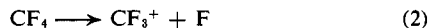(CF$_4$) = -217.8 kcal./mole[10] along with our estimated ΔH_f(CF$_4^+$).

An upper limit for I(CF$_4$) can also be determined in the following manner. Assume that the CF$_3^+$ ion from CF$_4$ is formed as indicated in reaction 2. Then

$$CF_4 \longrightarrow CF_3^+ + F \qquad (2)$$

Then I(CF$_4$) = A(CF$_3^+$) $-$ ΔH_f(F) $+$ [ΔH_f(CF$_4^+$) $-$ ΔH_f(CF$_3^+$)] neglecting any excess kinetic energy considerations. Using the range of A(CF$_3^+$) values of 15.2 to 15.4 e.v., as determined by the various workers, one may estimate that I(CF$_4$) = 14.9 to 15.1 e.v.

Table I. Heats of Formation of Various Ions

Ion	ΔH_t, kcal./mole				
	X = H[a]	X = CH$_3$[14]	X = Br[b]	X = Cl[b]	X = F[b]
CX$_4^+$	285	198	265	230[c]	(121)[d]
CX$_3^+$	262	185	244	216	109
CX$_2^+$	333	230	309	293	260
CX$^+$	360	285	338	350	321

[a] F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, Inc., New York, N. Y., 1957. [b] See ref. 4. [c] Calculated using I(CCl$_4$) = 11.47 e.v., as determined by K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957). [d] Estimated; see text.

A completely independent approach may be taken employing the quasi-equilibrium theory of mass spectra.[11] From the simpler expression, it can be determined that in order to explain the absence (or a very minute presence) of the parent ion in the mass spectrum of CF$_4$, [A(CF$_3^+$) $-$ I(CF$_4$)] could not be much greater than a few tenths of an electron volt. This strongly suggests that I(CF$_4$) $\simeq$ 15.0 e.v.

These estimates are in agreement with the observation that the ionization potential of a molecule is less than the appearance potential of any fragment ion from that molecule and thus indicates that I(CF$_4$) = 17.8 e.v. is much too high. A similar conclusion has been reached by Melton and Joy, who have recently employed their energy calibrated molecular orbital method[12] to calculate I(CF$_4$) and obtain a value of 14.36 e.v.[13] Our present calculations indicate I(CF$_4$) = 14.7 to 15.1 e.v. and lead us to conclude that the 120,900-cm.$^{-1}$ (15.0 e.v.) beginning of continuous absorption in CF$_4$ is to be attributed to an ionization process. It is also obvious that this problem should be studied by means other than electron impact. Hopefully, a study by photoionization techniques with mass analysis of the ionic products will provide additional conclusive information about the threshold formation of CF$_3^+$ or CF$_4^+$ ions.

(10) W. M. D. Bryant, *J. Polymer Sci.*, **56**, 277 (1962); Supplement No. 15 of the JANAF Thermochemical Data Tables lists ΔH_f(CF$_4$) = $-(220.5 \pm 2.5)$ kcal./mole; this will cause I(CF$_4$) to change by only 0.1 e.v.
(11) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Natl. Acad. Sci. U. S.*, **38**, 667 (1952).
(12) C. E. Melton and H. W. Joy, *J. Chem. Phys.*, in press.
(13) C. E. Melton, private communication.

Robert W. Kiser, Don L. Hobrock

*Department of Chemistry, Kansas State University
Manhattan, Kansas 66504*

Direct Observation of the Charge Neutralization Reaction in a γ-Irradiated Organic Glassy Solid

Sir:

Recently, the formation of trapped ionic intermediates in γ-irradiated organic glasses at low temperatures has been demonstrated in spectrophotometric observation[1-5] and by electron spin resonance measurements.[6] It has also been shown that these ionic intermediates including trapped electrons may play an important role in radiation chemistry.

Light irradiation ejects electrons from trap centers and some of these electrons recombine with positive holes. It may be significant to observe directly such charge neutralization processes for the study of the elementary processes in radiation chemistry.

We have observed the charge neutralization processes in both pure 3-methylpentane and a mixture of 3-methylpentane and vinyl acetate, γ-irradiated at 77°K., using the electron spin resonance technique. Figures 1a and 1b show the e.s.r. spectrum of an unbleached pure 3-methylpentane sample and that of the same sample bleached by visible light, respectively. Figures 2a and 2b show the e.s.r. spectrum of an unbleached mixture of 3-methylpentane and 20 mole % vinyl
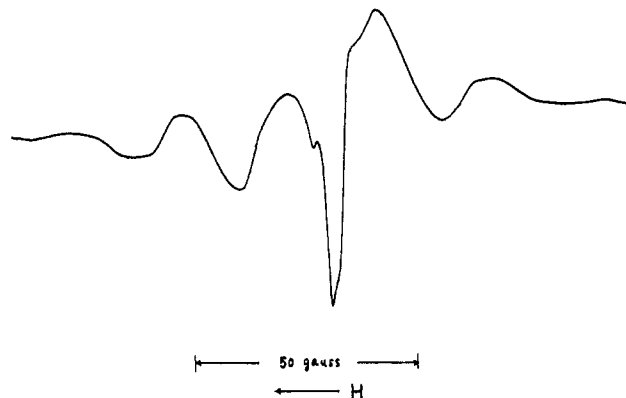
Figure 1a. Unbleached pure 3-methylpentane. The sample was irradiated and measured at 77°K. (radiation dose, 6 × 10^5 rads).
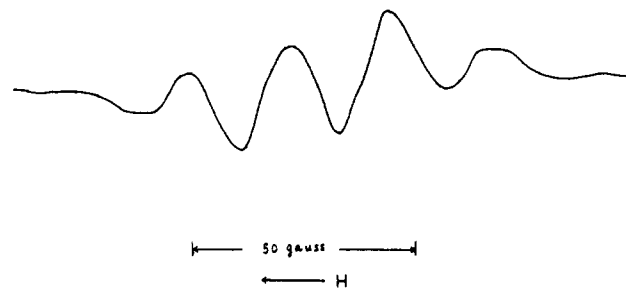
Figure 1b. Bleached pure 3-methylpentane. The sample was irradiated and measured at 77°K. (radiation dose, 6 × 10^5 rads).

(1) M. R. Ronayne, P. J. Guarino, and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 4230 (1962).
(2) J. P. Guarino, M. R. Ronayne, and W. H. Hamill, *Radiation Res.*, **17**, 379 (1962).
(3) W. H. Hamill, J. P. Guarino, M. R. Ronayne, and J. A. Ward, *Discussions Faraday Soc.*, **36**, 169 (1963).
(4) M. Kondo, M. R. Ronayne, J. P. Guarino, and W. H. Hamill, *J. Am. Chem. Soc.*, **86**, 1297 (1964).
(5) E. P. Bertin and W. H. Hamill, *ibid.*, **86**, 1301 (1964).
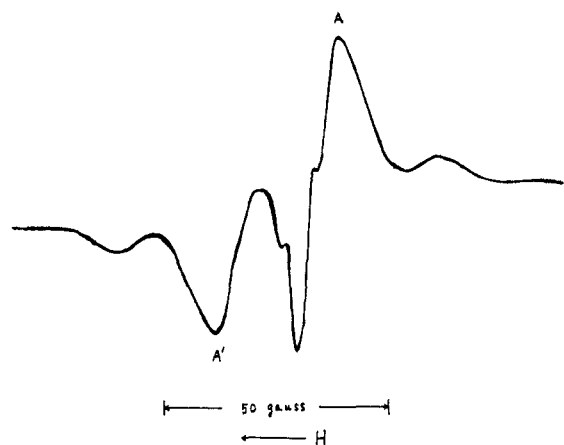(6) D. R. Smith and J. J. Pieroni, *Can. J. Chem.*, **42**, 2209 (1964).

Figure 2a. Unbleached 3-methylpentane + 20 mole % vinyl acetate. The sample was irradiated and measured at 77°K. (radiation dose, 8×10^5 rads).
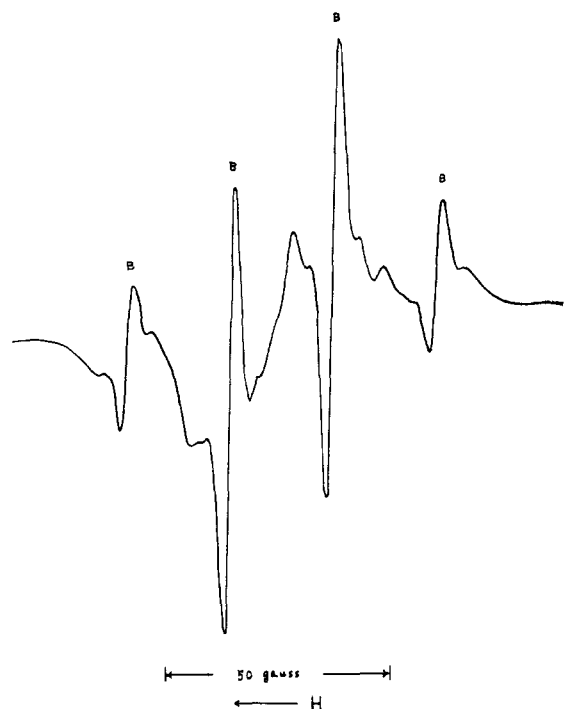

Figure 2b. Bleached 3-methylpentane + 20 mole % vinyl acetate. The sample was irradiated and measured at 77°K. (radiation dose, 8×10^5 rads).

acetate and that of the same sample bleached by visible light, respectively. The gain in the measurements is the same for Figures 1a and 1b and for Figures 2a and 2b.

In Figure 1a, a relatively narrow singlet is superimposed on a spectrum consisting of six absorption lines. In Figure 1b, only the spectrum consisting of six components in the intensity ratio 1:5:10:10:5:1 is obtained, which can be ascribed to the radical CH_3CH_2-$CHCH_2CH_3$. The methyl radical was not observed in pure 3-methylpentane under our experimental conditions. The singlet, centered at $g = 2.006$, which disappears by optical bleaching can be ascribed to trapped electrons.

In Figure 2a, an additional spectrum indicated with A and A' is superimposed on the spectrum obtained in

pure 3-methylpentane, as we can see from Figures 1a and 2a by comparing the relative intensities of the absorption lines in both figures. Bleaching causes the e.s.r. spectrum to change. The additional spectrum indicated with A in Figure 2a disappears by optical bleaching, being reasonably ascribed to the vinyl acetate ion (probably cation). In Figure 2b, the quartet indicated with B is superimposed on the multiline spectrum. The line separation of the quartet is 23 gauss in accord with that for the methyl radical obtained by Fessenden and Schuler.[7] Thus the quartet can be ascribed to the methyl radical which is produced by the neutralization reaction between the vinyl acetate cations and electrons and trapped in the special matrix (3-methylpentane–vinyl acetate system) used in the present study. The other multiline spectrum in Figure 2b consists of the absorption lines due to the radical produced from 3-methylpentane and those due to some radicals which are not identified.

A possible mechanism for the charge neutralization reaction observed in the 3-methylpentane–vinyl acetate system is given by

$$CH_2CHOCOCH_3{}^+ + e \longrightarrow CH_2CH + OCOCH_3$$

$$OCOCH_3 \longrightarrow CO_2 + CH_3$$
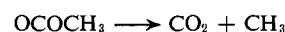
Hamill, et al.,[3] have suggested prompt decomposition of the acetoxy radical in explaining their experimental results. The second step shown above is consistent with their interpretation. The complicated nature of the e.s.r. spectrum of the mixture makes it difficult to identify the vinyl radical[7] definitely.

(7) R. W. Fessenden and R. H. Schuler, J. Chem. Phys., **39**, 2147 (1963).

Kenji Fueki, Zen'ichiro Kuri
Department of Synthetic Chemistry, Faculty of Engineering
Nagoya University, Chikusa-ku, Nagoya, Japan

Evidence for a Permanent Dipole Moment in Hemoglobin from Kerr Effect Optical Dispersion

Sir:

The electric dipole moment is an important parameter in the study of protein structure in solution because it is related to charge distribution, α-helical structure, and other factors. Efforts to obtain permanent dipole moments of globular proteins from dielectric constant data have yielded uncertain results because obscuring effects such as proton fluctuations[1] and ion atmosphere polarization[2] may occur. This communication describes a preliminary investigation of the Kerr effect optical dispersion of horse hemoglobin solutions. Knowledge of the three-dimensional structure of the hemoglobin molecule[3,4] suggested the possibility of using the known orientation of the four heme groups to investigate the direction of orientation of the molecule in a field. Assuming the molecular conformation and dimensions to be the same in solution as in the crystal,

(1) J. G. Kirkwood and J. B. Shumaker, Proc. Natl. Acad. Sci. U. S., **38**, 855 (1952).
(2) C. T. O'Konski, J. Phys. Chem., **64**, 605 (1960).
(3) D. J. E. Ingram, J. F. Gibson, and M. F. Perutz, Nature, **178**, 906 (1956).
(4) M. F. Perutz, M. G. Rossmann, A. F. Cullis, H. Muirhead, G. Wells, and A. C. T. North, ibid., **185**, 416 (1960).