Dielectric Relaxation Process of Rigid Molecules[1]

Sir:

We wish to report the results of recent work in our laboratory which may have a considerable bearing on our present understanding of the dielectric absorption due to molecular reorientation. We studied the dielectric absorption of several small rigid polar molecules, namely, the halogen-substituted benzenes and naphthalenes, in supercooled decalin at audio- and radiofrequencies. All these rigid molecules show a very broad distribution of relaxation times. The Cole-Cole plots for a solution of chlorobenzene in decalin at several temperatures, which also represent the general behavior found in our study, are shown in Figure 1. We find that the distribution of relaxation times (distribution parameter, α) increases with decreasing temperature or increasing solvent viscosity. The enthalpy of activation for dielectric relaxation is closely similar in all these molecules, and the differences in their relaxation times seem mainly due to the entropy factors.

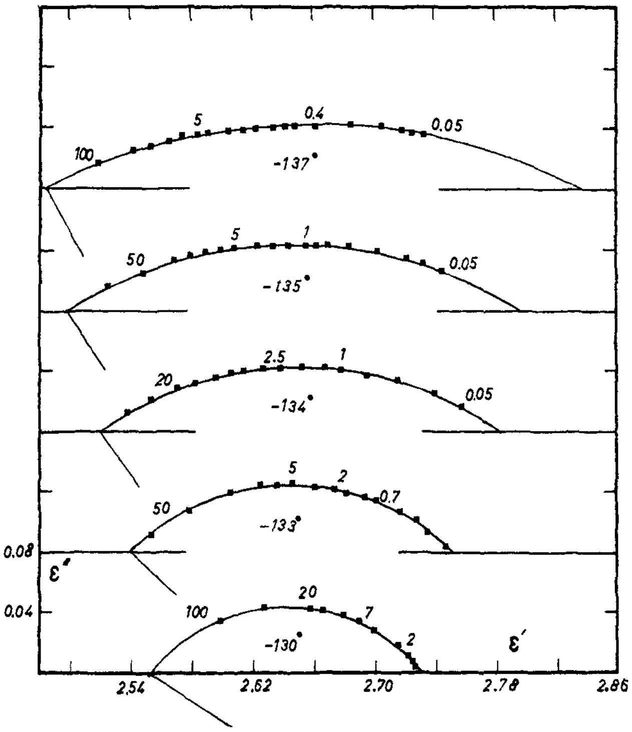

Figure 1. Cole-Cole plots for 7.8 mole % solution of chlorobenzene in decalin at several temperatures. Curves have been shifted upward as shown by the ordinate. Figures near the data points are the frequencies in kHz. Figures below the arcs are the the rounded-off temperatures in °C.

At ambient temperature these molecules in benzene and n-heptane show a single relaxation time ($\alpha = 0$) at the microwave frequencies. However, it has often been observed that, in viscous solvents, such as Nujol, they show a small distribution of relaxation times.[2] This small distribution has often been suggested to originate from a fluctuation in the environment of a reorienting dipole. We believe that the very broad distribution found at low temperatures in our study cannot, however, be due to a fluctuation of environment.

We propose the following picture of dielectric relaxation in solutions of rigid molecules in nonpolar solvents. This picture includes the effect of viscoelastic relaxation of the solvent on the reorientation of a dipole. Liquids show viscoelastic relaxation in the same frequency range in which dielectric absorption due to molecular processes is found,[3] the viscoelastic relaxation time being $\tau_{\mathrm{ve}} = \eta/G_\infty$, where η is the steady-flow viscosity, and G_∞ is the high-frequency shear modulus, $\approx 1 \times 10^{10}$ dynes/cm^2. On application of a periodic electric field, as in dielectric measurements, a rotating molecule displaces the solvent and thus causes local alternating shear stress in the solvent. A dipole thus transforms a periodic field to a periodic mechanical stress on the solvent. As a result of viscoelastic relaxation, the dynamic viscosity of the solvent in the immediate vicinity of the reorienting dipole is lowered. The over-all effect is that the dipole reorients in a medium whose dynamic viscosity is frequency dependent, decreasing with increasing frequency. The dipole thus reorients with a time that decreases with increasing frequency. This would give rise to a distribution of relaxation times in the dielectric absorption spectrum. The breadth of distribution would then be directly related to the steady-flow viscosity of the solvent. In benzene and n-heptane solutions, whose steady-flow viscosity is already very low, there will be a very small or zero distribution but, in viscous solvents, one should find a broad distribution. An additional advantage of this picture is that it explains the often-found lack of agreement with the Debye theory when the dependence of relaxation time on the macroscopic viscosity is examined.[2] In fact, the classical Debye model seems to be valid; what need to be considered are the additional processes which occur at the microscopic level on application of a periodic field.

It follows from this picture that no dielectric absorption due to molecular reorientation in solutions should occur with a single relaxation time, although, in solvents of very low viscosity, the distribution is very small and, within experimental error, is indistinguishable from zero. This represents a crucial experiment: if a molecular reorientation process in viscous liquids, or in polymers, shows a single dielectric relaxation time, the theory is refutable.

Details of the experimental results with a discussion of dielectric relaxation will be reported at a later date.

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(1) This research was supported in part by the U. S. Army Research Office (Durham). Reproduction in whole or in part by or for the U. S. Government is permitted.

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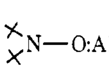
Free-Radical Molecular Complexes

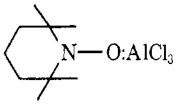
Sir:

We have discovered that aliphatic nitroxide free radicals form monomeric molecular complexes with strong Lewis acids. These complexes contain a nitroxide which is datively bonded through a "lone pair" of electrons but which retains its unpaired electron. They are thus different from several previously studied nitroxide complexes[1-3] but are quite analogous to a recently reported protonated aliphatic nitroxide.[4] These molecular complexes are stable in solution and demonstrate well-resolved hyperfine interactions with the principal nucleus of the acid as well as with nuclei of the nitroxides. The paramagnetism of these novel complexes offers a new technique for studying the nature of Lewis acid-base interactions. The unpaired spin serves as a microscopic probe of variations in the electron density of the paramagnetic base as well as the electronic structure of the acid.

In this preliminary communication we describe the complexes between the nitroxides di-*t*-butylnitroxide (I) and 2,2,6,6-tetramethylpiperidine-N-oxyl (II) with aluminum chloride to give complexes of the forms III and IV.



III



IV

Nitroxide complexes with $AlCl_3$, as well as with other Lewis acids, are prepared in rigorously anhydrous conditions on a vacuum line by a procedure to be described.[5] Although the aluminum chloride complexes are stable at room temperature over a period of weeks, other complexes, such as those with the boron trihalides, are much less stable and must be observed at lower temperatures.[5]

The solution electron spin resonance (esr) spectra of I and II consist of three lines produced by interaction of the unpaired electron with a single ^{14}N nucleus (Figure 1A). Under conditions of low resolution species III and IV exhibit 18-line spectra in which each of the three ^{14}N lines is split into six by interaction with a single ^{27}Al nucleus (Figure 1B). Upon complexation the ^{14}N hyperfine coupling constants of the parent nitroxides increase and the *g* values decrease (Table I).

Table I. Isotropic *g* Values and Hyperfine Coupling Constants (in Gauss) for Parent Nitroxides and $AlCl_3$ Adducts[a,b]

	g	a_N	$a_{^{13}C}$	a_{Al}
I	2.00606	15.33	4.26[c]	
II	2.00608	15.50	5.7[d]	
III	2.00525	20.15	5.50	11.40
IV	2.00504	19.86	6.4	8.80

[a] CCl_4 solution unless stated otherwise. [b] Uncertainties are estimated to be ±0.00005 for *g*; ± 0.1 for coupling constants except as noted. [c] R. J. Faber, F. W. Markley, and J. A. Weil, *J. Chem. Phys.*, **46**, 1652 (1967); uncertainty given as ±0.03; benzene solution. [d] R. Brière, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 3273 (1965); water solution.

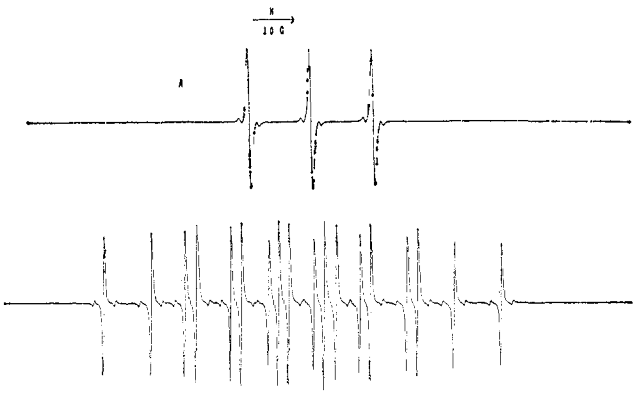


Figure 1. Low-resolution esr spectra of (A) di-*t*-butylnitroxide (I) and (B) di-*t*-butylnitroxide complexed with aluminum chloride (III) in carbon tetrachloride solutions at room temperature.

Under conditions of high resolution, however, each of the 18 component lines of III consists of at least 7, and almost certainly more, hyperfine lines. These small splittings must result from the protons on the aliphatic nitroxide and not the chlorines of the Lewis acid as evidenced by similar splittings which we have now observed in high-resolution esr spectra of the protonated form of II, species V.[5]

Although aluminum chloride is undoubtedly dimeric (Al_2Cl_6) in CCl_4 solution,[6] the observation of splitting from a single ^{27}Al nucleus in the nitroxide complexes with aluminum chloride suggests interaction with an $AlCl_3$ monomer. This view is supported by the fact that nitroxide complexes with BF_3 give spectra with hyperfine splittings from one nitrogen nucleus and one boron nucleus.[5] BF_3 molecules show little tendency to dimerize in solution.[7]

The increase in the ^{14}N hyperfine splitting and the decrease in *g* value upon complexation of the parent nitroxides are similar to changes upon protonation and indicate that the site of complexation is the nitroxide oxygen atom.[4] Bonding an acid to the oxygen atom draws the bonding π electrons toward the oxygen but shifts the unpaired antibonding electron toward the nitrogen atom. This process increases the nitrogen π-electron spin density (ρ_N) and therefore the nitrogen hyperfine splitting. The magnitude of the ^{27}Al coupling constant reflects the covalency in the bond between acid and base. These couplings may be compared with those of group II and group III metal ions complexed with *o*-semiquinone radical.[8] We defer consideration of a number of features of the spectra, such as the changes in the ^{13}C and proton splittings of the nitroxide upon complexation; these are more profitably discussed in conjunction with results for a number of Lewis acid complexes. We further defer discussion of the line-width variation evident in Figure 1B.[5]

Changes in the ^{14}N hyperfine coupling constant for a given nitroxide complexed with different Lewis acids will reflect the actual electronic structure within the adducts. That is, such changes will reflect the strength of the particular acid in a Lewis acid complex *as formed*,

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(5) B. M. Hoffman and T. B. Eames, to be published.

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(7) G. A. Olah in "Friedel-Crafts and Related Reactions," G. A. Olah, Ed., Interscience Publishers, New York, N. Y., 1963, p 201.

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as opposed to measurements of the thermodynamic stability of adducts with respect to their constituents, which depend on a reorganization energy. For example, upon protonation, a_N(I) increases by a factor of 1.37 to a_N(V) = 21.8 ± 0.2,[4] whereas a_N(I) increases by a factor of 1.28 upon complexation with aluminum chloride. Further information is gained by consideration of the size of a suitably normalized coupling constant to the central nucleus of the Lewis acid.[5] Steric hindrance from the nitroxide methyl groups may be taken account of by using different aliphatic nitroxides which are still less hindered. Also, structural differences in the aromatic and aliphatic nitroxides lead to markedly different changes in coupling constants upon protonation.[4,9] Exploring these differences upon adduct formation gives us yet another probe into the electronic structure of the Lewis acid adducts.

Acknowledgment. We are indebted to Professor D. F. Shriver for many invaluable discussions and to D. Barry for synthesizing the parent nitroxides. This research was supported by the Advanced Research Projects Agency of the Department of Defense through the Northwestern University Material Research Center.

[9] H. Hogeveen, H. R. Gersmann, and A. P. Praat, *Rec. Trav. Chim. Pays-Bas*, 86, 1063 (1967).

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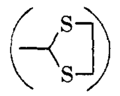
Neighboring Sulfur Participation in the Acetolysis of Benzyl Chlorides[1]

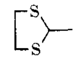
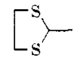
Sir:

Neighboring sulfur participation has long been known in the case of the solvolysis of β-chloroethyl sulfides.[2] However, similar participation has never been reported for benzyl chlorides having sulfur-containing *ortho* substituents. We now report rates of acetolysis of some *ortho*- or *para*-substituted benzyl chlorides and striking rate enhancement by the *o*-dithiacyclopentyl group.



Substituted benzyl alcohols were synthesized by conventional methods and converted into the corresponding chlorides by thionyl chloride in benzene with the use of a small amount of 2,6-lutidine. All of the chlorides were checked for purity by analysis and nmr spectra: *o*-dithiacyclopentylbenzyl chloride (V) (*Anal.* Calcd for $C_{10}H_{11}S_2Cl$: Cl, 15.36. Found: Cl, 15.24) nmr (τ) 2.10 (m, 1 H, Ar), 2.75 (m, 3 H, Ar), 3.98 (s, 1 H, CH), 5.30 (s, 2 H, CH_2), 6.57 (m, 4 H, CH_2CH_2); *p*-dithiacyclopentylbenzyl chloride (VI) (*Anal.* Calcd for $C_{10}H_{11}S_2Cl$: C, 52.05; H, 4.80; S, 27.79; Cl, 15.36. Found: C, 52.31; H, 4.98; S, 27.86; Cl, 15.32) nmr (τ) 2.67 (m, 4 H, Ar), 4.45 (s, 1 H, CH), 5.51 (s, 2 H, CH_2), 6.63 (m, 4 H, CH_2CH_2).

Table I. Rates of Acetolysis of Benzyl Chlorides at 60° [a]

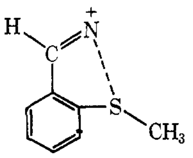
Substituent	k_1, sec^{-1}	*o*/*p* ratio	Rel *o*/*p* ratio
o-CH_3O (I)	3.2×10^{-6}	0.0017	1
p-CH_3O (II)	1.9×10^{-3}		
o-CH_3S (III)	3.6×10^{-7}	0.018	11
p-CH_3S (IV)	2.0×10^{-5}		
o-  (V)	3.9×10^{-5}	220	130,000
p-  (VI)	1.8×10^{-7}		

[a] Initial concentration 0.05 *M*; in the presence of 0.06 *M* sodium acetate.

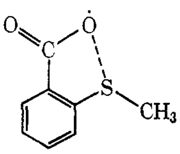
Rates of acetolysis of substituted benzyl chlorides were measured in the presence of a slight excess of sodium acetate at 60°, the reaction being followed titrimetrically by the Volhard method. All reactions obeyed the first-order rate equation up to 40–50% reaction and gave the corresponding acetates as a sole product except in the case of compound V where, besides the acetate, appreciable amounts of polymeric materials were produced beyond 60% reaction.

First-order rate constants, *ortho*:*para* rate ratios, and relative *ortho*:*para* rate ratios are listed in Table I. The *o*-methoxy compound I reacts at about $^1/_{500}$ the rate of the *p*-methoxy compound II, presumably due to steric hindrance to solvation of the transition state. The *o*-methylmercapto III is again considerably less reactive than the corresponding *para* compound IV, but the *ortho*:*para* ratio becomes slightly higher than in the methoxy case. The rate for the *o*-dithiacyclopentyl compound V, however, exceeds that of the corresponding *para* compound VI by a factor of 220. Assuming that the relative *ortho*:*para* rate ratio is a measure of the extent of the participation of the *ortho* substituents, dithiacyclopentyl is 130,000 times more effective in facilitating the solvolytic reaction than methoxy is. Allowing for the relative bulkiness of these two groups, this factor would be still greater.

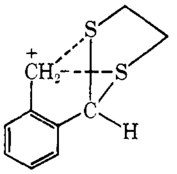
Participation of *o*-methylmercapto is reported in two cases, which results in about 10,000 times rate enhancement: degradation of esters of *syn*-benzaldoximes to the corresponding benzonitriles[3] and thermal decomposition of *t*-butyl perbenzoates.[4] In view of these facts the present result, *i.e.*, much participation in the



VII



VIII



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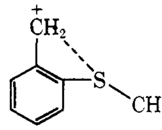

X

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[3] R. I. Crawford and C. Woo, *Can. J. Chem.*, 43, 3178 (1965).

[4] W. G. Bentrude and J. C. Martin, *J. Am. Chem. Soc.*, 84, 1561 (1962).