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this and the ambiguity in the excitation energies hinders any numerical estimate of the hybridization. It is interesting, however, to note the close resemblance with nuclear quadrupole coupling effects in molecules⁷ in that

⁷ C. H. Townes and B. P. Dailey, J. Chem. Phys. 17, 782 (1949).

both of them are essentially dependent upon the fraction of the unbalanced p electrons on the atom in question.

We have benefited from many interesting discussions with Dr. H. S. Gutowsky. In addition, Dr. Gutowsky's encouragement and help to one of us (A.S.) while at Illinois is deeply appreciated and gratefully acknowledged.

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Bromination of Hydrocarbons. VII. Bromination of Isobutane. Bond Dissociation **Energies from Bromination Kinetics***

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The kinetics of the gas phase photochemical bromination of isobutane to yield 2-bromo 2-methylpropane was investigated in the temperature range 40-95°C and the reaction found to proceed through an atom and radical chain mechanism analogous to that observed with a number of other hydrocarbons. The thermal reaction was studied at 112 and 130°C and shown to have the same mechanism except for the mode of production of bromine atoms. Bromination was inhibited by hydrogen bromide, a product of the reaction, and also by oxygen. The dissociation energy of the tertiary C-H bond in isobutane was found to be 89.6 kcal/mole at $0^{\circ}K$, in agreement with the idea that tertiary bonds are considerably weaker than primary bonds. A general review of activation energies of bimolecular reactions involved in bromination is given as well as a recapitulation of values of C-H and C-C bond dissociation energies derived from bromination studies.

INTRODUCTION

FROM studies of the kinetics of the gas phase bromination of hydrocarbons and the accompanying inhibition of the reaction by hydrogen bromide it has been possible to determine carbon-hydrogen bond dissociation energies and also enthalpies of formation of the corresponding radicals.¹⁻⁴ In addition, it was possible to compute carbon-carbon bond dissociation energies from these data.³⁻⁵ Thus far these studies have been confined to the bromination of primary carbon-hydrogen bonds in several aliphatic compounds¹⁻³ and also in the alkyl side chain of toluene.^{4,6} It was of interest, therefore, to extend this method to a hydrocarbon containing another type of carbon-hydrogen bond. The compound selected was isobutane which contains a tertiary C-H bond. This would be expected to brominate at a much faster rate than the primary bonds.

MATERIALS

Because of the sensitivity of gas-phase bromination to traces of oxygen, all materials used in the kinetic studies were purified and degassed in a grease-free high vacuum system by the procedure described previously.⁴ The starting materials were: Phillips Petroleum Company research grade isobutane having a purity of 99.88 ± 0.06 mole percent,⁷ Baker and Adamson analytical reagent grade bromine, and Mathieson anhydrous hydrogen bromide of a stated purity of 99.5 percent.

The products of the reaction were identified by means of their infrared spectra obtained with a Perkin-Elmer Model 21, double beam, recording infrared spectrophotometer using a 0.1-mm sodium chloride absorption cell. For comparison spectra the following compounds were purified by fractional distillation: Eastman Kodak Company 2-bromo 2-methylpropane (b. pt. 72.9° at 740 mm), Columbia Organic Chemicals Company 1-bromo 2-methylpropane (b. pt. 37.0°C at 115 mm), and Eastman Kodak Company 1,2-dibromopropane (b. pt. 47.0°C at 30 mm). 1,2-dibromo 2-methylpropane (b. pt. 66°C at 50 mm) was prepared by a procedure suggested by J. Howald. The solvent for all spectrophotometer measurements was Baker and Adamson reagent grade

⁷ According to the manufacturer's certificate quoting the determination of purity by the National Bureau of Standards.

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¹G. B. Kistiakowsky and E. R. Van Artsdalen, J. Chem. Phys. 12, 469 (1944).

² H. C. Andersen and E. R. Van Artsdalen, J. Chem. Phys. 12, 479 (1944).

³ E. I. Hormats and E. R. Van Artsdalen, J. Chem. Phys. 19, 778 (1951).

⁴ Anderson, Scheraga, and Van Artsdalen, J. Chem. Phys. 21, 1258 (1953).

⁵ E. R. Van Artsdalen, J. Chem. Phys. 10, 653 (1942).

⁶ Swegler, Scheraga, and Van Artsdalen, J. Chem. Phys. 19, 135 (1951).

carbon disulfide dried with anhydrous magnesium sulfate.

The reaction mixtures from a considerable number of photochemical runs were combined for the infrared analysis. The brominated product was freed of isobutane, hydrogen bromide, and bromine by washing with aqueous sodium bisulfite and water. This aqueous mixture was extracted with carbon disulfide and dried with anhydrous magnesium sulfate. The resulting solution contained approximately 1 mole percent of brominated hydrocarbon.

EXPERIMENTAL

The design of the apparatus was based on that used previously in the investigation of the bromination of neopentane.³ The reaction was carried out in a cylindrical Pyrex cell having a volume of 103 cc and a surface area of 122 cm². It was kept in an air thermostat in which the temperature could be maintained constant within ± 0.1 °C.

The rate of both the photochemical and thermal reactions was determined by following the rate of disappearance of bromine photometrically, using a system in which a pair of calibrated polaroids was "in series" with the reaction cell. The photometer employed light at 4358A from a General Electric AH-4 mercury vapor lamp as a measuring beam and an RCA 931A photomultiplier tube as light sensitive element. The light intensity from the AH-4 lamp was sufficiently low so that no measureable photochemical activation was induced by the measuring system. The photochemical reaction was interrupted at regular time intervals by means of a shutter to permit making the photometric determination of the amount of bromine remaining. In these experiments the light intensity on the photomultiplier tube was kept constant by decreasing the transmission of the polaroids as the transmission through the cell increased because of the disappearance of bromine during the course of the reaction. The bromine concentration at any time was therefore obtainable from the polaroid setting required to maintain constant light intensity on the photomultiplier tube. The system was calibrated before each run by determining the polaroid settings at a series of bromine pressures. An alternate reference optical path served to check on the constancy of the light intensity of the photometer lamp. Because the *thermal* reaction could not be interrupted for transmission measurements the rate of disappearance of bromine was followed by measuring the increase in photocell output at constant polaroid setting. Again each run was preceeded by a calibration.

The photochemical reaction was initiated by light from a General Electric AH-5 mercury vapor lamp. Corning filters were used in conjunction with a water filter to yield light of which 96 percent was between 4047 and 5780A. It has been shown⁸ that light absorbed at

wavelengths shorter than 5780A is effective in dissociating bromine molecules and that bromine atoms produced by predissociation show about the same reactivity as those dissociated in a primary act. In the temperature range employed here the absorption coefficient of bromine is essentially independent of temperature.9 The activating beam was at right angles to the measuring beam, and it could be interrupted at will by a shutter so that the bromine pressure at any time during the reaction could be determined. It was established that the total amount of reaction depended only on the total time of illumination, and not on the frequency of the interruptions, other things being constant. This is of course true only as long as the periods of illumination and of darkness are very long compared to the time required to attain the steady-state concentrations of atoms and radicals, which was the case in this investigation. To assure constant light intensity for all the photochemical experiments, the output of the AH-5 lamp was monitored by means of a circuit similar to that described by Wood.¹⁰

The reaction cell was attached to an all-glass highvacuum system in which all stopcocks exposed to either bromine or hydrogen bromide were lubricated with Du Pont Perfluorolube FCX-334. All other stopcocks were lubricated with Apiezon "N." Initial pressures of all reactants were measured using a quartz spiral manometer as a null point instrument.

No pyrolysis of isobutane^{11,12} or tertiary butyl bromide¹³ occurs in the temperature range employed here. Also no appreciable thermal reaction occurred at the highest temperatures used in the photochemical experiments.

Initial rates of reaction were determined by short extrapolations to zero time of reaction; these initial rates of reaction were used in all subsequent calculations of rate constants, inhibition effects, and temperature coefficients. Thus, the effects of secondary bromination were eliminated.

RESULTS

According to the work of Hass, McBee, and Weber¹⁴ on the chlorination of simple paraffin hydrocarbons it may be expected that bromination of isobutane would take place predominantly at the tertiary carbon atom at the temperatures employed here. The work of Vaughan and Rust¹⁵ on the oxidation of aliphatic hydrocarbons and the studies of Moore and Wall¹⁶ on the reaction

⁹ Acton, Aickin, and Bayliss, J. Chem. Phys. 4, 474 (1936).

 ¹⁰ L. A. Wood, Rev. Sci. Instr. 7, 157 (1936).
 ¹¹ A. D. Stepukhovich, J. Gen. Chem. (USSR) 15, 341 (1945).
 ¹² E. W. R. Steacie and I. E. Puddington, Can. J. Research 16B,

^{260 (1938).} ¹³ G. B. Kistiakowsky and E. H. Stauffer, J. Am. Chem. Soc. **59**, 165 (1937).
 ¹⁴ Hass, McBee, and Weber, Ind. Eng. Chem. 27, 1190 (1935);

^{28, 333 (1936).} ¹⁵ W. E. Vaughan and F. R. Rust, U. S. Patent No. 2,395,523

⁽¹⁹⁴⁵⁾

⁸ W. Jost, Z. Physik. Chem. B3, 95 (1929). See also reference 1.

¹⁶ W. J. Moore and L. A. Wall, J. Chem. Phys. 17, 1325 (1949).





between hydrogen atoms and isobutene gave further support to the feeling that the principal point of attack would be the tertiary carbon atom. This anticipated result was borne out by infrared analysis¹⁷ of the products of the photochemical reaction.

If the tertiary hydrogen is replaced by bromine the product is 2-bromo 2-methylpropane. If the bromination were allowed to continue some of this product would be converted to 1,2-dibromo 2-methylpropane. On the other hand, if bromination takes place on a primary carbon 1-bromo 2-methylpropane would be formed. Another possible product could arise if the tertiary butyl radical, postulated as an intermediate in the free radical bromination at the tertiary carbon atom, were unstable and decomposed into methyl radicals and propylene. If so, the latter, upon bromination, would yield 1,2dibromopropane. The infrared spectra of 1 mole percent solutions of each of these brominated hydrocarbons in carbon disulfide are reproduced in part in Figs. 1 and 2. Several peaks were readily identified and quantitative criteria were established for the smallest concentrations of each of these brominated hydrocarbons in carbon

¹⁷ We are indebted to Professor D. F. DeTar and Mr. T. Wentink for aid in the infrared analyses.

disulfide which would give unambiguously discernible peaks. Their wavelengths, good to $\pm 0.02\mu$, are shown next to the peaks in Figs. 1 and 2.

A comparison of the several curves leads to the conclusion that the principal product of the reaction between bromine and isobutane is 2-bromo 2-methylpropane (see Figs. 1b and 1c). The two extra peaks at 9.08μ and 10.16μ of Fig. 1c indicate that between 5 and 10 percent of the main product was brominated further to give 1,2-dibromo 2-methylpropane (see also Fig. 2a). Since the reaction was generally allowed to proceed until about one-fourth of the initial amount of bromine was used up, this result is not unreasonable.

From the established limits of detectability it may further be concluded that much less than 5 percent of the brominated product is 1,2-dibromopropane on the basis of the peaks at 8.46μ and 9.97μ (Fig. 2c), and that much less than 5 percent is 1-bromo 2-methylpropane on the basis of the peak at 7.60μ (Fig. 2b). No trace of any of these peaks was visible in the reaction products although they were discernible in reference solutions at the corresponding concentrations.

On the basis of these results the gas phase bromination of isobutane may be represented by the following over-all reaction

$$tBH+Br_2=tBBr+HBr,$$
 (I)

where tB represents the tertiary butyl radical $(CH_3)_3C_{\cdot}$, and tBH and tBBr represent isobutane and tertiary butyl bromide, respectively. It is, therefore, valid to base the kinetic study on the observed rate of disappearance of bromine in light of Eq. (I).

The empirical rate law for the initial part of the photochemical reaction at constant light intensity was determined at 78.3°C and found to be

$$-d(\mathrm{Br}_2)/dt = k_p(\mathrm{Br}_2)^{\frac{1}{2}}(tBH)(P)^{-\frac{1}{2}},$$
 (II)

where k_p is the photochemical rate constant and P is the total pressure of reactants. Values of k_p at several temperatures are given in Table I. The two series of measurements correspond to different apparatus constants, involving also changes in incident light intensity, which appear in k_p .

The bromination was found to be inhibited by HBr, and the rate law was modified to

$$-\frac{d(Br)_2}{dt} = \frac{k_p(Br_2)^{\frac{1}{2}}(tBH)(P)^{-\frac{1}{2}}}{1+n(HBr)/(Br_2)}.$$
 (III)

Data on the inhibited reaction are presented in Table II, where the values of n were computed from the known values of k_p at each temperature from the data of series B of Table I. Both the measurements in series B for uninhibited runs and those of Table II for inhibited runs were made at the same light intensity and with the same apparatus constant.

The temperature dependence of k_p and n are shown in Figs. 3 and 4, respectively. The data have been treated

 TABLE I. Photobromination of isobutane at constant light intensity (wavelength 4047-5780A).

	Initial (mm	pressures at <i>t</i> °C)	Initial rate $(-d[Br_2]/dt)$	
t°C	Br ₂	<i>tB</i> H	(mm/min)	<i>kp</i> (min ⁻¹)
		Series A, lig	ht intensity I_0'	
49.9	29.2	147.8	1.22	0.0203
	29.1	143.6	1.21	0.0205
	17.2	242.9	1 25	0.0200
	17.3	241.7	1.24	0.0198
				0.0202 ± 0.0002
64.1	30.9	141.3	2,65	0.0443
	30.1	139,9	2.50	0.0425
	30.0	138.5	2.55	0.0436
	29.7	136.5	2.52	0.0437
				0.0435 ± 0.0005
78.3	29.8	104.4	4.40	0,0894
	30.0	106.7	4.37	0.0874
	30.0	158.7	5.55	0.0877
	30.0	219.0	6.55	0.0862
	30.3	220.5	6.63	0.0865
	29.9	323.8	8.30	0.0882
	29,5	324.2	8.20	0.0876
	14.5	154.1	3.90	0.0863
	18.0	157.4	4.45	0.0883
	18.4	157.4	4.55	0.0894
	43.1	147.4	6.15	0.0877
	49.2	147.0	6.50	0.0883
				0.0878 ± 0.0008
94.9	31.3	143.7	11.20	0.184
	30.7	140.2	10.68	0.180
	31.3	138.9	12.30	0.206
	30.5	138.8	10.40	0.177
	18.7	199,6	11.00	0.188
	18.4	189.6	11.50	0.204
	18.2	189.2	10.20	0.182
				0.189 ± 0.007
		Series B, lig	ght intensity Is	
40.3	20.2	226.1	2.60	0.0340
10.0	20.6	165.4	2 38	0.0369
	28.0	162.8	2.03	0.0325
	28.5	162.8	2.08	0.0331
	29.6	161.8	2.17	0.0341
				0.0341 ± 0.0009
48.7	28.7	185.8	3,75	0.0552
	27.9	182.7	3.85	0.0579
	30.1	181.9	3.93	0.0573
	27,9	181.3	3.85	0.0581
	27.9	181.6	3,80	0.0573
				0.0572 ± 0.0008
66.2	32.2	115.0	8.45	0.157
	29.7	116.5	8.00	0.152
	30.0 31.5	215.5 213.9	10.05	0.133 0.140
	01.0	#10,7	*U,/ U	0.146.1.0.000
				0.140±0.009
84.9	29.6	160.7	22.4	0.353
	30.3	160.3	22.8	0.356
	30.9	160,3	22.9	0.355
				0.354 ± 0.001

TABLE II. Photobromination of isobutane at constant light intensity, I_0 (wavelength 4047-5780A); inhibition by hydrogen bromide.

	In	itial pressu (mm at t °C	ire 2)	Initial rate $(-d\Gamma Br_{\circ})/dt$	
t°C	Br ₂	HBr	tBH	(mm/min)	nª
40.3	28.2	48.6	209.7	1.34	0.391
	27.1	59.4	199.3	1.51	0.176
	27.5	47.1	145.7	0.975	0.467
	28.7	61.7	139.8	1.00	0.318
	29.1	58.8	200.0	1.19	0.407
	29.0	60.3	138.3	0.950	0.371
					0.355 ± 0.072
48.7	27.6	61.3	163.4	1.57	0.436
	28.2	59,6	165.3	1.48	0.535
	28.5	57.0	161.4	1.52	0.531
	29.0	61.0	158.6	1.55	0.475
	29.3	46.6	160.4	1.84	0.475
					0.490 ± 0.034
66,2	28.7	65.3	197.7	2.85	0.957
	28.8	65.4	198.3	2.95	0.916
	29.4	47.1	212.1	4.10	0.881
	29.0	51.9	200.7	3.26	1.053
					0.952 ± 0.053
84.9	29.8	63.0	214.0	5.00	1.76
	29.4	61.5	212.4	5.20	1.67
	29.9	60.7	211.2	5.10	1.78
	29.9	25.2	209.6	10.05	1.76
	30.1	109.6	189.7	2.85	1.68
	18.5	60.6	201.4	2.65	1.80
	47.2	45.1	200.3	10.75	1.73
					1.74 ± 0.04

* The values of n were calculated using the values of k_p given in series B, Table I, for the corresponding temperatures.

by the method of least squares and the following equations were obtained:

For series A

$$\log_{10}k_p = 6.3101 - 2588/T.$$
 (IV)

For series B

$$\log_{10}k_p = 6.6463 - 2541/T.$$
 (V)

It should be noted that Eqs. (IV) and (V) give k_p in



FIG. 3. Temperature dependence of photobromination of isobutane for two series of measurements.

min⁻¹. For n

$$\log_{10}n = 5.1062 - 1742/T.$$
 (VI)

From Eqs. (IV) and (V) the experimental activation energy is 11.7 ± 0.1 kcal/mole. From Eq. (VI) the apparent activation energy of inhibition is 8.0 ± 0.2 kcal/mole.

The effect of change of incident light intensity on the rate of the photochemical reaction was investigated at 78.3 °C by introducing a calibrated screen of 25.9 percent transmission into the light path. The results are shown in Table III. Assuming that $k_p = kI^a$, where k is independent of light intensity and a is the experimental order in light intensity, then the ratio of rate constants at light intensities I_0' and $0.259I_0'$ is $(I_0')^a/(0.259I_0')^a = 0.0878/0.0438$ giving a value of a = 0.53, which indicates a half-power dependence on light intensity.

Oxygen in small amounts inhibited the reaction. In large amounts the initial inhibition was followed by a rapid disappearance of bromine.

The thermal reaction was studied at two temperatures with no HBr present initially. Values of the specific



FIG. 4. Temperature dependence of inhibition by hydrogen bromide of photobromination of isobutane.

reaction rate constant k_t for the thermal reaction were computed from the empirical rate law

$$-d(\mathrm{Br}_2)/dt = k_t(\mathrm{Br}_2)^{\frac{1}{2}}(tB\mathrm{H}) \qquad (\mathrm{VII})$$

and are given in Table IV. These data give an activation energy of 35.6 kcal/mole which must be regarded as only an approximate value since only 3 runs were carried out at 112.4°C and data at only 2 temperatures are available for this computation.

Three thermal runs were carried out with HBr added initially, the inhibition constant n being computed from the equation

$$-\frac{d\left(\mathrm{Br}_{2}\right)}{dt} = \frac{k_{t}\left(\mathrm{Br}_{2}\right)^{\frac{1}{2}}\left(tB\mathrm{H}\right)}{1+n\left(\mathrm{HBr}\right)/\left(\mathrm{Br}_{2}\right)}.$$
 (VIII)

The data are shown in Table V. n was found to be approximately 4.3. Subsequent discussion will show that at any given temperature the value of n should be the same for both the thermal and the photochemical reaction. Extrapolation of the photochemical data would lead to a value of 6.1 for n at 130.2°C, the temperature (1)

of these experiments. Since so few runs were carried out on the inhibited thermal reaction more confidence must be placed in the value of *n* obtained photochemically. It should also be pointed out that even in the photochemical experiments the value of n is not determinable with high precision. The agreement shown here between the values 4.3 and 6.1 is therefore quite good.

DISCUSSION

The experimental data presented above can be accounted for by the following mechanism:

or

$$Br_2 + h\nu = 2Br \tag{1}$$

$$Br_2 + M = 2Br + M \tag{1a}$$

$$Br+tBH=HBr+tB$$
 (2)

$$tB + Br_2 = tBBr + Br \tag{3}$$

$$tB + HBr = tBH + Br$$
 (4)

(5) $2Br+M=Br_2+M$.

The usual steady-state assumption for the concentrations of Br atoms and tB radicals leads to the

TABLE III. Photobromination of isobutane at reduced light intensity, 0.259I₀' (wavelength 4047-5780A).

	Initial pressure (mm at t°C)		Initial rate $(-d[Br_1]/dt)$		
t°C	Br:	<i>tB</i> H	(mm/min)	<i>k</i> _p (min ^{−1})	
78.3	30.0 30.2	144.6 144.2	2.60 2.65	0.0434 0.0441	
				0.0438	

following rate expressions:

For the photochemical reaction initiated by step (1)

$$-\frac{d(\mathrm{Br}_2)}{dt} = \frac{k_2 k_1^{\frac{1}{2}}}{k_5^{\frac{1}{2}}} \frac{(tBH)(\mathrm{Br}_2)^{\frac{1}{2}}(M)^{-\frac{1}{2}}}{[1+k_4(\mathrm{HBr})/k_3(\mathrm{Br}_2)]}.$$
 (IX)

For the thermal reaction initiated by step (1a)

$$-\frac{d(\mathrm{Br}_2)}{dt} = \frac{k_2 k_{1a}^{\frac{1}{2}}}{k_5^{\frac{1}{2}}} \frac{(tBH)(\mathrm{Br}_2)^{\frac{1}{2}}}{[1+k_4(\mathrm{HBr})/k_3(\mathrm{Br}_2)]}.$$
 (X)

These rate expressions derived from the postulated mechanisms agree with the empirical rate laws [Eqs. (III) and (VIII)] if one sets M=P, $n=k_4/k_3$, k_p $=k_2(k_1/k_5)^{\frac{1}{2}}$, and $k_t=k_2(k_{1a}/k_5)^{\frac{1}{2}}$. It should be noted that $k_{1a}/k_5 = K$, the equilibrium constant for the thermal dissociation of bromine molecules, and one may therefore write $k_t = k_2 K^{\frac{1}{2}}$. Also, k_1 is used here as a short-hand notation for the expression $k_{app}\alpha I_0$ where k_{app} is a temperature-independent apparatus constant and α is the absorption coefficient of Br₂ for light of incident intensity I_0 for the wavelength range employed.

The reasons for not considering other possible ele-

TABLE IV. Thermal bromination of isobutane.

t°C	Initial p (mm at Br2	ressure t°C) tBH	Initial rate (-d[Br2]/dt) (mm/sec)	$k_i([cc/mole]^{\frac{1}{2}} sec^{-1})$
130.2	33.4	171.0	0.0460	0.233
	34.5	168.6	0.0430	0.218
	34.6	164.6	0.0465	0.241
	33.9	166.3	0.0490	0.258
	21.8	164.9	0.0350	0.228
	21.7	165.7	0.0360	0.234
	53.4	154.1	0.0565	0.252
	65.4	145.4	0.0560	0.239
	45.4	152,7	0.0480	0.234
	33.8	120.6	0.0325	0.232
	33.0	260.4	0.0720	0.241
	34.0	371.0	0.1025	0.238
				0.237 ± 0.007
112,4	32.7	242.9	0.0089	0.0314
	32.0	204.7	0.0071	0.0301
	32.4	203.3	0.0072	0.0305
				0.0307 ± 0.0005

mentary reactions in the over-all mechanism have been discussed previously.^{1,3,4} Also, while the infrared analyses indicated that about 5 to 10 percent of the 2-bromo 2-methylpropane was further brominated to give 1,2dibromo 2-methylpropane, this secondary bromination does not influence the rate constants since the latter were calculated from the *initial* rate of disappearance of bromine. In addition, these analyses show that no consideration need be given to products other than tBBr.

It is readily apparent that on the basis of the proposed mechanism the value of $n = k_4/k_3$ should be the same for both the photochemical and thermal bromination at any given temperature. Within the large experimental error involved in the determination of this inhibition constant this similarity is seen to exist.

As shown previously,¹⁻⁴ the experimental activation energy of 11.7 kcal/mole for the photochemical reaction may be assigned to step (2). Since the thermal rate constant is $k_t = k_2 K^{\frac{1}{2}}$ it follows that the experimental activation energy, $E_A = 35.6$ kcal/mole, of the thermal reaction may be written

$$E_A = E_2 + \frac{1}{2}\Delta H \tag{XI}$$

where ΔH is the heat of dissociation of Br₂. At 394°K, the mean temperature of the thermal runs, $\Delta H = 46.2$

TABLE V. Thermal bromination of isobutane at 130.2°C; inhibition by hydrogen bromide.

Initial pressure (mm at 130.2°C)			Initial rate	
Br	HBr	tBH	(mm/sec)	nª
34.2	64.5	198.7	0.00685	3.79
34.1	59.3	197.6	0.00580	4.83
32.8	61.8	198.9	0.00604	4.20

* *n* was calculated using the value $k_t = 0.237 \text{ (cc/mole)}^{\frac{1}{2}} \text{ sec}^{-1}$.

TABLE VI. Activation energies of bimolecular reactions involved in brominations.*

Reaction	E_A (kcal/mole)	Temp. range (°C)	Reference
H_2+Br	17.2 ± 0.6	160-218	ь
H+HBr	0	160-218	b
CH₄+Br	17.8 ± 0.4	150-230	с
CH ₁ +HBr	about 2	150-230	с
CH ₃ Br+Br	15.6 ± 1.0	150-230	с
$C_2H_6 + Br$	13.3 ± 0.5	35-90	d
$C_2H_5 + HBr$	assumed 0.8		d
C_5H_{12} +Br	17.8 ± 0.3	98-152	е
C _s H ₁₁ +HBr	9.6 ± 2	98-152	е
C ₆ H ₅ CH ₂ +Br	7.2 ± 0.6	82-132	f
C ₆ H ₅ CH ₂ +HBr	5.0 ± 1.2	82-132	f
$i - C_4 H_{10} + Br$	11.4 ± 0.2	40-95	this work
t-C4H9+HBr	7.7 ± 0.3	40- 85	this work

* All_activation energies have been obtained from photochemical reactions. They have been corrected for the temperature dependence of the frequency factor by subtracting RT/2 from the experimental activation

energies. ^b M. Bodenstein and H. Luetkemeyer, Z. Physik. Chem. 114, 208 (1925). See reference 1.
 d See reference 2.

See reference 3.

See reference 4

kcal/mole¹⁸ giving a value of 12.5 kcal/mole for E_2 . Considering the small number of thermal runs at 112.4°C, the appreciably different temperature regions, and the fact that only two temperatures were employed, this may be considered good agreement with the more reliable photochemically determined value of 11.7 kcal/mole.

It has also been shown 1-4 that the apparent activation energy of inhibition by HBr, 8.0 kcal/mole, is equal to E_4-E_3 and that E_3 may be regarded as negligibly small. Therefore, we may write

$$E_4 - E_3 \cong E_4 = 8.0$$
 kcal/mole.

The activation energies for steps 2 and 4 are listed, together with the analogous steps involved in previous bromination studies in this series, in Table VI.

The mechanisms proposed here for the photochemical and thermal reactions appear to be well substantiated by (a) the analysis of the reaction products, (b) the good precision of the rate constants, and (c) the agreement between the values of E_2 and n obtained from both the photochemical and thermal experiments. An interesting aspect of the reaction mechanism is made evident if one attempts to compute a steric factor on the basis of the collision theory. If the thermal rate constant k_t is represented in terms of K and k_2 , and if k_2 is written in

TABLE VII. Heats of formation and dissociation in isobutane.

Т°К	$\Delta H_f(tB)$ kcal/mole	D(tB-H) kcal/mole
0	13.4+0.6	89.6±0.6
298	7.5 ± 0.5	91.1 ± 0.5
335	7.1 ± 0.5	91.3 ± 0.5

¹⁸ U. S. National Bureau of Standards, Selected Values of Chemical Thermodynamic Properties, Series III, Washington, D. C., 1948, and Circular 500, Washington, D. C., 1952. the Arrhenius form, it is found that the frequency factor A_2 is 3.76×10^{17} (cc/mole) sec⁻¹ at 403.4°K (130.2°C). Using 3.0A as the collision diameter of the bromine atom³ and 4.6A for that of the isobutane molecule,¹⁹ the collision number at that temperature is found to be $Z_2 = 1.37 \times 10^{14}$ (cc/mole) sec⁻¹. Then if one introduces a steric factor s_2 to account for the discrepancy $(A_2 = s_2 Z_2)$, s_2 is found to be 2740, an abnormally high result. One may explain this large steric factor on a basis similar to that used to account for the extremely large rates of many unimolecular gas reactions. If several vibrational degrees of freedom can contribute to the energy of activation of the bimolecular reaction step 2 then the fraction of the molecules activated on collision will be greater^{19a} than $e^{-E/RT}$. If approximately 4 degrees of vibrational freedom contribute, then k_2 will be several thousand times larger than that computed from the collision number and the simple factor $e^{-E/RT}$, in agreement with the value 2740. The computed factor, s_2 , would not be regarded as a steric factor in light of such an explanation but rather as a manifesta-

TABLE VIII. Carbon-hydrogen bond dissociation energies at 0°K.

Bond	Dissociation energy (kcal/mole)	Reference
CH ₃ -H	101.6±1.0*	b
CH ₂ Br-H	99 ±2.5 [∗]	ь
$C_2H_5 - H$	98.5±2.0*	с
(CH ₃) ₃ CCH ₂ -H	$94.0 \pm 2.5^{*}$	d
$(CH_3)_2C-H$	89.6 ± 0.6	this work
$C_6H_5CH_2-H$	88.1 ± 1.4	e

Recomputed from original data using the more recently determined heat of formation of HBr (see reference 18). ^b See reference 1. ^c See reference 2.

^d See reference 3. • See reference 4.

tion of the contribution of vibrational degrees of freedom to the energy of activation.

BOND DISSOCIATION ENERGIES

As used here the term "bond dissociation energy" refers to the enthalpy change for the dissociation of a particular bond in a molecule to yield two atomic or molecular fragments.

Since the number of molecules of reactants and products are equal for the reaction tBH+Br=tB+HBr, we may equate the enthalpy change to $E_2 - E_4$ to obtain $\Delta H_{335} = 3.7$ kcal/mole at 335°K, the mean temperature of the photochemical experiments. This may be combined with the heat of formation of hydrogen bromide¹⁸ in the following manner:

tBH+Br=tB+HBr HBr=H+Br	$\Delta H_{335} = 3.7 \text{ kcal/mole} \\ = 87.6 \text{ kcal/mole}$
tBH = tB + H	$\Delta H_{335} = 91.3 \text{ kcal/mole}$

¹⁹ T. Titani, Bull. Chem. Soc. Japan, 5, 98 (1930).
 ^{19a} See, for example, L. S. Kassel, Kinetics of Homogeneous Gas Reactions, Chemical Catalog Company, Inc., Chap. II, III (1932).

to give the bond dissociation energy D(tB-H) = 91.3kcal/mole at 335° K. The tertiary C-H bond dissociation energies in isobutane at several temperatures are given in Table VII. In computing enthalpy changes at temperatures other than 335°K National Bureau of Standards data¹⁸ were used, and it was assumed that the heat capacities of isobutane and the tertiary butyl radical are approximately equal. The value at 0°K is compared in Table VIII to those for primary C-Hbonds which were also determined from bromination kinetics.

It is of interest to consider further the value for isobutane. As expected it is considerably lower than that for the various aliphatic primary C-H bonds and is roughly comparable to the strength of that bond in the aliphatic side chain of toluene. Numerous investigators, e.g., Kossiakoff and Rice,20 have concluded on the basis of such evidence as thermal decompositions, resonance stabilization, the isomerization of free radicals, etc. that the strength of the tertiary C-H bond should be about four kilocalories lower than that of the primary. This conclusion is borne out by the present work.

TABLE IX. Heats of formation of radicals at 0°K from bromination kinetics.

Radical	ΔH_f kcal/mole	Reference
methyl	34.0±1.0ª	b
ethvl	30.4 ± 2.0^{a}	с
t-butyl	13.4 ± 0.6	this work
neopentyl	11.1±2.5*	d
benzyl	53.9 ± 1.4	e

* Recomputed from original data and more recent heats of formation. ^b See reference 1. See reference 2.

^d See reference 3. ^e See reference 4.

The value of 89.6 kcal/mole agrees well with the value of 89.5 kcal/mole $(3.8_8 \pm 0.1 \text{ ev})$ which Stevenson²¹ obtained for the same bond by the electron impact method. Both of these values are somewhat higher than the 86.0 kcal/mole reported by Butler and Polanyi,²² based upon extensive studies of the rate of pyrolysis of certain alkyl halides. The difference may be due to their assumption about the dependence of the heat of substitution on the nature of the R group in the reaction RH+X=RX+H as R varies in the alkane series. This discrepancy has also been discussed by Stevenson.²¹

Using the value of 89.6 kcal/mole for the dissociation energy of the tertiary carbon-hydrogen bond in isobutane the heat of formation of the t-butyl radical can

TABLE X. Carbon-carbon bond dissociation energies at 0°K.

Bond	Dissociation energy (kcal/mole)
CH ₃ -CH ₃	84.5±2.0
$C_2H_5-CH_3$	83.9 ± 3.0
$C_2H_5 - C_2H_5$	84.1 ± 4.0
Np-CH ₃	79.7 ± 3.5
$Np-C_2H_5$	79.5 ± 4.5
$tB - CH_3$	78.7 ± 1.6
$tB-C_2H_5$	78.4 ± 2.6
tB-tB	67.9 ± 1.2
$C_6H_5CH_2-CH_3$	74.0 ± 2.4
$C_6H_5CH_2-C_2H_5$	74.5 ± 3.4

be calculated.

$$\Delta H_f(tB) = \Delta H_f(tBH) - \Delta H_f(H) + D(tB - H)$$

= -24.6- (+51.6)+89.6
= +13.4 kcal/mole at 0°K.

For this computation the heats of formation of isobutane and hydrogen were obtained from the data of the Bureau of Standards.^{18,23} The low value of the heat of formation of the *t*-butyl radical at 335°K (Table VII) indicates that this radical is fairly stable. The decomposition of t-butyl radicals into methyl radicals and propylene is improbable since the reaction is endothermic to the extent of about 29 kcal/mole at 0°K. Even the slight increase in entropy which probably accompanies this reaction will not make the free energy change favorable for decomposition. Also, the rearrangement of t-butyl to isobutyl radical is unlikely; in fact, according to the work of Moore and Wall¹⁶ it is likely that the rearrangement of isobutyl to *t*-butyl radicals is favored. All of these factors are in accord with the absence of bromides other than tBBr in the reaction products as found in the infrared analyses.

The heats of formation of other radicals have been calculated in the same manner and are given in Table IX.

It is now also possible to calculate various carboncarbon bond dissociation energies. For example, in neopentane (NpH)

$$D(tB - CH_3) = \Delta H_f(tB) + \Delta H_f(CH_3) - \Delta H_f(NpH)$$

= +13.4+34.0- (-31.3)
= +78.7 kcal/mole.

Similar calculations can be carried out for other compounds and the results are shown in Table X. Again, the heats of formation were obtained from data of the National Bureau of Standards.^{18,23} It is interesting to observe the magnitude of the lowering of the dissociation energy of aliphatic carbon-carbon bonds by the introduction of chain branching or a phenyl group.

²⁰ A. Kossiakoff and F. O. Rice, J. Am. Chem. Soc. 65, 590 (1943).

²¹ D. P. Stevenson, Discussions Faraday Soc. 10, 35 (1951)

²² E. T. Butler and M. Polanyi, Trans. Faraday Soc. 39, 19 (1943).

²³ U. S. National Bureau of Standards Circular 461, Selected Values of Properties of Hydrocarbons, Washington, D. C., 1947.