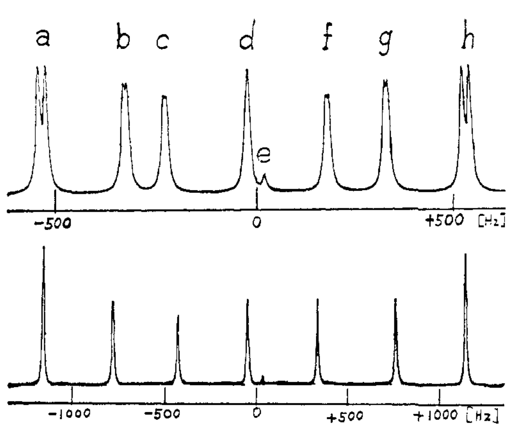

Figure 2. Computer simulated spectra corresponding to those given in Figure 1. The parameters used are given in Table II.

Table I to one enantiomer, and the lines in row 2 to the other. The spin-Hamiltonian parameters[4] which fit the observed spectra are listed in Table II. In addition the following indirect coupling constants were used: $J_{AB} = +4.6$, $J_{AC} = +3.6$, and $J_{BC} = +2.1$ Hz. The computer simulations are given in Figure 2. We also give in Table II the parameters for pure 3,3,3-trichloropropylene oxide. One may note in Table II that the chemical shifts in the isotropic pure solute are between those found for the two nematic solvents. This is consistent with our finding[2] that one of these solvents orients benzene parallel to the magnetic field, and the other perpendicular to it.[6]

Table II. Parameters of Spin Hamiltonian in Hertz

Solvent	Chemical shifts δ_B	Chemical shifts δ_C	Dipolar interactions D_{AB}	Dipolar interactions D_{AC}	Dipolar interactions D_{BC}
Cholesteryl mixture			−505.0	+347.5	−14.0
	+0.8	−27.5	−520.5	+363.0	−15.5
Hexyloxyazoxybenzene	−16.0	−57.0	+1218.5	−707.0	+27.5
Pure trichloropropylene oxide	−7.3	−48.0	0	0	0

A few isolated observations confirming the above interpretation follow. (1) Nonoptically active solute molecules, such as benzene, give only single, sharp lines in the compensated solvent. (2) We have observed line doubling also for racemic 2,3-epoxypropanal. (3) The same doubling of lines for compound I was found in compensated mixtures of cholesteryl chloride and a number of different cholesteryl esters.

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(6) It should be pointed out that the anisotropy in the chemical shift in Table II should not be interpreted as a property of the solute molecule only. Shifts due to the susceptibility of the solvent must be considered too, and the customary assumption of a spherical cavity in which the solute molecule fits is quite unrealistic in the anisotropic solvents.

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Saturation and Removal of Electron Trapping Sites in Hydrocarbon Glasses[1]

Sir:

The nature of the trapping sites at which electrons are stabilized in γ-irradiated organic glasses at 77°K is still highly speculative,[2,3] although the electrons may be observed by their infrared[4] and esr absorption spectra[5] and by electrical conductivity[6] and luminescence[7] during warm-up of trapping matrices.

This communication reports evidence that, in each of three glassy hydrocarbons (methylcyclohexane (MCH), 3-methylpentane (3MP), and 3-methyloctane (3MO)), increasing γ dose causes the electron concentration to increase, pass through a maximum, and then *decrease*. The effect in MCH is illustrated in Figure 1. It is contrary to the expectation that the concentration should reach a steady state at which the rate of thermal and "radiation-catalyzed"[8] neutralization of ion pairs is equal to their constant rate of production. It seems to indicate that (1) the matrix contains only a limited number of trapping sites; (2) electrons trapped in these sites are vulnerable to reaction with some product of the irradiation; and (3) when such reaction occurs, the site is either removed or remains occupied in such a way that it cannot trap another electron.

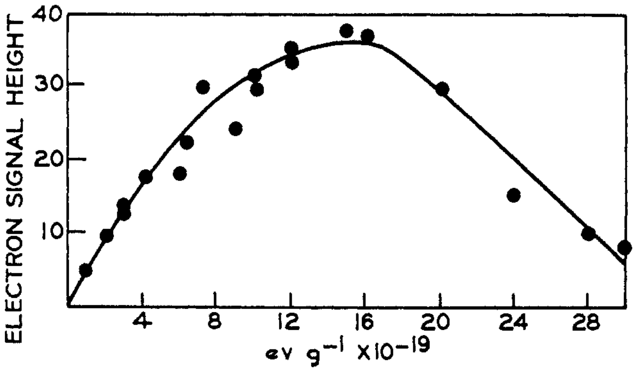

Figure 1. Height of esr e^- singlet as function of γ dose in MCH (later portions of curve would be slightly higher if corrected for Suprasil and radical background).

Reactions which might conceivably occur between trapped electrons and species produced by the ionizing radiation are: (1) $R + e_t^- \rightarrow R^-$; (2) $H^+ + e_t^- \rightarrow H$; (3) $RH^+ + e_t^- \rightarrow RH$; (4) $e^- + e_t^- \rightarrow (e^-)_2$; (5) $H + e^- \rightarrow H^-$.

Reaction 5 seems best able to account for the experimental observations. Trapped H atoms have been

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(1) This work was supported in part by the U. S. Atomic Energy Commission under Contract AT(11-1)-1715 and by the W. H. Vilas Trust of the University of Wisconsin.

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(4) J. B. Gallivan and W. H. Hamill, *J. Chem. Phys.*, **44**, 1279 (1966).

(5) (a) K. Tsuji, H. Yoshida, and K. Hayashi, *ibid.*, **46**, 810 (1967); (b) M. Shirom, R. F. C. Claridge, and J. E. Willard, *ibid.*, **47**, 286 (1967); (c) J. Lin, K. Tsuji, and F. Williams, *J. Am. Chem. Soc.*, in press.

(6) B. Wiseall and J. E. Willard, *J. Chem. Phys.*, **46**, 4387 (1967).

(7) (a) M. Burton, M. Dillon, and R. Rein, *ibid.*, **41**, 2228 (1964); (b) K. Funabashi, P. J. Herley, and M. Burton, *ibid.*, **43**, 3939 (1966).

(8) (a) R. M. Iyer and J. E. Willard, *ibid.*, **46**, 3501 (1967); (b) P. Ogren, Ph.D. Thesis, University of Wisconsin, 1967.

observed in radiolyzed CH_4 at 4°K[9] but are never found in hydrocarbons at 77°K, implying that they are sufficiently mobile to migrate to trapped electrons. It is plausible that the hydride ion should remain in the trap originally occupied by the electron, precluding the trapping of another electron.

Reactions 1 and 3 cannot be important because trapped radicals in these media have half-lives much too long to allow significant migration to trapped electrons. Reaction 2, which might occur if positive charge moves through the matrix by a chain of proton transfers, would produce H atoms which would diffuse out of the trapping sites. (It can only explain the observations if the energy of neutralization destroys the sites.) Dielectron formation (4) in these nonpolar media seems to be excluded by coulombic repulsion.

To test whether trapped free radicals affect electrons produced during subsequent irradiation, we have irradiated a sample of MCH glass at 77°K to a dose of 1.4×10^{20} eV g^{-1}, which produced the maximum electron esr signal. This signal was then removed by tungsten light, with no change in the free-radical esr signal. A subsequent 1.4×10^{20} eV g^{-1} irradiation doubled the intensity of the free-radical signal and produced a new electron signal approximately equivalent to that produced by the first irradiation. This shows that, within the sensitivity of detection, neither mobile electrons produced by photobleaching nor those produced by γ-irradiation react significantly with the prevailing concentration of trapped radicals to form anions.

To determine whether the species formed in removing the trapped electrons, and which preempts the trapping sites, can be removed by light, with regeneration of the traps, W. G. French of our laboratory has irradiated a sample of MCH to a dose of 4.4×10^{20} eV g^{-1}, at which point only a very small electron esr signal remained. The sample was then exposed to the light of a 150-W tungsten lamp at 25 cm for 15 min (<10 sec exposure would have bleached a full electron signal). An additional 8×10^{19} eV g^{-1} γ-irradiation did not produce a new electron signal, indicating that the inactivated traps are not regenerated by such illumination.

The transmission of MCH at 77°K from 11,500 to 16,000 Å as a function of γ dose has been determined by A. C. Ling, of our laboratory. These tests indicate a rise to a maximum in electron concentration followed by a decrease at higher doses similar to that observed by esr.

Assuming $G(e^-) = 0.7$ during the initial linear portion of the growth curves in the hydrocarbons, the trapped-electron concentrations at the maxima are about 10^{-4} mole fraction. In a preprint kindly sent to us while the present work was in progress, Lin, Tsuji, and Williams[5c] show that the electron concentration in γ-irradiated 3-methylhexane at 77°K reaches a maximum at a dose of about 8.5×10^{19} eV g^{-1} and a concentration of about 10^{-4} mf. Limited data indicate an apparent decrease in concentration at higher doses.

The electron esr signal in γ-irradiated methyltetrahydrofuran (MTHF) reaches a plateau at 2×10^{20} eV g^{-1} which shows no decrease up to at least 5.6×10^{20} eV g^{-1}. This indicates either that many more electron trapping sites are available in this more polar medium than in the hydrocarbons (possibly the electron can be trapped in a polarized envelope anywhere in the medium) or that the entity which removes e_t^- in hydrocarbons cannot do so in MTHF.

In contrast to the electron signals, the free-radical esr signals from MCH, 3MP, 3MO, and MTHF matrices grow linearly with dose to at least 4×10^{20} eV g^{-1}. C_2H_5 radicals produced by dissociative electron capture during γ-irradiation of 1.5 mole % C_2H_5 in 3MP or MCH show a still different pattern;[10] at a dose rate of 2×10^{18} eV g^{-1} min^{-1} their concentration approaches a steady state at 4×10^{20} eV g^{-1}. The decrease in G value with increasing dose must result from radiation-catalyzed[8,10] removal processes.

The experimental methods used in this work were similar to those described earlier.[5b]

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Stereoelectronic Requirements for the Type II Cleavage of *cis*- and *trans*-4-*t*-Butylcyclohexanones[1,2]

Sir:

Intramolecular type II photoeliminations, whereby a ketone or aldehyde possessing hydrogen on a γ-carbon atom yields an olefin and carbonyl compound,[3] have been the topic of much recent work.[4-7] It is now known that both singlet and triplet states of branched alkyl ketones may participate in this reaction.[4,6] Although there has been much speculation on the geometry and electronic structure of the excited n,π^* states of ketones, only recently have the stereoelectronic requirements for reactions of these states been investigated.[1] We wish to report such a study of the type II cleavage of *cis*- and *trans*-4-*t*-butylcyclohexanones.

Irradiation of cyclohexane solutions of *cis*- and *trans*-2-*n*-propyl-4-*t*-butylcyclohexanones (**1** and **2**) results in strikingly different photochemistry, both qualitatively and quantitatively. Thus, vapor chromatography of the reaction mixtures indicates that the major intramolecular path for photodecomposition of **1** results in formation of 4-*t*-butylcyclohexanone, while photolysis of **2** yields **1** as the major product, presumably as the result of α cleavage followed by epimerization.[8]

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[2] The authors gratefully acknowledge the generous support of this work by the Air Force Office of Scientific Research (Grant AFOSR-1000-66) and the National Science Foundation (Grant GP-4280).

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