The limiting yield of induced intersystem crossing is $\phi_{isc}^{lim} = k_3/(k_2 + k_3)$. For iodobenzene, bromobenzene, and 2-bromoethanol the limiting isomerization yields are nearly the same as those for bromoalkanes, indicating that the exciplex formed in eq 2 is almost entirely diverted away from the normal path (eq 3) to triplet formation (eq 4). It appears significant that a prominent external heavy atom effect is observed for such a wide variety of quenchers. These results also emphasize the distinction between exciplex formation and decay processes and indicate the role substituents can play in introducing alternate channels for radiationless decay.[23]

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Electron Paramagnetic Resonance Study of Conformation in β-Haloalkyl Radicals

Sir:

We wish to report the preparation and observation by epr of the β-chloro- and β-bromo-*tert*-butyl radicals, $ClCH_2\dot{C}(CH_3)_2$ (I) and $BrCH_2\dot{C}(CH_3)_2$ (II), by x-irradiation of isobutyl chloride and isobutyl bromide, respectively, in a matrix of adamantane-d_{16} at 77°K. Alkyl radicals with β-chlorine substituents are known to prefer an eclipsed conformation (1) in solution,[1,2] and it has been suggested[2] that bromine would have the same effect on radical structure, but no well-characterized β-bromo radicals have previously been reported. In fact, we find that whereas radical I does prefer the eclipsed conformation 1 in an adamantane matrix as well as in solution,[1] radical II prefers the staggered conformation 2, and furthermore the ultimate fates of the two radicals are quite different upon warming the sample.

The second-derivative epr spectrum of radical I is shown in Figure 1, together with a computer simulation based on the parameters of Table I. The chlorine hfs is smaller and the g value is larger in adamantane than in solution.[1] The positive temperature dependence of

Table I. Epr Parameters of β-Halogenated *tert*-Butyl Radicals

Radical	$ClCH_2C(CH_3)_2$	$BrCH_2C(CH_3)_2$
Temp	$-58°$	$-71°$
a_X, G	19.5 (^{35}Cl)	6.7 (^{81}Br)
	16.2 (^{37}Cl)	6.3 (^{79}Br)
a_H (CH$_2$), G	6.3	21.4, 42.7
		(av 32.0)
a_H (CH$_3$), G	21.1	21.4
g	2.0044	2.0010

(1) K. S. Chen, I. H. Elson, and J. K. Kochi, *J. Amer. Chem. Soc.*, 95, 5341 (1973).
(2) (a) D. J. Edge and J. K. Kochi, *J. Amer. Chem. Soc.*, 94, 6485 (1972). The tentative identification of the 2-bromoallyl radical (a_{Br} = 1.35 G, g = 2.00181) in this paper is supported by the similar values found for the β-bromo-*tert*-butyl radical. (b) It has been stated that for radicals of the type $R_nMCH_2CH_2$ where M is from the first row of the periodic table the preferred geometry will be staggered and where M is from rows 2, 3, or 4 the preferred geometry will be eclipsed. D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, 95, 6459 (1973).
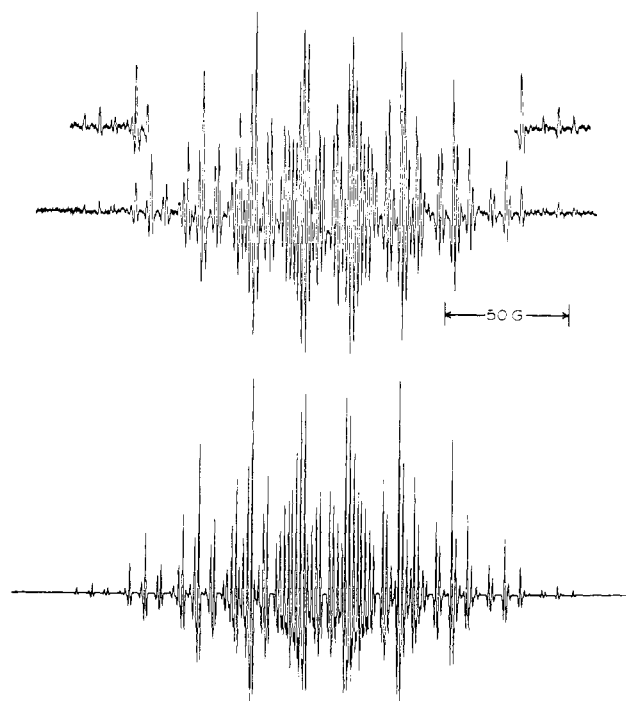

Figure 1. Second-derivative epr spectrum of the $ClCH_2\dot{C}(CH_3)_2$ radical in $C_{10}D_{16}$ at $-58°$ (top) compared with its computer simulation (bottom): line width = 0.60 G, relative abundances of ^{35}Cl: $^{37}Cl = 3:1$.

the methyl proton hfs, like that of *tert*-butyl radical,[3] indicates a nonplanar equilibrium radical site geometry while the negative temperature dependence of the chlorine hfs demonstrates a less favorable overlap of the chlorine with the unpaired electron orbital as the conformation is changed from the equilibrium position. The absence of line width alternation and the small size and equivalence of the methyl proton hfs indicates that the chlorine prefers to be eclipsed with the unpaired electron orbital.

The spectrum of radical II can best be fitted by computer simulation with the assumption of six equivalent methyl protons, one methylene proton with hfs accidentally equal to the methyl proton hfs, one methylene proton with hfs twice this value, and resolved ^{79}Br and ^{81}Br hfs in the ratio of their natural abundances. The broadened lines to be expected for the two methylene protons in the region of intermediate rate of exchange are present in the spectrum; however, the radical reacts irreversibly with the matrix before the high temperature limit (which would make the methylene protons equivalent with hfs equal to 32 G) is reached. The parameters are given in Table I and the spectrum together with the computer simulation is shown in Figure 2. The assignment of the methylene proton hfs was checked by preparation of the deuterated species $BrCD_2\dot{C}(CH_3)_2$.
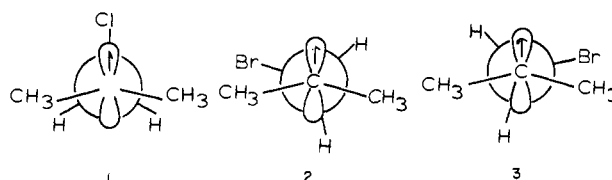
(3) D. E. Wood, L. F. Williams, R. F. Sprecher, and W. Lathan, *J. Amer. Chem. Soc.*, 94, 6241 (1972); D. E. Wood and R. F. Sprecher, *Mol. Phys.*, 26, 1311 (1973).
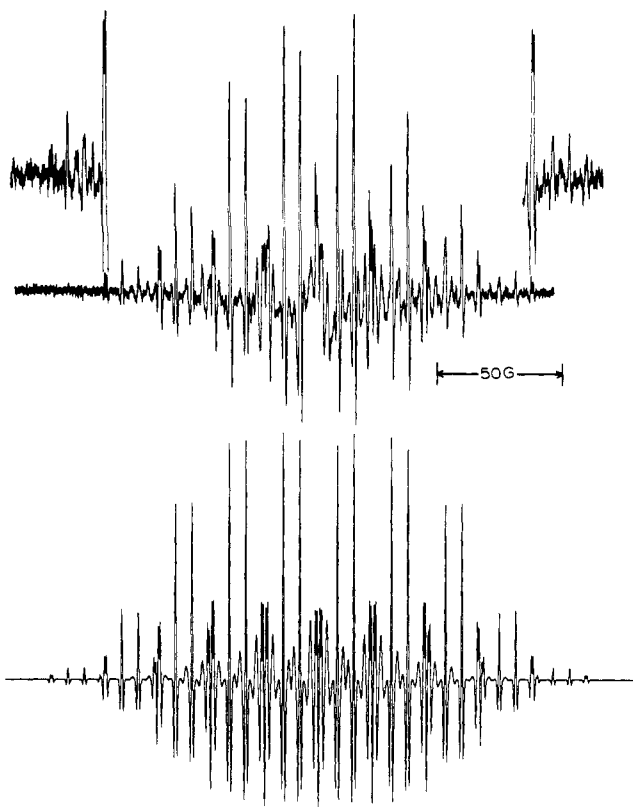
Figure 2. At the fast exchange limit the methylene protons of the β-bromo-*tert*-butyl radical should give a 1:2:1 pattern. At an intermediate rate of exchange the "two" intensity lines are broadened relative to the "one" intensity lines. The sum of the computed "one" intensiy lines and the broadened "two" intensity lines are shown together with the experimental second-derivative epr spectrum of the radical in adamantane-d_{16} at $-71°$: line widths = 0.70 G (narrow) and 1.40 G (broadened), relative abundances of $^{79}B:^{81}Br = 1:1$.
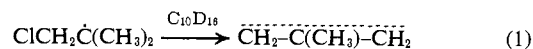
With use of the relation $a = A + B \cos^2 \theta$ for β-protons, we calculate the dihedral angles, θ, for the two methylene protons to be 45 and 15°, thus leading to the two equivalent conformations **2** and **3** with the bromine atom nearly in the nodal plane of the unpaired electron orbital. This explains the low hfs of bromine. Interconversion between **2** and **3** leads to the line width alternation as shown in Figure 2. The β-fluoro-*tert*-butyl radical is not yet reported[4] but the β-fluoroethyl radical in solution has been shown to prefer a staggered conformation[2a] similar to the one we have found for II, and indeed the limiting β-proton hfs of 28 G found for the former is quite close to the average value of 32 G in II.

Upon being cooled to $-150°$ the spectrum of II became noticeably anisotropic but the bromine hfs increased to only $\sim$8 G. In view of this it seems unlikely that the parameters reported by Symons[5] for a radical in γ-irradiated *tert*-butyl bromide (Br hfs $\sim$280 G and β-H hfs $\sim$12.5 G) correspond to radical II. Radical I was stable almost to room temperature at which point it decomposed to give the 2-methylallyl

(4) Since the submission of this communication the β-fluoro-*tert*-butyl radical has been prepared at University of Connecticut and it is found to prefer conformation 1. Details of the epr spectra and theoretical studies will be reported at a later date.
(5) A. R. Lyons and M. C. R. Symons, *J. Amer. Chem. Soc.*, **93**, 7330 (1971).

radical[6] (eq 1), while the bromo radical disappeared above $-70°$ by reaction with the matrix to form the deuterio-*tert*-butyl radical (eq 2) or the *tert*-butyl radical

$$ClCH_2\dot{C}(CH_3)_2 \xrightarrow{C_{10}D_{16}} \dot{CH}_2-C(CH_3)-CH_2 \quad (1)$$

$$BrCH_2\dot{C}(CH_3)_2 \xrightarrow[-70°]{C_{10}D_{16}} DCH_2\dot{C}(CH_3)_2 \quad (2)$$

in ordinary adamantane. Hydrogen atom exchange with the adamantane matrix has been observed previously with other radicals.[7,8] The high reactivity of radical II may explain the previous failure to observe it.[2a]

Further work in the conformation and reactions of β-haloalkyl radicals is in progress.

(6) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **90**, 7157 (1968).
(7) D. M. Camaioni and D. W. Pratt, *J. Amer. Chem. Soc.*, **94**, 9258 (1972).
(8) R. V. Lloyd and D. E. Wood, *J. Amer. Chem. Soc.*, **96**, 659 (1974).

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Conductivity Measurements on One-Dimensional Systems

Sir:

In recent years the anisotropic electrical properties of one-dimensional inorganic and organic systems have received considerable attention.[1-5] The conductivity, σ, has been frequently used to monitor the electrical transport properties of these systems. There are important differences between the conductivity of one- and three-dimensional systems. Calculation of the conductivity, σ, of a three-dimensional substance, *e.g.*, copper wire, is made in a straightforward manner, eq 1,

$$\sigma = \frac{l}{RA} \quad (1)$$

where R is the observed resistance (ohm), l the length (cm), and A the cross-sectional area (cm^2) through which the measurement is made. For three-dimensional metals, *e.g.*, copper wire, the intrinsic resistivity arises from phonon coupling and electron scattering at the surface. For a typical piece of wire the former term predominates. The contribution of the electron scattering at the surface to the resistivity is directly propor-

(1) K. Krogmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 35 (1969).
(2) I. F. Shchegolev, *Phys. Status Solidi A*, **12**, 9 (1972).
(3) H. R. Zeller, *Advan. Solid State Phys.*, **13**, 31 (1973).
(4) T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev.*, **1**, 99 (1972).
(5) J. S. Miller and A. J. Epstein, *Progr. Inorg. Chem.*, in press.