Energy Migration in γ-Irradiated Crystalline Solids at 77°K.[1]

W. Van Dusen, Jr., and F. K. Truby

Contribution from the Sandia Laboratory, Albuquerque, New Mexico
Received October 12, 1964

The γ-radiolysis of 0.2 M methyl bromide in cyclohexane has been examined at 77°K. The results are consistent with an interpretation of dissociative electron capture by the solute and an ion–molecule reaction between matrix molecules.

Introduction

In an effort to determine the importance of energy migration in polycrystalline solids we have examined 0.2 M methyl bromide in a cyclohexane matrix at 77°K. This system has been studied using e.s.r. techniques[2a] and conventional radiation chemical analysis[2b] of the gaseous and liquid phase products of the thawed irradiated samples. The results are consistent with the interpretation of dissociative electron capture by the solute and an ion–molecule reaction between the cyclohexane ion and a cyclohexane molecule.

Experimental

Phillips research grade cyclohexane was purified by passage through a 1-m. column filled with 28–200 mesh silica gel. As determined by gas chromatographic analysis, this procedure removed the olefinic impurities but did not affect 2,4-dimethylpentane (0.005 mole %) nor methylcyclopentane (0.005 mole %). Methyl bromide, obtained from the Matheson Co., Inc., and specified to be 99.5 mole % pure, was further purified by several freeze–pump–thaw cycles using an ethyl bromide mush. Cyclohexane was dried over P_2O_5 followed by trap-to-trap distillation using an ethyl bromide mush. The methyl bromide was metered into a calibrated volume and then simultaneously distilled with the cyclohexane into the irradiation cell[2] at 77°K. and sealed from the line when the pressure of the system was 5×10^{-5} mm. or less. The samples were then thawed, vigorously shaken, refrozen in liquid nitrogen, and irradiated.

The samples for chemical analysis were irradiated at 77°K. by γ-rays from a 2000-c. Co^{60} source at a dose rate of 5.65×10^{17} e.v./g. min. For e.s.r. studies, the samples were irradiated under similar conditions, but the γ-rays were from a 10,000-c. Co^{60} source at a dose rate of 6.00×10^{18} e.v./g. min. The dose rate was determined by the Fricke dosimeter $G_{Fe(III)} = 15.6$.

The procedure used for chemical analysis has been described[2b] except that methane and hydrogen were determined by mass spectrometric measurement on a CEC 21-130 mass spectrometer. The yields of cyclohexene and dicyclohexyl were measured from separate samples because it was found that cyclohexene yields

from samples analyzed after microstill reflux were lower than from unrefluxed samples. Analyses for cyclohexene and dicyclohexyl were performed on a Beckman GC-2 gas chromatograph, with a flame ionization detector utilizing a 12-ft. β,β'-oxydipropionitrile–30% silver nitrate column (Beckman No. 70322) and a 2.5-ft. Apeizon L column (Beckman No. 70009), respectively.

E.s.r. studies were carried out using a conventional bridge-type e.s.r. spectrometer with a cavity operating in the TE_{012} mode at 9.2 kMc./sec. A magnetic field modulation of 5.0 kc./sec. was utilized in such a manner as to record the first derivative of the resonance absorption. Sample temperature during e.s.r. measurement was maintained at 77°K. by the use of a thin-walled, unsilvered, quartz liquid nitrogen dewar inserted directly into the microwave cavity.

Results

The chemical results are presented in Table IA as relative product yields obtained by dividing the yields of the various products observed by the corresponding product yield produced in pure degassed cyclohexane irradiated at room temperature at the same dose. The methane yields reported are based on a comparison with the hydrogen yield in pure cyclohexane irradiated at room temperature. All chemical and e.s.r. samples were slowly frozen in liquid nitrogen, producing crystalline-appearing solids. No difference was found in the e.s.r. signals for slowly frozen and rapidly frozen samples. The high dose irradiations at liquid nitrogen temperatures produced a purplish color in the crystalline solid which disappeared rapidly upon exposure at 77°K. to the fluorescent light of the room. The exact nature of this color is unknown, but it seems plausible to associate it with the negative ion. No color was observable in the lower dose samples.

Table I. Methyl Bromide (0.2M) in Cyclohexane

Temp. of irradiation, °K.	Dose, e.v./g. $\times 10^{-18}$	$R(H_2)$	$R(CH_3\cdot)$	$R(CH_4)$	R(cyclo-C_6H_{10})	R(cyclo-$C_6H_{11})_2$
		A.	Chemical Results[a]			
77	1.7	0.86		0.12	Too small	to measure
77[b]	1.7	0.86		0.03		
77	8.5	0.83		0.05	0.62	0.67
77[b]	8.5	0.80		0.04		
77	76.0	0.85		0.02	0.67	0.62
77[b]	76.0	0.86		0.03		
		B.	E.s.r. Results[c]			
77	0.5		1.00			
77	1.5		0.82			
77	6.0		0.58			
77	25.0		0.31			

[a] Dose rate = 5.65×10^{17} e.v./g. min. [b] Bleached with 3500-Å. light. [c] Dose rate = 6.00×10^{18} e.v./g. min.
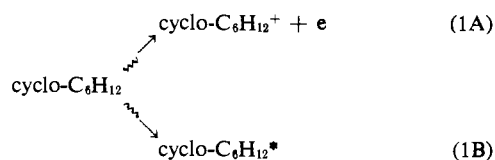
(1) This work was supported by the United States Atomic Energy Commission. Reproduction in whole or in part is permitted for any purpose of the U. S. Government.
(2) (a) F. Truby, *J. Chem. Phys.*, 40, 2768 (1964); (b) K. Jones, W. Van Dusen, and L. Theard, *Radiation Res.*, 23, 128 (1964).

The e.s.r. results have been obtained at 77°K. over the dose range 5.0×10^{17} to 2.5×10^{19} e.v./g. The e.s.r. signal obtained is shown in Figure 1. This signal is interpreted as consisting of two superimposed resonances, one from the cyclohexane matrix and the other from the solute. Bleaching with 3000–5000-Å. light (2.49 to 4.15 e.v.) eliminates one of the e.s.r. signals. The remaining signal is essentially identical with that observed by Ayscough and Thomson[3] in cyclohexyl iodide and by Smaller and Matheson[4] in pure cyclohexane. This species, due to bond breakage in the cyclohexane matrix, has been identified as the cyclohexyl radical.[3,5] It is also observed that the matrix signal is essentially unaffected by bleaching. This has been established by the observation that for the bleaching conditions used, the outer resolved peaks in Figure 1a did not change noticeably in intensity or position. Since the solute signal is dose dependent (Table IB), while the matrix signal is not, the relative intensity of the matrix signal with respect to the solute signal was varied. However, the subtraction procedure described below always yielded the same line shapes for the two resonances regardless of the ratio of the intensity between the solute and matrix e.s.r. signals. Therefore, it must be concluded that no significant changes in matrix signal are encountered during bleaching. The resonance obtained by subtraction of the matrix signal from Figure 1a is shown in Figure 1b. This resonance is identified as the methyl radical[5–8] and arises from the solute. The methyl radical yields as a function of dose shown in Table IB are normalized to the yield obtained at the lowest dose. Examination of the e.s.r. data revealed that while the methyl radical yield is nonlinear with dose in the range examined, the matrix signal intensity is linear with dose. By double integration of the e.s.r. derivative curves it has been found that for a dose of approximately 0.5×10^{18} e.v./g. the number of methyl radicals observed equals within experimental error the number of radicals produced in the cyclohexane matrix.

Discussion

Inasmuch as the mole fraction of methyl bromide for these experiments was 0.023, the fact that approximately equal damage in the form of radical formation was observed at low dose in the methyl bromide as in the matrix indicates that energy migrates from the matrix to the solute at 77°K. At the relatively high concentration[9] of methyl bromide used, we suggest that the methyl bromide undergoes dissociative electron capture (reaction 2). Hydrogen atom attack of the methyl

$$\text{cyclo-}C_6H_{12} \overset{\text{cyclo-}C_6H_{12}^+ + e \quad (1A)}{\underset{\text{cyclo-}C_6H_{12}^* \quad (1B)}{}}$$

Figure 1. (a) E.s.r. curve at 9.2 kMc./sec. of 0.2 M methyl bromide in cyclohexane γ-irradiated at 77°K. to a dose of 2.5×10^{19} e.v./g.; (b) methyl radical spectrum obtained by subtraction of bleached spectrum from unbleached spectrum (curve a).

$$\text{CH}_3\text{Br} + e \longrightarrow \text{CH}_3 + \text{Br}^- \qquad (2)$$

bromide cannot be important at low dose since the bleaching experiments produced a low yield of methane while positive charge transfer from cyclohexane to methyl bromide would be endothermic. Negative ion formation has been observed spectrophotometrically in γ-irradiated glasses at 77°K.,[10] and in the liquid phase such processes are well known and lead to methane formation.[11] The decrease of the methyl radical yield with dose may be due to a bleaching effect of the radiation. This is consistent with the chemical results where bleaching at low doses decreases the methane yield. At high doses radiation bleaching tends to reduce or eliminate the effects of light bleaching.

As the yields of methane decrease at low temperature, there is an increase in the yields of cyclohexene and dicyclohexyl. A chain reaction similar to that proposed for liquid methyl iodide–cyclohexane[12] solutions must be ruled out as the yield of cyclohexyl bromide is negligible.[13]

In the solid at 77°K. the bromine negative ion must exist in the close proximity of the methyl radical. Upon bleaching with light the electron is released from the negative ion and recombines with the positive hole. The methyl radical and the bromine atom must then recombine before they can escape the cage[14] and undergo other reactions. Recombination of the negative ion with the methyl radical is ruled out on the basis of the endothermicity of the reaction.[15] For low-irradiation doses, where bleaching caused by γ-irradiation would be less in evidence, warm-up of the samples without optical bleaching may allow some of the bromine ions to escape their cages before neutralization and recombination take place thus giving rise to a higher methane yield than observed for bleached samples.

If the positive hole were on the cyclohexane molecule, such a configuration would be paramagnetic and as such

(3) P. Ayscough and C. Thomson, *Trans. Faraday Soc.*, **58**, 1477 (1962).

(4) B. Smaller and M. Matheson, *J. Chem. Phys.*, **28**, 1169 (1958).

(5) R. Fessenden and R. Schuler, *ibid.*, **39**, 2147 (1963).

(6) W. Gordy and C. McCormick, *J. Am. Chem. Soc.*, **78**, 3243 (1956).

(7) C. Jen, N. Foner, E. Cochran, and V. Bowers, *Phys. Rev.*, **112**, 1169 (1958).

(8) T. Cole, H. Pritchard, N. Davison, and H. McConnell, *Mol. Phys.*, **1**, 406 (1958).

(9) E. Collinson, J. Conlay, and F. Dainton, *Discussions Faraday Soc.*, **36**, 153 (1963).
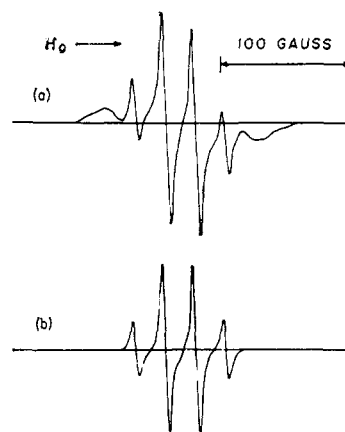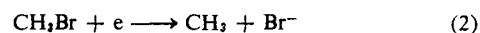
(10) E. Bertin and W. Hamill, *J. Am. Chem. Soc.*, **86**, 1301 (1964).

(11) W. Hamill, "Comparative Effects of Radiation," M. Burton, J. Kirby-Smith, and J. L. Magee, Ed., John Wiley and Sons, Inc., New York, N. Y., 1960.
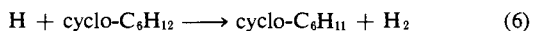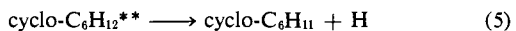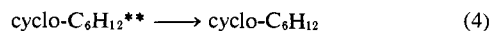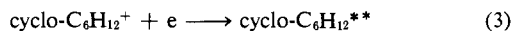
(12) R. Schuler, *J. Phys. Chem.*, **61**, 1472 (1957).

(13) W. Van Dusen, Jr., unpublished results.

(14) J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

(15) W. Hamill, *Discussions Faraday Soc.*, **36**, 292 (1963).

would contribute to the matrix e.s.r. signal. This must be ruled out since the matrix signal remains constant during bleaching. Charge neutralization during bleaching would either produce a neutral molecule which would then decrease the e.s.r. matrix signal or result in bond rupture producing a cyclohexyl radical which would give an e.s.r. signal different from that of the postulated positive ion. The above reactions are shown in steps 3–6, where $C_6H_{12}**$ is a cyclohexane molecule plus the energy of recombination.
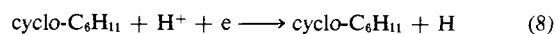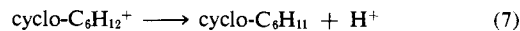
$$cyclo\text{-}C_6H_{12}^+ + e \longrightarrow cyclo\text{-}C_6H_{12}** \qquad (3)$$

$$cyclo\text{-}C_6H_{12}** \longrightarrow cyclo\text{-}C_6H_{12} \qquad (4)$$

$$cyclo\text{-}C_6H_{12}** \longrightarrow cyclo\text{-}C_6H_{11} + H \qquad (5)$$

$$H + cyclo\text{-}C_6H_{12} \longrightarrow cyclo\text{-}C_6H_{11} + H_2 \qquad (6)$$

The data are, therefore, consistent with the interpretation of the positive ion at 77°K. being a protonated free radical,[16] the cyclohexyl radical, and a proton. Such a configuration should given an e.s.r. signal of only the cyclohexyl radical. When the electron is returned to the radical ion, the proton is neutralized forming a hydrogen atom, which, because of its ability to diffuse at this temperature,[17] is ordinarily not detected by e.s.r. measurements at 77°K.,[18] thus leaving the cyclohexyl radical signal unchanged during charge neutralization (reactions 7 and 8).

(16) W. Busler, D. Martin, and F. Williams, *Discussions Faraday Soc.*, **36**, 102 (1963).
(17) D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance," Butterworths Scientific Publications, London, 1958, pp. 223, 224.
(18) J. Willard; *Discussions Faraday Soc.*, **36**, 291 (1963).

$$cyclo\text{-}C_6H_{12}^+ \longrightarrow cyclo\text{-}C_6H_{11} + H^+ \qquad (7)$$

$$cyclo\text{-}C_6H_{11} + H^+ + e \longrightarrow cyclo\text{-}C_6H_{11} + H \qquad (8)$$

However, reaction 7 is highly endothermic and, therefore, ruled out. Alternatively, the results may be explained by an ion–molecule reaction involving proton transfer from a cyclohexane ion to a cyclohexane molecule (reaction 9).

$$cyclo\text{-}C_6H_{12}^+ + cyclo\text{-}C_6H_{12} \longrightarrow cyclo\text{-}C_6H_{13}^+ +$$
$$cyclo\text{-}C_6H_{11} \quad (9)$$
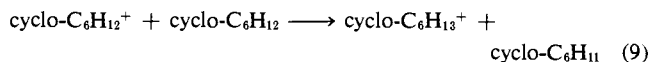
The e.s.r. matrix signal would be that of the cyclohexyl radical, and neutralization would occur with the protonated cyclohexane giving cyclohexane and a hydrogen atom (reaction 10).

$$cyclo\text{-}C_6H_{13}^+ + e \longrightarrow cyclo\text{-}C_6H_{12} + H \qquad (10)$$
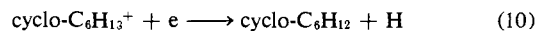
Reaction 9 is energetically favorable if the cyclohexane has a proton affinity of approximately 70 kcal./mole. Lampe and Field[19] have calculated the proton affinity for n-hexane as 103 kcal./mole. It must be further postulated that hydrogen formation by hydrogen atom abstraction from the matrix does not occur at liquid nitrogen temperature in this system because of an activation energy of about 8 kcal./mole[20] for this reaction. Therefore, the hydrogen atom must exist as a mobile entity, only undergoing reaction on an increase in temperature, or combining with other radicals or hydrogen atoms[21] as it diffuses through the matrix.

(19) F. Lampe and F. Field, *Tetrahedron*, **7**, 189 (1959).
(20) H. Schiff and E. W. R. Steacie, *Can. J. Chem.*, **29**, 1 (1951).
(21) V. Voevodskii and Y. Molin, *Radiation Res.*, **17**, 366 (1962).

Moderator Effects on Recoil Tritium Reactions with Methyl and Methyl-d_3 Fluorides[1]

E. K. C. Lee, George Miller, and F. S. Rowland

Contribution from the Department of Chemistry, University of Kansas, Lawrence, Kansas. Received March 28, 1964

The isotopic variations between CH_3F and CD_3F in recoil tritium reactions have been investigated for the O_2-scavenged compounds, and for O_2- and I_2-scavenged mixtures with a large excess of He^4. The relative yields of $HT:CH_2TF:CH_3T$ from CH_3F are 185:100:33, and of $DT:CD_2TF:CD_3T$ from CD_3F 187:100:31, but the absolute yields of all products from CH_3F are higher than from CD_3F. The ratios of CH_2TF/CH_3T and CD_2TF/CD_3T are only slightly affected by the presence of He^4 moderator, indicating that the reactions forming the compounds occur at about the same average kinetic energy for the tritium. The isotope effect in substitution for H or D favors H replacement by 1.27 ± 0.04 in a large excess of He^4. This fact implies that the primary source of the isotopic variation must lie in probability integral isotope effects, i.e., a larger probability for reaction per collision with CH_3F than for CD_3F and/or a larger range of tritium energy within which

reaction is possible. The average energy losses in nonbonding collisions are greater for tritium atoms in CH_3F than in CD_3F ($\alpha_{CH_3F}/\alpha_{CD_3F} = 1.23 ± 0.08$).

Introduction

Recoil tritium atoms react with methyl fluoride (or CD_3F) by the three important hot reactions of abstraction of H, substitution of T for H, and substitution of T for F, as in eq. 1–3. Each of these reactions is initiated

$$T* + CH_3F \longrightarrow HT + CH_2F \qquad (1)$$

$$T* + CH_3F \longrightarrow CH_2TF + H \qquad (2)$$

$$T* + CH_3F \longrightarrow CH_3T + F \qquad (3)$$

by tritium atoms possessing excess kinetic energy remaining from the initial nuclear recoil and is of considerable interest in the understanding of the kinetics and mechanisms of such high energy reactions. An additional hot reaction, the abstraction of F to form