

# Chemical Yields of Nuclear Reactions of Bromine as an Indication of Aggregation and Complexing of Bromine in Organic Matrices at 77°K<sup>1</sup>

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**Abstract:** Organic yields from the Br<sup>80m</sup> isomeric transition indicate that when solutions of bromine in *n*-hexane are frozen to a polycrystalline solid at 77°K the bromine is dispersed as Br<sub>2</sub> at concentrations of 2 × 10<sup>-5</sup> mf (mole fraction) and below, but is present as (Br<sub>2</sub>)<sub>n</sub> clusters of nearly uniform size at all concentrations in the range of 5 × 10<sup>-4</sup> to 1 × 10<sup>-2</sup> mf. Formation of these clusters appears to be dependent upon a preferred size of Br<sub>2</sub> aggregate in the crystal lattice, rather than an equilibrium of the type  $n\text{Br}_2 \rightleftharpoons (\text{Br}_2)_n$  in solution. Alkyl halides, benzene, and ethanol, at concentrations equivalent to the bromine, lessen clustering by complex formation. Similar clustering of bromine occurs in polycrystalline *n*-pentane but not in glassy 3-methylpentane or in polycrystalline benzene. The organic yield from the Br<sup>79(n,γ)</sup>Br<sup>80m</sup> process in (Br<sub>2</sub>)<sub>n</sub> clusters in polycrystalline *n*-C<sub>6</sub>H<sub>14</sub> is lower than that from the Br<sup>80m</sup> → Br<sup>80</sup> isomeric transition process, suggesting that the recoil atom may not escape its parent cage and that radiolytic effects following internal conversion contribute more effectively to the organic yield than does recoil energy. Bromine, but not I<sub>2</sub>, reacts with the stable unsaturated products formed by radiolysis of polycrystalline *n*-C<sub>6</sub>H<sub>14</sub> by reactor radiations. The extent of this reaction is the same when the bromine is added after melting the irradiated solid as when it is present during irradiation, indicating the absence of reaction with free radicals.

When Br<sup>80m</sup> undergoes isomeric transition (Br<sup>80m</sup> (4.4 hr) → Br<sup>80</sup> (18 min)), the Br<sup>80</sup> atoms are positively charged as a result of emission of conversion electrons and Auger electrons.<sup>2</sup> In a variety of gaseous, liquid, and solid organic media they are able to react to form organic bromides.<sup>3</sup> About 40% of the transition events lead to organically bound Br<sup>80</sup> when 10<sup>-2</sup> mf (mole fraction) Br<sub>2</sub>(Br<sup>80m</sup>) is present in liquid hydrocarbons.<sup>4</sup> By contrast, the organic yield from 10<sup>-2</sup> mf Br<sub>2</sub>(Br<sup>80m</sup>) in polycrystalline *n*-C<sub>6</sub>H<sub>14</sub> at 77°K is only about 4%, but is raised to 19% by the additional presence of 10<sup>-2</sup> mf *n*-propyl bromide.<sup>5</sup> In the present work a further study of this low yield, as a function of concentration of bromine and additives, has shown that chemical yields from nuclear transformations can give useful information about the state of aggregation of a solute and its tendency to become chemically complexed.

## Experimental Section

Phillips Pure Grade hydrocarbons were further purified by stirring for 48 hr with concentrated sulfuric acid followed by washing, drying, and fractional distillation. The freshly purified hydrocarbons showed negligible reaction with Br<sub>2</sub> on several hours standing in the dark. The compounds *n*-C<sub>3</sub>H<sub>7</sub>Br, *i*-C<sub>3</sub>H<sub>7</sub>Br, *n*-C<sub>3</sub>H<sub>7</sub>I, and CCl<sub>4</sub> were purified by preparative gas chromatography. Malinckrodt AR Br<sub>2</sub> was used as received.

Br<sub>2</sub> containing Br<sup>80m</sup> was prepared by neutron irradiation of Br<sub>2</sub> in the University of Wisconsin reactor. It was dissolved in the desired hydrocarbon, with or without additives present. Aliquots of the solution were placed in glass-stoppered tubes or prepared in

degassed form on a vacuum line, and frozen under liquid nitrogen. Following 2 hr of standing in the solid state a known volume of CCl<sub>4</sub> containing inactive Br<sub>2</sub> was added to the reaction tube, followed by sulfite solution. Aliquots of the organic and aqueous layers were counted in annular jackets surrounding a G.M. tube. The organic phase was counted immediately and the aqueous phase after the Br<sup>80m</sup> → Br<sup>80</sup> equilibrium had been reestablished. Corrections for relative counting efficiencies of the annular jackets, decay, and contribution of Br<sup>82</sup> to counting rates were applied. Operations prior to extraction were done in the dark to avoid photochemical bromination.

For *n,γ* activation, samples sealed under vacuum in quartz ampoules were irradiated in the rabbit facility of the reactor at a flux of 1 × 10<sup>12</sup> neutrons cm<sup>-2</sup> sec<sup>-1</sup>. To maintain them at low temperature during the short irradiations they were irradiated in polyethylene bottles filled with mineral oil frozen in liquid nitrogen. The temperature rose to 85°K at 1 min after removal from the liquid nitrogen, 95°K at 2 min, and 113°K at 3 min. All irradiations were for 2 min or less.

## Results

**Isomeric Transition.** The experimental results from isomeric transition studies, summarized in Table I, confirm the earlier findings<sup>5</sup> that the organic yield from 10<sup>-2</sup> mf Br<sub>2</sub>(Br<sup>80m</sup>) in hexane at 77°K is about 4% and that this is raised to 19% when 10<sup>-2</sup> mf *n*-C<sub>3</sub>H<sub>7</sub>Br is also present. They show that the yield in the absence of additives remains at about 4% when the Br<sub>2</sub> concentration is reduced from 1 × 10<sup>-2</sup> to 5 × 10<sup>-3</sup>, 1 × 10<sup>-3</sup>, and 5 × 10<sup>-4</sup> mf, but increases to 8% at 1 × 10<sup>-4</sup> mf and to 55% at 2 × 10<sup>-5</sup> mf and below.

Over the 20-fold range of Br<sub>2</sub> concentration where the yield is 4% in the absence of additives, it is raised to about 19% when *n*-C<sub>3</sub>H<sub>7</sub>Br is present at a concentration equal to that of the Br<sub>2</sub>. When the concentration of *n*-C<sub>3</sub>H<sub>7</sub>Br is tenfold less than that of Br<sub>2</sub>, there is little or no enhancement of yield. At a constant *n*-C<sub>3</sub>H<sub>7</sub>Br concentration of 1 × 10<sup>-2</sup> mf with decreasing Br<sub>2</sub> concentrations, giving *n*-C<sub>3</sub>H<sub>7</sub>Br/Br<sub>2</sub>(Br<sup>80m</sup>) ratios of 2, 4, 6, 8, 10, the organic yield increases progressively to 24, 30, 33, and 38%. The data of Table II indicate that *i*-C<sub>3</sub>H<sub>7</sub>Br is more effective, *n*-C<sub>3</sub>H<sub>7</sub>Cl less effective, and C<sub>2</sub>H<sub>5</sub>OH much less effective than *n*-

(1) This work was supported in part by the U. S. Atomic Energy Commission (Contract AT(11-1)-32) and by the W. F. Vilas Trust of the University of Wisconsin.

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**Table I.** Effect of Br<sub>2</sub> Concentration and Added *n*-C<sub>3</sub>H<sub>7</sub>Br on the Organic Yields of the Br<sup>80m</sup> → Br<sup>80</sup> Isomeric Transition Process in Polycrystalline *n*-C<sub>6</sub>H<sub>14</sub> Matrices at 77°K

Br <sub>2</sub> only		Br <sub>2</sub> + <i>n</i> -C <sub>3</sub> H <sub>7</sub> Br		
Br <sub>2</sub> , mf	OY, % <sup>a</sup>	Br <sub>2</sub> , mf	<i>n</i> -C <sub>3</sub> H <sub>7</sub> Br, mf	OY, % <sup>a</sup>
4 × 10 <sup>-7</sup>	55.6	5 × 10 <sup>-3</sup>	5 × 10 <sup>-4</sup>	5.3
4 × 10 <sup>-6</sup>	53.9	1 × 10 <sup>-3</sup>	1 × 10 <sup>-3</sup>	19.1
2 × 10 <sup>-5</sup>	55.2	5 × 10 <sup>-3</sup>	5 × 10 <sup>-3</sup>	20.2
5 × 10 <sup>-6</sup>	17.0	1 × 10 <sup>-2</sup>	1 × 10 <sup>-2</sup>	19.0
6 × 10 <sup>-5</sup>	12.2	5 × 10 <sup>-3</sup>	1 × 10 <sup>-2</sup>	24.3
1 × 10 <sup>-4</sup>	8.1	2.5 × 10 <sup>-3</sup>	1 × 10 <sup>-2</sup>	29.7
5 × 10 <sup>-4</sup>	4.3	1.7 × 10 <sup>-3</sup>	1 × 10 <sup>-2</sup>	33.2
1 × 10 <sup>-3</sup>	4.2	1 × 10 <sup>-3</sup>	1 × 10 <sup>-2</sup>	38.0
5 × 10 <sup>-3</sup>	4.7	...	...	...
1 × 10 <sup>-2</sup>	4.9	...	...	...

<sup>a</sup> Average of several determinations; error ≤ 1%. OY, organic yield.

**Table II.** Effect of Solvent and Nature of Additive on the Organic Yields from the Br<sup>80m</sup> → Br<sup>80</sup> Isomeric Transition Process in Organic Matrices at 77°K<sup>a</sup>

Solvent	Additive, 5 × 10 <sup>-3</sup> mf	OY without additive, % <sup>f</sup>	OY with additive, % <sup>f</sup>
<i>n</i> -Pentane <sup>b</sup>	<i>n</i> -C <sub>3</sub> H <sub>7</sub> Br	4.2 <sup>e</sup>	20.1
Benzene <sup>b</sup>	<i>n</i> -C <sub>3</sub> H <sub>7</sub> Br	25.2	27.1
3-Methylpentane <sup>c</sup> (3MP)	<i>n</i> -C <sub>3</sub> H <sub>7</sub> Br	40.0	41.5
<i>n</i> -Hexane <sup>b</sup>	CCl <sub>4</sub>	4.7	4.5
	3MP	4.7	4.4
	C <sub>2</sub> H <sub>5</sub> OH	4.7	7.6
	<i>n</i> -C <sub>3</sub> H <sub>7</sub> Cl	4.7	13.2
	<i>n</i> -C <sub>3</sub> H <sub>7</sub> Br	4.7	20.2
	<i>n</i> -C <sub>3</sub> H <sub>7</sub> I	4.7	22.1 <sup>d</sup>
	<i>i</i> -C <sub>3</sub> H <sub>7</sub> Br	4.7	26.0
	C <sub>6</sub> H <sub>6</sub>	4.7	21.0

<sup>a</sup> Br<sub>2</sub>(Br<sup>80m</sup>) = 5 × 10<sup>-3</sup> mf in all cases. <sup>b</sup> Polycrystalline. <sup>c</sup> Glassy. <sup>d</sup> Negligible Br<sup>80m</sup> (4.4 hr) activity in the organic layer indicated that the reaction Br<sub>2</sub> + C<sub>3</sub>H<sub>7</sub>I → BrI + C<sub>3</sub>H<sub>7</sub>Br was unimportant under the conditions used. <sup>e</sup> A yield of 3.8% at 10<sup>-2</sup> mf Br<sub>2</sub> was also observed. <sup>f</sup> Average of several determinations; error ≤ 1%. OY, organic yield.

C<sub>3</sub>H<sub>7</sub>Br in increasing the organic yield, while CCl<sub>4</sub> and 3-methylpentane (3-MP) have no effect.

When polycrystalline *n*-C<sub>5</sub>H<sub>12</sub> is used in place of *n*-C<sub>6</sub>H<sub>14</sub> as the matrix for the isomeric transition of 5 × 10<sup>-3</sup> mf Br<sub>2</sub>(Br<sup>80m</sup>) at 77°K, the organic yield is unchanged at 4%, but when the matrix is polycrystalline benzene or glassy 3-MP, the yields are much higher (Table II) and are essentially unaffected by the presence of a concentration of *n*-C<sub>3</sub>H<sub>7</sub>Br equal to that of the Br<sub>2</sub>. In *n*-C<sub>6</sub>H<sub>14</sub> as solvent addition of a concentration of benzene equal to that of the Br<sub>2</sub> raises the organic yield from 4 to 21%.

**Radiative Neutron Capture.** Determination of the organic yields of the Br<sup>79</sup>(*n*, $\gamma$ )Br<sup>80</sup> process in hydrocarbons is complicated by reaction of bromine with products (probably olefins) of radiolysis by the reactor radiations. When Br<sub>2</sub> in polycrystalline *n*-C<sub>6</sub>H<sub>14</sub> at 77°K is irradiated, such reaction occurs with the stable products of the radiolysis and not with the free radicals. This was shown by experiments using Co<sup>60</sup>  $\gamma$  radiation and Br<sub>2</sub>(Br<sup>82</sup>). When Br<sub>2</sub> was present at 10<sup>-3</sup> mf in polycrystalline *n*-C<sub>6</sub>H<sub>14</sub> during irradiation, the amount of bromine which entered organic combina-

tion per gram of hexane per second of irradiation was the same as when the Br<sub>2</sub> was added to the irradiated hexane after melting (following the irradiation). The presence of 10<sup>-3</sup> mf I<sub>2</sub> during irradiation and melting did not reduce the amount of bromine which became organically bound when Br<sub>2</sub> was added after melting. The *G* value for Br<sub>2</sub> entering organic combination was 2.5. Using this value, and observed values for the organic retention of bromine when Br<sub>2</sub>(Br<sup>82</sup>) was added to *n*-C<sub>6</sub>H<sub>14</sub> which had been exposed in the rabbit facility, the dose rate to samples in the reactor was estimated to be 8 × 10<sup>18</sup> ev g<sup>-1</sup> min<sup>-1</sup>.

The corrected organic yields, given in the fourth column of Table III, are equal to the observed organic incorporation of Br<sup>80m</sup>, reduced by the per cent of activity that would have entered as a result of reaction with the radiolysis products. Table III shows that the fraction of the Br<sub>2</sub> which reacts with radiolysis products is negligible for a concentration of 1 × 10<sup>-2</sup> mf and an irradiation time of 5 sec, but increases with increasing irradiation time and decreasing concentration, as expected.

**Table III.** Organic Yields of the Br<sup>79</sup>(*n*, $\gamma$ )Br<sup>80m</sup> and the Br<sup>79</sup>(*n*, $\gamma$ )Br<sup>80m</sup> → Br<sup>80</sup> Reactions in Polycrystalline *n*-C<sub>6</sub>H<sub>14</sub> Matrices at 77°K

Reactor irradiation, sec	Br <sub>2</sub> , mf	Br <sup>80m</sup>		IT OY, %
		OY <sup>c</sup> obsd, %	OY cor, % <sup>a</sup>	
5	1 × 10 <sup>-2</sup>	0.8	0.8	
5	5 × 10 <sup>-3</sup>	0.9	0.9	
5	1 × 10 <sup>-3</sup>	1.1	0.95	5.2
5	1 × 10 <sup>-4</sup>	9.5	7.0	16.1
20	1 × 10 <sup>-3</sup>	1.8	0.9	
20	1 × 10 <sup>-4</sup>	17.0	7.0	16.6
30	1 × 10 <sup>-3</sup>	2.4	0.9	5.9
60	1 × 10 <sup>-3</sup>	4.4	1.2	6.3
60	1 × 10 <sup>-4</sup>	38.0	7.8	
120	1 × 10 <sup>-4</sup>	71.0	10.0	
120	1 × 10 <sup>-5</sup>	84.0	...	
120	5 × 10 <sup>-3</sup> Br <sub>2</sub> + 5 × 10 <sup>-3</sup> C <sub>6</sub> H <sub>6</sub>	22.6	21.2	
120	5 × 10 <sup>-3b</sup> <i>n</i> -C <sub>3</sub> H <sub>7</sub> Br	81.0		

<sup>a</sup> Corrected for reaction with radiolytic products, see text. <sup>b</sup> No Br<sub>2</sub> present. <sup>c</sup> OY, organic yield; IT, isomeric transition.

The fifth column of Table III shows the results of experiments in which the matrices containing Br<sub>2</sub> in *n*-C<sub>6</sub>H<sub>14</sub> were allowed to stand at 77°K for 2 hr after neutron irradiation to determine the isomeric transition organic yield from Br<sup>80m</sup> produced *in situ* by the (*n*, $\gamma$ ) reaction. The organic yield of the Br<sup>80m</sup> → Br<sup>80</sup> process was then determined from the ratio of the Br<sup>80</sup> (18 min) activity found in the organic fraction at the time of extraction to the total Br<sup>80m</sup> (4.4 hr) activity from the sample corrected to the same time.

## Discussion

**Clustering of Br<sub>2</sub> in Crystalline Hexane.** If bromine in *n*-C<sub>6</sub>H<sub>14</sub> at 77°K forms solid solutions with monomolecular dispersion, the organic yield from the isomeric transition might be expected to be independent of concentration over the range for which this condition holds. Such appears to be the case at concentration of 2 ×

$10^{-5}$  mf and below (Table I).<sup>6</sup> In the range of  $5 \times 10^{-5}$  to  $1 \times 10^{-4}$  mf, the yield decreases progressively as might be expected if the solubility of the  $\text{Br}_2$  was exceeded and separation from the hexane occurred by fractional crystallization. However, the constancy of the organic yield at 4% over the twentyfold concentration range from  $5 \times 10^{-4}$  to  $1 \times 10^{-2}$  seems to indicate that the  $\text{Br}_2$  is all present as dissolved  $(\text{Br}_2)_n$  clusters with a nearly constant value of  $n$ . Separation of the  $\text{Br}_2$  from the matrix by fractional crystallization or increase in the value of  $n$  would result in a decrease in organic yield with increasing total concentration of  $\text{Br}_2$  because the  $\text{Br}^{80\text{m}}$  atoms undergoing isomeric transition would be more and more protected<sup>7</sup> from reaction with the organic medium by other  $\text{Br}_2$  molecules. At  $10^{-1}$  mf  $\text{Br}_2$  the reported<sup>8</sup> organic yield of  $\text{Br}^{82}$  from the  $\text{Br}^{82\text{m}}$  isomeric transition is less than 1% rather than 4%, indicating that at this concentration the clusters are larger or fractional crystallization has occurred.

If it is assumed that the  $(\text{Br}_2)_n$  clusters in the concentration range of constant  $n$  represent an equilibrium of the type  $n\text{Br}_2 \rightleftharpoons (\text{Br}_2)_n$ , where  $K = [(\text{Br}_2)_n]/[\text{Br}_2]^n$ ,  $n$  may be evaluated by comparing the experimental dependence of organic yield on concentration with that which would be expected for various values of  $n$  coupled with various values of  $K$ . For this estimate it is assumed that the yield when all the bromine is monomolecularly dispersed is 55%, that the yield when it is all in  $(\text{Br}_2)_n$  units is 5%, and that the equilibrium distribution in the liquid hexane at the freezing point is frozen into the solid. Using these assumptions, plots were made of organic yield as a function of bromine concentration for various assumed values of  $n$  and  $K$  and these were compared with the plot determined from the experimental data. The values  $n = 5$  and  $K = 10^{17}$  show the closest agreement with the experimental curve throughout its range.

Intermolecular bonding between halogen molecules in the solid state has been suggested as probable on the basis of nuclear quadrupole moment evidence,<sup>9</sup> and the molecules  $\text{I}_4$  and  $\text{Br}_4$  have been postulated to account for features of the absorption spectra of iodine<sup>10</sup> and bromine<sup>11</sup> vapor. It would, however, be surprising if most of the bromine in  $n\text{-C}_6\text{H}_{14}$  at its freezing point is present as  $(\text{Br}_2)_5$ , as indicated by the above estimate. Experimental evidence against the equilibrium  $n(\text{Br}_2) \rightleftharpoons (\text{Br}_2)_n$  accounting for the lowering of the organic yield is furnished by the fact that the yield in glassy 3MP at 77°K is high (40%) even though this solvent does not become rigid on cooling until about 120°K (*i.e.*,

(6) Two types of evidence indicate that the monomolecular dispersion of  $\text{Br}_2$  at  $2 \times 10^{-5}$  mf, and below is due to the solubility of  $\text{Br}_2$  rather than to complexing by impurities. Activation analysis for halogens in the pure  $n\text{-C}_6\text{H}_{14}$  solvent showed the absence of alkyl halides, and the organic yield of the isomeric transition in polycrystalline  $n\text{-C}_6\text{H}_{14}$  containing  $2 \times 10^{-5}$  mf  $\text{Br}_2(\text{Br}^{80\text{m}})$  was the same for samples of  $n\text{-C}_6\text{H}_{14}$  which had been passed through columns of activated  $\text{Al}_2\text{O}_3$  as for those which had not.

(7) This protection may be substantial, even for small clusters where the  $\text{Br}^{80}$  is born on the surface, because exchange with  $\text{Br}_2$  and scavenging of radicals by  $\text{Br}_2$  as well as physical shielding are of importance.

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much below the 178°K freezing point of  $n$ -hexane). If such an equilibrium prevailed, it would be expected to favor more and possibly larger clusters at the lower temperature, giving a yield of  $\leq 4\%$  in 3MP glass. Polycrystalline  $n$ -pentane, like polycrystalline  $n$ -hexane, gives an organic yield of 4% in the range of  $10^{-2}$  mf  $\text{Br}_2$  and immediately below.

These results seem to indicate that the uniform clustering of  $\text{Br}_2$ , required to account for the range of constancy of the yield at 4%, must result from a peculiarity of the hydrocarbon lattice which gives preference to incorporation of a rather specific number of  $\text{Br}_2$  molecules at each solute site.

**Prevention of Clustering by Complexing Agents.** The effect of  $n\text{-C}_3\text{H}_7\text{Br}$  in raising the organic yield of the isomeric transition (Table I) must result from reducing cluster formation by complexing the  $\text{Br}_2$  rather than from an effect on the nature of the lattice sites in the crystals. This conclusion is necessary because the effect on the yield is dependent on the ratio of the concentration of  $n\text{-C}_3\text{H}_7\text{Br}$  to  $\text{Br}_2$  rather than on the absolute concentration of  $n\text{-C}_3\text{H}_7\text{Br}$ . Evidence for complex formation is also given by the fact that the color of polycrystalline  $n\text{-C}_6\text{H}_{14}$  containing equal amounts of  $\text{Br}_2$  and  $n\text{-C}_3\text{H}_7\text{Br}$  is different (lemon-yellow) from that containing only  $\text{Br}_2$  (orange-red). The complex is presumably similar to the charge-transfer complexes of iodine. Consistent with this analogy is the fact (Table II) that propyl chloride, propyl iodide, ethanol, and benzene also form complexes with  $\text{Br}_2$ , as indicated by their effect on the organic yield, while carbon tetrachloride and 3-methylpentane do not.<sup>12</sup> The fact that  $\text{Br}_2(\text{Br}^{80\text{m}})$  in polycrystalline benzene gives a much higher organic yield than in polycrystalline  $n$ -hexane is further consistent with known<sup>13</sup> complexing action by the benzene.

Earlier tests<sup>5</sup> have shown that the presence of  $10^{-2}$  mf  $n\text{-C}_3\text{H}_7\text{Br}$  in polycrystalline  $n\text{-C}_6\text{H}_{14}$  containing  $10^{-2}$  mf  $\text{Br}_2(\text{Br}^{80\text{m}})$  at 77°K raises the yield of  $n\text{-C}_3\text{H}_7\text{Br}$  only from 0.12 to 1.2% and of  $i\text{-C}_3\text{H}_7\text{Br}$  from 0.03 to 0.32%, while raising the total organic yield from 4 to 19%. A similar analysis of a system containing a tenfold excess of  $n\text{-C}_3\text{H}_7\text{Br}$  ( $10^{-2}$  mf) over  $\text{Br}_2(\text{Br}^{80\text{m}})$  ( $10^{-3}$  mf) has now shown that the  $n\text{-C}_3\text{H}_7\text{Br}^{80}$  yield is still only 3% while the total organic yield is 38%. Since 40–50% of the organic yield of bromine undergoing nuclear transformations in pure  $n\text{-C}_3\text{H}_7\text{Br}$  appears as  $n\text{-C}_3\text{H}_7\text{Br}$ ,<sup>3b</sup> the present results show that the  $\text{Br}^{80}$  from complexed  $\text{Br}$  reacts primarily with molecules of the hydrocarbon matrix rather than with the complexing molecules.

**Radiative Neutron-Capture Experiments.** If  $\text{Br}^{80\text{m}}$  atoms recoiling from the  $\text{Br}^{79}(n,\gamma)\text{Br}^{80\text{m}}$  process move several molecular diameters from their parent site one might expect that the organic yield from this process would be higher than that of the isomeric transition process in the concentration range where the latter remains at 4%, since the recoil might allow the tagged atom to escape from the  $(\text{Br}_2)_n$  aggregate into the surrounding organic medium. The observed yields (for short irradiations where  $\gamma$  effects are negligible) are, however, only 1% (Table III). This seems to

(12) Spectrophotometric evidence for charge-transfer complexes between alkyl halides and halogens is given by R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **74**, 1891 (1952).

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indicate that the recoil does not free the  $\text{Br}^{80\text{m}}$  from the parent  $(\text{Br}_2)_n$  unit, or that, if it does, the atom's capability of reacting with the organic medium is removed during the escape process. To test the latter possibility, samples were allowed to stand at  $77^\circ\text{K}$  for 2 hr following neutron irradiation. They were then extracted and the organic layer was analyzed for  $\text{Br}^{80}$  (18 min) which might have been produced by the isomeric transition of  $\text{Br}^{80\text{m}}$  atoms which had recoiled into the organic medium as a result of the  $n,\gamma$  process. The yields were very nearly those predicted on the assumption that the organic yield of the  $n,\gamma$  process is a true indication of the fraction of the  $\text{Br}^{80\text{m}}$  atoms which escape from the  $(\text{Br}_2)_n$  units.<sup>14</sup>

(14) In making this estimate it was assumed that the fraction of the  $\text{Br}^{80\text{m}}$  atoms escaping the clumps was twice the organic yield since approximately half would enter inorganic combination. It was further assumed that the organic yield for the isomeric transition of those which had escaped would be ca. 50%, which is the value for the organic yield of the isomeric transition in very dilute  $\text{Br}_2$  in *n*-hexane.

The fact that the organic yield from the  $n,\gamma$  process in polycrystalline *n*- $\text{C}_6\text{H}_{14}$  is lower (1%) than that of the isomeric transition process (4%) is unexpected. The most obvious interpretation would seem to be that the recoil atom, faced by a solid wall of close-packed surrounding molecules, has a very low probability of escape from the parent cage, and that it has less capability of reacting with the hydrocarbon matrix surrounding the surface of the cluster than does an atom produced by the isomeric transition. This difference in capability may result from the fact that essentially all of the isomeric transition events produce  $\text{Br}^{80}$  ions which emit conversion and Auger electrons which produce radiolytic fragments from the hydrocarbon matrix, whereas the fraction of  $\text{Br}^{79}(n,\gamma)\text{Br}^{80\text{m}}$  events which lead to charged  $\text{Br}^{80\text{m}}$  and electron emission may be no more than 12%.<sup>15</sup>

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## Kinetics of Thermal Deuterium Atom Reactions with Methane and Ethane<sup>1</sup>

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**Abstract:** Use of  $\text{NH}_3$  as a proton (deuteron) scavenger has permitted a study of the effects of temperature on homogeneous thermal D-atom reactions with  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  in  $\text{H}^3$   $\beta$ -ray irradiated gaseous  $\text{TD-D}_2\text{-CH}_4\text{-NH}_3$  and  $\text{TD-D}_2\text{-C}_2\text{H}_6\text{-NH}_3$  mixtures between 25 and  $220^\circ$ . Exchange products with  $\text{CH}_4$  are  $\text{CH}_3\text{D}$ ,  $\text{CH}_2\text{D}_2$ ,  $\text{CHD}_3$ , and  $\text{CD}_4$ , but ethane is not a detectable product below  $125^\circ$ .  $\text{C}_2\text{H}_5\text{D}$  is the only deuterated ethane formed by the atomic sequence in  $\text{D}_2\text{-C}_2\text{H}_6\text{-NH}_3$  mixtures at 25 to  $125^\circ$ . Exchange proceeds *via* H-atom abstraction in both systems. Above  $\sim 125^\circ$  a chain reaction sequence,  $\text{D}\cdot + \text{RH} \rightarrow \text{HD} + \text{R}\cdot$  (i),  $\text{R}\cdot + \text{D}_2 \rightarrow \text{RD} + \text{D}\cdot$  (ii), becomes dominant. Activation energies,  $E_i$  and  $E_{ii}$ , have been found to be  $8.5 \pm 0.5$  and  $12.0 \pm 0.7$  kcal/mole, respectively, for  $\text{RH} = \text{CH}_4$ , and  $6.5 \pm 0.5$  and  $13.5 \pm 1.0$  kcal/mole, respectively, for  $\text{RH} = \text{C}_2\text{H}_6$ . Estimates of  $\Delta S^\circ$  and  $\Delta H^\circ$  for *i* provide  $k_{(\text{D}\cdot + \text{CH}_4)} = 6 \times 10^{-11} e^{-8600/RT}$  cc/molecule sec between 25 and  $125^\circ$  and a collision theory (hard sphere,  $\sigma = 3 \text{ \AA}$ , two squared terms) steric factor of 0.1. Results also suggest that  $\text{D}_2$  is quite inefficient as a third body for collisional stabilization of excited methane and ethane molecules formed *via*  $\text{R}\cdot + \text{D}\cdot \rightarrow \text{RD}^*$ , even at  $\text{D}_2$  pressures near 1 atm.

Although the reactions of thermal hydrogen atoms with  $\text{CH}_4$  and with  $\text{C}_2\text{H}_6$  have been subjects of many investigations for over 30 years,<sup>3-9</sup> the activation energy for the homogeneous reaction with  $\text{CH}_4$  has yet to be established within reasonable limits.<sup>10</sup> Before

1958 values ranging from 4.5<sup>4</sup> to 15 kcal/mole<sup>3</sup> were reported. Recently, the range appears to have been narrowed to approximately 7 to 12 kcal/mole.<sup>5,6,8</sup> Little attention has been given to reactions of hydrogen atoms with  $\text{C}_2\text{H}_6$  during the last decade. Earlier values of  $E_A$  for ethane range from 6 to 9 kcal/mole.<sup>3</sup> This state of affairs attests to difficulties with production of hydrogen atoms at steady rates, avoidance of surface effects, and establishment of necessary relations between measured quantities and parameters of the elementary steps. Shortcomings of flow systems<sup>4,8</sup> for studies of homogeneous reactions and for temperature coefficient measurements are well known. Flame techniques,<sup>6</sup> in particular, as well as photolytic competitive methods,<sup>5</sup> are dependent upon knowledge concerning elementary steps whose kinetic parameters are seldom more firmly established than those to be determined. Investigations employing radiolytically generated hydrogen atoms<sup>7,9</sup> are subject to seriously misleading interpreta-

(1) Based on a dissertation presented in partial fulfillment of requirements for the Ph.D., The Ohio State University, 1965, by R. H. Lawrence, Jr., U.S.A.F., A.F.I.T. Program, 1961-1965.

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