[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, BROOKHAVEN NATIONAL LABORATORY, AND SAINT PETER'S COLLEGE]

Chemical Effects of Nuclear Activation of Bromine in the Propyl Bromides[1]

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Very similar retentions have been observed for the bromine isotopes, Br^{80} and Br^{82}, in (n,γ) activation of solid as well as liquid *n*-propyl and isopropyl bromide. This lack of isotopic separation appears to be in agreement with previous work on the alkyl iodides where (n,γ) produced I^{128} and $(n,2n)$ produced I^{126} were found to have comparable retentions. The retentions were also found to be the same for Br^{82} produced by capture of highly thermalized neutrons from a thermal column in the Brookhaven reactor and by capture of unmoderated cyclotron neutrons. In contrast to the similarity of yields in these other observations, 6-min. Br^{78} produced by $(n,2n)$ activation of the propyl bromides is found to have a somewhat higher retention than Br^{82} produced simultaneously by (n,γ) activation. This difference occurs in both solid and liquid samples and in liquid samples containing small amounts of added bromine. It appears that the higher retention for the Br^{78} isotope may result from the increased fragmentation produced by the very much more energetic recoil atom.

In previous work on the comparison of the chemical effects of various modes of nuclear activation of iodine in the alkyl iodides, little dependence of the retention values on the energy of the recoiling nucleus was observed.[3,4] In Szilard–Chalmers studies of the alkyl bromides, however, various conflicting reports on the separation of the bromine isotopes have appeared.[5] A comparative study of the retentions for (n,γ) and $(n,2n)$ activation of the propyl bromides was undertaken in order to provide information on possible effects of recoil energy in the bromide systems. Further studies of the retentions of Br^{80} and Br^{82} produced by thermal-neutron activation have also been carried out.

The chemical effects accompanying radiative neutron capture by bromine have been the subject of numerous investigations.[5] With the exception of the work in Libby's laboratory,[6–8] however, all studies have been confined to the liquid state. The various investigators now appear to agree that in carefully purified liquid bromides the basic retentions for the Br^{80}, Br^{80m} and Br^{82} isotopes are very nearly the same. Willard has shown, however, that retentions may be modified by irradiation of the sample and apparent isotopic differences may result if the irradiation is long compared to the radioactive half-life of the species involved.[9]

For solid alkyl bromides, Libby and co-workers[7,8] have reported that the retention of Br^{82} is considerably higher than that of Br^{80} and have ascribed the apparent isotopic separation to a difference in the degree of melting of the crystal by the recoiling atom. According to this proposed model, the more energetic recoil atoms melt a larger zone in the crystal and come to rest in a more liquid-like environment. Since the liquid bromides have lower retentions than the solid bromides, this increase in liquefaction appears as a decrease in the retention value. We have previously commented[4] that the lack of difference in retentions for (n,γ) and $(n,2n)$ activation of the solid iodides appears to be at variance with this model.

Experimental

Purification of Alkyl Bromides.—Because of the known effect of impurities, rigorous purification of the material for irradiation was deemed necessary. Matheson *n*-propyl bromide was treated with elemental bromine and stored for 4 weeks. The bromine was extracted with aqueous bisulfite and the material dried over anhydrous magnesium sulfate. It was then stirred with concentrated sulfuric acid for a period of two weeks, the acid being changed every two days. The *n*-propyl bromide was separated from the acid and washed with ice-water, aqueous bicarbonate, and further with water until the bromide layer was no longer opalescent, then dried over anhydrous magnesium sulfate and subjected to a rough preliminary distillation. The central portion of this distillate was fractionated in a 4-foot helix-packed all-glass column and the middle third used for the activation experiments. Two separate preparations of *n*-propyl bromide were made.

The treatment of the isopropyl bromide was similar except that the sulfuric acid treatment was stopped after two days because of oxidation of the bromide and the appearance of a strong odor of sulfur dioxide. After this short treatment with sulfuric acid, the isopropyl bromide was separated, washed, dried, treated again with bromine for four days and subsequently worked up for distillation.

Activation.—Thermal-neutron activations were carried out at the Brookhaven reactor in an irradiation facility[10] which is a low-gamma-background source (~150 Roentgens per hour) of highly thermalized neutrals. Twenty-five-ml. samples were exposed in silica containers to a neutron flux of 6.5×10^8 neutrons $cm.^{-2}$ $sec.^{-1}$ for five minutes.

Fast-neutron activations were carried out at the Brookhaven 60-inch cyclotron as previously described.[3] During these irradiations, the deuteron beam was very rapidly brought up to 40–50 microamperes and the entire irradiation completed within three minutes so that all activation occurred within a period short with respect to the 6-min. half-life of the Br^{78}. The activation processes important in the fast-neutron irradiations are given in Fig. 1. As these irradiations were carried out in Pyrex vessels the Br^{82} was produced here by activation with epithermal neutrons.

For both fast- and thermal-neutron bombardments the solid samples were immersed in liquid nitrogen baths during the irradiations. To all appearances these samples were quite crystalline; there was no evidence at all of the formation of a bromide glass. The solid samples were quickly melted immediately after the irradiation and remained in the liquid state for less than two minutes before subsequent work up and separation.

Retention Measurements.—Bromine (0.05 ml.) was added to the irradiated sample, a 10-ml. portion was retained for measurement of the *total* activity, and the remaining 15 ml. was extracted with 15 ml. of aqueous thiosulfate. Ten-ml. portions of the *organic* and *aqueous* extractable ac-

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[3] R. H. Schuler, *J. Chem. Phys.*, **22**, 2026 (1954).

[4] C. E. McCauley, G. S. Hilsdorf, P. R. Geissler and R. H. Schuler, THIS JOURNAL, **78**, 3246 (1956).

[5] *Cf.* J. E. Willard, *Ann. Rev. Nuc. Sci.*, **3**, 493 (1953).

[6] L. Friedman and W. F. Libby, *J. Chem. Phys.*, **17**, 647 (1949).

[7] M. S. Fox and W. F. Libby, *ibid.*, **20**, 487 (1952).

[8] F. S. Rowland and W. F. Libby, *ibid.*, **21**, 1495 (1953).

[9] J. C. W. Chien and J. E. Willard, THIS JOURNAL, **77**, 3441 (1955).

[10] H. J. Curtis, S. R. Person, F. B. Oleson, J. E. Henkel and N. Delihas, *Nucleonics*, **14**, No. 2, 26 (1956).

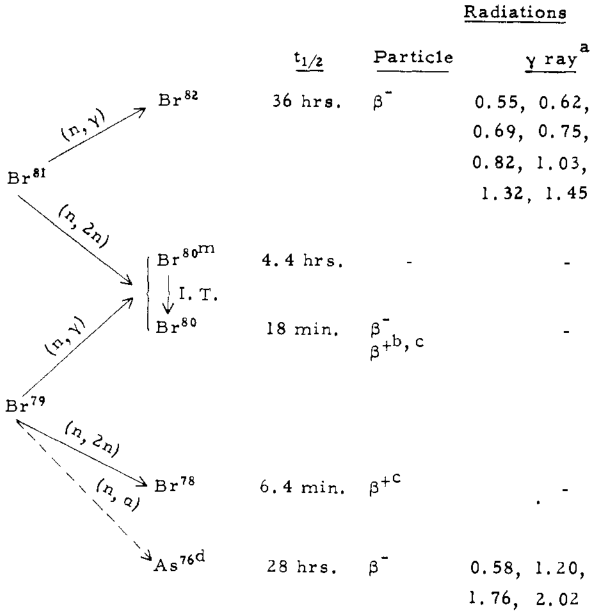

Fig. 1.—Fast-neutron activation of bromine: a, only pertinent high energy γ-rays are included; energy in Mev.; b, positron emission occurs at 2.8% of Br^{80} decays; c, gives 0.51 Mev. annihilation radiation; d, As^{76} produced by (n,α) activation of Br^{79} is a possible contaminant in the fast-neutron experiments and cannot be separated from 36-hr. Br^{82} by decay measurements. Other (n,α) and (n,p) produced contaminants can be eliminated by decay or energy considerations.

tivity were placed in stoppered volumetric flasks for counting. Cyclohexene (0.10 ml.) was added to the total and organic samples to fix the activity in organic combination.

In the fast-neutron experiments it was necessary to count the Br^{78} isotope with moderate selectivity because of the high background of concomitant activity produced by (n,γ) reactions. A scintillation spectrometer which consisted of a sodium iodide crystal detector and pulse height analyzer was used for this purpose. Figure 2 gives the measured pulse height distribution for the various isotopes of concern in these experiments.

The Br^{80} from the thermal-neutron activations was detected by the 0.51 Mev. annihilation radiation from its positron, though with only low efficiency because of the 2.8% abundance of this positron. The Br^{82} isotope could then be counted without waiting for complete decay of the short-lived isotopes by using the analyzer channel at 0.76 Mev. The high relative sensitivity of this counting arrangement for Br^{82} at 0.51 Mev., however, makes it impossible to obtain accurate data for the activities of the 4.4-hr. Br^{80m} isomer. In the fast-neutron experiments the Br^{78} isotope is also detected by its positron annihilation radiation. Here the high Br^{78} activity levels make it difficult to obtain significant retention values for either the 18-min. or 4.4-hr. bromine isotope.

Since As^{76} has a half-life very similar to that of Br^{82} it is expected that this activity, which is a possible (n,α) by-product in the fast-neutron experiments, might be produced in sufficient yield to complicate the measurements of Br^{82}. However as is seen in Fig. 2, any As^{76} contribution is minimized by counting the Br^{82} activity in the 0.76 Mev. spectrometer channel. The relative intensities in the 0.55 and 0.76 Mev. channels observed in the fast-neutron activation experiments were found to be almost identical to those given for Br^{82} in Fig. 2 showing that there was little production of As^{76} and that the contribution by this nuclide to the counting rate in the 0.76 Mev. channel was negligible. The activity level of C^{11}, which is produced from the fast-neutron bombardment of the carbon present was shown to be negligibly low by a similar activation of a sample of cyclohexane.

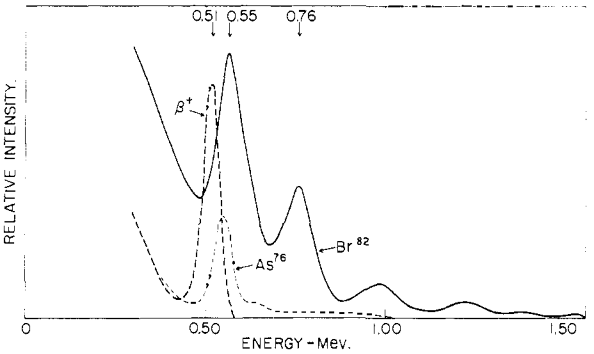

Fig. 2.—Relative pulse height intensity obtained with NaI γ-ray crystal spectrometer for thermal neutron produced Br^{82} and As^{76} and for positron annihilation radiation (from C^{11}).

Immediately after activation and separation, the activities of the various liquid samples were followed in the 0.51 Mev. channel. Consecutive 40-second counts were taken for about the first hour of decay. The activity due to Br^{82} was then determined from longer counts in the 0.76 Mev. channel and the retention of Br^{82} ($R_{Br^{82}}$) was determined from the relative activities of the total and organic samples. Since the counting medium was the same for each measurement, no correction was necessary for a difference in counting efficiency of the two samples. For the solid samples, where retention is high, the ratio of the activity of the aqueous extract to that of the total sample was taken as an auxiliary measure of the quantity $1 - R$. In general the sum of the aqueous and organic activity was very nearly equal to the total activity and thus showed that the counting efficiency was not very different for the aqueous and organic samples.

The 18-min. Br^{80} contribution in the thermal-neutron experiments was obtained by subtracting the contribution of 36-hr. Br^{82} ($C_{Br^{82}}$) from the total activity and the corresponding quantities $R_{Br^{82}}C_{Br^{82}}$ and $(1 - R_{Br^{82}})C_{Br^{82}}$ from the organic and aqueous components. A similar correction was made for the very small contribution of 4.4-hr. Br^{80m} assuming that its retention was the same as for Br^{82}. The residual activities, when corrected for decay of the 18-min. isotope to a common time, showed no trend. For the various samples these corrected activities over the first half-life of decay were averaged and the retentions calculated.

In the fast-neutron experiments the retentions of Br^{82} and Br^{78} were obtained by an extension of the above procedure. After correction for the longer-lived activities, the resultant activity decayed with a 6.4-min. half-life. The retentions for Br^{78} were determined from the averages of the corrected activities for the first 15 minutes of counting.

In general a sufficient number of events were recorded to give the individual activity measurements a statistical significance of better than 1% except for the Br^{82} produced at the cyclotron where the activity level was lower and precision poorer (~2%).

Results

The results of the thermal-neutron experiments are given in Table I. It is seen that, in general, the retention values are substantially the same for the Br^{80} and Br^{82} isotopes in both liquid and solid samples. While the retentions for Br^{80} appear to be slightly higher than for Br^{82} in the liquid samples and slightly lower in the solid samples, possible differences are slight and of the order of the general experimental error.

Measurements also were carried out on the propyl bromide samples some four months after purification. Since the retentions of these samples were slightly lower than those of the fresh material, it seemed possible that the propyl bromides were slowly changing on aging. The *n*-propyl bromide was therefore stored in the dark further for three months and two additional solid phase measure-

TABLE I

THERMAL NEUTRON ACTIVATION EXPERIMENTS

	Sample and history	Retention, % Br^{80}	Br^{82}
n-Propyl bromide, liquid	A—fresh	35.8[a]	..
	B—fresh	37.8	36.5
	B—4 months old	34.2	32.5
Isopropyl bromide, liquid	A—fresh	24.2	23.5
	A—4 months old	24.0	21.2
n-Propyl bromide, solid	A—fresh	79.1	79.4
	B—fresh	73.9	75.6
	B—4 months old	71.5	72.8
	B—7 months old	74.3	73.8
	B—7 months old—washed[b]	75.9	74.9
Isopropyl bromide, solid	A—fresh	79.6	81.0
	A—4 months old	78.2	81.8
	Stock—washed[c]	80.7	81.4

[a] Activated with photoneutrons from 2 Mev. Van de Graaff generator. [b] Aged sample washed with thiosulfate, water and dried over anhydrous magnesium sulfate. [c] Untreated stock sample washed with thiosulfate, water and dried.

ments made, the first on a sample taken directly from the stock material, the second after thoroughly washing the propyl bromide with thiosulfate solution, water, and drying. The washed material appears to have a very slightly higher retention than the untreated sample although both values are nearly the same as for the fresh material. Once purified, the bromides appear to be quite stable toward chemical changes which affect their Szilard–Chalmers chemistry.

Retentions also were determined for solid isopropyl bromide on a sample which was not subjected to the normal purification but merely washed with aqueous thiosulfate, with water, dried and filtered. Somewhat surprisingly this sample showed the normal retention values and no isotopic difference.

The data from the fast-neutron experiments are given in Table II. It is seen that in all cases, for both liquid and solid samples, the retention of Br^{78} is greater than that of Br^{82}. The isotopic separation is most evident in the decay of the activities from the aqueous extract from the solid samples, where the Br^{78} contribution is less than one-half that of Br^{82}. For a sample of commercial *n*-propyl bromide which had only been ozonized briefly before washing and distillation, liquid-phase retentions of 54.4% for Br^{78} and 47.8% for Br^{82} were obtained. These high values undoubtedly indicate an impure sample. It is interesting however to note that the difference, 6.6%, is about the same as that found in the measurements reported in Table II. Figure 3 illustrates the results obtained from the fast-neutron activation of *n*-propyl bromide samples containing added molecular bromine. Data of Rowland and Libby[8] on the effect of bromine on the retention of (n,γ)-produced activity are given for comparison. The addition of Br_2 results in a decrease in the difference between the retention values although this effect is important only at relatively high concentrations (∼ 1 mole %).

TABLE II

FAST NEUTRON ACTIVATION EXPERIMENTS

	Retention, % Br^{78}	Br^{82}
n-Propyl bromide, liquid	43.9[a]	36.3[a]
	40.3	33.4
Isopropyl bromide, liquid	26.5	23.3
n-Propyl bromide, solid	94.0[a]	76.3[a]
	93.5[a]	76.1[a]
	90.5	73.9
Isopropyl bromide, solid	94.0	79.7
	93.2	81.3

[a] *n*-Propyl bromide sample A, all other sample B.

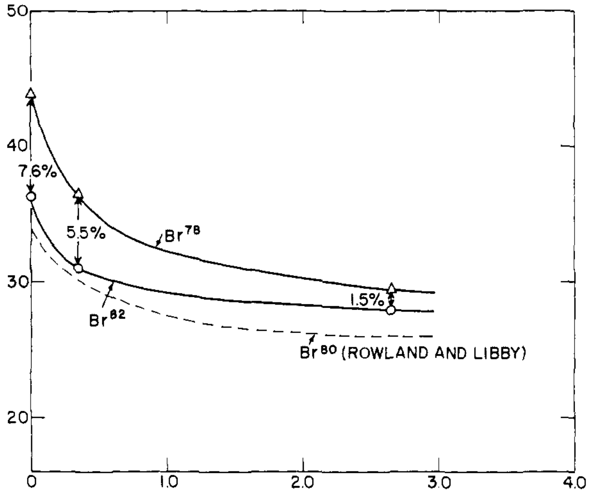

Fig. 3.—Effect of added bromine on the retention values of *n*-propyl bromide: Δ, retention of (n,2n) produced Br^{78}; O, retention of simultaneously produced Br^{82}. The data of Rowland and Libby (ref. 8) on Br^{80} are given by the dashed curve.

Discussion

A comparison of the bromine retention values obtained by various workers for (n,γ)-produced activity is given in Table III.[11] The present experiments show similar retentions for Br^{82} produced both by capture of highly thermalized neutrons from the reactor and the more energetic neutrons at the cyclotron. This comparison suffers of course from the relatively poor reproducibility obtained in the individual measurements on different samples. Both the Wisconsin[12] and Chicago[7] groups have previously reported the absence of a neutron energy effect in the liquid state.[13] No significant difference is observed in the present work between thermal-neutron-produced Br^{80} and Br^{82} in either solid or liquid samples. Here, of course, a direct comparison of the two activities in the same sample is somewhat more significant than the results from different experiments. The lack of isotopic separation is in agreement with the investigations of Libby and co-workers on liquid

[11] The data of Capron and co-workers (*cf.* P. C. Capron and L. J. Gilly, *J. chim. phys.*, **52**, 505 (1955)) which were in general obtained with unpurified samples, are not included.

[12] J. C. W. Chien and J. E. Willard, THIS JOURNAL, **76**, 4735 (1954).

[13] D. J. Apers and P. C. Capron, *J. Inorg. Nuc. Chem.*, **2**, 219 (1956), have recently reported that non-thermalized neutrons give a lower organic yield of Br^{80} than of Br^{82}. No difference in retention was observed for thermal neutrons.

TABLE III

COMPARISON OF VARIOUS RETENTION MEASUREMENTS

	Present work			Willard and co-workers	Libby and co-workers		
	Br^{80} Thermal	Br^{82} Thermal	Br^{82} Fast	Br^{80} Thermal	Br^{80}	Br^{80m}	Br^{82}
n-Propyl bromide, liquid	35.8		36.3				
	37.8	36.5	33.4	36^{a,e}	34.0^{c}	34.0^{c}	35.5^{d}
Isopropyl bromide, liquid	24.2	23.5	23.3	23.6^{b}	33.7^{d}	33.9^{d}	31.7^{d}
n-Propyl bromide, solid	79.1	79.4	76.2				
	73.9	75.6	73.9	...	...	78.2^{c}	86.7^{c}
							88.4^{d}
Isopropyl bromide, solid	79.6	81.0	80.5	...	81.6^{d}	79.9^{d}	94^{d}
						82.9^{c}	93.0^{c}

[a] Ref. 12. [b] Ref. 14. [c] Ref. 8. [d] Ref. 7. [e] Chien and Willard report similar retentions for Br^{80m} and Br^{82}.

bromides but in disagreement with their work on solid bromides.

For liquid *n*-propyl bromide, the various observers appear to agree on a retention of 33–37%. The retention of 23% found in the present investigation for liquid isopropyl bromide is in agreement with the recent data of Levey and Willard[14] although considerably lower than other previously reported values. Since impurities generally present tend to increase retentions, the lower values are presumably more significant. Isopropyl bromide appears to be more difficult to obtain in the required purity than *n*-propyl bromide and extreme caution had to be observed in the washing and distilling operations. As remarked in the paragraph on the preparation of the isopropyl bromide, concentrated sulfuric acid reacts with the bromide and it is conceivable that, in the previous investigation,[8] impurities were introduced which were not removed in the subsequent purification thus leading to the higher values. The lower retention for liquid isopropyl bromide suggests that the primary and secondary bromides may well fit a pattern similar to that pointed out by Levey and Willard for the corresponding iodides.[15]

For the solid bromides, the present values for Br^{80} and Br^{82} are in substantial agreement with the Br^{80} values reported by Rowland and Libby[8] although higher values are given by them for the retention of Br^{82}. If the period of activation is long with respect to the radioactive half-lives of the species involved, impurities might be expected to produce an apparent retention difference.[9] However in both the present and the previous work,[8] irradiations were short so that the retention of each isotope should be affected to very nearly the same extent by the presence of impurities. Similarly, it does not appear that the slightly different extraction procedure used previously can account for the observed separation. Other sources of artifacts, such as differences in counting efficiency, which might lead to apparent isotopic differences, appear to have been carefully eliminated in both investigations. The discrepancy between the present work and that of Rowland and Libby appears at this writing to be completely unresolved. Since comparison of (n,γ) and (n,2n) activations of bromides and iodides shows that only small retention differences result from large changes in recoil energy, it seems doubtful that more than slight differences in the chemical effects should accompany the possible differences in the energy of the recoils from (n,γ) activation of the two bromine isotopes.

The higher retentions observed in the (n,2n) activation experiments are of course in contradiction to the model proposed by Libby and co-workers.[7,8] The recoil energy here is known to be much greater than that in thermal neutron (n,γ) experiments ($\sim$ 100,000 e.v. as compared to $\sim$ 100 e.v.) and yet the retentions in the solid state are higher, not lower, than the retentions observed for less energetic recoils. It would seem that internal liquefaction of the crystal by the recoil is at least not the determining factor for the fate of the activated atom. We have previously pointed out,[4] in a comparison of (n,2n) activation of liquid and solid iodides, that the decreased activity as the parent species in the solid iodides also does not correspond to this liquefaction model.

The cause of the increased retention of Br^{78} is not wholly understood. It can result from any of a number of differences in the physical processes involved in the activation,[3,4] but the natural tendency is, of course, to ascribe it to the greater energy of the (n,2n) recoil. Neither the billiard-ball[16] nor the epithermal reaction[6,17] model predicts any energy dependence of the retention provided the recoil energy is above a certain minimum. A model involving disruption (random fragmentation)[5] of a large volume of the system might, however, lead to an energy dependence of retention provided there is an appreciable probability of diffusion of the radioactive atom so that it may react with an organic fragment originally formed at some distance. For the more energetic recoils the fragmentation background is greater and it might be expected that some of the activated atoms which escape organic combination in the (n,γ) case will be trapped by reaction with the fragments present, although in such a case one might perhaps have expected a more pronounced scavenging effect by inactive bromine (*cf.* Fig. 3). The apparent lack of effect of energy in the case of the iodides may be only a difference of degree, since differences of the order of a few per cent. would have been obscured in the intercomparison of work from different la-

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(14) G. Levey and J. E. Willard, THIS JOURNAL, **78**, 2352 (1956).

(15) G. Levey and J. E. Willard, *ibid.*, **74**, 6161 (1952).

(16) W. F. Libby, *ibid.*, **69**, 2529 (1947); J. M. Miller, J. W. Gryder and R. W. Dodson, *J. Chem. Phys.*, **18**, 579 (1950); P. C. Capron and Y. Oshima, *ibid.*, **20**, 1403 (1952).

(17) J. M. Miller and R. W. Dodson, *ibid.*, **18**, 865 (1950).

boratories. Chemical differences between the halogens may result in larger effects for bromine than for iodine. For example, Br_2 molecules containing active bromine can be incorporated into stable organic products by reacting with olefins to form vicinal dibromides while the analogous reaction is not possible for I_2. Other differences between the chemistry of iodine and bromine atoms may also lead to differences in the fates of the activated species.

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The Reaction of Methyl-d_3 Radicals with Cyclopropane and Cyclopentane

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The abstraction of hydrogen from cyclopropane by CD_3 radicals proceeds with an activation energy of 13.1 kcal. while the value for abstraction from cyclopentane is 9.3 kcal., the same as for abstraction of secondary H from *n*-butane. The mechanism of the decomposition of the cyclobutyl radical and the fate of the cyclopropyl radical are discussed.

The abstraction of hydrogen from cyclic hydrocarbons should proceed with an activation energy characteristic of the abstraction of secondary hydrogen from paraffins if the ring character does not affect the situation. It is of interest to know if a relatively unstrained ring such as cyclopentane conforms to this expectation, and a highly strained structure such as cyclopropane behaves differently. Trotman-Dickenson and Steacie's[1] data show that cyclopropane has a higher energy of activation for hydrogen abstraction than does cyclopentane. In this paper the energies of activation and the pre-exponential factors have been more precisely determined. In addition, the fate of the cyclopropyl and cyclopentyl radicals have been investigated to a limited extent.

Experimental

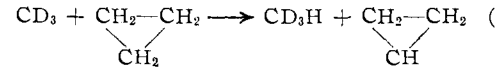
A mixture of acetone-d_6 and cyclopropane in the ratio 0.57 was made up and all cyclopropane experiments were carried out on this mixture. The acetone-d_6 was prepared by exchange with D_2O[2] and analyzed $D/(D + H) = 0.98$. Photolyses were carried out with a Hanovia Medium Pressure Mercury Arc with a quartz reaction vessel in a block aluminum furnace.[3] Methane analyses were made by expanding the fraction of the products volatile from liquid nitrogen into a mass spectrometer. A mixture of acetone-d_6 and cyclopentane in the ratio 1:10 was similarly photolyzed and the methane fraction analyzed.

The products of the photolysis of acetone-d_6 and cyclopentane were examined only by means of vapor phase chromatography. The products of the CD_3 + cyclopropane reaction were chromatographically separated and identified by the mass spectrometer.

Results and Discussion

The results of the methane analyses in the cyclopropane and cyclopentane studies are given in Tables I and II. Corrections have been made for CD_3H produced from the H impurity in the deuterated acetone. Reactions were carried to about 1% conversion of the acetone. The following reactions are of importance

$$CD_3 + CD_3COCD_3 \longrightarrow CD_4 + CD_2COCD_3 \qquad (1)$$



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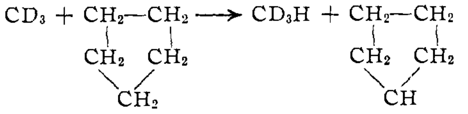

(3)

TABLE I

PHOTOLYSIS OF ACETONE-d_6 IN THE PRESENCE OF CYCLOPROPANE

T, °C.	T, min.	CD_3H/CD_4[a]	k_H/k_D
248	2	0.382	0.218
248	4	.384	.219
302	2	.461	.263
302	4	.454	.259
354	1	.507	.289
354	3	.508	.290
404	3	.573	.327

$$\frac{A_{d_6} + A_{d_5}}{\text{cyclopropane}} = 0.57$$

[a] Corrected for blank and for ^{13}C isotope.

TABLE II

PHOTOLYSIS OF ACETONE-d_6 PLUS CYCLOPENTANE MIXTURE

T, °C.	T, min.	CD_3H/CD_4[a]	k_H/k_D	$\frac{H_2}{CD_4 + CD_3H}$	HD/H_2
250	2	10.22	11.24	0.01	...
250	4	10.27	11.30	.01	...
306	2	8.48	9.33	.04	...
306	4	8.53	9.38	.03	...
357	1	7.36	8.10	.18	0.029
357	2	7.40	8.14	.18	.032
402	1	6.62	7.28	.28	.038
402	10	6.56	7.22	.27	.038

$$(A_{d_5} + A_{d_6})/CP = 1.10$$

[a] Corrected for blank and for ^{13}C isotope.

For the case of the acetone-d_6 cyclopropane mixtures, in the early stages of reaction

$$k_2/k_1 = (A_2/A_1)e^{(E_1 - E_2)/RT} = \frac{(CD_3H)(CD_3COCD_3)}{(CD_4)(C_3H_6)} = 0.57\,\frac{CD_3H}{CD_4} \qquad (1)$$

The data show that $E_1 - E_2 = -1.8$ kcal. and $A_2/A_1 = 1.3$. Since $E_1 = 11.3$ kcal., it follows that $E_2 = 13.1$ kcal., a much larger value than previously reported. Similarly

$$k_3/k_1 = (A_3/A_1)e^{(E_1 - E_3)/RT} \qquad (2)$$

Examination of the results reveals that $E_1 - E_3 = 2.0$ kcal. and that $A_3/A_1 = 1.65$. Since $E_1 =$

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[1] A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951).

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