

CONFORMATIONAL EFFECTS OF HALOGEN ON ALKYL RADICALS BY ESR

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Halogen substituents play a rather unique role in controlling the stereochemistry and kinetics of homolytic reactions. The influence exerted by bromine particularly in the β -position of an alkyl radical has been discussed extensively, and the effect has also been noted for iodine in the γ -position.¹ The esr spectra of the β -fluoro and the β -chloroethyl radicals in solution are characterized by unusually small hyperfine splittings (hfs) of the β -protons.² Furthermore, spectra obtained recently in solid solutions at 77°K appear to show rather large β -bromine and iodine splittings.³

We have used the temperature dependence of the esr parameters and selective line broadening as probes⁴ for the study of the conformational effects of halogen substituents on a variety of alkyl radicals in solution. For example, the esr spectrum of the β -fluoroethyl radical showed no change in the α -proton hfs between -98° and -146° C. Significantly, the temperature-dependent hfs of the β -protons showed a diametrically opposed trend from that of the β -fluorine. Furthermore, the slopes and curvatures of the β -proton and fluorine hfs plotted in Fig. 1 indicate that they are close to limiting values at the lowest temperatures

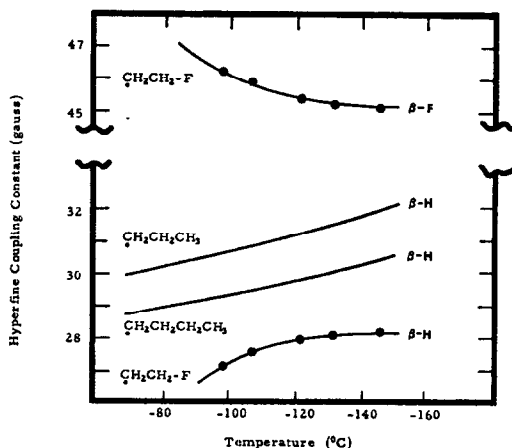
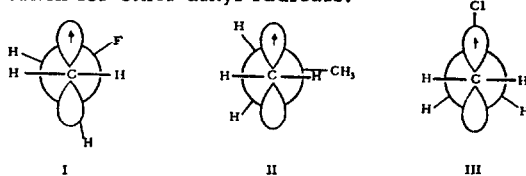
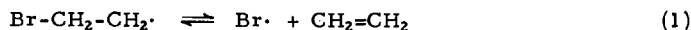


Figure 1. Temperature dependence of the β -proton and fluorine hfs of $\dot{C}H_2CH_2F$.

attained (-150°C) in solution, in contrast to the β -hfs for *n*-propyl and *n*-butyl radicals also shown for comparison. The limiting value of approximately 28 gauss represents the average hfs for the pair of β -protons in a conformation I in which the β -fluorine occupies a position about 50° from the plane defined by the *p*-orbital. This conclusion is based on a model in which the β -carbon is tetrahedral and the angular dependence of the hfs for the β -protons is the same as that commonly taken for other alkyl radicals.⁵



The *n*-propyl radical exists in a preferred conformation II in which the β -methyl group lies close to the nodal plane.^{4,5} The β -proton hfs is particularly small in the β -chloroethyl radical and the absence of any selective line broadening with temperature changes are only consistent with a symmetrical conformation III.^{2,6} After repeated attempts we have been unable to observe β -bromoalkyl (and iodoalkyl) radicals in solution under a wide variety of conditions which are highly effective with β -chloroalkyl radicals. These methods include the photolysis of β -bromopropionyl peroxide or its *t*-butyl perester,⁷ as well as di-*t*-butyl peroxide with alkyl bromides, vicinal dibromides with triethylsilane and HBr with various olefins.⁶ Part of the difficulty is due to its instability (eq 1). For example, we



find that photolysis of 3-bromopropionyl peroxide or the perester at temperatures as low as -150°C produces more than a 50% yield of ethylene.

The esr spectrum of the homologous γ -bromopropyl radical is readily observed from the photolysis of δ -bromobutyryl peroxide or the reaction of 1,3-dibromopropane with silyl radicals. The spectrum at -120°C consists of the expected triplets (22.28 G) of triplets (27.17 G) from splitting by the α - and β -protons, respectively. However, the outer lines (corresponding to $M_I = \pm 1$) of the triplet for the β -protons are broadened to a point they almost disappear at this temperature. A similar selective broadening of lines is shown by the γ -chloropropyl radicals in Fig. 2 which illustrates the dramatic effect of temperature. The onset of line broadening occurs approximately at the same temperature (ca. -100°C) that the hfs of both the β - and γ -protons increased markedly. The rather unusual alternation of linewidths is observed only in the spectra of γ -chloro and γ -bromopropyl radicals and is

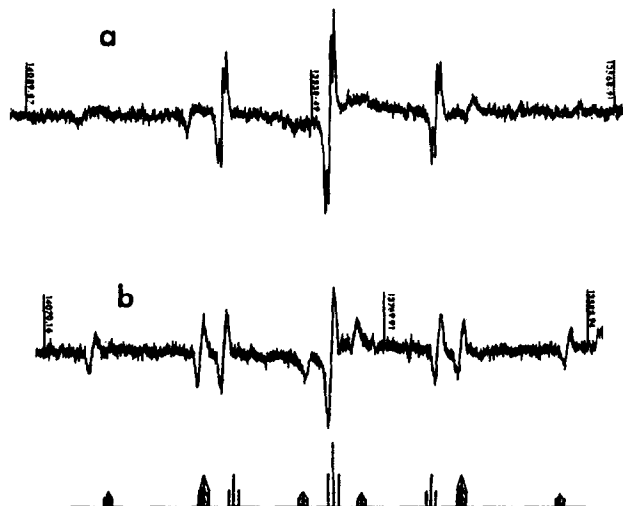


Figure 2. Temperature dependence of the selective broadening of lines in the esr spectrum of the γ -chloropropyl radical at (a) -132°C and (b) -94°C in cyclopropane solutions. The shaded portions of the stick spectrum correspond to the lines broadened by the in-phase modulation of the $M_I = \pm 1$ of the β -protons. The proton nmr field markers are in kilohertz.

clearly associated with the in-phase modulation of the β -hfs; i. e., both β -protons have hfs which are equivalent instantaneously, but are modulated between two limiting values.⁸ This linewidth effect is related to asymmetry around the $\text{C}_\beta\text{-C}_\gamma$ bond since the esr spectrum of the γ, γ, γ -trichloropropyl radical is invariant between -20 and -160°C .

We associate the magnitude and change of the hfs as well as the occurrence of selective line broadening at lower temperatures with unique conformational changes in the γ -chloro and γ -bromopropyl radicals. Two such conformations which are consistent with these observations are shown by IV and V. Alkyl radicals with γ -fluorine or oxygen substituents do not show this unusual behavior and exist in conformations similar to those of other alkyl radicals.



The effects of chlorine and bromine fall off beyond the γ -position. The proton hfs and the g -factors of the homologous (up to haloheptyl) radicals are essentially the same as those of the corresponding alkyl radicals. Furthermore, the general line broadening due to the presence of bromine gradually decreases until it disappears entirely in the 6-bromohexyl radical.

The conformations adopted by γ -chloro and γ -bromopropyl radicals contrast with conformations VI and VII of the isosteric n-butyl radical, whose esr spectrum shows



selective line broadening due to the out-of-phase modulation of the β -protons.⁴

ESR studies, thus, show that chlorine located in the β - and γ -positions has a profound effect on the conformation of the alkyl chain. An analysis of the unusually low g -factor (2.00214) indicates that a p - p homoconjugative interaction from the radical center to chlorine is a stabilizing influence in the β -chloroethyl radical.⁶ The g -factors of the γ , γ , γ -trichloro (2.00366) and γ -bromo-propyl (2.00368) radicals are also unusual and indicate a significant interaction between the halogen and the odd electron orbital. The mechanism of the odd electron delocalization in these γ -halopropyl radicals, however, is not yet clear.⁹

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9. The large positive shift (Δg) in the g -factor is not readily accounted for by either conformation IV or V, since p - p homoconjugation would lead to a negative Δg . Moreover, the stable conformation calculated for the γ -fluoropropyl cation [L. Radom, J. A. Pople, V. Buss and P. Schleyer, *J. Amer. Chem. Soc.*, 92, 6987 (1970)] will account for the positive Δg but is not consistent with the alternating linewidth observed.

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