slope.[25] Figure 5 also compares our data with those from de Maine[3] and Amako;[4] de Maine's data (from CCl_4 solution) do not agree either with our measurements in the nonpolar solvent, *n*-heptane, or with our measurements in the polar solvent, CH_2Cl_2. On the other hand, Amako's result[4] (in *n*-hexane) agrees quite well with ours in *n*-heptane. We believe that the larger temperature range covered in our work makes our resulting $\Delta H_f°$ somewhat more reliable than Amako's lower value,[4] and that the value of $\Delta H_f°$ is the same, within experimental error, in both *n*-heptane and *n*-hexane solvents.

Conclusion

Although the properties of the ethanol–I_2 complex are of basic importance for the understanding of complexes between alcohols (or other oxygen-containing donors) and halogens, we find on repetition of the earlier experiments[3,4] that the complex is considerably more stable (as measured by K_f, and especially by $-\Delta H_f°$) than indicated by the earlier work. We find no definite evidence indicating that competition between CT-complex formation between ethanol and I_2 and hydrogen-bond complex formation between two ethanol molecules affects these results. We do find some trends in the values of K_f (or in the ζ matrix of the Liptay method) using the simple Liptay–Scott analysis of the data in *n*-heptane. These trends can be eliminated by making reasonable assumptions concerning the change in ϵ_{13}, the molar absorptivity of free I_2, as the nature of the solvent changes due to the addition of the ethanol. However, the values of the molar absorptivity of the CT band of the complex, and the values of $\Delta H_f°$, do not depend very strongly upon how the corrections are made for these trends.

We have found, furthermore, that the frequency of maximum absorption of the CT band in a nonpolar solvent is higher (by about 3000 cm^{-1}, or 0.3 eV) than that reported earlier, and its intensity is much greater than that reported earlier (*f* and *D* are found to be about twice as large as those estimated earlier).

We find this evidence for much stronger interaction than was believed earlier to be more consistent with the large "blue shift" of the visible band and with other indications of stronger interaction. In general we believe our results are consistent with other ideas[25] about complexes and fit better with these than did the earlier indications[3,4] of only weak interaction.

Acknowledgments. Financial support from Public Health Service Research Grants No. GM-10168 and GM-14648 is gratefully acknowledged. We are also grateful to the University of Iowa Computer Center and to the Graduate College for support of the computing.

Electron Spin Resonance Studies of Steric Effects in Tetrakis(alkylthio)ethylene Cation Radicals[1a,b]

David H. Geske[1c] and Margaret V. Merritt[1d]

Contribution from the Department of Chemistry, Cornell University,
Ithaca, New York 14850. *Received May 3, 1969*

Abstract: The temperature dependence of the esr spectra of cation radicals of the type $(RS)_2C^+{=}C(SR)_2$, I^+, has been investigated (R = methyl, ethyl, isopropyl, and phenyl). The radicals were produced by oxidation of the parent ethylenes with aluminum chloride in methylene chloride. The esr room-temperature spectrum of the methyl derivative, Ia^+, was attributed to interaction with 12 equivalent protons: $|a_H| = 2.70$ G. The spectrum observed at −90° was analyzed in terms of interaction with two sets of six equivalent protons: $|a_H| = 0.93$ G, $|a_H| = 4.22$ G. At intermediate temperatures, the spectrum exhibited an alternating line-width effect. These results are in accord with a temperature-dependent intramolecular process which can be formally described as an interconversion of two identical conformers of Ia^+ (see eq A). The line-width variation was analyzed using the theory of Freed and Fraenkel to obtain k, the rate constant for the interconversion process, $E_a = (8.6 \pm 0.6)$ kcal mole^{-1}. A similar temperature dependence of the methylene proton coupling constant in the ethyl derivative, Ib^+, was observed and similarly interpreted. In addition, restricted rotation about two of the ethyl carbon–sulfur bonds is postulated to account for the low-temperature spectrum of Ib^+. It is suggested that the alkyl proton coupling constants in this type radical can be related to the sulfur spin density, ρ_S, by the following expression: $a_H = Q^H{}_{S-C-H}\rho_S\langle\cos^2\theta\rangle$. The ^{13}C coupling constant was observed in the esr spectrum of Ia^+ enriched in ^{13}C at the ethylenic position: at +30°, $a_C = +3.72$ G; at −90°, $a_C = +3.87$ G.

Few cation radicals of thioethers have been observed.[2,3] Zweig, *et al.*, have investigated the cation radicals of 1,4-bis(methylthio)benzene[2] and 1,2,4,5-tetrakis(methylthio)benzene and have suggested that the coupling constant of the methyl protons β to the sulfur is related to ρ_S by the expression $a_H = Q^H{}_{SCH_3}\rho_S$, $Q^H{}_{SCH_3} = 21$ G/e. In a reexamination of Zweig's work, Forbes and Sullivan concluded that the

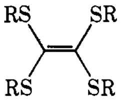
---

(1) (a) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968. (b) Abstracted from the Ph.D. Thesis of M. V. M., Cornell University, 1968. (c) Deceased, Dec 4, 1967. (d) Du Pont Teaching Fellow, 1966–1967, Cornell University Fellow, 1967–1968. Address correspondence to author at the Mellon Institute, 4400 Fifth Ave., Pittsburgh, Pa. 15213.

(2) A. Zweig and W. G. Hodgson, *Proc. Chem. Soc.*, 417 (1964).

(3) A. Zweig, W. G. Hodgson, W. H. Jura, and D. L. Maricle, *Tetrahedron Letters*, 1821 (1963).

cation radical of 1,4-bis(methylthio)benzene, as well as the corresponding diethyl compound, exists as a mixture of *cis* and *trans* isomers.[4] They used a value of $Q^{H}{}_{S-C-H} = 18.5$ G/e in comparing the experimental coupling constants with those calculated from ρ_S. They implied that the magnitude of the alkyl proton coupling is dependent upon the dihedral angle between the plane of the *C–H* proton bond and the p_z–π orbital of the adjacent sulfur. This esr study of the cation radicals of some tetrakis(alkylthio)ethylenes (I) was undertaken to investigate further the properties of this class of radicals and the mechanism of spin transmission.



Ia, R = methyl
b, R = ethyl
c, R = isopropyl
d, R = phenyl

Experimental Section

Materials. Trifluoroacetic acid (Distillation Products Industries) and anhydrous aluminum chloride (Fisher Certified) were used without further purification. Acetonitrile, obtained from Standard Oil Co. of Ohio, was purified by a slight modification of the method described by Mann and coworkers.[5] Methylene chloride (Fisher Certified) was purified by stirring *ca.* 12 hr over calcium hydride. It was then filtered and distilled *in vacuo* into a storage flask where it was kept under vacuum and distilled *in vacuo* as needed. Nitromethane (Fisher Certified) was purified by an identical procedure except that the drying over calcium hydride was carried out at reflux temperatures. The supporting electrolyte for all electrochemical experiments was tetraethylammonium perchlorate (Distillation Products Industries) at *ca.* 0.1 *M* concentration. This material was recrystallized three times from water and dried at 100°.

Tetrakis(methylthio)ethylene (Ia). Ia was prepared by reaction of methyl orthothioformate with sodamide (Fisher Certified) as described by Hine and coworkers.[6] The methyl orthothioformate was synthesized from formic acid (K and K Laboratories) and methyl mercaptan (Matheson) in the sealed tube reaction of Houben and Schultze.[7] Ia was purified by recrystallization from methanol and vacuum sublimation at *ca.* 50°: mp 60–61° (lit.[8] 61.5°); nmr ($CDCl_3$) δ 2.38 ppm (s) (lit.[6] δ 2.39 ppm).

[Ethylene-^{13}C]-Tetrakis(methylthio)ethylene. Ethylenic-^{13}C-labeled Ia was prepared by the above method modified appropriately for a small-scale reaction; 0.5 g of formic acid, 51.9% enriched in ^{13}C, was supplied by Merck Sharp and Dohme of Canada, Ltd. A fourfold excess of methyl mercaptan was used in the reaction. The overall yield of labeled Ia based on formic acid was 10%. A mass spectrum of the product confirmed the expected extent of isotopic enrichment.

Tetrakis(ethylthio)ethylene (Ib). Ib was synthesized by a method, described by Frohling and Arens,[9] similar to that used to prepare Ia. Ib was purified by vacuum sublimation at *ca.* 40°: mp 52.5–53.0° (lit.[9] 53.5–54°); nmr ($CDCl_3$) δ 1.22 ppm (t, 12, J = 7.2 Hz), δ 2.88 ppm (m, 8, J = 7.2 Hz).

Tetrakis(phenylthio)ethylene (Ic). Ic was prepared by the above method. The resulting compound was purified by recrystallization from heptane, followed by vacuum sublimation at *ca.* 140°: mp 151–153° (lit.[9] 153–154°); nmr ($CDCl_3$) δ 7.36 ppm (m).

Tetrakis(isopropylthio)ethylene (Id). Id had not been previously reported; it was prepared by the method of Frohling and Arens from isopropyl orthothioformate.[9] Isopropyl mercaptan (Aldrich Chemical Co.) and ethyl formate (Distillation Products Industries) were used to synthesize the orthothioformate, yield 20%. The resulting oil was used without further purification in the subsequent reaction to form the ethylenic compound. Data for isopropyl orthothioformate: ir (neat) 1380 and 1360 (isopropyl doublet), 1050 cm^{-1} (C–O); nmr (neat) δ 1.23 (d, 18, J = 6.3 Hz), 3.85 (m, 3, J = 6.3 Hz), 4.85 ppm (s, 1). The yield of Id based on orthothioformate was *ca.* 10%. Id was purified by recrystallization from methanol, followed by vacuum sublimation at *ca.* 70%: mp 82.5–84.0°; nmr (CH_2Cl_2) δ 1.27 (d, 24, J = 6.6 Hz) and 3.53 ppm (m, 4, J = 6.6 Hz); mass spectrum (70 eV, *m/e* (relative intensity) 324 (1), 281 (1), 239 (0.2). *Anal.* Calcd for $C_{14}H_{28}S_4$: C, 51.80; H, 8.69; S, 39.55. Found: C, 51.12; H, 8.66; S, 39.55.[10]

It should be noted that attempts to prepare tetrakis(*t*-butylthio)ethylene were unsuccessful. The product of the reaction of *t*-butyl orthothioformate with sodamide in liquid ammonia yielded a material whose mass spectrum exhibited a parent ion of *m/e* 310. The molecular ion of the desired product should have *m/e* 380. No further characterization of this material was attempted.

Electrochemistry. Voltammetric measurements were made with a controlled-potential three-electrode polarograph, which has been previously described.[11] A rotating platinum microelectrode (rpe) was used and potential measurements were made *vs.* the aqueous saturated calomel electrode (sce) under conditions of "long immersion".[12] The precision of such measurements is assumed to be ±5 mV.[13]

Values of limiting currents were compared with that obtained for the one-electron oxidation of iodide ion in acetonitrile with the rpe used.[14] A Hewlett-Packard function generator, Model 202 A, was used to produce a triangular sweep in conjunction with the three-electrode polarograph for cyclic voltammetry studies. A shielded-disk platinum electrode, *ca.* 5 mm in diameter, was used in the cyclic voltammetry measurements.

Electron Spin Resonance. Esr measurements were made with a Varian V-4502 X-band spectrometer as previously described.[11] A Varian V-4531 multipurpose cavity was used routinely; *g*-value measurements were made, however, with the Varian dual sample cavity; DPPH (g = 2.0036) was used as a reference.

Radicals generated *in situ* in the resonance cavity in an electrochemical flow cell were produced by electrolytic oxidation at a platinum gauze electrode as has been previously described.[15] The Glarum–Marshall "two electrode potentiostat" was used for electrochemical oxidation.[16]

The concentration and stability of radicals produced by aluminum chloride oxidations were extremely dependent on the method of preparation; consequently the preparation is given in detail. *Ca.* 1 mg of the substrate was placed in a 3-mm o.d. cylindrical Pyrex tube of a two-compartment sample cell; ~6 mg of aluminum chloride was put in the second compartment. *Ca.* 1 ml of solvent was distilled *in vacuo* onto the aluminum chloride. The solvent was allowed to melt; solid particles were allowed to settle; and the supernatant liquid was decanted onto the substrate. This solution was thoroughly mixed and the 3-mm sample tube was inserted into the resonance cavity.

Trifluoroacetic acid oxidations were performed by distilling *in vacuo ca.* 1 ml of the acid, followed by 1 ml of solvent onto *ca.* 1 mg of substrate in a 3-mm o.d. sample tube. The solution was mixed and the sample tube was inserted into the resonance cavity.

The Ia$^+$ radical was generated in several media. In each system, the observed coupling constants were identical within experimental error. The signal intensity and radical stability were, however, extremely dependent on the method of preparation. The intensity and stability were low in the following systems: flow electrolysis in acetonitrile, sulfuric acid, ammonium persulfite–trifluoroacetic acid, aluminum chloride–acetonitrile, methanesulfonic acid;[17] they were high in the following systems: aluminum chloride–nitro-

---

(4) P. D. Sullivan and W. F. Forbes, *Can. J. Chem.*, **46**, 317 (1968).

(5) J. O'Donnell, J. Ayres, and C. Mann, *Anal. Chem.*, **37**, 1161 (1965).

(6) J. Hine, R. P. Bayer, and G. G. Hammer, *J. Am. Chem. Soc.*, **84**, 1751 (1962).

(7) J. Houben and K. M. L. Schultze, *Ber.*, 44, 3235 (1911).

(8) P. Fetkenheuer, H. Fetkenheuer, and H. Lecus, *ibid.*, 60, 2535 (1927).

(9) A. Frohling and J. E. Arens, *Rec. Trav. Chim.*, 81, 1009 (1962).

(10) Galbraith Laboratories, Inc., Knoxville, Tenn.

(11) K. Kuwata and D. H. Geske, *J. Am. Chem. Soc.*, 86, 2102 (1964).

(12) J. F. Coetzee and G. R. Padmanabhan, *J. Phys. Chem.*, 66, 1709 (1962).

(13) D. H. Geske, J. Ragle, M. Banbenek, and A. Balch, *J. Am. Chem. Soc.*, 86, 987 (1964).

(14) D. H. Geske, *J. Phys. Chem.*, 63, 1062 (1959).

(15) T. M. McKinney and D. H. Geske, *J. Am. Chem. Soc.*, 87, 3013 (1965).

(16) S. Glarum and J. Marshall, *J. Chem. Phys.*, 41, 2182 (1964).

(17) P. A. Malachesky, L. S. Marcoux, and R. N. Adams, *J. Phys. Chem.*, 70, 2064 (1966).

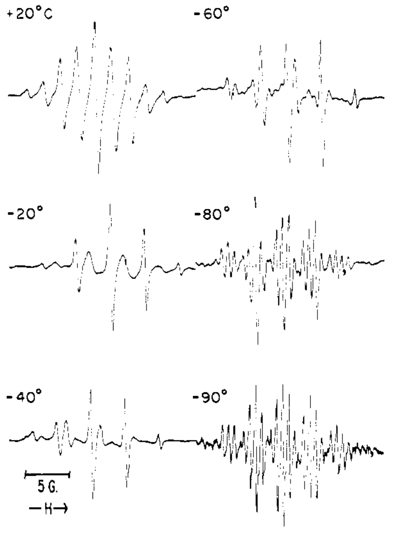


Figure 1. Esr spectra of Ia$^+$.

methane,[18] aluminum chloride–methylene chloride, trifluoroacetic acid–nitromethane,[19] trifluoroacetic acid–methylene chloride.

Oxidation with aluminum chloride in methylene chloride proved to be the most satisfactory method of radical generation for these reasons: (1) a large concentration of radicals was produced; (2) the radical appeared to be relatively stable in this medium (little or no decrease in the esr signal intensity was observed during an 8-hr period); (3) the low freezing point of methylene chloride makes this system amenable to study over a wide temperature range. Consequently, aluminum chloride in methylene chloride was used as the method of radical generation for all esr studies unless otherwise specified. It should be mentioned that the mechanism of this oxidation is unknown.

Hückel molecular orbital calculations and simulations of esr spectra were done using standard programs[20,21] executed on a Control Data Corp. 1604 computer and an International Business Machines 360-65 computer.

Results

Electrochemistry. The data obtained from electrochemical studies are contained in Table I.

Table I. Electrochemical Data

Solvent	Sub-strate	$E_{1/2}$, V^a	$E_{3/4} - E_{1/4}$, mV	i_l/C, μA/mmol^b
CH_3CN	Ia	0.89	51	7.6
	Ib	0.93	51	8.0
	Ic	0.97	64	6.6
	Id	1.18	199	3.8
CH_3NO_2	Ia	0.83	57	5.8
	Ib	0.87	72	5.1
	Id	1.08	64	4.5

^{a} Measured at a rotating platinum electrode (rpe) *vs.* sce. ^{b} i_l/C = 4.81 μA for one-electron oxidation of iodide in acetonitrile with rpe used.

Electron Spin Resonance. The coupling constants and *g* values of the radicals studied are reported in Table II. All temperature effects were completely reversible.

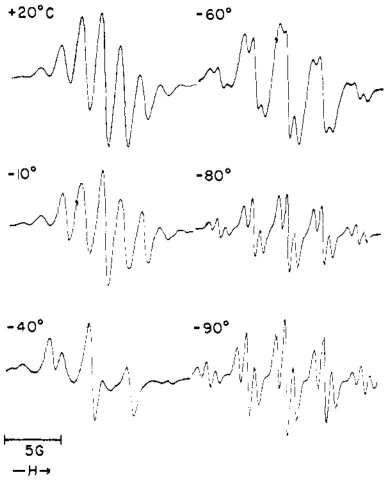


Figure 2. Esr spectra of Ib$^+$.

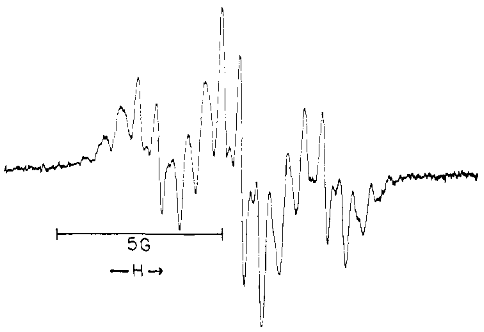


Figure 3. Esr spectrum of Ic$^+$ at −90°.

Ia$^+$. The esr spectra of Ia$^+$ recorded at various temperatures are shown in Figure 1. Nine of the observed 13 lines seen at +20° are shown; this spectrum may be assigned to interaction with 12 equivalent protons. The spectrum observed at −90° consists of seven multiplets of major lines, each containing a seven-line multiplet. This spectrum is attributed to hyperfine splittings from two groups of six equivalent protons. The spectra observed at intermediate temperatures exhibit an alternating line-width effect.

Ib$^+$. The esr spectra of Ib$^+$ observed at various temperatures are shown in Figure 2. The nine-line spectrum observed at +20° may be attributed to eight equivalent protons. The spectrum observed at −90° consists of five major lines each consisting of a triplet; this spectrum may be assigned to interaction from one group of four equivalent protons and from one group of two equivalent protons. The spectra observed at intermediate temperatures exhibit an alternating line-width effect.

Ic$^+$. The esr spectrum of Ic$^+$ observed at −90° is shown in Figure 3. A single broad line was observed at 0 and 50°; at 50° the radical was produced by aluminum chloride oxidation in nitromethane. The spectrum observed at −90° exhibited three major lines attributed to two equivalent protons. Resolution was not sufficient to assign unambiguously the small splittings of *ca.* 0.9 G. Attempts to simulate this spectrum did demonstrate, however, that the small splittings could not be attributed to coupling from the two additional isopropyl protons alone.

Id$^+$. The esr spectrum of Id$^+$ at all temperatures consisted of a single line with a width of *ca.* 2 G. The

(18) W. F. Forbes and P. D. Sullivan, *Can. J. Chem.*, **44**, 1501 (1966).

(19) A. Raymond and G. K. Fraenkel, *J. Phys. Chem.*, **71**, 4570 (1967).

(20) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

(21) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **38**, 1999 (1963).

Table II. Esr Results $AlCl_3$–CH_2Cl_2

	Coupling constants						
	+20°		−90°		g value[c]		
Radical	$\|a_H\|$, G	n[b]	$\|a_H\|$, G	n[b]	+20°	−90°	Color of soln
Ia^+	2.69 ± 0.02	12	0.93 ± 0.04 4.22 ± 0.07	6 6	2.0097	2.0092	Yellow
Ib^+	2.09 ± 0.03	8	3.08 ± 0.05 0.88 ± 0.03	4 2	2.0095	2.0092	Yellow
Ic^+			2.48 ± 0.03	2		2.0093	Yellow
Id^+					2.0089	2.0088	Green

[a] Precision is expressed in terms of the standard deviation. [b] Number of equivalent nuclei. [c] The error in the g-value determinations is less than the uncertainty in the g value of DPPH: 2.0037 ± 0.0001.

line width can probably be attributed to unresolved splittings from the phenyl protons. Attempts to resolve ^{33}S and ^{13}C splittings were unsuccessful.

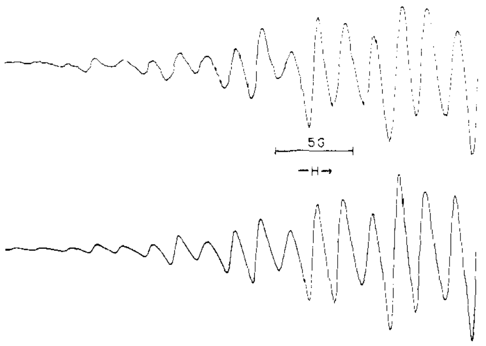


Figure 4. Low-field half of esr spectrum of [^{13}C]-Ia at +30° (top) with computed spectrum (bottom) using the parameters contained in the text.

[^{13}C]-Ia^+. The esr spectra of [ethylenic-^{13}C]-Ia^+ recorded at +30 and −90° are shown in Figures 4 and 5, respectively, with computer simulations of the spectra using $a_c = +3.72$ G at +30° and $a_c = +3.87$ G at −90° with three labeled species: 50% singly labeled [^{13}C]-Ia^+, 25% doubly labeled [^{13}C]-Ia^+, and 25% unlabeled Ia^+. The percentage of enrichment in ^{13}C was known to a precision of ±5%. It was found that changing the per cent of singly labeled [^{13}C]-Ia^+ to 55%, and the other percentages accordingly, produced no significant change in the simulated spectrum.

The sign of the carbon coupling constant was determined by examination of the variation in line width of the ^{13}C lines with magnetic field. The high-field lines are broader than the corresponding low-field lines. Consequently the carbon coupling constant is positive if ρ_c is positive.[22]

Discussion

Electrochemistry. Nitromethane has approximately the same dielectric constant (35.9) as acetonitrile (37.5). Consequently, the observed difference in the electrochemical behavior of the tetrakis(alkylthio)ethylenes between these solvents is puzzling. Although the half-wave potentials vary in the same manner, the values of $E_{3/4} - E_{1/4}$ and i_l/C suggest that these compounds undergo a two-electron electrochemically irreversible oxidation at the rpe in acetonitrile and a one-electron electrochemically reversible oxidation in nitromethane. No cathodic current was observed in cyclic voltammetry studies of these compounds in nitromethane, whereas the ratio of anodic current to cathodic current was approximately one in acetonitrile. These observations were particularly surprising in that radicals generated in nitromethane by chemical oxidations were extremely stable.

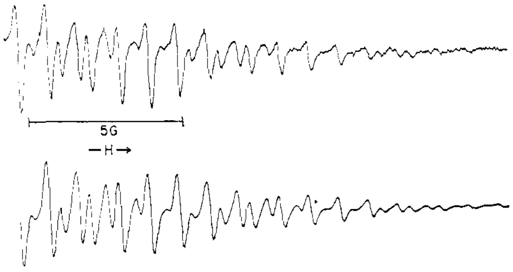


Figure 5. High-field half of esr spectrum of [$^{13}C_1$]-Ia^+, −90° (top) with computed spectrum (bottom) using the parameters contained in the text.

Temperature Effects and Stereochemistry in Ia^+ and Ib^+. Ia^+. Alternating line-width effects in esr are a reasonably common phenomena; they are indicative of inter- and intramolecular rate processes. The various sources of the effect have been recently reviewed by Fraenkel.[23] The effect in the case of Ia^+, since only one species is present at both high and low temperatures, can be ascribed to a decrease in the rate of an intramolecular motion so that the methyl protons are nonequivalent at low temperatures. This process, which is probably a hindered rotation, can be formally described as a decrease with decreasing temperature in the rate of interconversion of two equivalent rotational isomers of Ia^+ in which two pairs of methyl groups are nonequivalent. This formalism simplifies the treatment of the line-width variation; *vide infra*. At −90° the rate of interconversion is slow so that two different methyl proton coupling constants are observed. At 20° the rate of interconversion is sufficiently rapid so that the methyl protons appear equivalent. The coupling constant at +20° is the approximate average of those measured at −90°.

The time scale here is defined in terms of the lifetime, τ, of one conformer and the difference in the methyl proton coupling constants in this conformer. A spec-

---

[22] E. de Boer and E. Mackor, *J. Chem. Phys.*, 38, 1450 (1963).

[23] G. K. Fraenkel, *J. Phys. Chem.*, 71, 139 (1967).

trum attributable to one conformer is observed if $\tau \gg (\gamma/|a_{\mathrm{I}} - a_{\mathrm{II}}|)^{-1}$, a_{I} and a_{II} are the methyl coupling constants observed at −90°, and γ is the gyromagnetic ratio of the electron. In this case "slow interconversion" implies a $\tau \gg 1.9 \times 10^{-7}$ sec, or the rate of interconversion $k \ll 5.2 \times 10^{6}$ sec^{-1}. A spectrum from a freely rotating averaged species will be seen if $\tau \ll (\gamma/|a_{\mathrm{I}} - a_{\mathrm{II}}|)^{-1}$; *i.e.*, $\tau \ll 1.9 \times 10^{-7}$ sec or $k \gg 5.2 \times 10^{6}$ sec^{-1}. The region in which τ is comparable to 1.9×10^{-7} sec leads to alternating line-width effects. In this region both the position and the intensities of the lines are changing.

The possibility existed that the nonequivalence of the methyl protons in Ia$^+$ might result from an interaction of Ia$^+$ with an aluminum chloride species, *e.g.*, a charge-transfer complex. An alternating line-width effect was observed in the esr spectrum of Ia$^+$ generated in trifluoroacetic acid in methylene chloride at 0, −10, −20, and −30°. No observations could be made below −30° because this mixture froze at lower temperatures. The observation of an alternating line-width effect in the absence of aluminum chloride indicates that the motional effects reflected in the esr spectra of Ia$^+$ and the different methyl proton coupling constants cannot be attributed solely to some specific interaction with an aluminum chloride moiety, but are associated with the cation radical itself. The motion may be a simple rotation of the methyl groups about carbon–sulfur bond or some concerted motion of these alkylthio groups. It is not possible to specify completely the stereochemistry of the low-temperature conformer or the molecular process that produces the alternating line-width effect. Molecular models reveal that Ia$^+$ is sterically very crowded; in a planar structure, protons a are closer to a nonbonded sulfur containing protons b than *vice versa.* It is possible that the nonequivalence of the methyl proton coupling constants at −90° is due to differences in nonbonded interactions of the methyl protons with sulfurs.

Ib$^+$. The temperature dependence of the esr spectrum of Ib$^+$ is partially explicable by use of a model similar to that used to describe the esr spectrum of Ia$^+$; *i.e.*, one in which some motion in the C–S–alkyl fragment is restricted at −90° so that the ethyl groups are nonequivalent. At room temperature, interconversion of the two identical conformers with nonequivalent ethyl groups is rapid, and an esr spectrum is observed in which the eight methylene protons appear equivalent. At −90°, however, coupling with only six protons is observed; the coupling constant of the two remaining methylene protons must be less than 200 mG, the measured line width. If we assume, *vide infra*, that the primary mode of spin transmission to the alkyl protons in these cations is *via* direct interaction of these protons with the sulfur p_z–π orbital, *i.e.*, hyperconjugation, the structure shown in Figure 4, containing two groups of nonequivalent ethyl groups, is a representation of the low-temperature conformer. We suggest that the ethyl groups containing protons a are freely rotating and that these four protons account for the five major lines in the spectrum at −90°. In order for protons b and c to be nonequivalent, there must be restricted rotation about the adjacent S–CH$_2$ bonds as well as in the ethylenic C–S ethyl fragments. Overlap of protons c with the sulfur p_z–π orbital is minimal; *i.e.*, the angle between that orbital and the C–H$_c$ plane is *ca.* 90°. Consequently, $a_{\mathrm{H_c}} < 200$ mG and $a_{\mathrm{H_b}} = 0.88$ G. Molecular models reveal that the ethyl groups containing protons b and c are sterically more hindered than those containing protons a.

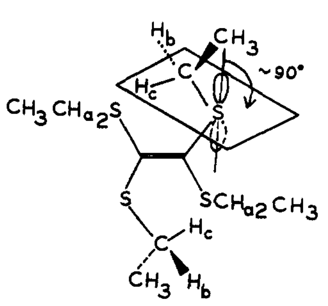
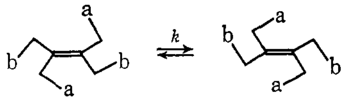


Figure 6. Low-temperature conformer of Ib$^+$.

Rate Constants for Restricted Motion in Ia$^+$ and Ib$^+$. The line-width theory developed by Freed and Fraenkel was used to analyze the variation in line widths in the spectra of Ia$^+$ to obtain the rates of the intramolecular process which interconverts the alkyl groups.[24] A two-jump model (eq A) was used to describe this process.



(A)

This model is not meant to imply a specific molecular geometry; rather it is merely intended to show the interconversion of two identical conformers in which protons a are different from protons b. The analysis of the line-width variation was used to obtain k, the rate of interconversion of the two conformers, *i.e.*, the rate of the restricted motion in the Ia$^+$ radical.

The line widths of the $M = \pm 1$, $M = 0$ ($M = \pm 1$ and $M = 0$ are total quantum numbers) lines were measured from the esr spectra recorded at +20, +10 0, and −10°. There was no variation within experimental error between the width of $M = \pm 1$ lines. (A difference in these widths would have allowed evaluation of the sign of a_{H}.[22]) The difference in the line widths between the $M = \pm 1$ lines and the $M = 0$ line was used to determine the spectral density, j_{t}, the contribution the rotational modulation makes to the observed line width.

The contributions made by j_{t} to the line widths of components of the $M = \pm 1$ and $M = 0$ lines are given in Table III. The total line width of any one com-

Table III. Secular Line Widths, Two-Jump Isotropic Modulation[a]

M	D_{k}[b]	$(T_{2,\mathrm{k}}^{(\mathrm{m})})^{-1}$, sec^{-1}
±1	12	$25j_{\mathrm{t}}$
	180	$9j_{\mathrm{t}}$
	600	j_{t}
0	2	$36j_{\mathrm{t}}$
	72	$16j_{\mathrm{t}}$
	450	$4j_{\mathrm{t}}$
	400	$0j_{\mathrm{t}}$

[a] This table was excerpted from ref 24. [b] Degeneracy of hyperfine component.

---

(24) J. H. Freed and G. K. Fraenkel *J. Chem. Phys.*, **39**, 326 (1963).

ponent is the sum of a residual line width, $(T_2')^{-1}$, which includes all contributions other than that from the motional process, and the contribution from the motional effect, $(T_{2,k}^{(m)})^{-1}$, which is dependent on the total quantum number M. For example, the component of the $M = 0$ line with a degeneracy, D_k, of 2 exhibits a line width of $(T_2')^{-1} + (T_{2,k}^{(m)})^{-1} = (T_2')^{-1} + 36j_t$. In estimating j_t, we assumed that only the component of the $M = \pm 1$ lines making a contribution j_t to the line width of these lines, and the component of the $M = 0$ line with no motional contribution to the line width of the $M = 0$ line were narrow enough to be observed in the measured esr spectrum. All other components of these lines were assumed to be too broad to make any observable contribution. With these assumptions, the spectral density j_t is then simply the difference between the measured line widths of the $M = 0$ line (w_0) and $M = \pm 1$ lines ($w \pm 1$).

$$j_t = \Delta w = w_{\pm 1} - w_0 \qquad (1)$$

The validity of these assumptions was checked by comparing the measured intensity ratio of these lines (I = integrated intensity) with that calculated using the value of j_t above.

$$\frac{I_0}{I_{\pm 1}} = \frac{w_0 + j_t^2}{w_0}(2/3) \qquad (2)$$

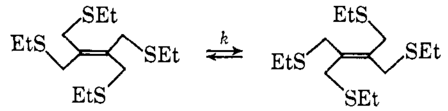
Reasonable agreement between the calculated and observed values of $I_0/I_{\pm 1}$ was obtained. Furthermore, the use of the values of j_1 from above to calculate the contributions to the line width from the individual components revealed that the contributions from the neglected components were indeed too broad to be observed relative to those used in the determination of j_t. For example, at −10°, the contributions from the neglected components ranged from 1.64 to 10.35 G. The measured line width of the $M = 1$ line was 0.72 G; $j_t = 0.41$ G.

The rates of the interconversion process were calculated from the following expression

$$k = \frac{\gamma_e^2(a_I - a_{II})^2}{8j_t} \qquad (3)$$

a_I and a_{II} are the coupling constants at −90°.

An Arrhenius plot of these rates was used to obtain an activation energy for the interconversion process: $E_A = (8.6 \pm 0.6)$ kcal/mole; $k = (5.8 \pm 0.9) \times 10^7$ sec^{-1} at −10°. The frequency factor was calculated to be 8.8×10^{14} sec^{-1}, a value that is not unreasonable for a unimolecular process.[25] A two-jump model was also used to obtain the rate constants k for the interconversion of the conformers of Ib$^+$ from the line-width variations. The values were obtained from the line-width variation in the two low-field end lines. (There was no significant difference in the widths of the low- and high-field lines.) The difference in the line widths yields k;[24] $k = 0.7 \times 10^6$ sec^{-1} at −90°. An Arrhenius plot of these rate constants yields an activation energy of (4.0 ± 4.0) kcal/mole^{-1}, a value within experimental error of that found for a similar process in the Ia$^+$ radical. One expects that the activation energy for the ethyl radical should be larger than for the methyl radical because of the larger size and consequent larger steric requirements of the ethyl fragment.



Q^H_{S-C-H}. As noted in the introductory section, Sullivan and Forbes have implied that the magnitude of coupling constant of alkyl protons β to sulfur is dependent upon the dihedral angle between the plane of the *C–H* proton bond and the p_z–π orbital of the adjacent sulfur. Examination of the low-temperature esr spectrum of Ib$^+$ seems to substantiate this angular dependence of alkyl proton β to sulfur suggested by Sullivan and Forbes. The observation of three unique coupling constants for the methylene protons at −90° seems to require that rotation about two of the S–CH$_2$ bonds is restricted and that the alkyl proton coupling constants are angularly dependent. Consequently, we suggest that the alkyl proton coupling constant may be related to ρ_S by the following expression.

$$a_H = Q^H_{S-C-H}\rho_S\langle\cos^2\theta\rangle \qquad (4)$$

This angular dependence suggests that hyperconjugation is the mechanism by which unpaired spin density is transmitted from the sulfur to the alkyl protons. Hyperconjugation would require that the value of the proton coupling constants and Q^H_{S-C-H} have a positive sign;[26] however, we were not able to evaluate the signs of the alkyl proton coupling constants. Kreilick has recently determined that $Q^H_{OCH_3}$ has a positive value.[27] Since the bonding in ethers and thioethers, and hence the spin transmission mechanism, should be qualitatively similar, Kreilick's observation is consistent with a hyperconjugation mechanism of spin transmission.

Since it appears that the magnitude of the methyl proton coupling constants in Ia$^+$ is partially dependent on nonbonded interactions, we cannot obtain a reliable estimate of Q^H_{S-C-H} from our data.

[Ethylenic-^{13}C]-Ia. The ^{13}C coupling constants are reported in the Experimental Section. The near invariance of the ^{13}C coupling constant with temperature suggests that there is no gross redistribution of spin density with temperature since this coupling constant is probably a function of the spin density of both sulfur and of carbon.[28] Insufficient data are available for further evaluation.

Acknowledgments. Support for this research from the National Science Foundation through Grant GP-7783 and Grant GP-1687 for partial support for purchase of the esr spectrometer are gratefully acknowledged. The helpful criticisms of J. H. Freed, B. C. Gilbert, and W. E. Geiger are gratefully acknowledged. Dr. T. M. McKinney's assistance in the preparation of the manuscript was greatly appreciated.

---

[25] I. Amdur and G. G. Hammes, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 14.

[26] J. P. Colpa and E. de Boer, *Mol. Phys.*, 7, 333 (1964).

[27] R. W. Kreilick, *J. Am. Chem. Soc.*, 90, 5991 (1968).

[28] M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, 35, 1312 (1961).