Radiation-Induced Trapped Electrons in Saturated Hydrocarbons Studied by Optical and Electron Spin Resonance Spectroscopy[1,2]

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Abstract: A comprehensive study is reported on the production of trapped electrons in several saturated hydrocarbon glasses by γ irradiation and photoionization. Optical and esr detection methods have been used to determine radiation-chemical yields and to follow thermal decay. For glasses of high viscosity, the trapped electron is thermally stable at 77°K. $G(e^-)$ for 3-methylhexane is found to be 0.89 by optical and 0.87 by esr determinations. A satisfactory correlation is also obtained for the corresponding yields in other hydrocarbon glasses, but the absolute values are lower. The magnitude of the yield appears to be influenced by the constitution of the glassy state, and semicrystalline hydrocarbons give the lowest G values. Thermal decay of the trapped electron in 3-methylpentane and in 3-methylpentane–isopentane mixtures at 77°K has been examined in considerable detail. Under conventional experimental conditions, a faster decay is observed by esr compared to the results obtained by optical study on the same material. The possibility is raised that this apparent difference may be due to sample size. Although the absolute values for the half-decay times $t_{1/2}$ as determined by optical and esr methods do not agree, each set of experimental results shows that $t_{1/2}$ depends on the half-power of viscosity.

It has come to be recognized in radiation chemistry that molecular ionization in the condensed phase leads to the production of localized electrons in several solvent systems.[4] Contrary to many earlier reports and suppositions, recent work has demonstrated that this phenomenon is not restricted to polar solvents. Therefore, since it is impossible to prepare solvent-trapped electrons in pure alkanes by ordinary chemical methods based on the use of alkali metals or other electron donors, the radiation technique affords the opportunity for a unique study of the factors affecting the production and properties of the trapped electron, (e^-), in saturated hydrocarbons.

Optical studies of (e^-) in irradiated 3-methylpentane (3-MP) glasses have been reported in considerable detail by Hamill and his coworkers.[5-7] More recently, several groups have detected the authentic electron spin resonance (esr) signal of (e^-) in 3-MP under various conditions of irradiation and temperature.[8-12] In the present work, we have employed both of these detection techniques in irradiation studies of several alkane glasses, utilizing photoionization and high-energy radiation sources. Information is presented in this paper on the radiation-chemical yield, $G(e^-)$, for several γ-irradiated hydrocarbon glasses, and on the thermal stability of (e^-) as a function of glass viscosity and temperature. Because our preliminary work[9] indicated some appreciable differences between the results of optical and esr observations on γ-irradiated 3-MP at 77°K, we now report a more detailed comparison of the findings obtained by these two physical methods.

Experimental Section

Materials. Tetrahydro-2-methylfuran (MTHF) and 2-methylbutane, referred to here as isopentane (IP), were obtained from Eastman Organic Chemicals. The following hydrocarbons were obtained in the best available grade from Matheson Coleman and Bell: 3-methylpentane (3-MP, Chromatoquality); 3-methylhexane (3-MHX); 3-methylheptane (3-MHP); 4-methylheptane (4-MHP); methylcyclopentane (MCP, Chromatoquality); methylcyclohexane (MCH, Spectroquality); methylcyclohexane-d_{14} (Deuteroquality). Small samples (1 ml) of 3-MHX (99.5%), 3-ethylhexane (99.5%), 2,3-dimethylhexane (99.7%), and 3-methyloctane (99%) were obtained from Chemical Samples, Co., Columbus, Ohio, and used as received. For the photoionization studies, N,N,N′,N′-tetramethyl-*p*-phenylenediamine was isolated from the dihydrochloride salt (Eastman). Biphenyl (Eastman) was used as received.

Purification and Preparation of Samples. MTHF was washed with sodium hydroxide solution and water, dried with calcium sulfate, and distilled immediately before use. Those hydrocarbons available in bulk quantities were purified according to the following directions. The material was first passed through a column containing a fine grade of silica gel which had been activated immediately before use by heating for over 12 hr at 250–300°; the middle portion was collected and subjected to a careful fractional distillation at atmospheric pressure using either a Nester–Faust spinning-band or a packed distillation column. For the higher hydrocarbons, it was found that the optical transmission in the 200–220-nm region could be improved significantly after distillation by further passage through silica gel. The measured optical densities in a 1-cm cell for 3-MHX were 0.07, 0.28, and 0.70 at 220, 210, and 200 nm, respectively; corresponding values were 0.09 (230 nm) and 0.75 (220 nm) for 3-MHP and 0.20 (220 nm) for 4-MHP. It is evident that treatment with silica gel reduces the olefin content well below 10^{-3} *M*. Analyses by gas-liquid chromatography revealed that 3-MP contained considerably less than 0.5% impurity, and that the contaminants in 3-MHX, 3-MHP, and 4-MHP probably consisted of the corresponding saturated hydrocarbon isomers.

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[3] Research Participants at the Radiation Laboratory, University of Notre Dame, summer 1967.

[4] For a concise review of the work in polar solvents, see J. H. Baxendale, *Current Topics Radiation Res.*, 3, 1 (1967).

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The same general procedure of sample preparation was followed for both optical and esr studies. Solutions containing TMPD were made up externally either by solvent extraction from an alkaline aqueous solution of the dihydrochloride followed by drying with anhydrous potassium carbonate,[13] or by dissolving a known weight of crystalline TMPD previously obtained by sublimation of the free base.[14] The solution was injected through a rubber septum cap fitted to a side arm of the optical cell (or esr sample tube) already connected to the vacuum line. The side arm was sealed off at a constriction, and the solution was degassed by standard techniques. All the solvents and hydrocarbons were dried on the vacuum line by flash distillation onto a fresh mirror formed by vaporization of liquid sodium–potassium alloy. In handling TMPD solutions, care was taken not to pump directly on the solid TMPD remaining behind in the sample tube during the solvent-drying procedure.

γ- and Ultraviolet-Irradiation Techniques. Two cobalt-60 sources of γ radiation were used. For the esr studies, a Gammacell-200 source at the University of Tennessee provided a maximum dose rate of 2.9×10^{17} eV g^{-1} min^{-1}. Samples could be irradiated either at 77°K in a conventional dewar containing liquid nitrogen, or below 77°K (*ca.* 70°K) by bubbling helium gas through liquid nitrogen in the irradiation dewar, as described to us by Willard and his coworkers.[11] A 0.5-pt Thermos bottle with a narrow neck was a very suitable dewar for this purpose. In optical studies at the Radiation Laboratory of the University of Notre Dame, a γ source giving a dose rate of 1.4×10^{18} eV g^{-1} min^{-1} was employed. The uv source was a high-pressure mercury arc lamp (General Electric Co. A-H6 or B-H6), and the irradiation arrangement has been described.[10]

Optical Measurements. The apparatus and techniques were identical with those developed by Hamill and his coworkers, and these methods are described in their publications.[5–7,15] Cells were fabricated from 1-cm^2 extruded quartz (Suprasil) tubing. For some irradiations, it was desirable to use cells with shorter path lengths (5 and 2 mm), and these were constructed specially, the actual path lengths being determined by calibration against the standard 1-cm cells, making use of the overtone C–H vibration bands at *ca.* 1195 and 1396 nm in the (blank) absorption spectrum of the unirradiated hydrocarbon. After γ or uv irradiation, the cell was quickly transferred in the dark to the optical dewar in the compartment of the Cary 14R spectrophotometer, and the decay of (e^-) was followed at 77°K by repeated scanning of the near-infrared absorption band from 2000 to 700 nm. Following these measurements, the sample was photobleached *in situ* by radiation of $\lambda > 1000$ nm, as provided by the intense beam from the IR-2 spectrophotometer lamp after filtration (Corning filters No. 2030 and 4308). Accordingly, the absorption spectra were recorded before and after bleaching without disturbing the position of the cell. When biphenyl was present, the visible–uv region of the spectrum was also scanned.

Esr Measurements. A Varian-4502 spectrometer was used. The microwave frequency was *ca.* 9459 MHz, this value being determined by the use of a transfer oscillator (ACTO-Model 1255) and a 50-MHz counter (Model 1037) supplied by the Systron-Donner Corp. The spectrometer could be operated at one of several modulation frequencies. Most of the measurements were made at 100 kHz, but microwave power saturation studies were also carried out at 400 Hz, and for some systems at 200 Hz. In all cases the modulation amplitude was 1.7 G or less. The low-power arrangement of the microwave bridge was installed with a 3-db directional coupler (Hewlett-Packard X 752 A) in the arm of the sample cavity. A thermistor probe (Hewlett-Packard X 486 A) was attached to the directional coupler and connected to a power meter (Hewlett-Packard Model 431 C) for direct observation of microwave power. The power level corresponding to the "total attenuation of 35 db" referred to in our preliminary studies[9,10] was found to be about 0.01 mW. Spectra were recorded as first-derivative signals using a response time of 0.3 or 1 sec. A Varian "strong pitch" sample served to check the spectrometer sensitivity from day to day. The magnetic-field scan was made by means of the Varian "Fieldial" attachment and calibrated according to the known hyperfine splitting constant (a_N = 13.0 G) for peroxylamine disulfonate, prepared by dissolving Frémy's salt in aqueous sodium carbonate.

After γ irradiation, the sample tubes were transferred to the unsilvered tail section of a quartz dewar located in the cavity of the spectrometer. In some of the experiments to be described, a stream of helium gas was passed through a fine capillary tube into the liquid nitrogen at the bottom of the esr dewar so as to reduce the sample temperature below 77°K. The samples were kept in the dark during γ irradiation, transfer, and subsequent esr measurements.

All the photoionization studies to be reported in the present work were carried out with light of 300- to 360-nm wavelength. The optical filters have been described.[10] In the esr studies of photoionization, the sample could be irradiated directly in the cavity, and this technique enabled the trapped-electron concentration to be monitored continuously during as well as after irradiation.[10] Only the latter type of measurement is possible by means of the usual optical detection technique.

The photobleaching of samples used in esr studies was generally carried out with a 250-W Kenmore (Sears, Roebuck and Co.) Heat-Ray ir lamp, using the same filtration system described for the optical work. Thermal bleaching was studied in the case of 3-MHX samples using the Varian V-4557 variable-temperature accessory.

Results

It is difficult to obtain the true radiation-chemical yield, $G(e^-)$, in circumstances where the trapped electron undergoes appreciable thermal decay during the time of γ irradiation and subsequent transfer to the spectrometer. The problem is aggravated by the fact that this decay does not conform to a characteristic kinetic order, so that extrapolation from initial measurements becomes uncertain. In this report, optical and esr observations are presented first for various systems under conditions where the trapped electron is relatively stable to thermal decay. The results of thermal decay studies are then described in detail.

The near-infrared absorption spectra for several γ-irradiated hydrocarbon glasses are shown in Figure 1, the spectrum for 3-MP being identical with that given by Gallivan and Hamill.[5] Comparison with the other hydrocarbons shows that the maximum at *ca.* 1600 nm in the absorption band for 3-MP shifts to slightly longer wavelengths (1650–1700 nm) for the higher hydrocarbons. These spectra were recorded within about 10 min following irradiation in the γ source, the scan beginning in most cases after about 3–4 min. At 77°K, the decay of the absorption was almost negligible over this interval of time except in the case of 3-MP (*vide infra*). For γ-irradiated 3-MHX, the optical density increased linearly with dose (Figure 2), at least up to 3×10^{18} eV g^{-1}. By assuming that the value for the molar extinction coefficient of the trapped electron absorption at 1600 nm in 3-MP,[5] $\epsilon(e^-) = 3.0 \times 10^4$ M^{-1} cm^{-1}, applies at $\lambda_{\max}$ to the other hydrocarbons used in this work, $G(e^-)$ values of 0.07, 0.30, 0.55, 0.58, and 0.89 are calculated for MCP, MCH, 4-MHP, 3-MHP, and 3-MHX, respectively. The measured optical density for 3-MP in Figure 1 refers to the value about 4 min after irradiation, and this corresponds to $G(e^-) = 0.60$, in precise agreement with the results of Skelly and Hamill.[16] Following a 1-min dose of 1.4×10^{18} eV g^{-1}, the decay curve (in Figure 11 below) for optical absorption in 3-MP can be extrapolated to give $G(e^-) = 0.65$ at zero time after irradiation, but the previous reservations must apply to the adoption of this value.

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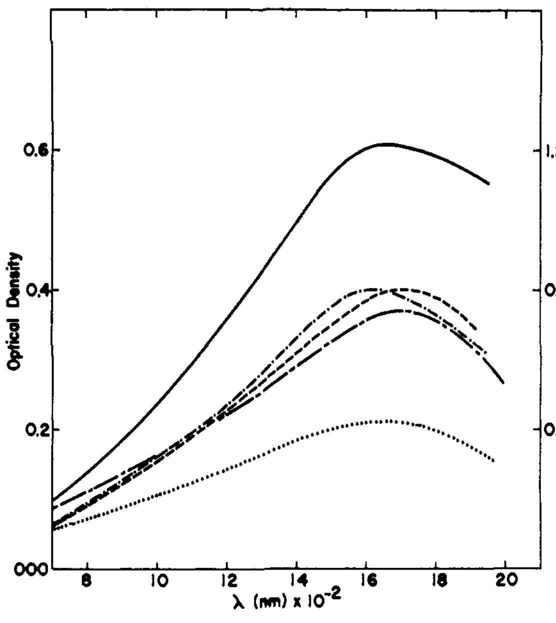

Figure 1. Optical absorption spectra for γ-irradiated hydrocarbon glasses at 77°K: ——, 3-methylhexane, λ_{max} 1650 nm, path 1 cm, dose 1.4×10^{18} eV g^{-1}; —·—, 3-methylpentane, λ_{max} 1600 nm, path 1 cm, dose 2.8×10^{18} eV g^{-1}; — — —, 3-methylheptane, λ_{max} 1700 nm, path 0.2 cm, dose 7.0×10^{18} eV g^{-1}; — – —, 4-methylheptane, λ_{max} 1700 nm, path 0.2 cm, dose 7.0×10^{18} eV g^{-1}; ...., methylcyclohexane, λ_{max} 1650 nm, path 0.2 cm, dose 1.4×10^{19} eV g^{-1}. The right-hand ordinate scale refers to the spectra of 3-methylpentane and methylcyclohexane.

No optical absorption was produced in the near-infrared when 3-MHX and 3-MHP glasses containing 0.15 mole % biphenyl (φ) were irradiated. The absorption band characteristic of the biphenyl negative ion (ϕ^-) at 408 nm was formed in each case, and the results are compared in Table I with the value of $G(\phi^-)$ obtained for 3-MP by Guarino and Hamill.[17]

Table I. Yields of Biphenyl Anion[a] in γ-Irradiated Hydrocarbon Glasses at 77°K

Hydrocarbon[b]	Optical density at 408 nm	Path length, cm	Dose, eV g^{-1}	$G(\phi^-)$
3-Methylheptane	1.12	0.21	7.0×10^{18}	1.23
3-Methylhexane	1.04	1.0	1.05×10^{18}	1.60
3-Methylpentane[c]			1.10×10^{18}	1.57

[a] Based on $\epsilon(\phi^-) = 3.7 \times 10^4\ M^{-1}\ cm^{-1}$ (ref 15). [b] 0.15 mole % biphenyl present. [c] Reference 17.

Turning to the esr studies, early attempts to measure the yield of trapped electrons in γ-irradiated 3-MP at liquid nitrogen temperature were thwarted by the rapid thermal decay of the signal which could only be followed after the sample had been transferred to the esr dewar. Actually, the signal intensity as first measured some 3 min after a 10-min γ irradiation (total dose = 3×10^{18} eV g^{-1}) was already much weaker in the case of pure 3-MP compared to 3-MP glasses containing various alkylamines, where the rate of decay was much slower.[9] Further, the decay of the trapped electron signal at 77°K following photoionization in pure 3-MP was observed to take place immediately after uv irradiation with a value of $t_{1/2}$ between 2 and 4 min.[10] Among other things, these observations suggested that considerable decay of the signal had occurred in 3-MP at 77°K during the *ca.* 3-min interval between γ irradiation and esr measurements. It should be added that this development was unexpected, because the decay of the optical absorption attributed to the trapped electron in 3-MP was known[5] to be much slower ($t_{1/2} \approx$ 45 min) at 77°K. Our subsequent attempts to clarify this apparent discrepancy are taken up later in this report.

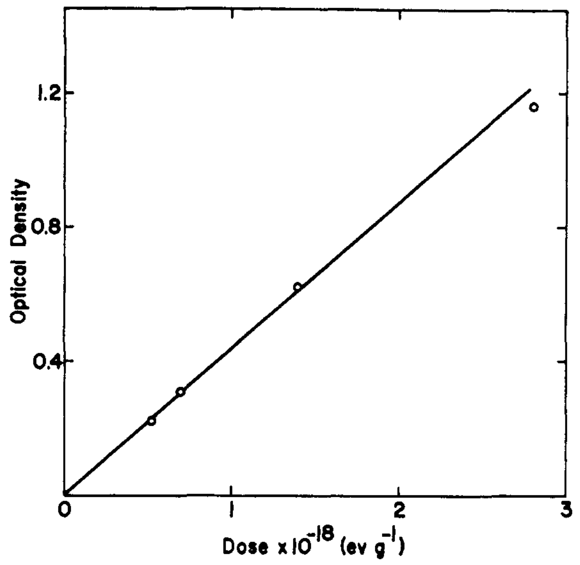

Figure 2. Dose dependence of optical density at 1650 nm in γ-irradiated 3-methylhexane (path length 1 cm) at 77°K; dose rate 1.4×10^{18} eV g^{-1} min^{-1}.

The esr signal of the trapped electron in 3-MP is thermally stable at temperatures of *ca.* 70°K and below. Shirom, Claridge, and Willard[11] have reported no detectable decay after 300 min at 72°K following γ irradiation. Also, Smith and Pieroni[12] obtained a strong stable esr signal due to the trapped electron after γ irradiation and storage at 4.2°K, although these authors could not detect the signal using conventional techniques of γ irradiation and measurement at 77°K. In this work, we have used the cryogenic cooling technique[18] of bubbling helium gas through liquid nitrogen to attain a stationary-state temperature of *ca.* 70°K in the esr and irradiation dewars. We confirm that the esr signal of the trapped electron in 3-MP is stable for at least 1 hr at this temperature, and this allows studies to be made on the dose dependence and the esr saturation behavior.

The evidence supporting the assignment of the singlet to the trapped electron has been given previously,[8–12] and only one further point needs to be examined here. Johnson and Albrecht[19] drew attention to the possibility that the esr singlet attributed to the trapped electron in various glasses might well be confused with the signal of the carbon dioxide radical anion ($CO_2\cdot^-$). These authors[19] cited evidence from their own work on $CO_2\cdot^-$, and from Smith and Pieroni's study[20] of

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Table II. Line Widths for Esr Singlet of Trapped Electrons in Organic Glasses at 77 °K

Glass	ΔH_{ms}, G	Glass	ΔH_{ms}, G
3-Methylpentane[a]	3.9 ± 0.2	2-Methyltetrahydrofuran[b]	4.2 ± 0.2
3-Methylhexane	3.8 ± 0.2	Methylcyclohexane	4.4
3-Methylheptane	4.0 ± 0.2	Methylcyclohexane-d_{14}[c]	3.3
4-Methylheptane	4.1 ± 0.1	3-Ethylhexane	3.9
3-Methyloctane	4.2	2,3-Dimethylhexane	4.1

[a] Reference 8 gives 3.7 G; our measurements were made at 71 and 77 °K, but there was no definite trend with temperature. [b] Reference 20 gives 4.5 G. [c] Polycrystalline sample gave weak and poorly resolved signal.

the trapped electron in γ-irradiated MTHF, to indicate that the microwave power saturation behavior is similar in the two cases. Our results presented in Figures 3 and 4 disagree with this summation,[19] at least under comparable conditions of irradiation and esr measurement. We find (Figure 3) that the $CO_2\cdot^-$ signal increases linearly with the square root of power below 0.01 mW and reaches maximum intensity at a power of 0.2 mW. These results are fully consistent with the data obtained by Willard and coworkers[11] at 100 kHz. Assuming a loaded-cavity Q value of 6900, we can transform the power measurements to H_1, the microwave magnetic field in gauss, by means of the numerical equation[21]

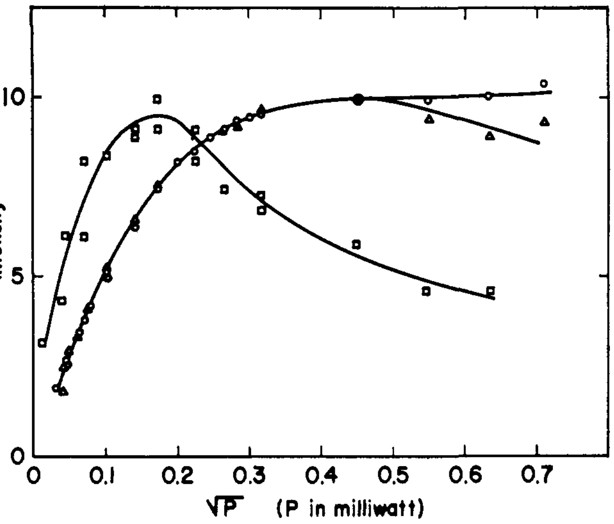

Figure 3. Microwave power saturation curves for (e^-) and $CO_2\cdot^-$ in 3-methylpentane (3-MP). Plot of relative esr signal intensity *vs.* square root of microwave power: ○ 0.2 mole % CO_2 in 3-MP, γ dose 8.7×10^{18} eV g^{-1}, modulation frequency 400 Hz, 77 °K; △ 0.2 mole % CO_2 in 3-MP, γ dose 8.7×10^{18} eV g^{-1}, modulation frequency 200 Hz, 77 °K; □ 3-MP, γ dose 1.2×10^{19} eV g^{-1}, modulation frequency 400 Hz, 71 °K.

$$H_1 = 3.7 \times 10^{-2}\sqrt{P}$$

where P is in milliwatts. Hence the maximum intensity of the $CO_2\cdot^-$ signal corresponds to a value of $H_1 = 0.017$ G, in excellent agreement with Johnson and Albrecht's own finding (at 100 kHz) of 0.015 ± 0.005 G. Thus it appears that our results for the saturation curve of the trapped electron in MTHF (Figure 4) are at variance with the measurements of Smith and Pieroni;[20] their published curve passes through a maximum at $H_1 = 0.023$ G whereas the maximum in Figure 4 occurs at $H_1 = 0.0063$ G. The samples of MTHF used in the two studies received comparable γ-irradiation doses, so this is not the reason for the discrepancy. Smith and Pieroni used 20-Hz modulation whereas our work was done at 200 Hz; in their paper[20] they also quote some experiments in which no detectable saturation of the signal occurred with 100-kHz modulation at $H_1 = 4.8 \times 10^{-3}$ G, a behavior which is more in keeping with our results. It is interesting to note that Zimbrick and Kevan[22] obtained a maximum in the signal intensity at $H_1 = 4.5 \times 10^{-3}$ G for the trapped electron in 10 M sodium hydroxide "ice" at 77 °K. These authors used 40-Hz modulation frequency to satisfy the slow-passage requirement. Although further work is needed on this general problem, it appears that the saturation behavior of trapped electrons is largely unaffected by the nature of the glassy matrix, *i.e.*, by whether the latter is molecular or ionic in structural character.

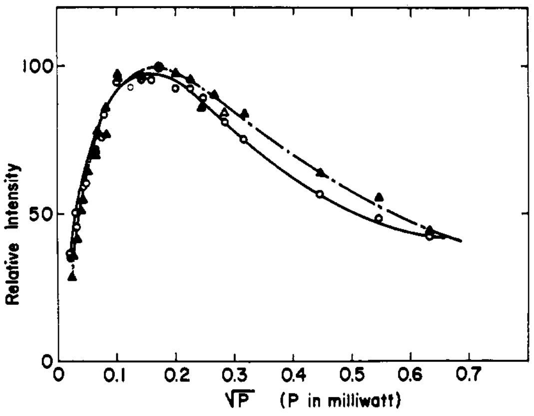

Figure 4. Microwave power saturation curves for (e^-) at 77 °K. Plot of relative esr signal intensity *vs.* square root of microwave power at 200 Hz modulation frequency: ○ 3-methylhexane, γ dose 1.7×10^{19} eV g^{-1}; ▲ methyltetrahydrofuran, γ dose 2.1×10^{19} eV g^{-1}.

It is evident from Figures 3 and 4 that the saturation curves for the trapped-electron signal in 3-MP, 3-MHX, and MTHF almost coincide with each other. In every case examined, the part of the curve corresponding to power levels below saturation was relatively unaffected by increasing the modulation frequency to 100 kHz, and most of the routine measurements were made at this frequency and a power level of 0.01 mW. Calculations of trapped-electron concentrations and G values have been made by comparison against γ-irradiated MTHF as a standard using the G

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(20) D. R. Smith and J. J. Pieroni, *Can. J. Chem.*, **43**, 876 (1965).

(21) *Cf.* A. T. Bullock and L. H. Sutcliffe, *Trans. Faraday Soc.*, **60**, 2112 (1964).

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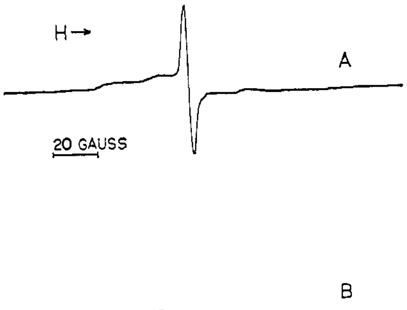

Figure 5. Electron spin resonance first-derivative spectra of γ-irradiated 3-methylhexane (dose, 2.9×10^{18} eV g^{-1}) at 77°K before and after bleaching with infrared light. The spectra were recorded at the same sensitivity and a power of 0.01 mW with modulation frequency of 100 kHz.

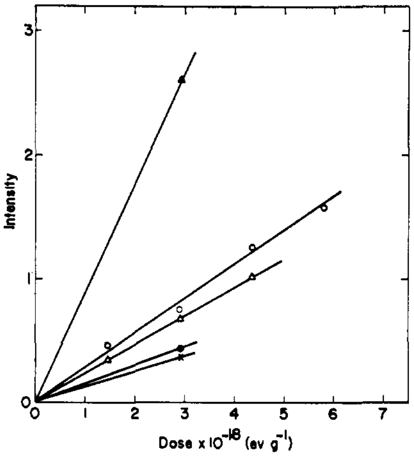

Figure 6. Dose dependence of (e^-) intensity in γ-irradiated hydrocarbon glasses at 77°K measured by esr spectroscopy: ▲, methyltetrahydrofuran; ○, 3-methylhexane; △, 3-methylheptane; ●, 4-methylheptane; ×, methylcyclohexane. The unit of the intensity scale corresponds to a concentration of (e^-) = 3×10^{16} spins g^{-1}.

value of 2.6, a reference which seems to be fairly well established by optical[15] and esr[23] methods. The signal intensity was taken to be proportional to the product of the amplitude and square of the line width, assuming the line shape (found to be Gaussian) to remain unchanged. The values for the line width are given in Table II, from which it is clear that there is hardly any variation; the ΔH_{ms} value for 3-methylpentane is the average of over 50 determinations. There was also no significant difference in the g value (2.002 ± 0.001) of the trapped electron in these various glasses within the limits of accuracy possible in this work.

The esr spectra of γ-irradiated 3-MHX as recorded before and after bleaching with infrared light are shown in Figure 5. For this hydrocarbon, the radiation-induced singlet is particularly strong relative to the underlying radical signal and this, coupled with the stability of the trapped electron in this matrix at 77°K, makes the 3-MHX glass very suitable for extended studies on the dependence of trapped-electron concentration on γ-irradiation dose. To begin with, it is clear from Figures 6 and 7 that, in the dose region where the intensity of the esr singlet is proportional to the irradiation dose, the G yield for trapped electrons is higher for the pretreated 3-MHX than for any other hydrocarbon examined in this work. All the hydrocarbon glasses included in Figure 6 give stable trapped electrons at 77°K over the short irradiation times involved. In the case of γ-irradiated 3-MP, linearity of concentration against dose can only be obtained at a lower temperature such as to obviate the effect of thermal decay; the results obtained at 71°K are shown in Figure 7. A summary of $G(e^-)$ values calculated from the esr data is given in Table III, together where possible with the corresponding yields derived by the use of the optical method.

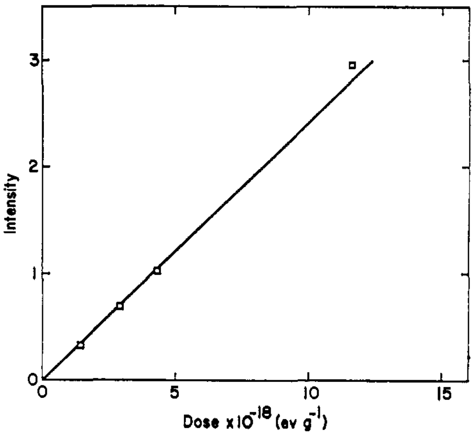

Figure 7. Dose dependence of (e^-) intensity in γ-irradiated 3-methylpentane at 71°K measured by esr spectroscopy (intensity scale as in Figure 6).

Table III. 100-eV Yields of Trapped Electrons in γ-Irradiated Organic Glasses at 77°K

Glass	Esr[a] $G(e^-)$	Optical[b] $G(e^-)$
3-Methylpentane	0.69[c]	0.65[d]
3-Methylhexane	0.87	0.89
3-Methylhexane[e]	0.54	
3-Methylheptane	0.68	0.58
4-Methylheptane	0.44	0.55
3-Methyloctane[e]	0.41	
2,3-Dimethylhexane[e]	0.35	
3-Ethylhexane[e]	0.23	
2-Methyltetrahydrofuran	2.6[f]	2.6[g]
Methylcyclopentane[h]		0.07
Methylcyclohexane	0.38	0.30
Methylcyclohexane-d_{14}[h]	0.29	

[a] Reproducibility of esr data is ±10%. [b] The optical determinations for all the hydrocarbon glasses have been calculated using $\epsilon(e^-) = 3.0 \times 10^4\ M^{-1}\ \mathrm{cm}^{-1}$ at $\lambda_{\max}$ (ref 5). [c] At 71°K. [d] Extrapolated for decay (see text). [e] These samples were obtained in small lots (1 ml) and used as received (see Experimental Section). [f] This value[23] is used as a standard for the esr determinations. [g] Reference 15. [h] Polycrystalline, at least in part.

Irradiation doses exceeding 5×10^{19} eV g^{-1} (0.8 Mrad) in 3-MHX result in pronounced deviations from the linear concentration–dose relation found at lower doses. This behavior is illustrated in Figure 8, where the intensity values (ordinate) refer to the same absolute scale as that used in Figures 6 and 7. A maximum in the intensity curve occurs at a dose of about 8.5×10^{19} eV g^{-1}, and this corresponds to a concentration of γ-induced trapped electrons in the region

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(23) D. R. Smith and J. J. Pieroni, *Can. J. Chem.*, 43, 2141 (1965).

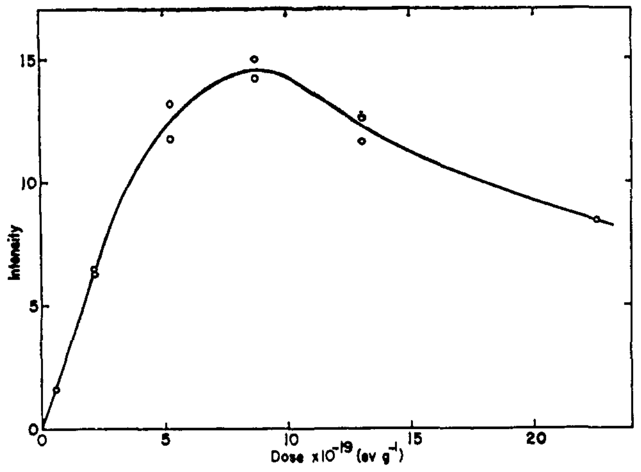

Figure 8. Dose dependence of (e$^-$) intensity in γ-irradiated 3-methylhexane at 77°K measured by esr spectroscopy (intensity scale as in Figure 6).

of 7.5×10^{-4} *M*. At higher doses, the concentration appears to decline but more experimental points are needed to verify these particular results. In any event, it seems clear there is a definite upper limit to the number of physically trapped electrons which can exist in a hydrocarbon glass under prolonged exposure to γ irradiation at 77°K. It may be of some practical interest to mention that this maximum concentration of trapped electrons attained for 3-MHX under γ irradiation exceeds the steady-state concentration (*ca.* 5×10^{-5} *M*) set up during the photoionization of various glasses, including 3-MP, under our standard experimental conditions.[10]

A noticeable difference emerges between the G(e$^-$) values obtained for the two samples of 3-MHX used in this work (Table III), the carefully pretreated samples giving a larger value than the sample reputed to be of 99.5% *isomeric* purity. While this effect may indeed be due to isomer composition, we cannot rule out the alternative possibility that the difference arises from electron capture by traces of foreign substances in the untreated sample.

The extent of correlation between the esr and optical data (Table III) was further explored by studying mixtures of 3-MP and MCH. At low concentrations of MCH in 3-MP, the γ irradiation and subsequent esr measurements were again carried out at 71°K, whereas thermal decay did not significantly affect the reliability of the optical results obtained at 77°K. Reasonable agreement between the yields obtained by the two experimental methods is indicated in Figure 9.

Thermal Decay Studies

Our earlier remarks on this subject have served to introduce the problem. Essentially, the general results show that the esr signal in 3-MP disappears at a faster rate than does the optical absorption when conventional techniques are used at 77°K. The possibility that this effect is more apparent than real must be considered very seriously, because the measurements by these physical methods were not carried out concurrently on the same sample. Unfortunately, some severe technical problems are posed by the design of a dual observation experiment with presently available equipment.

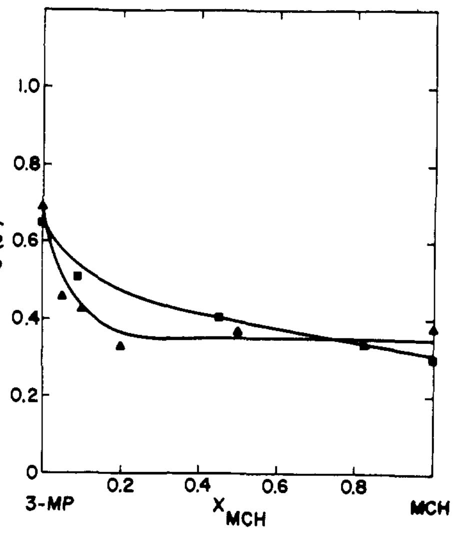

Figure 9. G(e$^-$) *vs.* mole fraction of methylcyclohexane in mixtures of 3-methylpentane and methylcyclohexane: ▲, from esr spectroscopy; ■, from optical spectroscopy.

Proceeding to consider some likely reasons for the discrepancy, the most obvious possibility is that the temperature of the sample in the esr dewar was above 77°K. This dewar is fabricated with an unsilvered tail section which fits into the cavity. The "boil-off" rate is somewhat variable in these dewars and the narrow esr sample tube (3.5 to 4 5 mm o.d.) is not always completely enveloped by an outside layer of liquid nitrogen. Temperature measurements by means of a differential thermocouple (copper–constantan junctions) were rather inconclusive insofar as they showed fluctuating readings between 77 and 78.2°K in the tail section. It has been pointed out[11] that liquid nitrogen may become contaminated with oxygen on standing in the atmosphere, and the temperature difference to which this gives rise could account for some variation in the observed decay times. However, it is difficult to accept this as the sole, or even the main, factor responsible for the marked and consistent *difference* in behavior between the optical and esr decay experiments.

The early part of the esr decay curve for 3-MP cannot be obtained following γ irradiation at 77°K, so samples were irradiated and transferred to the esr dewar at 71°K, where the signal is stable. Two different types of decay experiments were then carried out. In the first case, the supply of helium gas was stopped so that the temperature inside the esr dewar rose quickly to *ca.* 77°K. A decay curve ($t_{1/2} \approx 6$ min) obtained under these conditions[24] for 3-MP is illustrated in Figure 10 which also shows the decay at 77°K of the esr signal due to the trapped electron in the other γ-irradiated hydrocarbons. The comparative optical data are presented in Figure 11, and our results for 3-MP ($t_{1/2} \approx 45$ min) completely confirm those obtained earlier by Gallivan and Hamill.[5]

At this stage it occurred to us that the continuing uncertainty over the temperature of the sample[25] in

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[24] Decay times measured under these conditions are maximum values because of the time necessary for temperature to adjust upward to "77°K." Times may be measured from end of helium bubbling or from beginning of detectable decay but in either case, the decay time $t_{1/2}$ is prolonged in comparison to the value obtained from isothermal decay at "77°K."

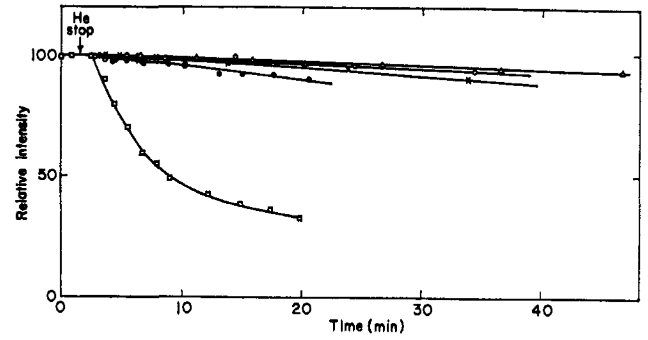

Figure 10. Thermal decay curves for (e^-) in various hydrocarbon glasses at 77°K after γ irradiation, as followed by esr spectroscopy. All curves have been normalized to the initial value of the measured intensity: □, 3-methylpentane, *irradiated at 71°K*, dose 3.5×10^{18} eV g^{-1}; ○, 3-methylhexane, dose 2.9×10^{18} eV g^{-1} at 77°K; △, 3-methylheptane, dose 2.9×10^{18} eV g^{-1} at 77°K; ●, 4-methylheptane, dose 2.9×10^{18} eV g^{-1} at 77°K; × methylcyclohexane, dose 2.9×10^{18} eV g^{-1} at 77°K. Dose rate = 2.9×10^{17} eV g^{-1} min^{-1}.

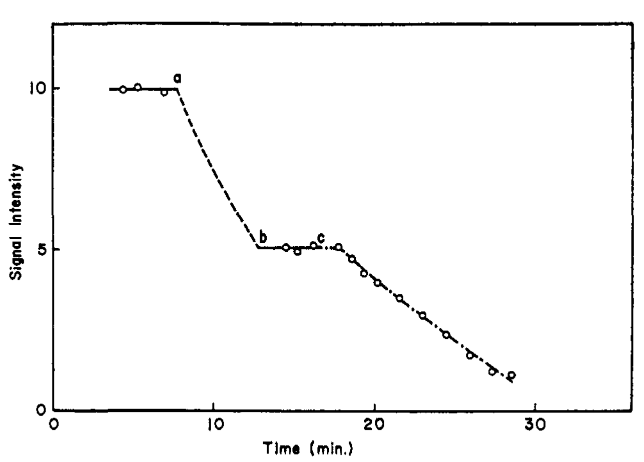

Figure 12. Thermal decay curve for (e^-) in γ-irradiated 3-methylpentane (dose 2.9×10^{18} eV g^{-1}): in esr dewar at 71°K, ——; transfer at (a) to conventional dewar at 77°K, - - -; return at (b) to esr dewar at 71°K, ——; helium bubbling stopped at (c) followed by decay at 77°K (see text), — — —. Sample irradiated at 71°K.

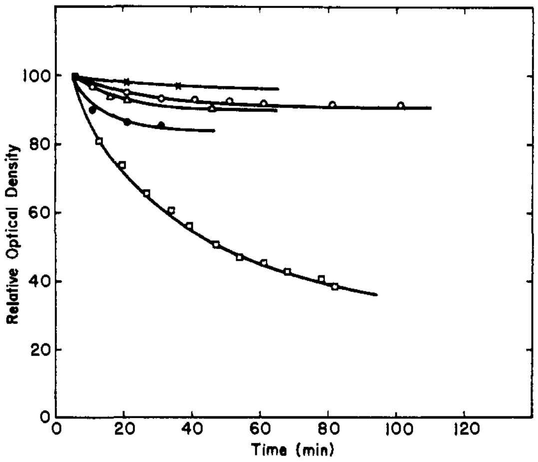

Figure 11. Thermal decay curves for (e^-) in various hydrocarbon glasses at 77°K after γ irradiation at 77°K, as followed by optical spectroscopy. All curves have been normalized to the initial value of the measured optical density at λ_{max}: □, 3-methylpentane, dose 2.8×10^{18} eV g^{-1}; ○, 3-methylhexane, dose 1.4×10^{18} eV g^{-1}; △, 3-methylheptane, dose 7.0×10^{18} eV g^{-1}; ●, 4-methylheptane, dose 7.0×10^{18} eV g^{-1}; ×, methylcyclopentane, dose 1.4×10^{19} eV g^{-1}. Dose rate = 1.4×10^{18} eV g^{-1} min^{-1}.

the esr dewar (without helium bubbling) could best be resolved by recourse to a second type of experiment in which the sample is transferred from the esr dewar at 71°K to a standard dewar containing liquid nitrogen for definite periods of time and then returned to the esr dewar (at 71°K) for measurement. The results of one such experiment are illustrated in Figure 12, from which it is obvious that the decay is almost as rapid as that recorded previously in the esr dewar after discontinuation of helium bubbling (Figure 10). This result was confirmed several times (see Table IV below). Thus it is clear that the special features of the esr dewar are *not* responsible for the observed effect, although we subscribe to the view that a greater degree of temperature fluctuation occurs in this type of dewar compared to the conventional kind. A word or two of caution should be inserted here about these experiments with 3-MP below 77°K. In some cases, the 3-MP sample became partly polycrystalline at the low temperature and did not revert immediately to the glassy state on warming to 77°K. Under these conditions, the subsequent decay at 77°K was very slow indeed. Another noticeable effect was that the yield of γ-induced trapped electrons was much smaller with these polycrystalline samples of 3-MP.

A parallel series of esr and optical decay studies was also carried out following the photoionization of TMPD in 3-MP and in mixtures of 3-MP and IP. A typical esr record is shown in Figure 13, in which the decay curve was traced out directly by holding the magnetic field H_0 constant at the value corresponding to peak amplitude of the first-derivative signal.[26] The graphical representation of another 3-MP run is given in Figure 14. Although the initial temperature was 71°K in this case so that the trapped electron was thermally stable, it is evident that a stationary-state concentration is quickly attained under optical excitation. The esr technique was very convenient for studying the relatively fast decays in 3-MP–IP mixtures at 77°K, and satisfactory signal-to-noise ratios could be obtained even for decay times of a few seconds. Optical studies necessitated the transfer of the optical dewar from the uv-irradiation housing into the spectrophotometer compartment, and normally about 1 min elapsed before measurements could begin. However, it was revealed again that for a 3-MP–IP sample of the same composition, the optical decay at 77°K was considerably slower. This comparison between esr and optical studies is illustrated in Figure 15 by the separate plots of $t_{1/2}$ *vs.* the known viscosity for 3-MP–IP mixtures.[14] Over almost the entire range of viscosity, the absolute $t_{1/2}$ for optical decay is about 20-fold greater than the corresponding value for the isothermal decay of the esr signal. Despite this quantitative difference, it is remarkable that in each case $t_{1/2}$ depends on a power of viscosity slightly greater than 0.5.

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(25) It has been suggested to us privately that microwave heating of the sample in the esr cavity might be responsible for the more rapid decay of the esr signal. At the low power (10 μW) involved, this does not seem very likely. In the course of our work we have not observed any significant increase in decay rate as a function of microwave power into the cavity, but a systematic study has not been carried out.

(26) R. W. Fessenden, *J. Phys. Chem.*, **68**, 1508 (1964).

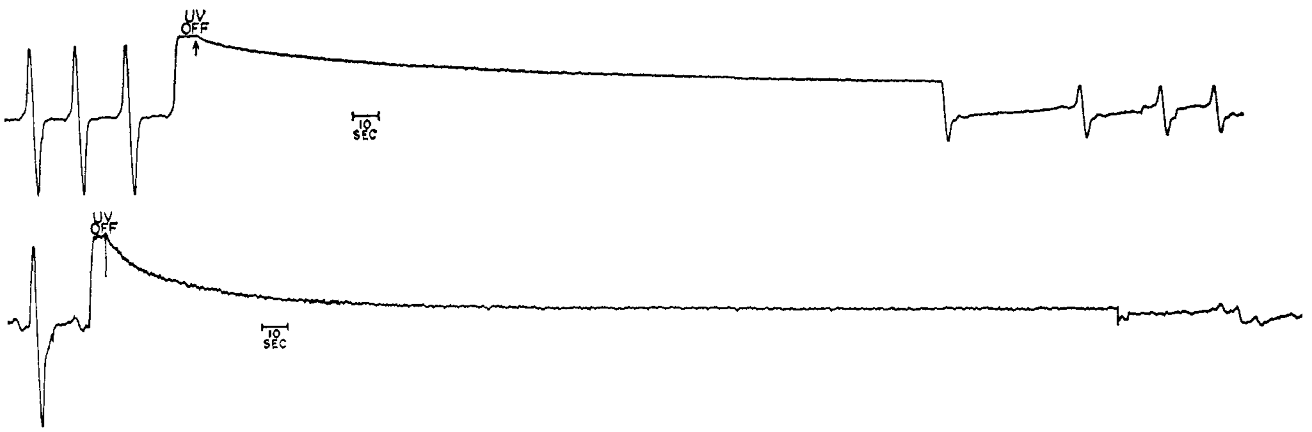

Figure 13. Esr spectra showing thermal decay for (e⁻) following photoionization of 0.02 mole % TMPD in hydrocarbon glass at 77°K. Upper trace refers to 3-methylpentane and the lower to 40 mole % isopentane in 3-methylpentane; gain sensitivity was 160 and 400, respectively.

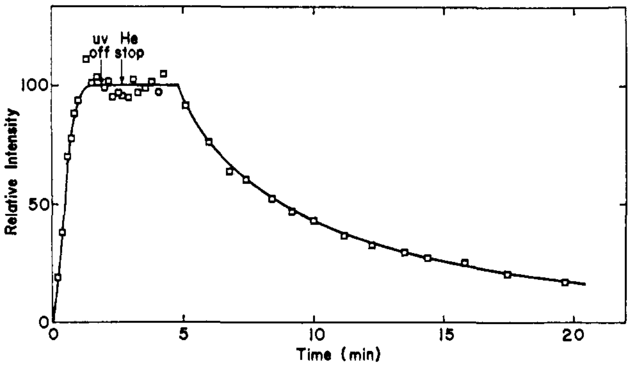

Figure 14. Growth and decay of (e⁻) in uv irradiation of 3-methylpentane containing 0.02 mole % TMPD. Photoionization at 71°K followed by decay at "77°K" (see text).

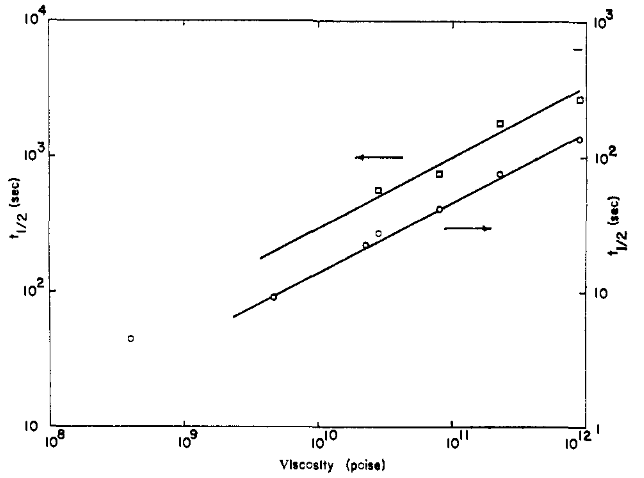

Figure 15. Viscosity dependence of $t_{1/2}$, the time for half-decay, for (e⁻) in 3-methylpentane–isopentane mixtures at 77°K following photoionization of 0.02 mole % TMPD solutions: ○, measurements by esr spectroscopy; □, measurements by optical spectroscopy. Right-hand ordinate refers to esr data.

A significant clue to the solution of the entire mystery surrounding the decay problem may be provided by the results of some recent esr experiments on 3-MP in which the sample tubes were narrower than those employed heretofore. The pertinent observations are summarized and compared in Table IV with other relevant data. While the observations are not conclusive, they do suggest that longer decay times are associated with larger samples. Since the optical studies on 3-MP have all been made with 1-cm² cells, the trend is in the right direction to bring the results into coincidence. A final answer[26a] to this vexatious problem must await further experimental work with suitable equipment involving the use of larger samples in the esr cavity.

Table IV. Decay of Trapped-Electron Esr Signal in 3-Methylpentane Glass at "77°K"

Irradiation	Sample tube o.d., cm	$t_{1/2}$,[a] min	% decay[b] (time, min)
γ	0.45	5.8 ± 1.8	52 ± 4[c] (6) 50 (5)
γ	0.39	2.5 ± 0.7	73 (6) 83 (7.7)
TMPD photoionization	0.45	7.6 ± 1.6	48 ± 4[d] (6)

[a] Half-decay time. Determination after cessation of helium bubbling in esr dewar (see text). Time in this case is counted from the stoppage of helium flow. [b] Determination by transfer to conventional dewar for stated time. [c] Mean of eight runs. [d] Mean of four runs.

Discussion

For reasons which must be apparent from the preceding analysis, we do not feel that a theoretical examination of the difference in absolute magnitude between the optical and esr decay studies is called for at this time. Therefore, we shall confine ourselves to remarks on the factors affecting the yields of trapped electrons in hydrocarbons, and on the mechanism of thermal recombination of charges.

The results in Table III demonstrate a quantitative correlation between the optical and esr determinations of G(e⁻) in several hydrocarbon glasses. A qualitative similarity in the bleaching behavior with infrared light[5,8–12] also supports the view that both detection

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(26a) Note Added in Proof. Coincidence in thermal decay rates of (e⁻) in γ-irradiated 3-MP at 77°K has now been established between optical and esr methods by the use of standard 1-cm⁻² cells in both cases. These more recent esr studies were made with a Varian V-4535 cylindrical cavity: K. Tsuji and F. Williams, submitted for publication.

techniques reveal the presence of the same entity. Other evidence[5,9,11] is the nonappearance of the optical absorption and esr signal in the presence of additives (biphenyl, methyl iodide, carbon dioxide) which are known to undergo electron capture. These observations amply confirm the earlier assignment[5] of the near-infrared absorption band in 3-MP to the physically trapped electron.

In Table III there is no discernible trend in the $G(e^-)$ values with minor changes in hydrocarbon structure, but the possibility that molecular structure *per se* has some influence cannot be dismissed at the present state of our knowledge.[27] However, it is abundantly clear that the yield often is affected by the characteristic ability of the hydrocarbon to form a glassy state. For example, the low yield of $G(e^-)$ for methylcyclopentane is strongly correlated with the largely polycrystalline nature of the sample. Methylcyclohexane (MCH) forms a transparent glass in narrow tubes and thin optical cells, but it has a tendency to "crack," and the yield is low. Of all the hydrocarbons used in this work, only 3-MP and 3-MHX formed consistently good, *i.e.*, optically clear, glasses on shock cooling to 77°K in 1-cm^2 optical cells, and it is suggestive that these hydrocarbons give the largest $G(e^-)$ values. In other work involving mixtures and polar compounds such as triethylamine, we have also noticed that $G(e^-)$ is affected by a transition from the glass into what might be described as the semicrystalline morphology of translucent samples. Unfortunately, there is no simple way of assessing the "degree of disorder" in a glass, so the observations have only a qualitative significance.

Both the variability of $G(e^-)$ with glass structure and the fact that $G(e^-)$ is much less than the corresponding yield obtained by electron capture with biphenyl (Table I) suggest that the number density of preexisting physical traps in the glass is the limiting factor to the $G(e^-)$ attained in hydrocarbons. This conclusion is similar to that reached by Funabashi, Herley, and Burton[28] from luminescence studies on γ-irradiated 2-MP and 3-MP glasses.

The present work demonstrates rather conclusively that trapped electrons can be thermally stable in hydrocarbons of sufficiently high viscosity. In some ways it is unfortunate that many low molecular weight hydrocarbons have glass transition points[29] close to 77°K, for the large change in viscosity caused by small temperature changes in this region[30] causes the thermal decay to become very sensitive to differences of only a few degrees. A case in point is 3-MHX; the trapped electron in this glass decays less than 10% in 60 min at 77°K, but at 84°K, $t_{1/2}$ is of the order of 10 min. It has been pointed out before[31] that thermal decay rates for the recombination of ions and electrons at the glass transition temperature are in order-of-magnitude agreement with numerical estimates based on a simple diffusive model of charge recombination.

A remarkable dependence of $t_{1/2}$ on the 0.51 ± 0.05 power of viscosity is revealed by Figure 15 irrespective of which detection method was used to follow the kinetics of thermal decay. A similar phenomenological relation has been obtained by Leone and Hamill[32] from studies of recombination luminescence at much lower viscosities.

Our main concern in this paper has been to establish the experimental facts as accurately as possible, and speculation concerning the interpretation of some of the findings has been kept to a minimum. Much more work is necessary on a variety of systems before detailed answers can be given to the fundamental questions surrounding the mechanism of electron trapping and the kinetics of thermal decay.

Acknowledgment. We are much indebted to Professor Milton Burton for the opportunity to carry out a part of this research at the Radiation Laboratory of the University of Notre Dame. Our thanks are also due to Professor W. H. Hamill for the use of many items of optical equipment. Discussions with several staff members at the Radiation Laboratory contributed significantly to the progress of the work.

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(27) A most surprising recent result is that no trapped electron can be observed (by esr) in a γ-irradiated polyisobutylene glass of low molecular weight containing *no* antioxidant. We are indebted to Mr. R. B. Taylor for the preparation of this sample. The polymer was obtained by the radiation-induced polymerization of highly purified dry, isobutylene at 27°, as described by R. B. Taylor and F. Williams, *J. Am. Chem. Soc.*, **89**, 6359 (1967).

(28) K. Funabashi, P. J. Herley, and M. Burton, *J. Chem. Phys.*, **43**, 3939 (1965).

(29) M. R. Carpenter, D. B. Davies, and A. J. Matheson, *ibid.*, **46**, 2451 (1967).

(30) M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).

(31) F. Williams and K. Hayashi, *Nature*, **212**, 281 (1966).

(32) Private communication from Professor W. H. Hamill; J. A. Leone and W. H. Hamill, submitted for publication.