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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[CONTRIBUTION FROM THE COMBUSTION BRANCH, CODE 5059 MICHELSON BRANCH, U. S. NAVAL ORDNANCE TEST STATION]

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

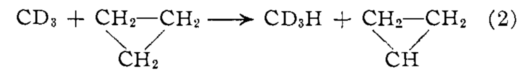
A mixture of acetone-d_6 and cyclopropane in the ratio 0.57 was made up and all cyclopropane experiments were carried out on this mixture. The acetone-d_6 was prepared by exchange with D_2O[2] and analyzed $D/(D + H) = 0.98$. Photolyses were carried out with a Hanovia Medium Pressure Mercury Arc with 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

$$CD_3 + CD_3COCD_3 \longrightarrow CD_4 + CD_2COCD_3 \quad (1)$$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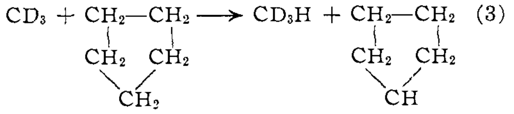
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TABLE I
PHOTOLYSIS OF ACETONE-d_6 IN THE PRESENCE OF CYCLOPROPANE

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

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

[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

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

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

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

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).

[2] J. R. McNesby, T. W. Davis and A. S. Gordon, THIS JOURNAL, **76**, 823 (1954).

[3] J. R. McNesby and A. S. Gordon, *ibid.*, **76**, 4196 (1954).

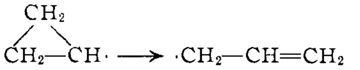
11.3 kcal., E_3 = 9.3 kcal., which is just equal to the value obtained for the abstraction of secondary H from *n*-butane.[4]

The gas chromatographic analysis of the reacted mixture showed that CD_3 radicals failed to sensitize the isomerization of cyclopropane at 375°. This result is to be expected in view of the intramolecular nature of the isomerization.[5-7] The reaction

$$\cdot CH_2CH{=}CH_2 + HR \longrightarrow CH_3CH{=}CH_2 + R\cdot \quad (4)$$

does not proceed under the conditions of the experiments. That allyl radicals are indeed present in the reaction is demonstrated by experiments described below.

The products of the photolysis of acetone-d_6 in the presence of cyclopropane consist principally of CO, methane, ethane, C_4H_8 and methyl ethyl ketone, as well as another partially identified product which may be hexadiene. No hydrogen is observed at any temperature up to 404°. The product C_4H_8 could be butene-1 or methylcyclopropane depending upon the relative concentrations of the allyl and cyclopropyl radicals, as determined in part by the velocity of (5).


(5)

Since the mass spectrum of methylcyclopropane is not available, the following gas chromatography experiment was carried out to determine whether the C_4H_8 product was butene-1 or methylcyclopropane. An amount of butene-1 corresponding approximately to the amount of C_4H_8 in the products was introduced into the reaction mixture after reaction. Since there is a ten-degree difference in the normal boiling points of methylcyclopropane and butene-1, two peaks in the C_4H_8 region would be observed if the reaction product were methylcyclopropane and one if the product were butene-1. A 1.5% squalane–Pelletex column six feet in length was employed with temperature programmed from −196° to room temperature.[8] Under the conditions of the experiment the characteristic elution temperature for butene-1 is −44°. The column used is capable of completely separating propylene and cyclopropane, the former emerging first. The result of the experiment was an enlarged single chromatogram peak with an elution temperature of −44°. This result indicates that the cyclopropyl radical isomerizes to allyl at 375°.

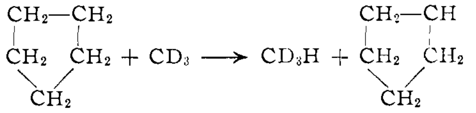
The butene-1, methyl ethyl ketone and ethane fractions from the above gas chromatographic analysis were each trapped and analyzed by the mass spectrometer.[8] The butene-1 fraction was found to contain three D atoms while the methyl ethyl ketone contained eight. The ethane was found to be C_2D_6 and must have been produced by recombination of methyl radicals. The butene arises from

$$CD_3 + \cdot CH_2{-}CH{=}CH_2 \longrightarrow CD_3CH_2CH{=}CH_2 \quad (6)$$

while the methyl ethyl ketone is formed by recombination of acetonyl and methyl radicals.

$$CD_3 + CD_2COCD_3 \longrightarrow CD_3CD_2COCD_3 \quad (7)$$

In the reaction between CD_3 and cyclopentane, hydrogen is an important product above 300° as may be seen in Table II. The presence of hydrogen in the products implies that cyclopentene or a diolefin is also present in the products. Examination of the chromatogram of the products of the reactions at 375° failed to reveal such a product. It is possible that pentadiene is obscured by the cyclopentane parent. The chromatogram shows ethylene to be an important product at 375°. Under the same experimental conditions, the photolysis of acetone-d_6 forms about 5% of the ethylene formed in the photolysis of the acetone-d_6 and cyclopentane mixture. Butene-1 and ethane are present in much smaller concentrations and only trace amounts of propylene are present. These observations are in harmony with these reactions.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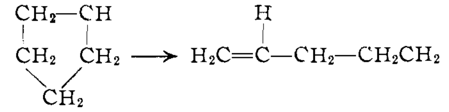
(9)

$$H_2C{=}C{-}CH_2{-}CH_2CH_2\cdot \longrightarrow C_2H_4 + H_2C{=}CHCH_2\cdot \quad (10)$$

The allyl radical is quite stable and does not abstract H appreciably at this temperature. Instead it prefers to react with other radicals, forming hexadiene and butene-1.

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[4] J. R. McNesby and A. S. Gordon, THIS JOURNAL, **78**, 3570 (1956).

[5] E. S. Corner and R. N. Pease, *ibid.*, **67**, 2067 (1945).

[6] R. H. Lindquist and G. K. Rollefson, *J. Chem. Phys.*, **24**, 725 (1956).

[7] J. R. McNesby and A. S. Gordon, *ibid.*, **25**, 582 (1956).

[8] C. M. Drew, J. R. McNesby, S. R. Smith and A. S. Gordon, *Anal. Chem.*, **28**, 979 (1956).