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Electron Capture Processes in the γ -Radiation of Organic Halides in Hydrocarbon Rigid Matrices¹

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Relative electron capture cross sections of chloromethane derivatives have been determined by competition with biphenyl anion in 3-methylpentane-2-methylpentene-1 mixtures, at liquid nitrogen temperatures. A species with λ_{\max} at 680 m μ appears to be 2-methylpentene-1 cation. Irradiation of iodine, hydrogen iodide, methyl iodide, *n*-butyl iodide, or *p*-diiodobenzene in 3-methylpentane produces species with λ_{\max} 770, 530, and 390 m μ . Methyl iodide also has an absorption band at 430 m μ , due to a species of cationic character, probably CH₂I⁺. The band at 390 m μ is assigned to I⁻. In alkane glass with *p*-diiodobenzene the solvent shows an 1800 m μ band, attributed to solvated electrons, which enhances the 390 m μ band upon selective illumination. Bromides yield analogous results.

Introduction

It has been found that certain solvents such as 3-methylpentane (3MP), 2-methylpentene-1 (2MP-1), and 2-methyltetrahydrofuran (MTHF) among others, form noncrystalline rigid matrices at liquid nitrogen temperatures, and that these are highly suitable for studies in radiation chemistry.² Evidence has been found for the formation of naphthalene anion by cobalt-60 γ -radiation, with absorption maxima essentially the same as those of chemically prepared sodium naphthalenide.^{2,3} Similar results were obtained for biphenyl. Irradiation of pure MTHF gave an absorption maximum at 1300 m μ , shown to be due to solvated electrons² for which the 100 e.v. yield is approximately 3. Evidence has been found for the stabilization of otherwise short-lived species such as free radicals and hydrocarbon cations.⁴⁻⁶

Halogen-containing molecules RX are expected to react with slow electrons *via* dissociative capture, forming free radicals R and halide ions X⁻. In cases where the resultant species do not have characteristic absorption spectra, the electron capture cross sections of the parent molecule may be determined by its competition for electrons with solutes whose spectra are known.

Assuming, in competitive electron capture, that the number *N* of anions formed is proportional to the product of capture cross section σ and concentration *C* we have the relationship

$$N_X/N_Y = \sigma_X C_X / \sigma_Y C_Y \quad (1)$$

where Y = reference solute and X = competitive solute. Equation 1 may be rewritten

$$\frac{N_Y + N_X}{N_Y} = 1 + \frac{\sigma_X C_X}{\sigma_Y C_Y} \quad (2)$$

In cases where plateau values indicate that all electrons within a certain energy range are being captured, we may write

$$N_Y + N_X = G_e^0 \times \text{dose} \quad (3)$$

(1) The Radiation Laboratory of the University of Notre Dame is operated under contract with the Atomic Energy Commission.

(2) P. S. Rao, J. R. Nash, J. P. Guarino, M. R. Ronayne, and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 500 (1962).

(3) G. J. Hoijtink and P. J. Zandstra, *Mol. Phys.*, **3**, 371 (1960).

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(5) M. R. Ronayne, J. P. Guarino, and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 4230 (1962).

(6) W. H. Hamill, J. P. Guarino, M. R. Ronayne, and J. A. Ward, *Discussions Faraday Soc.*, September, 1963.

where G_e^0 is the yield of electrons of suitable energy range. Hence, in another form

$$\frac{1}{G_{Y^-}} = \frac{1}{G_e^0} + \frac{\sigma_X C_X}{G_e^0 \sigma_Y C_Y} \quad (4)$$

The slope of a plot of C_X vs. $1/G_{Y^-}$ gives the value $\sigma_X/G_e^0 \sigma_Y C_Y$, from which the ratio of cross sections σ_X/σ_Y may be determined.⁴

Experimental

Methods of solvent purification, outgassing, γ -irradiation and the measurement of absorption spectra have been previously reported.⁵ Organic halides were distilled over activated charcoal through Dry Ice-acetone traps. Biphenyl was purified by recrystallization. Peroxy compounds were removed from 2-methylpentene-1 by treatment with NaK alloy. Silica gel was employed to free 3-methylpentane from alkenes. Gas chromatographic analysis showed less than 0.05% unsaturates remaining in 3MP. Ultrapure 1 \times 1 cm. silica cells were used in a Cary Model 14-R recording spectrophotometer to obtain absorption spectra. In cases where the visible and near-infrared regions were being investigated, Pyrex cells were sometimes used. Cells were kept immersed in liquid nitrogen during irradiation and spectrophotometry. All spectra and optical densities of irradiated samples reported are those obtained when the individual spectra before irradiation are subtracted from those after irradiation. The only exceptions to this practice are those values involving interrupted illumination, shown in Fig. 8 and 9.

Results

The anion band of biphenyl at 410 m μ was used for competition studies.⁴ Figure 1 shows the resultant plateau established when the concentration of biphenyl was varied, in 25% 2MP-1-75% 3MP (by volume), at -196°, with a total dose of 10¹⁸ e.v./g. At constant 0.2 mole % of biphenyl varied quantities of chloroform, methylene, and methyl chlorides were added, with the results shown in Fig. 2 and 3. The ratios of the slopes (and hence of the capture cross section) are: $\sigma_{\text{CHCl}_3}/\sigma_{\text{CH}_2\text{Cl}_2}/\sigma_{\text{CH}_3\text{Cl}} = 5.0:3.1:1$.

When 1 mole % of methyl chloride in 25% 2MP-1-75% 3MP is irradiated to 6.5 \times 10¹⁸ e.v./g., a broad absorption band results, beginning at ca. 1500 m μ , rising to a maximum at about 680 m μ , dropping to a minimum at 460 m μ , and rising off scale at about 280 m μ . Table I lists other systems which gave this same spectrum, while Fig. 4 and 5 show the effect of the addition of methyl chloride on the 680 and 1800 m μ bands of the system 25% 2MP-1-75% 3MP. The 680 m μ band rises rapidly when methyl chloride is added and begins to plateau at approximately 2% added solute. The 1800 m μ band diminishes rapidly and disappears at about 0.5% methyl chloride. With no added

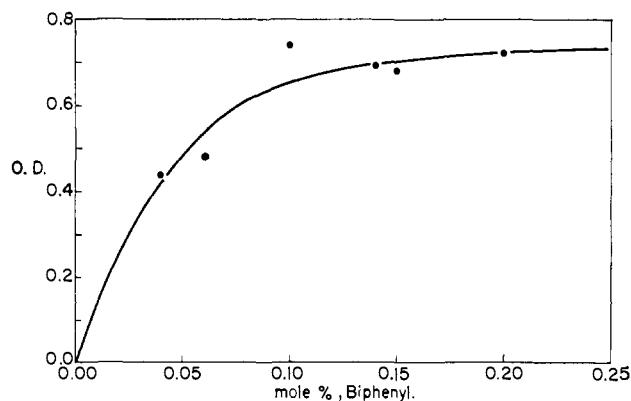


Fig. 1.—Mole % biphenyl in 25% 2-methylpentene-1-75% 3-methylpentane vs. O.D.₄₁₀.

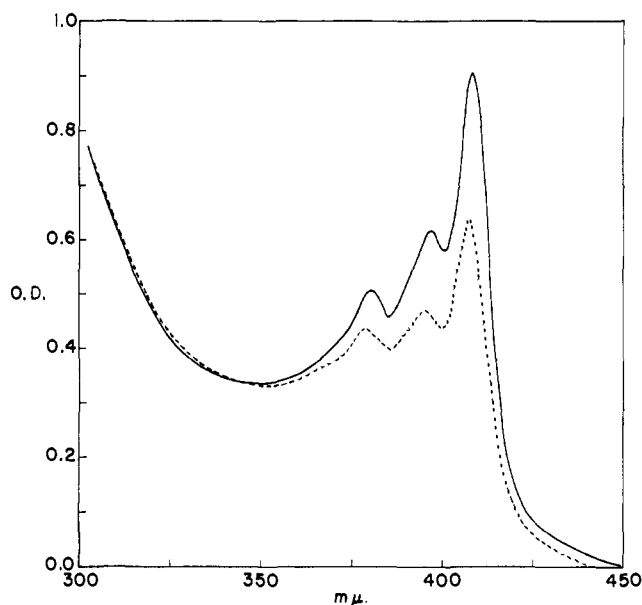


Fig. 2.—Effect of addition of CH_3Cl to biphenyl in 25% 2-methylpentene-1-75% 3-methylpentane: —, 0.2% $(\text{C}_6\text{H}_5)_2$; - - -, 0.05% CH_3Cl + 0.2% $(\text{C}_6\text{H}_5)_2$, 1.1×10^{18} e.v./g.

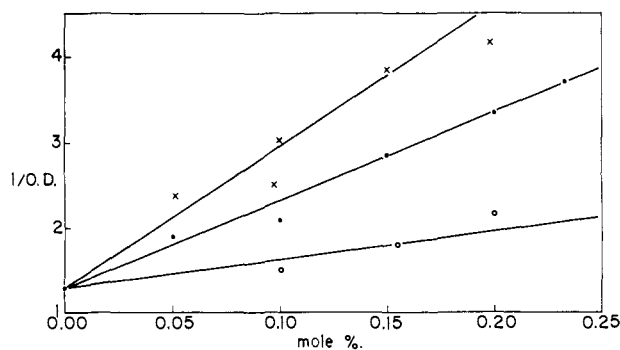


Fig. 3.—Mole % chloromethane derivatives vs. $1/\text{O.D.}_{410}$; O, CH_3Cl ; ●, CH_2Cl_2 ; X, CHCl_3 .

solute, the 680 $m\mu$ band appears as a low intensity shoulder on the tail of the 1800 $m\mu$ band.

The following systems gave no appreciable absorption maxima in the 660-690 $m\mu$ range: 0.2% chloroform, 0.2% or 1% methyl chloride in 3MP only; 1% triethylamine or 1% triethylamine plus 1% methyl chloride in 25% 2MP-1-75% 3MP; pure 3MP. In pure 2MP-1, there was a slight absorption in this region, but with insufficient intensity to be conclusive.

Figure 6a shows the absorption spectrum of 1% methyl iodide in 3MP after a dose of 6.15×10^{18} e.v./g., fol-

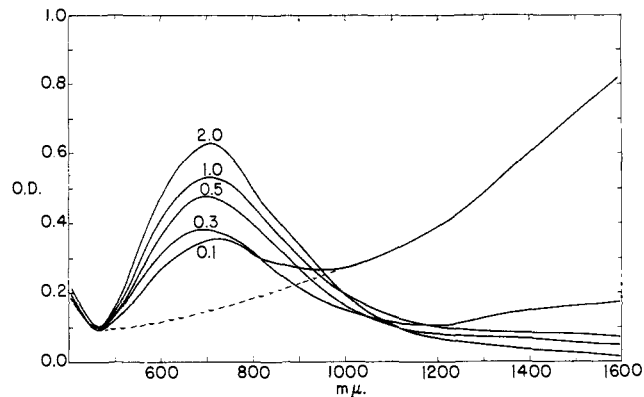


Fig. 4.—The effect of the addition of 0.1-2 mole % CH_3Cl on the 680 $m\mu$ cation band in 25% 2-methylpentene-1 + 75% 3-methylpentane. The longer wave length absorption is due to solvated electrons.

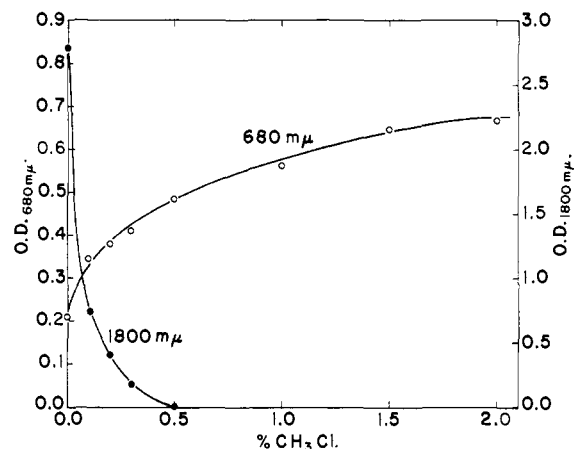


Fig. 5.—The dependence of the 680 $m\mu$ cation band and the 1800 $m\mu$ solvated electron band on the concentration of electron acceptor.

lowed by illumination with Corning filter No. 3385, which transmits light from 530 $m\mu$ to longer wave lengths (all spectra reported hereafter are of samples irradiated with this same dose). The concentration effect of methyl iodide is shown in Fig. 6b. Figure 7

TABLE I

SYSTEMS INVOLVING 680 $m\mu$ BAND IN 25% 2MP-1-75% 3MP AT -196° , 6.5×10^{18} e.v./g.

Solute	Mole % solute	λ_{max} , $m\mu$	O.D. ^a
...	...	690	0.12
CH_3Cl	0.2	650	.10
CH_2Cl_2	.2	660	.20
CHCl_3	.2	670	.21
CH_3Cl	1.0	690	.41
CH_3Br	1.0	690	.39

^a Measured with respect to minimum at 460 $m\mu$.

shows 0.01% iodine in 7.5% toluene-92.5% 3MP, with added amounts of CH_3Cl . The 390 $m\mu$ band, for which optical density was 1.34, has been completely eliminated by the addition of 0.1% methyl chloride. For 1% hydrogen iodide in 3MP, the increase in optical density at 390 $m\mu$ was 1.27. At room temperature, a solution of iodine and methyl iodide in 3MP has a λ_{max} at 520 $m\mu$. At -196° an absorption maximum at 460-490 $m\mu$ was detected for iodine alone, or iodine plus methyl iodide, butyl iodide, hydrogen iodide, or toluene.

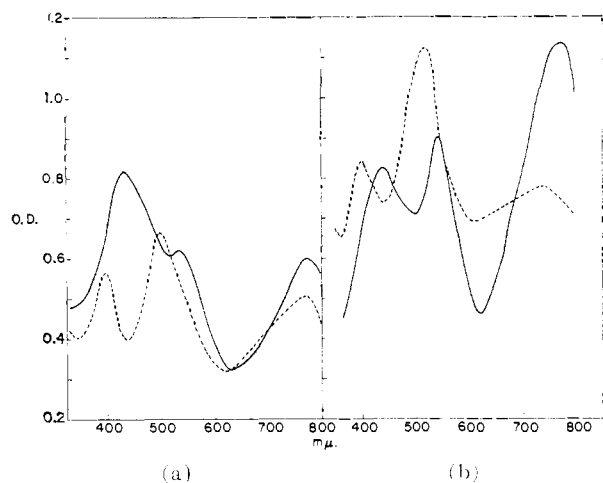


Fig. 6.—(a) 1 mole % CH_3I in 3-methylpentane, 6.5×10^{14} e.v./g. (b) 1.5 mole % CH_3I in 3-methylpentane, 6.5×10^{18} e.v./g.; dashed curve, after bleaching.

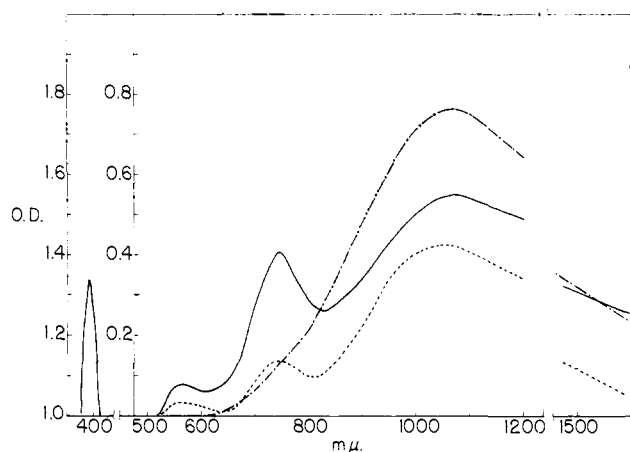


Fig. 7.—Irradiation of 0.01 mole % I_2 in 7.5% toluene-92.5% 3-methylpentane: —, I_2 only; ---, I_2 + 0.1 mole % CH_3Cl ; - · - ·, I_2 + 1.0 mole % CH_3Cl , 6.5×10^{18} e.v./g.

Table II shows the effect of the addition of methyl chloride and toluene on the 430 $m\mu$ band of irradiated methyl iodide.

TABLE II

EFFECT OF THE ADDITION OF METHYL CHLORIDE AND TOLUENE ON 430 $m\mu$ BAND OF IRRADIATED CH_3I IN 3MP, -196° , 6.5×10^{18} E.V./G.

Added solute	% added solute	O.D. ₄₃₀
CH_3Cl	1.5	0.94
CH_3Cl	1.0	.79
CH_3Cl	0.5	.72
None	..	.65
$\text{C}_6\text{H}_5\text{CH}_3$	0.25	.50
$\text{C}_6\text{H}_5\text{CH}_3$	0.50	.36
$\text{C}_6\text{H}_5\text{CH}_3$	1.00	.22

Addition of carbon tetrachloride to methyl iodide in 3MP enhances the three bands of methyl iodide as

Solute	O.D. ₃₇₀	O.D. ₅₃₀	O.D. ₄₃₀
1.0% CH_3I	0.55	0.55	0.74
1.0% CH_3I + 1.0% CCl_4	0.65	0.72	1.02

It will be noticed that the greatest effect is found in the 430 $m\mu$ band.

The effect of short, equal, successive periods of illumination with Corning filter no. 3385 upon the spectrum of products formed by irradiating methyl iodide in

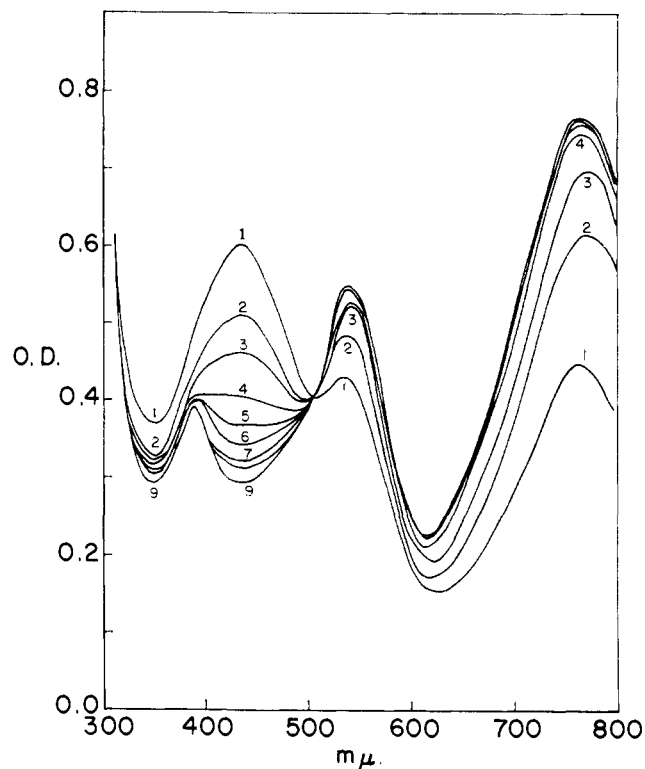


Fig. 8.—Effect of progressive illumination of irradiated CH_3I in 3-methylpentane: 1, 6.5×10^{18} e.v./g.; 2, bleached, 2 min.; 3, bleached, 4 min.; etc.

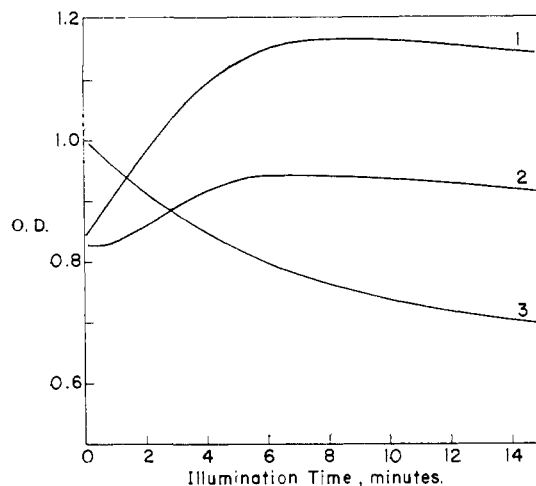


Fig. 9.—Plot of O.D. vs. illumination time for 1% CH_3I in 3-methylpentane, 6.5×10^{18} e.v. g., 3385 filter: 1, 765 $m\mu$; 2, 530 $m\mu$; 3, 430 $m\mu$.

3MP appears in Fig. 8 and 9. When 0.01% *p*-diiodobenzene in 3MP was irradiated with a dose of 6.5×10^{18} e.v./g., a 390 $m\mu$ band (O.D. 0.48) appeared together with the broad band at λ_{max} 1800 $m\mu$, attributed to the solvated electron in some hydrocarbon matrices.⁷ At 1600 $m\mu$, the optical density of the solvent alone, for the dose mentioned above, was 1.0. In 0.01% *p*-diiodobenzene it was 0.41. When bleached with Corning filter no. 2600, which transmits light from 730 to 1030 $m\mu$, it decreased to 0.09, while that of the 390 $m\mu$ band increased to 0.54.

Irradiation of 1% methyl bromide in 3MP gives bands at 570 and 400 $m\mu$. Upon illumination with Corning filter No. 3385, the 400 $m\mu$ band bleached and

a 360 $m\mu$ band became evident. With 10% *sec*-butyl bromide, irradiation produced bands at 610 and 360 $m\mu$. Illumination caused the first to shift to 580 $m\mu$ but the second remained unchanged.

Discussion

The description of competitive electron attachment by two solutes according to eq. 1-4 requires that all electrons capable of attachment by solute molecules will, in fact, be attached by one solute or the other. As a matter of convenience the concentration of biphenyl, the reference solute, should be constant and sufficient to attach all electrons even when no second solute is present. Reference to Fig. 1 demonstrates that 0.2 mole % biphenyl fulfills this condition.

Analysis of data for the 680 $m\mu$ absorption in alkane-alkene systems indicates: (1) this band appears only when 2-methylpentene-1 is present; (2) it is enhanced by addition of known electron acceptors and increases in intensity when their concentration increases; (3) the presence of a substance of low ionization potential and high proton affinity, such as triethylamine, prevents the formation of this band even if large amounts of an electron acceptor, such as methyl chloride, are present. Consistent with these facts and with others is the assignment of the 680 $m\mu$ band to a cation of 2-methylpentene-1.

In systems containing iodine, hydrogen iodide, or organic iodides the band at 390 $m\mu$ can be assigned to I^- . The anionic character of the color center at 390 $m\mu$ is attested by its failure to appear when methyl chloride is present and by its enhancement when the electron band, in the run with diiodobenzene, was

optically bleached. Moreover it corresponds to an absorption threshold at 404 $m\mu$ for I^- in the gaseous state which has been reported recently.⁸

The marked effect of methyl iodide concentration upon the spectrum of radiation products, shown in Fig. 6, suggests an aggregation of permanent dipoles in the nonpolar medium which may be pronounced at low temperature. Single and dimeric (or higher) molecular aggregates of methyl iodide could give rise to various products with relative yields depending upon concentration.

The run with *p*-diiodobenzene tests this possibility since it is nonpolar, and extensive aggregation of molecules in glasses at -196° is less likely than for methyl iodide. Hence, products involving two or more atoms of iodine, *e.g.*, I_2 , I_2^- , or I_2^+ , are less likely. In fact, one band at 390 $m\mu$ was detected in the 350-800 $m\mu$ region.

The band at 430 $m\mu$ in glasses containing methyl iodide does not appear with other alkyl iodides. It is a cationic color center since addition of methyl chloride enhances O.D.₄₃₀ while toluene decreases it. The bands at 530 and 765 $m\mu$ appear to arise from different species since carbon tetrachloride did not enhance O.D.₅₃₀ and O.D.₇₆₅ proportionately. The species absorbing at 430 $m\mu$ both decomposes spontaneously and undergoes photolysis to form the other two color centers (Fig. 8 and 9).

Acknowledgment.—We are indebted to Mr. James B. Gallivan for gas chromatographic analyses.

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Gas Phase Radiolysis of Pentaborane-9¹

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Mass spectral analysis of the products produced by deuteron irradiation of pentaborane-9 shows that hydrogen, diborane, and decaborane-16 are formed in addition to polymeric materials. As a result of experiments involving the use of deuterium as a tracer, the rare gases as sensitizing agents, and iodine as a scavenging agent, a mechanism is proposed in which it is postulated that BH_3 , which is produced by the radiation fragmentation of B_5H_9 molecules, abstracts hydrogen in stepwise fashion from pentaborane-9, giving BH_3 and B_3H_3 radicals. BH_3 dimerizes to give diborane and two B_3H_3 radicals couple to give decaborane-16.

Introduction

In previous studies, Schmied and Koski³ and Hall and Koski⁴ reported that when certain boron hydrides are exposed to ionizing radiation such as protons or deuterons, new products are formed as a result of the coupling of hydride fragments. When pentaborane-9 is irradiated, decaborane-16 is produced, and when decaborane-14 is irradiated, icosaborane-26 ($B_{20}H_{26}$)⁴ is produced. These studies were limited to the synthetic aspect of the reactions and no details of the radiation and chemical processes involved were reported. In the present study, attention is primarily directed

to the radiation chemistry of the system. The G -values of the various products, the influence of iodine as a scavenging agent, and the effect of rare gas sensitization are reported and a mechanism is suggested.

Experimental

The irradiations were performed with 2-Mev. deuterons from an electrostatic generator. The irradiation cell was constructed of Pyrex tubing with a volume of about 125 cc. and it was attached by means of a Kovar seal to a brass flange which in turn was bolted to the accelerator. The cell window was 0.0001 in. thick nickel foil. The dose delivered to the sample was measured by ethylene dosimetry.⁵ $G = 1.2$ at 20 cm. pressure of ethylene was taken as a reference point.

The pentaborane-9 was purchased from the Callery Chemical Corp. and was purified by trap-to-trap distillation until mass spectroscopic analysis revealed no significant impurities. Matheson research grade rare gases were used. The deuterium (purity

(1) This work was done under the auspices of the United States Atomic Energy Commission.

(2) At present a postdoctoral fellow at the National Bureau of Standards.

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