Bromination of Hydrocarbons. I. Photochemical and Thermal Bromination of Methane and Methyl Bromine. CarbonHydrogen Bond Strength in Methane

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The photochemical bromination of methane was studied in the temperature range 423–503°K and found to proceed through the following chain mechanism:

$$(1) \quad Br_2 + h\nu = Br + Br$$
$$(2) \quad Br + CH_4 = CH_3 + HBr$$
$$(3) \quad CH_3 + Br_2 = CH_3Br + Br$$
$$(4) \quad CH_3 + HBr = CH_4 + Br$$
$$(5) \quad Br + Br + M = Br_2 + M.$$

Bromination of methyl bromide is analogous and from 7.5 to 10 times more rapid in this temperature range. Hydrogen bromide inhibits bromination of methane but not of methyl bromide. Thermal bromination was studied at 570°K and found to follow the same mechanism as photochemical reaction, except that bromine atoms are produced thermally. The activation energy of photochemical bromination of methane is 17.8 kcal./mole and that of methyl bromide is 15.6 kcal./mole. Varying efficiencies of different molecules as third bodies in the homogeneous recombination of bromine atoms are discussed. Configurations of activated complexes have been assigned and by statistical mechanical calculations shown to be reasonable. Activation energies and other data have been combined to arrive at a value for the C—H bond strength in methane of 102 kcal./mole at room temperature.

SUBSTITUTION reactions of bromine with paraffins are known to yield bromo-paraffins and hydrogen bromide. They have not been studied kinetically heretofore. Coehn and Cordes[1] have investigated the photochemical chlorination of methane and reported that it is analogous to the hydrogen chloride reaction. Other writers[2] have suggested that bromination should take place in a similar type of chain mechanism. It was felt that a thorough study of the bromination of paraffins might lead to valuable methods for determining strengths of several carbon-hydrogen and carbon-carbon bonds. This has proved to be the case.[3]

REAGENTS AND MATERIALS

Methane of extremely high purity was prepared jointly with Dr. E. E. Roper by decomposition of a methyl grignard reagent with

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[1] A. Coehn and H. Cordes, Zeits. f. physik. Chemie **B9**, 1 (1930).
[2] H. J. Schumacher, X. Congr. Int. di Chimica **IV**, 464 (1938); J. W. T. Spinks, Chem. Rev. **26**, 129 (1940).
[3] Andersen, Kistiakowsky, and Van Artsdalen, J. Chem. Phys. **10**, 305 (1942). E. R. Van Artsdalen, *ibid*. **10**, 653 (1942); H. C. Andersen and G. B. Kistiakowsky, *ibid*. **11**, 6 (1943).

ethanol. It was anticipated that oxygen would inhibit photochemical bromination, hence great pains were taken to exclude air, preparation being accomplished under vacuum conditions using reagents repurified especially. The methane was distilled from a trap in liquid air to one in liquid nitrogen ($-188°$ to $-197°$) and showed a distillation pressure between 12 and 12.5 mm. Vapor pressure determinations with different amounts vaporized indicated that the methane was extremely pure.

Mallinckrodt bromine, A.R. grade, was purified further by storing over pure potassium bromide to eliminate chlorine. It then was distilled under vacuum through a drying tube containing P_2O_5. Alternate freezing and melting of the sample under high vacuum was carried out to eliminate traces of air. In a final distillation the middle third was retained for this investigation.

A sample of methyl bromide, about 99.8 percent pure, was donated for this work by The Dow Chemical Company. It was purified further by repeated bulb-to-bulb distillations under vacuum until no further change in its vapor pressure in a dry-ice acetone bath could be detected. Its vapor pressure at 0°C was 677 mm. Approximately 95 percent was distilled from a dry-ice bulb into a reservoir flask. The vapor pressure of the 5 percent residuum was 674 mm. Kemp and Egan[4] give 675.8 mm as the vapor pressure at 0°C.

Hydrogen bromide was prepared by the direct union of electrolytic hydrogen and A.R. grade bromine, according to the method outlined by Ruhoff, Burnett, and Reid.[5] Repeated bulb-to-bulb distillations (dry-ice to liquid air) were made of the product under vacuum, voiding considerable hydrogen bromide. The purified material formed a clear, colorless liquid and a perfectly white solid. Its vapor pressure was 320 mm at $-81°C$.

EXPERIMENTAL METHOD

Bromination was followed by observing the rate of disappearance of bromine from the reaction system. For this purpose a photoelectric photometer of balanced construction was used.

Light of wave-length greater than 4360A was eliminated by Corning violet filter, No. 511. Immediately prior to each set of measurements, the photometer was calibrated against known pressures of bromine measured with a quartz spiral null-point manometer against a glass scale mercury manometer. In general it was possible to reproduce bromine partial pressures to ±0.1 mm. Ability to rotate the photometer between two fixed paths, one of which passed through the reaction cell and the other through a comparison cell, made it possible to check the zero setting of the photometer immediately before and after each individual determination of bromine concentration.

A Pyrex glass reaction cell of about 82-cc volume and 106-cm^2 wall area was supported in a fixed position in an electrically heated glass air bath which was made large in comparison with the cell in order to minimize thermal gradients. Temperature was measured to 0.1° with a thermocouple and controlled to $\pm0.2°$–0.3°. Dead space was about 2–2.5 cc which is not serious for these bromination reactions in which there is no volume change.

The reaction mixture was illuminated in the photo experiments by blue light (from a 750-watt Mazda projection lamp) filtered through 0.5″ of water and 4.54-mm Corning blue-green filter No. 430 to eliminate red and infra-red radiation. Constant amperage through the lamp circuit was maintained by manual rheostat control. The axis of illumination was perpendicular to the photometer path. All lamps, air bath windows, and filters were cleaned with alcohol prior to each set of measurements.

Bromine predissociation in the band region yields two normal bromine atoms, while dissociation in the continuum gives one normal atom and one excited atom. Jost[6] has shown that there is no very appreciable difference between using light in the band region or in the continuum to activate photochemical formation of hydrogen bromide, indicating that the electronic excitation energy is not useful in the reaction. Most of the radiation in our experiments was in the continuum. Bromine was the only substance present which absorbed any light of the wave-lengths used.

[4] J. D. Kemp and C. J. Egan, J. Am. Chem. Soc. 60, 2097 (1938).
[5] Ruhoff, Burnett, and Reid, *Organic Syntheses* (John Wiley & Sons, Inc., New York, 1935), Vol. XV, p. 35.
[6] W. Jost, Zeits. f. physik. Chemie B3, 95 (1929).

It is known that at the temperatures employed in this research no thermal decomposition of either methane or methyl bromide occurs.[7] An *a posteriori* calculation indicates that dark reaction (thermal bromination) should be undetectable in the course of an hour at 483°K. Experimentally no dark reaction at this temperature was observed over a period of half an hour, in which time photochemical bromination was practically complete. Therefore the photoreaction was stopped by inserting a metal shield between light source and reaction cell while bromine concentrations were determined with the photometer. In this way repeated measurements of bromine concentration could be made after each desired interval of illumination. In the case of thermal brominations photometer readings had
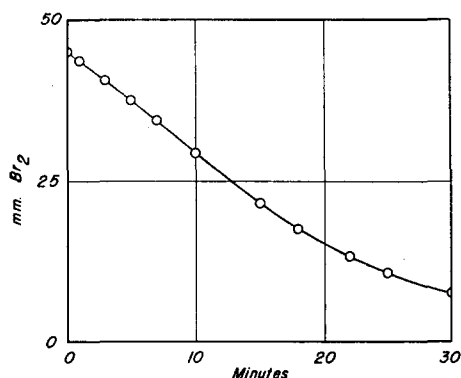

FIG. 1. Photochemical bromination of methane. 483°K. Initial pressures, CH_4 641 mm; Br_2 45.0 mm.

to be taken "on the fly," that is, while the reading was changing. In all cases reproducibility was satisfactory.

Bromine concentrations were measured at suitable times and from them rates of reaction during small time intervals were determined and an extrapolation made to obtain the rate at zero time. Rate constants were calculated from this rate at zero time. This method was employed because at the start of the reaction there are no products of reaction present to complicate the kinetics. It is known that all of the bromomethanes can be produced by photobromination, hence it is essential in a kinetic study to measure the rate of formation of a particular compound. The plot of a typical experiment is given in Fig. 1.

EXPERIMENTAL RESULTS

It was found experimentally that the rate of photobromination of methane was proportional to methane concentration, to the square root of bromine concentration, and inversely proportional to the square root of total pressure. In analogy with the hydrogen bromide synthesis it is plausible to expect the rate determining step in methane bromination to involve the reaction of a bromine atom, produced either thermally or photochemically, with a methane molecule. On this basis the initial rate should be proportional to methane concentration and to the square root of bromine concentration, or in the case of the photoreaction, to the square root of absorbed light intensity. The Lambert-Beer law is known to apply quite accurately in the case of bromine up to a partial pressure of 50 mm,[8] about the maximum employed here, hence absorbed light intensity is proportional to bromine concentration. The inverse proportionality with total pressure in the photochemical bromination is in accord with a three-body mechanism for destruction of bromine atoms.

Table I gives values of initial rate constants (k') for photobromination calculated by means of the equation

$$-d[Br_2]/dt = k'[CH_4][Br_2]^{\frac{1}{2}}[1/P]^{\frac{1}{2}}. \quad (A)$$

k' is a rate constant multiplied by absorption coefficient and an apparatus constant. P is the total pressure. The three series of experiments are not comparable in terms of absolute rate because design and adjustment of the optical system were altered slightly between them. Series A and B show clearly that the initial rate constant remains unchanged over a threefold variation in both CH_4 and Br_2 partial pressures as well as total pressure. However, this equation cannot be used to evaluate rate constants during any appreciable part of the reaction because of secondary reactions and inhibition by the hydrogen bromide produced.

A direct test of the dependence of rate on the intensity of incident radiation was made by inserting between the light source and reaction cell a screen calibrated to transmit 44.5 percent

[7] H. P. Meissner and H. J. Schumacher, Zeits. f. physik. Chemie **A185**, 435 (1940).

[8] M. Bodenstein and H. Lütkemeyer, Zeits. f. physik. Chemie **114**, 208 (1924).

TABLE I. Photobromination of methane.

	$T°K$	Initial pressures (mm at $T°K$) CH$_4$	Br$_2$	k'(sec.$^{-1}$) $\times 10^4$
Series A	503	547	53.5	7.0
		618	41.7	7.3
		613	40.5	7.3
		555	41.1	7.2
		553	41.1	7.0
		456	41.5	7.2
		311	43.0	7.3
		284	40.5	7.2
		279	40.8	7.0
		210	40.9	7.7
		473	25.1	7.8
		280	21.5	7.0
		497	16.3	7.3
				7.25
Series B	483	641	45.0	1.38
		514	44.4	1.39
		210	44.4	1.41
				1.40
Series C	483	492	44.4	2.94
		488	45.1	3.03
		486	46.2	2.89
		486	43.6	2.53
		483	44.1	2.84
		450	45.8	2.71
				2.82
	453	424	45.7	0.816
		419	51.1	.816
		418	45.5	.830
		418	45.4	.764
				0.807
	423	406	45.2	0.196
		400	44.9	.185
				0.190

of incident radiation. If the rate is proportional to the square root of absorbed light and with validity of the Lambert-Beer law this screen should reduce the velocity of bromination to $(0.445)^{\frac{1}{2}}=0.667$ or 66.7 percent of its value in absence of the screen. Experimentally the rate was reduced to 68.3 percent of its normal value. This is within experimental error of 66.7 percent and is considered as additional proof that the rate depends upon the square root of absorbed light intensity, which latter is proportional to the bromine concentration.

It was found that hydrogen bromide, a product of the reaction, inhibits bromination. The following equation was found to apply to photobromi-

nation of methane in the presence of HBr,

$$-\frac{d[Br_2]}{dt}=\frac{k'[CH_4][Br_2]^{\frac{1}{2}}[1/P]^{\frac{1}{2}}}{1+\dfrac{k_4[HBr]}{k_3[Br_2]}}. \quad (B)$$

Table II shows results of experiments made to study the effect of inhibition by HBr. Values of k' were taken from experiments run in absence of HBr. The experiments at 310°K were of very long duration (two months), and were carried out in sealed tubes, analysis being made chemically instead of photometrically. They are subject to lower accuracy than those at the two higher temperatures. In any case it is difficult to determine the ratio k_4/k_3 with high accuracy because the rate is rather insensitive to relatively large changes in HBr concentration.

Bodenstein and Lütkemeyer,[8] employing an analogous expression, found for the hydrogen-bromine reaction a value of $k_4/k_3=0.10$ which is temperature independent. It is seen in Table II that at high temperature HBr inhibits bromination of CH$_4$ more strongly than that of H$_2$ and that this inhibition has a definite temperature coefficient.

An experiment was performed at 453°K to determine whether oxygen exerts an inhibitory action. To a reaction mixture of 371 mm of CH$_4$ and 45.7 mm of Br$_2$, carefully dried and CO$_2$-free air was admitted corresponding to 1.6 mm of O$_2$. A calculation using $k'=0.807$

TABLE II. Photobromination of methane. Inhibition by HBr.

$T°K$	Initial pressures (mm at $T°$) CH$_4$	HBr	Br$_2$	k_4/k_3
483	363	121	46.6	0.212
	385	96	47.7	.204
423	254	138	41.6	.154
	248	116	42.1	.111
310	298	143	48.4	.089
	281	135	48.4	.064

$\times 10^{-4}$ sec.$^{-1}$ showed that if this behaved as an inert gas the initial rate of disappearance of Br$_2$ should have been 0.60 mm/min. The experimental value was 0.4 mm/min., indicating strong inhibition by oxygen. However, this inhibition

was present at the start of the reaction only, the rate having increased to 0.6 mm/min. after about 1.5 mm of Br_2 had been consumed. The reaction was normal from then on. This experiment is in agreement with known behavior of oxygen in other brominations and bromine sensitized oxidations.[2]

Series C of Table I gives data for a 60° temperature interval which have been used to calculate the activation energy of photochemical bromination of methane. Before such data may be employed with assurance it is necessary to answer two questions: (1) Does the absorption coefficient of bromine vary appreciably over the temperature range in question, and (2) is the ideal gas law sufficiently exact under the conditions of the experiment? The second question was tested by applying the Berthelot equation to Br_2. Deviations between it and the ideal gas law in our pressure ranges were considerably less than 0.5 percent, hence the ideal gas law was used. Bodenstein and Lütkemeyer[8] have shown that the absorption coefficient of bromine varies about 5 percent between room temperature and 490°K at 5350A, decreasing with shorter wavelength to 1 percent variation at 5000A. Relatively little light of wave-length greater than 5000A was used. Consequently no correction was made for temperature dependence of the absorption coefficient over our smaller temperature interval. In Fig. 2, log k' has been plotted against $1/T$ giving a good straight line. The slope of this line gives 18.25 kcal. for the uncorrected energy of activation. Taking the mean temperature of 453°K, $RT/2 = 0.45$ kcal. leaving 17.8 kcal. by subtraction from 18.25 for the corrected energy of activation.[9]

The photochemical bromination of methyl bromide corresponds to the second step in the over-all bromination of methane. It was studied kinetically in the same manner as was methane. The rate of disappearance of bromine follows the kinetic expression

$$-d[Br_2]/dt = k''[CH_3Br][Br_2]^{\frac{1}{2}}[1/P]^{\frac{1}{2}}. \quad (C)$$

Rate constants are given for three series of experiments in Table III. Series C has been used to evaluate the activation energy as in the

case of methane, the data being plotted in Fig. 2. The corrected value for the activation energy is 15.6 kcal./mole. The effect of hydrogen bromide was investigated at both 483°K and 423°K. No inhibition was observed.
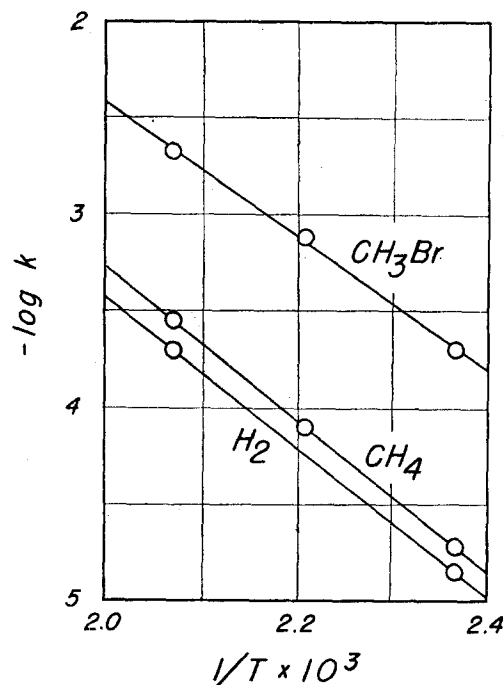

FIG. 2. Temperature coefficients. Each circle represents average of all runs at that particular temperature.

The rate constants for bromination of methane and methyl bromide being known separately, it is possible to calculate what the rate should be in mixtures of methane and methyl bromide. Satisfactory agreement was obtained between experiment and calculation when tested.

Several experiments at both 483 and 423°K were made on the photochemical hydrogen-bromine reaction in order to check our method on a very well studied reaction. Good reproducibility was obtained. The activation energy calculated from these experiments was 17.5 kcal./mole in agreement with Bodenstein's value of 17.6 kcal./mole. The data are plotted in Fig. 2.

The rates of thermal bromination of methane, methyl bromide and hydrogen were measured at 570°K. The method of measurement was essentially the same as that used in the photochemical experiments. Data are recorded in Table IV.

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[9] This correction is based on the simple bimolecular rate equation, $k = Z'T^{\frac{1}{2}}e^{-E/RT}$.

Rate constants were calculated from the initial rate of reaction using the equation:

$$-d[Br_2]/dt = k[CH_4][Br_2]^{\frac{1}{2}}. \quad (D)$$
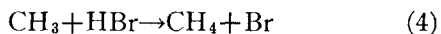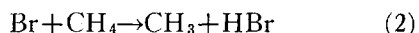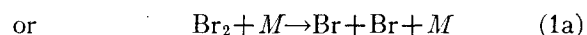
It is observed that the rate is independent of total pressure and that concordant values of k are obtained over a twofold variation of partial pressures.

The data of Bodenstein and Lind[10] were used to calculate a rate constant for the hydrogen reaction at 570°K of $k = 0.022$ which is in good agreement with our value of $k = 0.0196$. A difference of 1 to 1.5° in the temperature scales would bring the two values into excellent agreement.

DISCUSSION

The following chain is postulated as the reaction mechanism operative in bromination of methane.

$$Br_2 + h\nu \rightarrow Br + Br \quad (1)$$

or $\quad Br_2 + M \rightarrow Br + Br + M \quad (1a)$

$$Br + CH_4 \rightarrow CH_3 + HBr \quad (2)$$

$$CH_3 + Br_2 \rightarrow CH_3Br + Br \quad (3)$$

$$CH_3 + HBr \rightarrow CH_4 + Br \quad (4)$$

$$Br + Br + M \rightarrow Br_2 + M \quad (5)$$

. . . .

$$Br + CH_3Br \rightarrow CH_2Br + HBr \quad (2a)$$

$$CH_2Br + Br_2 \rightarrow CH_2Br_2 + Br \quad (3a)$$
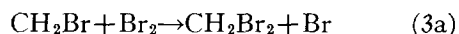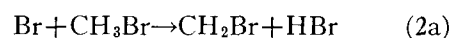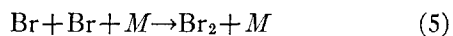
$$CH_2Br + HBr \rightarrow CH_3Br + Br \quad (4a)$$
etc.

At sufficiently low pressures one would expect chain termination to result from diffusion of bromine atoms to the wall followed by heterogeneous recombination. This is not the case in our experiments, for the rate then would be first order with respect to Br_2 concentration instead of 0.5 order.

Reactions involving production of hydrogen atoms have been ruled out on the basis of energetic considerations. Some would involve Walden type inversions which are known to have high activation energies. For example, it has been shown[11] that the reaction $CH_4 + H \rightarrow CH_3 + H_2$ requires 8

[10] M. Bodenstein and S. C. Lind, Zeits. f. physik. Chemie **57**, 168 (1906).

[11] Gorin, Kauzmann, Walter, and Eyring, J. Chem. Phys. **7**, 633 (1939).

TABLE III. Photobromination of methyl bromide.

	$T°K$	Initial pressures (mm at $T°K$) CH$_3$Br	Br$_2$	k''(sec.$^{-1}$) $\times 10^3$
Series A	503	337	52.4	5.36
		159	41.8	5.15
		347	40.6	5.19
Series B	483	381	43.2	1.07
		453	42.8	1.02
		398	42.6	1.08
		298	32.9	1.15
		211	29.0	1.17
Series C	483	259	48.5	2.07
		287	45.9	2.21
		255	45.2	2.25
		472	44.1	1.93
				2.12
	453	331	45.5	0.754
		336	44.5	.769
				0.762
	423	317	45.0	0.209
		308	44.4	.199
		295	42.8	.198
				0.202

TABLE IV. Thermal brominations at 570°K.

	Initial pressures (mm at 570°K) X	Br$_2$	k(cc mole^{-1})$^{\frac{1}{2}}$ sec.$^{-1}$
A. $-CH_4$	517	53.0	0.0247
	331	55.5	.0250
	317	48.1	.0249
	227	51.0	.0240
	353	25.0	.0253
	325	22.0	.0247
			0.0248
B. $-H_2$	431	51.2	0.0193
	405	52.0	.0198
			0.0196
C. $-CH_3Br$	352	52.7	0.156
	210	53.2	.163
	342	25.6	.162
			0.160

to 11 kcal. activation energy while the Walden inversion $CH_4 + H \rightarrow CH_4 + H$ requires 35 to 40 kcal. Thus there is good evidence against reactions of the type $CH_4 + Br \rightarrow CH_3Br + H$.

Using the above reaction mechanism and assuming steady state concentrations of chain-propagating radicals, one can derive the ex-

pression

$$\frac{d[CH_3Br]}{dt} = \frac{k_2[CH_4](n/k_5[M])^{\frac{1}{2}}}{1 + \frac{k_4[HBr]}{k_3[Br_2]}}, \quad (E)$$

where n represents the number of absorbed light quanta and $[M]$ is the total concentration of all molecules present. It is clear that $n = k_{ap}\alpha I[Br_2]$, where k_{ap} is a temperature independent apparatus constant, I is the intensity of incident radiation, and α is the absorption coefficient of bromine. Because I was a constant in any set of experiments we may write $k' = k_2(k_{ap}\alpha I/k_5)^{\frac{1}{2}}$. Hence, Eq. (E) is seen to be equivalent to Eq. (B). It is based on methyl bromide as the only bromomethane formed and is, therefore, a first-order approximation only. Considering secondary bromination to produce methylene bromide with negligible inhibition of this step

TABLE V. Frequency factor and entropy of activation at 570°K.

Reaction	A Expt.	Z' Collision theory	S Expt.	S Calc.
$Br+H_2$	1.14×10^{12}	11.7×10^{12}	-2.31	
$Br+CH_4$	1.48×10^{12}	7.2×10^{12}	-1.81	-1.84
$Br+CH_3Br$	1.35×10^{12}	5.9×10^{12}	-1.98	-1.94

by hydrogen bromide, the second-order approximation for the rate becomes

$$\frac{d[CH_3Br]}{dt} = \frac{k'[CH_4][Br_2]^{\frac{1}{2}}[1/P]^{\frac{1}{2}}}{1 + \frac{k_4[HBr]}{k_3[Br_2]}}$$

$$-k''[CH_3Br][Br_2]^{\frac{1}{2}}[1/P]^{\frac{1}{2}}, \quad (F)$$

where $k'' = k_{2a}(k_{ap}\alpha I/k_5)^{\frac{1}{2}}$. The rate of disappearance of bromine clearly will be the sum of the two terms on the right. This equation was found to fit our experimental data when applied by means of successive approximations.

From the postulated mechanism one derives the first-order approximation for the thermal reaction:

$$\frac{d[CH_3Br]}{dt} = \frac{k[CH_4][Br_2]^{\frac{1}{2}}}{1 + \frac{k_4[HBr]}{k_3[Br_2]}}, \quad (G)$$

in which $k = k_2(K_{eq})^{\frac{1}{2}}$ where K_{eq} is the equilibrium constant for dissociation of bromine. This reduces to Eq. (D) at zero time when the concentration of hydrogen bromide is zero.

Qualitatively we may observe that the rate of disappearance of bromine will increase for a time after the reaction begins because of the gradual increase in concentration of methyl bromide which is brominated from 7.5 to 10 times more rapidly than methane in the temperature range we investigated. Inhibition by hydrogen bromide becomes progressively more pronounced in the latter stages of bromination when its concentration becomes relatively high in respect to bromine. Acceleration by methyl bromide is more important than inhibition by hydrogen bromide. However, decreasing bromine concentration of itself also causes a decreasing rate of bromination. These effects are seen in Fig. 1.

It is evident from the form of the kinetic equation that the rate determining step is reaction (2) in the case of methane and (2a) in the case of methyl bromide. If this were not true the rate would depend on some other concentration functions. Energetic considerations also are in agreement. Reaction (3) will be exothermic to an appreciable extent because the $C-Br$ bond is stronger than the $Br-Br$ bond (45.2 kcal.) and because it is a free radical reaction it should require very low or zero activation energy. On the other hand, reaction (2) should be endothermic because the $C-H$ bond is certainly stronger than the $H-Br$ bond (85.6 kcal.). It must, therefore, require an activation energy at least equal to its endothermicity. On the basis of these considerations the activation energy of bromination of methane, 17.8 kcal., has been ascribed to reaction (2), while the corresponding value of methyl bromide, 15.6 kcal., has been assigned to reaction (2a).

The temperature dependence of inhibition by hydrogen bromide enables a determination of the difference in activation energies between reactions (3) and (4) and a reliable estimate of the activation energy of reaction (4). Employing the usual, simple bimolecular equation $k = AT^{\frac{1}{2}}e^{-E/RT}$, where A is a temperature independent frequency factor and E the activation energy, we express the logarithmic ratio of the rate constants of reactions (3) and (4) in the

TABLE VI. Rate constant ratios.

$T°K$	k_{CH_4}/k_{H_2} Experimental	Calc'd with efficiency 1:1	3.6:2.2	k_{CH_3Br}/k_{H_2} Experimental	Calc'd with efficiency 1:1	2.7:2.2	k_{CH_3Br}/k_{CH_4} Experimental	Calc'd with efficiency 1:1	2.7:3.6
Thermal 570	1.26			8.2			6.4		
Photo 483	1.39	1.05	1.35	10.5	9.6	10.5	7.5	9.0	7.7
453							9.3	10.9	9.4
423	1.33	1.01	1.30	14.2	12.8	14.0	10.6	12.5	10.7

form

$$\ln \frac{k_4}{k_3} = \ln \frac{A_4}{A_3} - \frac{E_4 - E_3}{RT}.$$

For these two similar reactions the assumption is made that the quantity $(E_4 - E_3)$ does not vary appreciably with temperature. Since A also is essentially temperature independent, the expression can be differentiated to give

$$d \ln \frac{k_4}{k_3} = \frac{E_4 - E_3}{RT^2} dT$$

which combined with inhibition data (Table II) yields $(E_4 - E_3) = 2$ kcal. For reasons already mentioned it is not unreasonable to assume that the activation energy of reaction 3 is zero, making 2 kcal. the activation energy of reaction 4 in good agreement with the value of 1.5 kcal. obtained by Andersen and Kistiakowsky[12] from experiments on the photolysis of methyl iodide in the presence of hydrogen bromide.

Absolute rates of thermal bromination at 570°K and data of Gordon and Barnes[13] on the thermal dissociation of molecular bromine have been used to calculate the temperature independent frequency factor A in the equation $k = A T^{\frac{1}{2}} e^{-E/RT}$ as applied to the rate determining single reactions of bromine atoms with hydrogen, methane, and methyl bromide. Experimental values of E determined in the photochemical brominations were used. The collision number Z was calculated by classical collision theory employing the following molecular diameters,

$H_2 = 2.76A$, $CH_4 = 3.2A$, $CH_3Br = 4.5A$, $Br = 3.0A$. Values of A and Z' $(=Z/T^{\frac{1}{2}})$ are given in Table V. It is interesting that A and Z' differ little from one another, the steric factor being approximately 0.1 to 0.2. This is in contrast to the reaction of hydrogen atoms with methane where a steric factor of the order of 10^{-2} to 10^{-3} is required.[11] A possible explanation of this difference may be found by considering the relative sizes of bromine and hydrogen atoms. The hydrogen atom presumably must approach the methane molecule more precisely oriented along the axis of a $C-H$ bond than is required in the case of the bromine atom.

Experimental entropies of activation were calculated from the data of thermal experiments at 570°K using a formula of Kistiakowsky and Ransom,[14]

$$k = \frac{k_B T}{h} e^2 e^{S/R} e^{-E/RT},$$

where S is the entropy of activation, k_B the Boltzmann constant, and h Planck's constant. "Theoretical" entropies of activation were calculated by statistical mechanical methods. Configurations of activated complexes were assigned by analogy with those calculated by Gorin, Kauzmann, Walter, and Eyring[11] for reaction between hydrogen atoms and methane. It was assumed that the minimum activation energy is required when a bromine atom approaches a methane molecule along the axis of a $C-H$ bond. No change in configuration of the CH_3 part of the molecule was assumed. Interatomic distances and vibrational frequencies were as-

[12] H. C. Andersen and G. B. Kistiakowsky, J. Chem. Phys. 11, 6 (1943).
[13] A. P. Gordon and C. Barnes, J. Chem. Phys. 1, 692 (1933).
[14] G. B. Kistiakowsky and W. W. Ransom, J. Chem. Phys. 7, 725 (1939).

signed as follows,

H₃————C——————H———————————Br
    1.09A   1.17A   1.86A

C−H stretching   3000 cm⁻¹   (4)

CH₃ torsional   1440   (6)

H−Br stretching   2200   (1)

Br−H−CH₃ bending   500   (2).

In the case of methyl bromide the assignments were

           1.09A
       H₂
        \
         \
           C———————H———————————Br.
        /
      /
    /
  Br 1.91A   1.17A   1.86A
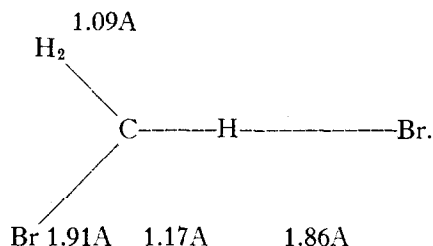
Frequencies of methyl bromide[15] plus others for bromine atom assignments were 3061 (2), 2900 (1), 2200 (1), 1450 (2), 1305 (1), 957 (2), 610 (2), and 105 (2). A comparison of experimental and "theoretical" entropies of activation is given in Table V. It is observed that these complexes have low, doubly degenerate bending frequencies which make large contributions to the entropy. Unfortunately they cannot be estimated with high precision. However, agreement between experimental and calculated entropies of activation indicates that the structures assigned to the activated complexes are reasonable.

Ratios of the experimental rate constants for thermal and photochemical reactions are shown in Table VI. Clearly in the case of thermal bromination these are ratios of the rate constants of reaction (2) and its prototypes, the equilibrium constant for dissociation of bromine cancelling out. However, for photochemical bromination they would represent the ratios of the bromine atom reactions only if all molecules were equally effective third bodies for homogeneous recombination of bromine atoms. That such is not the case is shown in Table VI. Ratios for photobromination calculated from thermal absolute rates and experimental activation energies on the assumption of equal efficiencies do not

[15] D. P. Stevenson and J. Y. Beach, J. Chem. Phys. 6, 25 (1938).

agree with experiment. Rabinowitch and Wood[16] have studied the influence of various molecules on recombination of bromine atoms and report that the efficiencies of hydrogen and methane are in the ratio 2.2:3.6, respectively. When these values are used in calculating rate constant ratios excellent agreement with experiment is obtained as shown in Table VI. We deduced from our experiments that the efficiency of methyl bromide on the same basis as hydrogen and methane was 2.7, the results being indicated in the table. It is surprising that methyl bromide efficiency should be less than that of methane. However, this quantity is very susceptible to a small difference in the values of activation energies. A recalculation assuming an activation energy of 16.2 kcal., i.e., 0.6 kcal. above our accepted value of 15.6 kcal., for bromination of methyl bromide yields an efficiency of 3.9. It can be said that our experiments confirm the work of Rabinowitch and Wood and indicate that the efficiencies of methyl bromide and methane are roughly equal. In the inhibition experiments with hydrogen bromide no account has been taken of varying efficiency of methane and hydrogen bromide. Work of Hilferding and Steiner[17] combined with that of Rabinowitch and Wood indicates that the efficiencies of methane and hydrogen bromide are equal. Differing efficiencies would change the absolute value of the inhibition constant but should not affect its temperature coefficient.

The experimental rate constant ratios of photochemical bromination in Table VI can be used as an estimate of the relative quantum yields. If the quantum yield for hydrogen bromide synthesis is one[18] then it is about 1.4 for formation of methyl bromide.

CARBON-HYDROGEN BOND STRENGTH

Values for activation energies of reactions (2) and (4) may be combined to obtain the heat of reaction at the mean experimental temperature

[16] E. Rabinowitch and W. C. Wood, Trans. Faraday Soc. 32, 907 (1936).
[17] K. Hilferding and W. Steiner, Zeits. f. physik. Chemie B30, 399 (1935).
[18] See, for example, W. A. Noyes, Jr., and P. A. Leighton, The Photochemistry of Gases (Reinhold Publishing Corporation, New York, 1941).
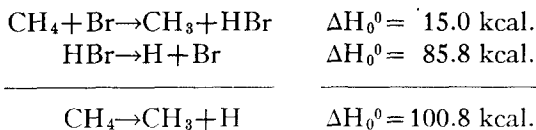
453°K for $CH_4 + Br \rightarrow CH_3 + HBr$. Because the numbers of molecules of products and reactants are equal, we may write

$$\Delta H_{453}^0 = \Delta E_{453}^0 = (E_2 - E_4) = (17.8 - 2) = 15.8 \text{ kcal.}$$

ΔH_0^0 was calculated using the following values of $(H_{453}^0 - H_0^0)$.

	$H_{453}^0 - H_0^0$
CH₄	3.83 kcal./mole
CH₃	3.75 kcal./mole
HBr	3.15 kcal./mole
Br	2.25 kcal./mole
H	2.25 kcal./mole.

Values for CH_4 and HBr are from a review by Pitzer,[19] H and Br were calculated for free atoms with translational degree of freedom only, and the value for CH_3 is that for CH_4 diminished by 0.3 times the vibrational contribution. We thus obtain $\Delta H_0^0 = 15.0$ kcal. This may be combined with the value 85.8 kcal. for the heat of dissociation of hydrogen bromide[20] to obtain the carbon-hydrogen bond strength as follows:

$CH_4 + Br \rightarrow CH_3 + HBr$	$\Delta H_0^0 = 15.0$ kcal.
$HBr \rightarrow H + Br$	$\Delta H_0^0 = 85.8$ kcal.
$CH_4 \rightarrow CH_3 + H$	$\Delta H_0^0 = 100.8$ kcal.

The value of ΔH^0 at any temperature may be calculated in similar manner. We obtain the following rounded values for the carbon-hydrogen bond strength at the indicated temperatures.

$T°K$	$D(CH_3-H)$
0	101 kcal.
293	102 kcal.
453	103 kcal.

Although quite divergent values of the carbon-hydrogen bond strength in methane have been reported, a considerable body of evidence points to its being in the range 100 to 104 kcal./mole.[21] The agreement between our value and that of Stevenson[21g] derived from electron impact critical potentials is particularly impressive. Thus two entirely different experimental methods of determining the carbon-hydrogen bond strength agree within their experimental errors (about 1 kcal.). Semi-empirical calculations of H. A. Taylor and Burton[21e] by the Voge method yield the value of 102.1 kcal. if one assumes the zero-point energy of CH_3 to be three-quarters that of methane.

Similar assumptions regarding activation energies lead to the conclusion that the substitution of bromine for one hydrogen in methane lowers the bond strength by about 2 to 3 kcal. von Braunwarth and Schumacher[22] found an activation energy of the order of 10 kcal. for bromination of bromoform, which indicates that the introduction of 3 bromine atoms into methane lowers its C–H bond strength by about 7–8 kcal. Probably the introduction of two bromine atoms lowers this bond strength about 5–6 kcal.

[19] K. Pitzer, Chem. Rev. 27, 39 (1940).

[20] $D(H-Br) = 85.8$ kcal. by combination of the heat of dissociation of $H_2 = 102.48$ kcal. [H. Beutler, Zeits. f. physik. Chemie B29, 315 (1935)] with that for $Br_2 = 45.22$ kcal. and heat of formation of HBr from its elements $= 11.99$ kcal. (reference 13).

[21] (a) L. Pauling and J. Sherman, J. Chem. Phys. 1, 606 (1933), 100 kcal.; (b) R. G. W. Norrish, Trans. Faraday Soc. 30, 103 (1934), 103 kcal.; (c) F. O. Rice and K. K. Rice, Aliphatic Free Radicals (Johns Hopkins Press, Baltimore, 1935), p. 75, 100 kcal.; (d) F. Patat, Zeits. f. physik. Chemie B32, 290 (1936), 102.5 kcal.; (e) H. A. Taylor and M. Burton, J. Chem. Phys. 7, 572 (1939), 102.1–103.7; (f) E. C. Baughan and M. Polanyi, Nature 146, 685 (1940), 103.6 kcal.; (g) D. P. Stevenson, J. Chem. Phys. 10, 291 (1942)—101 kcal.

[22] von Braunwarth and H. J. Schumacher, Kolloid Zeits. 89, 184 (1939).