the additional hfs must be added to eq 1.

$SnCl_4$. Although $SnCl_4$ reacts irreversibly with nitroxides at room temperature to form $(R_2NO^+)Cl^-$,[15] when mixed with either DTBN or TMPN in toluene at ~−90°, it forms a relatively stable molecular complex. The fluid solution epr spectrum of the DTBN·$SnCl_4$ complex is shown in Figure 1B. The center triplet, with a_N greater than that of DTBN itself (Table I), results from ^{14}N hfs in complexes whose Sn nucleus has no nuclear spin (~84% natural abundance). In addition, in the wings there is a less intense doublet of triplets from the complexes which contain Sn nuclei with spin ${}^1/_2$ (^{117}Sn, 7.7% natural abundance; ^{119}Sn, 8.7% natural abundance). The doubling of each line of the outer triplet results from the fact that ^{117}Sn and ^{119}Sn have slightly different nuclear gyromagnetic ratios. The separation between the lines of the outer triplets is identical with the separation between the lines of the center triplet (a_N). If the wings are blown up,

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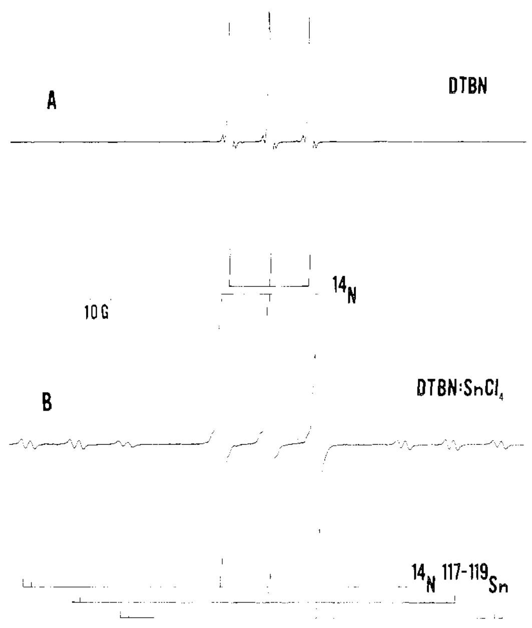

Figure 1. Epr spectra in toluene fluid solution: (A) DTBN; (B) DTBN·$SnCl_4$. Stick diagram indicates the minority nuclear isotope species, $^{14}N^{117}Sn$ (6.1%) and $^{14}N^{119}Sn$ (7.0%).

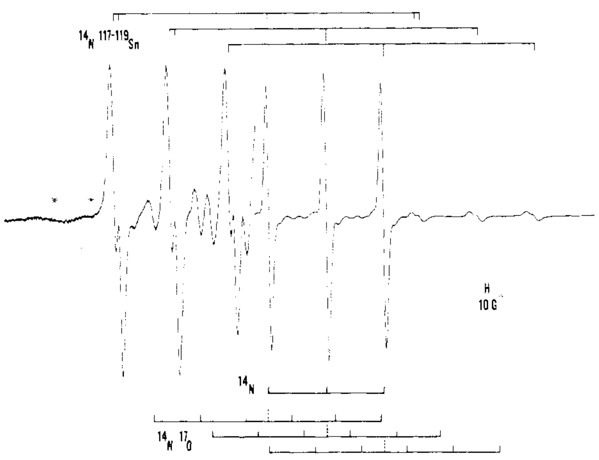

Figure 2. Fluid-solution (toluene) epr spectrum of TMPN(^{17}O)·$SnCl_4$. The signal amplitude of the low-field portion of the spectrum is 31 times that of the remainder. Stick diagrams for the several predominant isotopic species are labeled with the nuclei for which splittings are observed: ^{14}N (78.5%), $^{14}N^{17}O$ (8.6%), $^{14}N^{119}Sn$ (6.9%), $^{14}N^{117}Sn$ (6.0%). The asterisks indicate a portion of the spectrum resulting from the $^{14}N^{17}O^{117-119}Sn$ species (1.4%).

an additional doublet of triplets is observed which comes from complexes which contain ^{115}Sn ($I = {}^1/_2$, 0.35% natural abundance). The ratios of the three tin hfs values agree with those of the different nuclear gyromagnetic ratios; therefore, only the hfs of the most abundant isotope, ^{119}Sn, is reported in Table I.

The paramagnetic center possessing this spectrum is shown to be a chemically unaltered, complexed nitroxide by the fact that addition of a stronger Lewis base such as pyridine displaces the DTBN giving an epr signal of the uncomplexed nitroxide. The new signal has approximately the same intensity as that of the complex.

The fluid solution epr spectrum of the TMPN·$SnCl_4$ complex is qualitatively similar to that of DTBN·$SnCl_4$ but has broader lines, as does the parent nitroxide. This results in poorer resolution of the partially overlapping $^{117-119}Sn$ lines. The TMPN(^{17}O)·$SnCl_4$ complex isotropic spectrum (Figure 2)

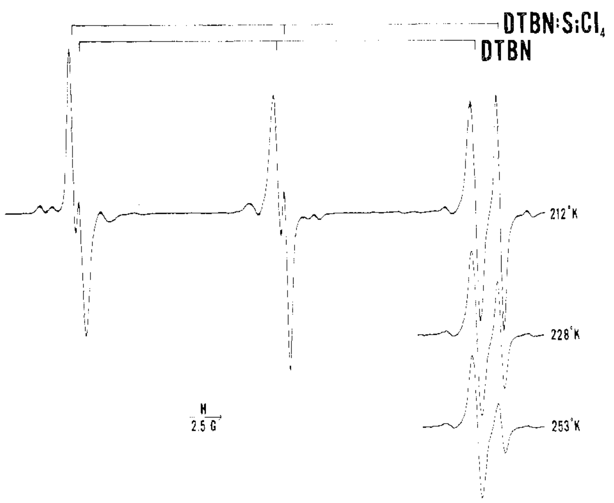

Figure 3. Fluid-solution epr spectra of DTBN dissolved in $SiCl_4$.

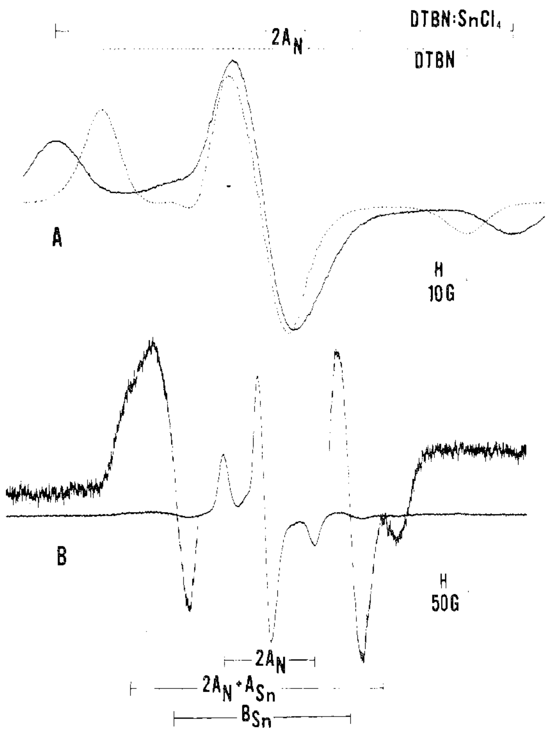

Figure 4. (A) Frozen toluene solution epr spectrum of DTBN in toluene (- - -) and DTBN·$SnCl_4$) (——). (B) Frozen toluene solution epr spectrum of DTBN·$SnCl_4$ on expanded scale. The outer sections of the spectrum result entirely from the $^{14}N^{117-119}Sn$ species and the signal amplitude for the overlay is increased 50 times.

was recorded at = −20°. At higher temperatures the complex decomposed rapidly and at a much lower temperatures the ^{17}O ($I = {}^5/_2$) lines were too broad to be measured. The spectrum is an even more complicated superposition than that of Figure 1B due to the presence of various species exhibiting hfs from ^{17}O. The observed isotopically different species are, in order of abundance, ^{14}N (78% of total spectrum; 3 lines expected, 3 lines observed), $^{14}N^{17}O$ (8.6%; 18 lines expected, 13 observed), $^{14}N^{119}Sn$ (6.7%; 6 lines expected, 6 lines observed), and $^{14}N^{117}Sn$ (6.0%; 6 lines expected, 6 lines observed). Broad lines resulting from $^{14}N^{17}O$-$^{117-119}Sn$ (1.4%; 36 lines expected, 4 lines observed) are also detected.

Coupling constants for a nitroxide–Lewis acid complex exhibit temperature dependences which vary in magnitude with

Table I. Spin-Hamiltonian Parameters for Complexed R_2NO^a

DTBN

Lewis acid	a_N, G	A_N, G	g_{iso}	a_M, G
$Ti(OPh)_4$	16.3^b	37.3	2.00574	<0.6
$GeCl_4{}^c$	16.35	37.4	2.00566	<0.5
$SiCl_4{}^d$	16.54	37.0	2.00559	<2.0
S	16.6^b	37.7	2.00576	~2.1
SiF_4	16.8^b		2.00558	<2.4
$SnBr_4$	18.1^b		2.0076^e	142.0^f
$SnCl_4$	18.63	43.5	2.00521	151.0^f
$TiCl_4$	19.11	45.2	2.00493	<0.7
$Al(i\text{-}Bu)_3{}^g$	18.56		2.00535	<0.5
$AlCl_3{}^h$	20.47	47.0^i	2.0050^e	13.28
$BF_3{}^h$	20.61		2.0048^e	9.11
$BCl_3{}^h$	21.24		2.0055^e	12.19
$BBr_3{}^h$	21.58		2.0093^e	12.89
CH_3OH^j	16.18	36.8	2.00574	
$PhOH^j$	16.90	38.3	2.00558	
$3\text{-}FPhOH^j$	17.05	38.7	2.00553	
$(CF_3)_2CHOH^j$	17.35	39.6	2.00546	
F_5PhOH^j	17.48	39.8	2.00545	

TMPN

Lewis acid	a_N, G	A_N, G	a_O, G	A_O, G	g_{iso}	a_M, G
$GeCl_4{}^c$	16.6^f	$\gtrsim 37.0$			2.0058^e	$\lesssim 1$
$SiCl_4{}^d$	16.5^f	$\gtrsim 37.4$			2.0058^e	$\lesssim 1$
SiF_4	16.6^f				2.0057^e	$\lesssim 4$
$SnCl_4$	18.53	42.7	14.72^k		2.0054^e	119.0^f
$Al(i\text{-}Bu)_3$	18.23				2.0055^e	$\lesssim 1$
$BF_3{}^h$	20.34				2.0049^e	7.96
$BCl_3{}^h$	21.18				2.0058^e	10.35
$BBr_3{}^h$	21.41					10.89
CH_3OH^j	16.28	36.9	18.28	67.1	2.00583	
$3\text{-}FPhOH^j$	17.16	38.4	17.30	63.4	2.00561	
$(CF_3)_2CHOH^j$	17.42	39.3	17.05	62.7	2.00559	

[a] In Toluene at 183°K except as noted. [b] Error is ±0.1 G. [c] In $GeCl_4$ at 220°K. [d] In $SiCl_4$ at 220°K. [e] Error is ±0.0001. [f] Error is ±0.2 G. [g] From J. E. Huheey, *J. Phys. Chem.*, 70, 2086 (1966). [h] From ref 4b; in toluene at 213°K. [i] From A. H. Cohen, T. B. Eames, and B. M. Hoffman, to be submitted for publication; error is ±0.7 G. [j] With Lewis acid as solvent at room temperature. [k] At 253°K.

the nucleus considered. As found for the group III nitroxide complexes a_N and a_M (when observed) decrease with increasing temperature and may be fit to an equation of the form $a_i(T) = a_N{}^0 + b_iT$ (Table II).[4b] These results may be contrasted with those of Scheidler and Bolton,[16] who have shown that for bis(trifluoromethyl) nitroxide the ^{14}N splitting increases linearly with increasing temperature.

In comparing the temperature dependence for different nuclei, it is necessary to consider normalized coefficients $\tilde{b}_i = (b_i/A_i{}^{iso}) \times 100$, where $A_i{}^{iso}$ is the theoretically calculated splitting for a single electron in the valence-shell s orbital of atom i.[17] The $\tilde{b}_i$ values (Table II) thus correspond to percentage s-orbital spin densities. Temperature variations for metal nuclei ($\tilde{b}_M$) are generally greater than those for nitroxide nuclei ($\tilde{b}_N$).

For the $DTBN \cdot MX_3$ complexes the $\tilde{b}_N$ values for BCl_3, BBr_3, and $AlCl_3$ are similar while that for BF_3 is considerably larger. Representative values are included in Table II. $\tilde{b}_N$ for the $DTBN \cdot SnCl_4$ complex falls between these values while $\tilde{b}_{Sn}$ is larger than any of the reported $\tilde{b}_M$ values for the MX_3 complexes.

The epr spectrum of a frozen solution of the $DTBN \cdot SnCl_4$ complex is shown in Figure 4. The central portion of the spectrum is a typical nitroxide-like pattern and is primarily associated with complexes containing Sn nuclei of $I = 0$. Additional features in the wings (Figure 4B) are due to tin nuclear hfs from those complexes containing $^{117-119}Sn$ nuclei ($I = {}^1/_2$, 16.4% total natural abundance). Computer simulations of these spectra show that the $^{117-119}Sn$ hfs' are isotropic ($A_{Sn} \approx a_{Sn} = 165$ G) to within a fairly large experimental error (±5 *G*) which arises from the overlapping of the spectrum of the $I_{Sn} = 0$ complexes. This value for a_N is considerably greater than the largest value observed in fluid solution, $a_N = 151.0$ G at $-90°$, but less than calculated from the temperature coefficient in Table II. Thus as expected, at low temperatures a_N is less temperature dependent.

The minimal anisotropy of the tin hfs shows only that π-electron spin density is also minimal. Since a single electron in a 5p orbital on the tin would produce an anisotropy of $|A_{Sn} - B_{Sn}| = 573$,[17] then the above error estimates show $|\rho_{Sn}{}^\pi| < 0.02$.

A nuclear spin dependence of line widths can be used to investigate further spin density on tin and the sign of a_{Sn}.[18] Each peak is associated with a value of (m_N, m_{Sn}), the nuclear spin quantum numbers for nitrogen and tin. Peak-to-peak line widths for the $^{119}SnCl_4 \cdot DTBN$ complex, given in Table III, can be fit to a polymomial of the form

$$W(\tilde{m}_N, \tilde{m}_{Sn}) = A + \sum_{N,Sn} B_i\tilde{m}_i + \sum_{N,Sn} C_i\tilde{m}_i{}^2 + E_{N,Sn}\tilde{m}_N\tilde{m}_{Sn} \qquad (2)$$

Because the signs of a_i are unknown in advance, eq 2 employs $\tilde{m}_i$, where $\tilde{m}_i$ and m_i differ only by a factor of ϵ_i, the negative of the sign of the hyperfine splitting (a_i): $\tilde{m}_i = -(a_i/|a_i|)m_i$. The line-broadening mechanisms which give rise to eq 2 arise from *g*-factor anisotropy (A), from anisotropic electron-nuclear dipolar interaction (C_i, E_{ij}), and from these two mechanisms in conjunction (B_i).

Table IV lists the least-squares parameters to eq 2 for the line widths given in Table III. Following the procedure previously described,[4b] use of appropriate ratios of the coefficients in Table V gives an estimate of the spin density on tin

$$\rho_{Sn}{}^\pi \approx \left(\frac{a_{Sn}}{|a_{Sn}|}\right)\begin{cases} +0.07 - 0.01\epsilon_{Sn} \pm 0.04\ (TMPN \cdot SnCl_4) \\ +0.06 - 0.01\epsilon_{Sn} \pm 0.03\ (DTBN \cdot SnCl_4) \end{cases} \qquad (3)$$

First, these estimates are consistent with the limits placed on $|\rho_{Sn}{}^\pi|$ from powder spectra. Second, the product $(a_{Sn}\rho_{Sn}{}^\pi)$ is positive. Taking into account the fact that $a_i \propto \gamma_i$ (gyromagnetic ratio) and $\gamma_{Sn} < 0$, this result is similar to that for the $DTBN \cdot AlCl_3$ complex. Although calculations are not available for the nitroxide-$SnCl_4$ complex, CNDO and INDO[19] calculations give a negative $\rho_M{}^\pi$ for the BF_3-nitroxide complex. If $\rho_{Sn}{}^\pi$ is negative, then a_{Sn} is negative.

Occasionally, when a $TMPN \cdot SnCl_4$ sample was warmed above $-40°$, a second paramagnetic species was observed; no second species was found for $DTBN \cdot SnCl_4$. This second species, with a ^{14}N hfs indistinguishable from that of low-temperature species, was only detected by its 10% increase in a_{Sn}. There was no evidence for equilibrium between the two species and all $TMPN \cdot SnCl_4$ epr parameters reported here pertain to the low-temperature species. Both the $DTBN \cdot SnCl_4$ and $TMPN \cdot SnCl_4$ complexes decompose slowly at $-50°$

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(18) See G. K. Fraenkel, *J. Phys. Chem.*, 71, 139 (1967).

(19) D. L. Beveridge and P. A. Dobosh, *J. Chem. Phys.*, 48, 5532 (1968), and references therein.

Table II. Constants Calculated from Least-Squares Fit of DTBN·MX_n Hfs to the Equation $a_i(T) = a_i^0 + b_iT$

MX_n[a]	a_N^0	$-b_N \times 10^3$	$-\tilde{b}_N \times 10^4$ [d]	a_M^0	$-b_M \times 10^3$	$-\tilde{b}_M \times 10^4$ [d]
$SnCl_4$	19.23 ± 0.02	3.5 ± 0.1	6.4 ± 0.2	195.9 ± 0.3	268 ± 1	36.0 ± 0.1
$SnBr_4$[b]		9 ± 7	15 ± 10	173 ± 18	230 ± 100	30 ± 13
BF_3[c]	22.26 ± 0.04	7.7 ± 0.2	14.0 ± 0.3	14.01 ± 0.04	23.1 ± 0.1	31.9 ± 0.1
BCl_3[c]	21.60 ± 0.02	1.8 ± 0.1	3.2 ± 0.2	14.32 ± 0.02	10.1 ± 0.1	13.9 ± 0.1

[a] For SnX_4 and BX_3 complexes, M = ^{119}Sn and ^{11}B, respectively. [b] Estimated from two points. [c] Representative data from ref 4b. [d] See text for definition.

Table III. Derivative Peak-to-Peak Line Widths (G) for $SnCl_4$ Complexes of DTBN and TMPN ($T = -91°$)[a]

		$\tilde{m}_N$		
	$\tilde{m}_{Sn}$	−1	0	+1
TMPN	$-^1/_2$	3.60	3.70	5.85
	$+^1/_2$	3.84	3.10	4.45
DTBN	$-^1/_2$	2.32	2.32	4.07
	$+^1/_2$	2.47	2.01	3.02

[a] Determined as described in the Experimental Section. Estimated uncertainties ±0.1 G.

Table IV. Least-Squares Parameters (G) of Eq 2 for $R_2NO\cdot{}^{119}SnCl_4$ Complexes

	TMPN	DTBN
$A + C_{Sn}/4$[a]	3.4	2.17
B_N	0.72	0.58
B_{Sn}	−0.59	−0.40
C_N	1.04	0.81
$E_{N,Sn}$	−0.82	−0.60

[a] Because $I_{Sn} = {}^1/_2$, C_{Sn} cannot be separately determined (see eq 2).

and very rapidly at room temperature to diamagnetic materials.

$SnBr_4$. Upon mixing in toluene at −90°, $SnBr_4$ forms a complex with DTBN whose epr spectrum also exhibits both nitrogen and tin hfs. Even at low temperatures this complex readily formed a second and sometimes a third species as evidenced by a doubling or tripling of the ($^{119\text{-}117}Sn$, ^{14}N) lines as well as the ^{14}N central triplet. We report only data for the initial, low-temperature species.

Table I shows that both a_N and a_{Sn} for this complex are less than those of $SnCl_4$·DTBN but that the g value is significantly larger. The g-value increase upon changing Br for Cl is similar to that found in BX_3 complexes and is attributed to a small, but finite spin density on the halogen atoms; bromine has a much larger spin-orbit coupling constant than chlorine.

Both a_N and a_{Sn} decreased linearly with temperature, with the variation in a_{Sn} much greater than that of a_N. Because of the low stability of this complex data were only available over a narrow temperature range, limiting the accuracy with which the hfs variations could be fit (Table II).

$(t\text{-Bu})_2SnCr(CO)_5$. Since the Lewis acid $(t\text{-Bu})_2SnCr(CO)_5$ [compound S] is unstable without a coordinated base, it is originally isolated as a tetrahydrofuran (THF) adduct.[20] The isotropic epr spectrum of DTBN in toluene with a large excess of S·THF was a superposition of two triplets, one the spectrum of DTBN and the other the spectrum of the DTBN·S complex, indicating that the complex was in equilibrium with its components and that DTBN can successfully compete with THF for this acid. The ^{14}N hfs of the complex (Table I) is larger than that for DTBN, but considerably smaller than for the two SnX_4 complexes. Weak shoulders on the S·DTBN triplet indicate that the tin hfs values are quite small: $a_{Sn} \approx 2.1$ G.

Although the concentrations of reagents were not accurately known, and thus equilibrium constants were unavailable, the ratio R^S = [DTBN·S]/[DTBN] could be measured as a function of temperature. Since 1 mol of the THF is produced per mole of S·DTBN formed, then the equilibrium expression for the displacement reaction is

$$K^S{}_{dis} = \frac{[S\cdot DTBN][THF]}{[DTBN][S\cdot THF]} = \frac{[S\cdot DTBN]^2}{[DTBN][S\cdot THF]} \tag{4a}$$

$$= \frac{(R^S)^2}{1 + R^S}([DTBN]_{total}[S\cdot THF]^{-1}) \tag{4b}$$

With S·THF in large excess over $[DTBN]_{total}$, its concentration is effectively constant. Therefore, although the product of concentrations in parentheses, eq 4, was not well known, from a plot of $(R^S)^2/(1 + R^S)$ *vs.* inverse temperature we obtain the enthalpy for the displacement reaction (Table V). The reaction is exothermic, and thus, when they are dissolved in toluene, DTBN is a stronger Lewis base than is THF with respect to the Lewis acid S.

Since the spectra of radical and complex are superimposed, with the nonoverlapping high-field lines resolved and with no apparent line broadening, rates of complex formation and dissociation must be slow (less than ~10^6 sec^{-1}).

$[(t\text{-Bu})_2SnFe(CO)_4]_2$. In the presence of a base this dimer is in equilibrium with the monomer·base adduct[21]

$$[(t\text{-Bu})_2SnFe(CO)_4]_2 \overset{2B}{\rightleftharpoons} 2[(t\text{-Bu})_2SnFe(CO)_4]\cdot B$$

Preparation of a toluene solution with an excess of the dimer over DTBN did not give any indication of formation of the nitroxide adduct. Although with THF as solvent the dimer is cleaved, we did not attempt to try this cleavage with DTBN as solvent.

SiF_4. The epr spectrum of a toluene solution of DTBN with an excess of SiF_4 exhibited a superposition of the spectra from the complexed and uncomplexed nitroxide. The ^{14}N hfs (Table I) of the complex is slightly larger than that of the S complex. ^{29}Si ($I = {}^1/_2$, 8.5% natural abundance) hfs values were not observed.

Again, the resolution of two spectra, with a minimal increase in line width, indicates a slow exchange between complex and free nitroxide. The slow exchange makes it likely that ^{29}Si hfs values are not observed because a_{Si} is small. Because of the relatively low abundance of ^{29}Si (4.7%) the nonobservation of silicon hfs only requires a_{Si} to be less than about 2-3 times the line width, or about 2 G.

Both DTBN·SiF_4 and TMPN·SiF_4 rapidly decomposed to diamagnetic products even at −90°.

$SiCl_4$. The epr spectrum of a toluene solution of nitroxide with an excess of $SiCl_4$ or simply a solution of nitroxide in $SiCl_4$ itself (Figure 2) was again a composite of the spectra from the complex and uncomplexed nitroxide with no observable ^{29}Si hfs. The ^{14}N hfs of this complex is slightly

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(20) T. J. Marks, *J. Amer. Chem. Soc.*, **93**, 7090 (1971).

(21) T. J. Marks and A. R. Newman, *J. Amer. Chem. Soc.*, **95**, 769 (1973).

Table V. Thermodynamic Constants for DTBN-Lewis Acid Interactions

Lewis acid	Reaction	ΔH, kcal/mol	ΔS, cal/mol deg	ΔG,[a] kcal/mol	a_N,[a] G
$SiCl_4$[b]	Association	−3.1 ± 0.3	−10 ± 1.5	−0.9 ± 0.1	16.54
$GeCl_4$[c]	Association	−3.0 ± 0.2	−6.1 ± 0.9	−1.7 ± 0.1	16.35
$(t\text{-Bu})_2SnCr(CO)_5$[d]	THF displacement	−2.2 ± 0.2			16.6

[a] At 220°K. [b] In $SiCl_4$. [c] In $GeCl_4$. [d] In toluene.

smaller than for the SiF_4 complex but the exchange reaction is again slow and $a_{Si} < 2$ G. Both the DTBN and TMPN complexes were sufficiently stable to allow determination of the ratio $R^{SiCl_4} = [R_2NO \cdot SiCl_4]/[R_2NO]$ as a function of temperature. The equilibrium expression for the association reaction is

$$K_a^{SiCl_4} = \frac{[R_2NO \cdot SiCl_4]}{[R_2NO][SiCl_4]} = R^{SiCl_4}[SiCl_4]^{-1} \tag{5}$$

With silicon tetrachloride as the solvent $[SiCl_4]$ remains equal to the value which was measured for the pure material. From the temperature dependence of R^{SiCl_4} that of $K_a^{SiCl_4}$ may be obtained, and thus the enthalpy and entropy changes for the association reaction may be obtained.

Since DTBN·$SiCl_4$ has significantly narrower lines than does TMPN·$SiCl_4$, its spectrum is better resolved, allowing a more accurate determination of R^{SiCl_4}. Table V therefore lists only the thermodynamic parameters for the association reaction of $SiCl_4$ with DTBN.

For some samples, the ratio R^{SiCl_4} did not behave reversibly with temperature, suggesting the formation of other radical species. Equilibrium data were obtained only from samples exhibiting complete reversibility of this ratio.

Interestingly, in some of the samples for which decomposition occurred and thus samples which were unusable for evaluating K_a, the decomposition products appeared to catalyze the exchange between DTBN and the complex, causing a complete averaging of their separate spectra.

$GeCl_4$. The epr spectrum either of a toluene solution of DTBN with excess $GeCl_4$ or of a solution of DTBN in $GeCl_4$ was a composite very similar to those of the $SiCl_4$ and SiF_4 complexes. The value of a_N for the $GeCl_4$ complex is very slightly smaller than for the $SiCl_4$ complex and hfs values from ^{73}Ge ($I = ^9/_2$, 7.61% natural abundance) were also unobservably small. The complex in $GeCl_4$ as the solvent was sufficiently stable to obtain the association constant, $K_a^{GeCl_4}$, as a function of temperature, and the thermodynamic parameters are listed in Table V.

As with $SiCl_4$, for some $GeCl_4$ samples the ratio R^{GeCl_4} did not behave reversibly with temperature and these were not used to obtain equilibrium data.

$TiCl_4$. Mixing DTBN and excess $TiCl_4$ in toluene at −90° yielded a paramagnetic precipitate. At −30° this complex was sufficiently soluble to give a solution spectrum, a single triplet with a_N even larger than that of the $SnCl_4$ complex (Table I) and no splittings from titanium (for ^{47}Ti, $I = ^5/_2$, 7.75% abundance; for ^{49}Ti, $I = ^5/_2$, 5.5% abundance). The complex decays slowly at −30° ($t_{1/2} \approx 15$ min) largely to diamagnetic products but also in small part to an unidentified paramagnetic species.

Although this single spectrum could in principle be the result of rapid exchange between DTBN and a $TiCl_4$ complex with even larger splittings, of the R_2NO complexes observed to date almost all can be shown to exchange slowly, either by the observation of metal hfs or of a superposition spectrum. We therefore discard the possibility of exchange and assign the spectrum to the $TiCl_4$ complex itself. This means that $a_{Ti} < 0.7$ G.

In the presence of trace amounts of water $TiCl_4$ forms a hydrate which is a strong Bronsted acid, protonating the nitroxide. Similar behavior has been seen for MX_3 hydrates, where M is a group III atom.[22]

$TiBr_4$. Preparation of a sample in toluene at −90° by the standard procedure caused a large loss in the epr signal. The remaining observable species was a material insoluble at low temperature (−90°). This precipitate gave a powder spectrum typical of the protonated nitroxide with no indication of a $TiBr_4$ complex having been formed and decomposed before dissolving as the temperature was raised to −50°. This study was not pursued further.

$Ti(OPh)_4$. $Ti(OPh)_4$ formed a complex with DTBN which exhibited ^{14}N hfs but not $^{47-49}Ti$ hfs. The a_N (Table I) was similar to that of $GeCl_4$ and the complex was also in equilibrium with the free nitroxide, but not even the high-field line was sufficiently resolved to allow an accurate determination of the ratio $R^{Ti(OPh)_4}$ as a function of temperature. A slight broadening of the lines for DTBN in this system (~0.2 G) may mean that chemical exchange, although still slow, is faster than in the other equilibrium studies observed here.

H-Bonding Solvents. As has been observed previously, dissolving a nitroxide in a hydrogen-bonding solvent gives a typical three-line spectrum with an increased a_N.[13a] Superposition of spectra is not observed, for on the epr time scale there is rapid exchange between H-bonded and free nitroxide but epr and optical absorption studies on the DTBN–phenol system gave $K_a^{PhOH}(298°) = 6.5 \pm 0.2\ M^{-1}$.[23] An even larger value of K_a^{ROH} has been reported on the basis of calorimetric measurements for TMPN H-bonded adducts: $K_a^{ROH} \geqslant 27$ M^{-1} for phenol, 3-fluorophenol, and hexafluoro-2-propanol.[24] Thus for 10^{-3} M R_2NO dissolved in hydrogen-bonding liquids, where $[ROH] > 5$ M, the observed spectrum is essentially that of the $R_2NO \cdot HOR$ H-bonded adduct. The nitrogen hfs values for H-bonded DTBN are given in Table I.

***g* Values.** When DTBN and TMPN are perturbed in protic or aprotic solvents, g_{iso} varies linearly with a_N.[6b] In molecular complexes deviations from this relationship have been attributed to spin–orbit interaction of spin density on the acid and for the BX_3 (X = Cl, Br) complexes this deviation has been used to give an upper limit of 1% for the spin density on X. No information about spin density on boron was available because of the small spin–orbit coupling constant.[4b] Deviations in g_{iso} have also been used as evidence that protonated nitroxides in CH_2Cl_2 exist as tight ion pairs.[6b]

g_{iso} for the complexes studied here are listed in Table I. Deviations from the solvent relationship are uniformly small (⩽0.00015) except for $SnBr_4$ (see above), indicating minimal spin density on MX_4 in all the group IV acids studied here.

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(22) B. M. Hoffman and T. B. Eames, *J. Amer. Chem. Soc.*, **91**, 2169 (1969).

(23) Y. Murata and N. Mataga, *Bull. Chem. Soc. Jap.*, **44**, 354 (1971).

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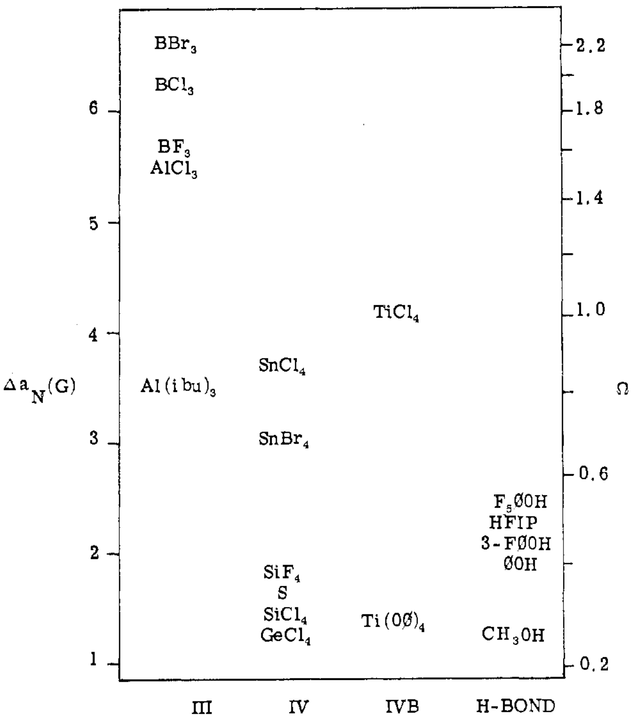

Figure 5. Lewis acids arranged by type and ordered by their change of the ^{14}N isotropic hfs of DTBN (see text) and by Ω (eq 7).

For $SnCl_4$ this result is consistent with the above more direct estimate from the anisotropic hfs. The greater deviations found in BX_3 complexes suggest that a noticeably greater π delocalization occurs in these acids.

Discussion

Several observations presented here give the most satisfying demonstration to date that the paramagnetic products of nitroxide-Lewis acid interaction are indeed molecular complexes. First, we have observed both ^{14}N and ^{17}O hfs from a nitroxide within a complex. Second, we have observed nitroxide and complex in a reversible equilibrium. Finally, the addition of pyridine to a nitroxide complex liberates the nitroxide base intact.

Although group IV tetrahalides (MX_4) generally form 2:1 base-acid complexes, because our experiments are all carried out with large excesses of acid, the complexes studied here are nevertheless 1:1. This conclusion is based on both the fluid- and frozen-solution epr spectra. If two radicals were complexed to a single metal atom, it is probable that they would exchange-couple through the metal. An interaction as small as $J \approx 10^{-4}$ cm^{-1} would be observable in a fluid-solution spectrum, but none is observed.

Even more definitive is the powder epr results. Two radicals complexed to a metal must exhibit a dipolar interaction between their spins and this "classical" interaction is calculable from a knowledge of the spin-density distribution on the nitroxides plus an estimate of the structure parameters.[25] Taking typical spin density distributions in a complex of $\rho_N^{\pi} \approx 0.7$ and $\rho_O^{\pi} \approx 0.3$ and N-O and M-O bond lengths of 1.3 and 2.2 Å, respectively, then the dipolar interaction for a *trans*-$(R_2NO)_2 \cdot MX_4$ complex would give rise to a fine-structure splitting of $2D \approx 480$ G. No such splitting is observed in the epr spectrum of any complex, confirming that the complexes studied are indeed single nitroxides complexed to Lewis acids.

As indicated above, a change in the R_2NO spin-density distribution upon complex formation can be taken as a measure of the acceptor strength of a Lewis acid. Since ^{14}N isotropic hfs values and spin densities for DTBN and TMPN are linearly related[6]

$$a_N = 20.3\rho_N^{\pi} + 3.6 \qquad (6)$$

the change in a_N (Δa_N) upon complexation is an equivalent measure. Figure 5 displays Δa_N for DTBN complexes of the group IV Lewis acids studied here, for some group III acids, and for hydrogen-bonding Lewis acids. As our reference, we take the indirectly measured value $a_N = 15.0$ G for gas-phase DTBN.[6b]

The same ordering may be placed on a scale with a more direct physical interpretation. Using a simple Huckel MO scheme, we can calculate $\Omega(A)$,[4b] the change in the effective electronegativity of the nitroxide oxygen upon complexation by acid A

$$\Omega(A) = \frac{|\alpha_O(A) - \alpha_O(0)|}{|\beta_{N-O}|} \qquad (7a)$$

$$= \Lambda(A) - \Lambda(0) \qquad (7b)$$

where β_{N-O} is the N-O resonance integral, $\alpha_O(A)$ and $\alpha_O(0)$ are the oxygen Coulomb integrals in the $R_2NO \cdot A$ complex and gas-phase DTBN, respectively, and

$$\Lambda = [2\rho_N^{\pi} - 1]/[\rho_N^{\pi}(1 - \rho_N^{\pi})]^{1/2}$$

Figure 5 also exhibits $\Omega(A)$ for Lewis acids studied.

For the group III trihalides, the ordering of acceptor strengths by Δa_N or Ω (Figure 5)[26] is in agreement with previous orderings on the basis of spectroscopic probes.[3] There is also qualitative agreement between acceptor strength as measured by Δa_N and Lewis acidity as indicated by the association constant for complex formation. For any MX_n acid studied with $\Delta a_N \gtrsim 3$ G, the association constant is immeasurably large, so that in the presence of excess acid no uncomplexed nitroxide is observed, while many acids with smaller Δa_N have measurable K_a. This agreement was also demonstrated for the TMPN H-bonded adducts in which the ^{14}N hfs was found to increase regularly with the enthalpy of formation and with the change in the O-H stretching frequency.[24]

For the group IV tetrahalides the ordering of acceptor strength on the basis of Δa_N (or Ω) is $SnCl_4 > SnBr_4 \gg SiF_4 \gtrsim SiCl_4 \gtrsim GeCl_4$. The tin halides have substantially larger Δa_N (Ω) than do SiX_4 or $GeCl_4$, and for M = Sn and Si, the ordering for MX_4 follows the electronegativity of X. These observations confirm the previous inferences,[7-9] as mentioned above, with the exception of our finding of $SiCl_4 \gtrsim GeCl_4$. The comparison of $SiCl_4$ and $GeCl_4$ is of some interest. Both by acceptor strength, Δa_N, and by the free energy of formation (220°K) the acids are quite similar; however, the ordering by acceptor strength is $SiCl_4 > GeCl_4$, which is the reverse of the ordering by Lewis acidity (ΔG).

To our knowledge, ours are the first equilibrium measurements for adduct formation by $SiCl_4$ and $GeCl_4$. Other measurements such as ΔH for formation of $MX_4(\text{isoquinoline})_2$ and ΔH for dissociation of $MX_4(N(CH_3)_3)$ also indicate that

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(25) N. Hirota and S. I. Weissman, *J. Amer. Chem. Soc.*, **86**, 2538 (1964).

(26) Reference 5 studied gallium and aluminum trihalides but used a different, less sensitive reference nitroxide and their results are not included in Figure 5. Within a large experimental error their results indicate $AlX_3 \gtrsim GaX_3$, but differences due to X are not distinguished.

they have relatively weak acidic properties but with $GeCl_4$ stronger than $SiCl_4$.[7,8,27] Thus the spectroscopic probe of the intact complex, Δa_N, seems to be measuring a somewhat different property than displayed in complex formation.

Although the groups attached to the tin atom of compound S make it an unusual Lewis acid, its study has afforded a direct comparison between R_2NO and a more conventional base. The ability of DTBN to compete favorably with THF (for compound S) but not with pyridine (for $SnCl_4$) established its Lewis base character within the framework of more ordinary chemical experience. Previous estimates of the basicity of R_2NO, obtained from measurement of ΔH_f for adducts of TMPN with H-bonding Lewis acids, indicate that TMPN is a stronger base than acetone.[24]

Comparing group IVb and IVa (Figure 5), we see than a_N for $TiCl_4$ is slightly greater than that for $SnCl_4$. Within group IVb, the great difference between Δa_N for $TiCl_4$ and $Ti(OPh)_4$ is perhaps somewhat surprising in view of the reported Mulliken electronegativities: Cl, 9.4; Br, 8.4; OPh, 8.5.[28] On the basis of these electronegatives and the fact that $\Delta a_N(TiCl_4) \gtrsim \Delta a_N(SnCl_4)$ one might predict that Δa_N for Ti(OPh) should be slightly greater than that for $SnBr_4$, whereas it is considerably less. This discrepancy may result from a sensitivity of the effective electronegativity of a group (*i.e.*, OPh) to the atom to which it is bonded. The use of a very sterically hindered reference base interacting with the relatively sterically hindered $Ti(OPh)_4$ may also serve to reduce Δa_N.

Although the results for nitroxide complexes with the group III trihalides have been previously detailed,[4] it is interesting to note in Figure 5 the large difference between Δa_N for this class of acids and for the group IV tetrahalides. We also see that even with the substantial reduction in Δa_N upon going from $AlCl_3$ to $Al(i\text{-}Bu)_3$[29] still $\Delta a_N(Al(i\text{-}Bu)_3) \approx \Delta a_N(SnCl_4)$.

Results for hydrogen-bonded, $R_2NO \cdot HOR$, adducts have been included primarily for illustrative purposes. These adducts form in the highly polar ROH, and thus the values of Δa_N may not be strictly comparable to those observed for the MX_n adducts. Nevertheless, it is interesting to note that the largest values of Δa_N produced by H bonding exceed those for the weaker acids of group IV. The Δa_N of the H-bonding Lewis acids ROH can be readily accounted for by the obvious differences in the electronegativities of the R groups.

We have studied R_2NO complexes with group IV Lewis acids and have compared our results with other measurements of their acceptor strengths as well as with the ordering of the group III Lewis acids. Changes in nitroxide ^{14}N hfs are a readily measured and convenient scale of relative acceptor strengths. Although in many cases the complexes are unstable at room temperature, they can usually be studied at low temperatures. This technique, applicable to the study of a wide variety of molecular Lewis acids in solution, can be further extended to the investigation of catalytically interesting surface acidic sites.[30]

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Registry No. $Ti(OPh)_4 \cdot DTBN$, 51202-21-2; $GeCl_4 \cdot DTBN$, 51176-02-4; $SiCl_4 \cdot DTBN$, 51176-03-5; S·DTBN, 51130-07-5; $SiF_4 \cdot DTBN$, 51176-04-6; $SnBr_4 \cdot DTBN$, 51176-05-7; $SnCl_4 \cdot DTBN$, 51176-06-8; $TiCl_4 \cdot DTBN$, 51176-07-9; DTBN, 2406-25-9; TMPN, 2564-83-2; $GeCl_4 \cdot TMPN$, 51176-08-0; $SiCl_4 \cdot TMPN$, 51176-09-1; $SiF_4 \cdot TMPN$, 51176-10-4; $SnCl_4 \cdot TMPN$, 51176-11-5.

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Reactions of Gaseous Inorganic Negative Ions. V. Dissociative Electron Capture and Ion-Molecule Reactions in Methylfluorosilanes[1]

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The negative ion mass spectra of methylfluorosilanes $(CH_3)_nSiF_{4-n}$ ($n = 4$–1) measured at low pressure and at low electron energies are characterized by the loss of atomic hydrogen and atomic fluorine from the parent molecule negative ion. The dominant ions are those formed by loss of hydrogen atoms. Elimination of neutral HF is a characteristic reaction of the $(P - H)^-$ ion where $(P - H)^-$ represents parent molecule ion minus a hydrogen atom. Negative ion-molecule reactions of the methylfluorosilanes with SF_6^- involve fluoride ion transfer. Rate constants and reaction cross sections have been measured as a function of primary ion energy. The reaction cross section shows a dramatic decrease in magnitude as fluorine is replaced by methyl groups in the series of compounds. The magnitude of the reaction cross section among the series of compounds varies in a manner similar to the known stability of the pentavalent methylfluoro anions in condensed phases.

Introduction

Primary and secondary negative ion formation in nonmetal fluorides has been studied by several investigators.[2,3] The investigations have had as their goal the characterization of negative ion formation processes, evaluation of ionic heats

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[1] Presented in part at the 21st Meeting of the American Society for Mass Spectrometry, San Francisco, Calif., May 1973.

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