

time being expressed in minutes. From these two rates, the activation energy calculated from the equation

$$A = \frac{RT_2T_1}{(T_2 - T_1)} \ln \frac{k_2}{k_1}$$

was found to be equal to 29,400 cal./mole. Using this value of the activation energy and the known rate at one temperature, the rate of thermal rearrangement at the temperature used in each experiment was calculated, and, by subtracting this from the over-all rate, the rate of rearrangement due to the ultrasonic vibrations alone was obtained.

In order to determine the effects of different frequencies upon the reaction, it was necessary to know the rates at which energy was being supplied to the solutions or some quantities directly proportional to these rates. The necessary data were obtained from calorimetric measurements. After concluding an experiment on an azide solution, water was placed in the same reaction tube, and an air-jacket (instead of a water-jacket) was used. A measured volume of water (50 cc.) was transferred to the tube and vibration was applied. The rate of temperature rise of the water was measured. The rate of rise, in degrees per minute, was converted into calories per second, assuming that the specific heat of water is constant and equal to 1.00. The absorption of heat by the glass could be ignored, for it would be the same in heating the azide solution as in heating the water.

This procedure determined a rate of addition of energy which was proportional to, but not equal to, the rate of supply of energy to the azide solu-

tion. Equality cannot be assumed, for the coefficients of acoustic absorption of the azide solution and of water must be different. The actual value of the proportionality factor is unimportant since the same azide concentration, the same solution volume and the same volume of water was used in each experiment. The proportionality factor may be assumed to be constant.

No linear relationship exists between energy input and energy supplied in vibrational form, for different crystals possess different degrees of efficiency in converting electrical into acoustical power, and with a given crystal the efficiency of the oscillator varies with the input of power. This makes it impossible to use oscillator input as a quantitative measure of the energy being supplied to the solution, and therefore the calorimetric data must be relied upon.

The results of five runs show that, within the limits of experimental error, the rate of rearrangement induced by ultrasonic vibrations is directly proportional to the energy absorbed by the solution, and is independent of the frequency of the vibrations.

Summary

The rate of rearrangement of benzazide in aniline solution has been studied at frequencies of 16, 275 and 478 kilocycles per second and with power inputs ranging from 100 watts to 250 watts. The rate of rearrangement has been found to be directly proportional to the energy of the vibration and independent of the frequency.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Photolysis of Methyl Bromide¹

BY ALVIN GORDON² AND H. AUSTIN TAYLOR

The photolysis of alkyl halides is a convenient source of hydrocarbon free radicals; the immediately ensuing secondary reactions yield data from which the properties and reactivities of those radicals can be deduced. Up to the present, such work has dealt almost entirely with the

(1) Paper presented before the Division of Physical and Inorganic Chemistry, St. Louis Meeting of the American Chemical Society, April, 1941.

(2) Abstract from a thesis presented in partial fulfillment of the requirements for the degree of doctor of philosophy at New York University, June, 1941.

iodides. The products finally obtained have been accounted for, in general, on the basis of probable secondary reactions, either between the radicals themselves, or between the radicals and the molecules present. Since the absorption spectra of methyl iodide and methyl bromide are qualitatively similar, the latter band being somewhat broader and displaced toward shorter wave lengths,³ it is to be expected that the primary

(3) Herzberg and Scheibe, *Z. physik. Chem.*, **B7**, 390 (1930).

absorption act would result in dissociation of the bromide as it does for the iodide.⁴ However, the difference in strengths of the C-I and C-Br bonds might be expected to alter the rates of the secondary reactions, and thus comparison of the products in the two cases might lead to a confirmation or modification of the previously assumed secondary processes. To this end, the photolysis of methyl bromide vapor has been studied alone, in the presence of nitric oxide, and also in the presence of silver.

Experimental

Apparatus.—The reaction vessel was a quartz cylinder flat on one end and constricted at the other for a quartz-to-Pyrex graded seal to the system. It was 10 cm. long and 2.7 cm. in diameter. A low pressure quartz-mercury arc, spiral in form,⁵ covered the reaction vessel, and was energized with a 0.265 KVA transformer. Pressure measurements were made using a Bodenstein quartz spiral gage in connection with a mercury manometer. As a light filter to remove principally 1849 Å. radiation, a solution of approximately normal acetic acid and normal sodium acetate was allowed to flow continuously over the cell during experiments.⁶ The remaining radiation was principally 2537 Å. The products of photolysis were withdrawn from the reaction cell by means of a mercury piston to a buret. Provision was made for collecting gases in a small tube over mercury. These gases were analyzed using the Blacet and Leighton micro-gas analyzer.⁷ The reaction system itself was protected by gold-leaf traps at all places open to contact with mercury.

Chemicals: Methyl Bromide.—Kahlbaum methyl bromide was distilled through a phosphorus pentoxide tube and through silver foil into a reservoir containing mercury and maintained at dry-ice temperature. Prior to use, it was repeatedly evacuated while frozen in liquid nitrogen, and occasionally pumped out for short intervals while cooled in dry-ice.

Nitric Oxide.—Nitric oxide was prepared by two methods during the work: the first, by the reaction of mercury with nitrosyl-sulfuric acid; and the second, by treatment of potassium iodide and potassium nitrite with sulfuric acid. It was purified by passage over moist potassium hydroxide and dried with phosphorus pentoxide.

Phosgene.—Tank phosgene was purified by repeated liquefaction and distillation and stored at dry-ice temperature.

Quantum Yield and Incident Light.—For the estimation of quantum yields the method of Etzler and Rollefson⁸ was adopted. These authors used data on the oxidation of phosgene.⁸ In their work as in this, a difficulty resulted from the fact that the light source was a helical coil which fitted around the cylindrical reaction vessel. To offset the

difficulty, they estimated the incident light intensity in two ways. In the first, they used the phosgene oxidation actinometer, assuming roughly that the diameter of the reaction vessel was the length of the light path, and taking the value of 1.8 for the quantum yield⁸ at 2537 Å. In the second, they used uranyl oxalate in the reaction cell. For the reaction they were studying, the phosgene oxidation actinometer gave a quantum yield of 0.55 while the uranyl oxalate actinometer gave 0.46. The agreement clearly justifies the use of the phosgene oxidation actinometer. At the same time it should be noted that the assumption concerning the length of the light path tends to give high values for the quantum yield.

The extinction coefficient ϵ , defined by the equation $I/I_0 = 10^{-\epsilon cl}$, where c is in moles per liter and l in cm., is 0.36 for phosgene and 1.26 for methyl bromide.⁹ Since the latter is a higher value than that of phosgene, the assumption concerning the length of the light-path will not be as much in error. The quantum yields in methyl-bromide photolysis calculated in this way and reported here may thus be slightly too high, but probably by less than 5%, and certainly within the limits of experimental error. The value for I_0 found by using the phosgene oxidation actinometer was 1.09×10^{18} quanta/sec. when water flowed over the cell, and 1.04×10^{18} quanta/sec. when the acetic acid-sodium acetate filter was used. The incident light values are somewhat less than those employed by Etzler and Rollefson.

Photolyses.—The photolyses were carried out statically in the quartz vessel which was repeatedly flamed out before each run. The arc was allowed to warm up to full intensity while the reaction vessel was shielded with an aluminum cylinder. Pressure readings were made during irradiation with the previously calibrated Bodenstein gage; the final pressure of the system was taken with the arc turned off. The products of the reaction were condensed in a trap in liquid nitrogen; *s*-butyl chloride mush (-131°) and dry-ice were used to obtain further fractionations. The gases uncondensed in liquid nitrogen were pumped off and analyzed, using the Blacet-Leighton technique.⁷ The only gases so found were methane and carbon monoxide. No ethane or unsaturated hydrocarbon was ever found. Bromine was distilled into potassium iodide and the resulting iodine titrated with standard thiosulfate. In some experiments the unchanged methyl bromide was absorbed in dimethylaniline.

In experiments using nitric oxide, methyl bromide at the required pressure was added to the reaction vessel, and there frozen in liquid nitrogen. Nitric oxide was admitted after thorough evacuation. The gases were then allowed to warm to room temperature and the total pressure recorded. During titration of the iodine liberated by bromine and nitrosyl bromide, some air oxidation of nitric oxide occurred and the resulting nitrogen tetroxide oxidized more iodide ion. To eliminate this difficulty, the nitrosyl bromide was converted to bromide ion by sodium bisulfite in nitric acid and the total bromide then titrated by the Volhard method. It was found, however, that merely bubbling methyl bromide and nitric oxide through water gave a solution containing bromide which could be

(4) West and Schlessinger, *THIS JOURNAL*, **60**, 961 (1938); *Iredale, Trans. Faraday Soc.*, **35**, 458 (1939).

(5) Etzler and Rollefson, *THIS JOURNAL*, **61**, 800 (1939).

(6) Cf. Ley and Arends, *Z. physik. Chem.*, **B17**, 177 (1932).

(7) Blacet and Leighton, *Ind. Eng. Chem., Anal. Ed.*, **3**, 266 (1931); **5**, 272 (1933); **6**, 334 (1934).

(8) Rollefson and Montgomery, *THIS JOURNAL*, **55**, 142 (1933).

(9) Fink and Goodeve, *Proc. Roy. Soc. (London)*, **A163**, 592 (1937).

titrated. The extent of this "blank" was determined and allowance for it was made in subsequent titrations.

In experiments using silver the procedure was the same as that with pure methyl bromide. The silver was cleaned with emery cloth, washed and dried. New silver was used for each run with two exceptions.

Experimental Results

Methyl Bromide.—The quantum yield of the photolysis of pure methyl bromide was calculated on the basis of bromine atoms produced. The calculations are based on the initial pressure of methyl bromide; the calculation for expt. 1 follows.

Press. CH_3Br = 67.2 mm. at 26° , hence

$$c \approx 0.00359 \text{ moles/liter}$$

$$l = 2.70 \text{ cm.}$$

$$I_0 = 1.03 \times 10^{18} \text{ quanta/sec.}; \epsilon = 1.26$$

$$\therefore I_0 - I = 3.15 \times 10^{18} \text{ quanta absorbed per sec.}$$

Time of exposure = 180 minutes

$$\therefore \text{Total quanta absorbed} = 3.40 \times 10^{20}$$

In the titration 0.2773 g. of $\text{Na}_2\text{S}_2\text{O}_3$ solution containing 0.0091 me./g. was required. Hence 1.53×10^{18} atoms of Br were produced.

$$\therefore \text{Quantum yield, } \gamma = 4.5 \times 10^{-3}$$

Since the amount of decomposition is only from 5–10%, the quantum yields given are minimum values compensated slightly as already indicated and not seriously in error. Table I summarizes the data so obtained. The average yield is seen to be $\sim 4 \times 10^{-3}$.

TABLE I

QUANTUM YIELD OF PHOTOLYSIS OF METHYL BROMIDE

Expt.	CH_3Br , mm.	Time, min.	Quantum yield ^a $\times 10^3$	Temp., $^\circ\text{C}$.
1	67.2	180	4.5	21.5
2	76.7	150	8.0	21.0
3	90.6	140	3.1	22.0
5	82.5	45	1.7	21.0
6	67.9	60	1.2	20.0
7	128.0	17	7.1	21.0
8	86.8	142	7.1	20.5
9	118.7	17	4.9	20.5
10	66.4	60	5.7	20.0
11	80.0	46	3.8	20.0
12	80.6	50	5.3	20.0
13	104.2	600	6.7	20.0
17	110.9	620	6.3	23.5
20	144.5	515	1.0	25.0
22	143.2	402	1.9	29.0

^a Quantum yields based on analysis of methane produced run $\sim 10^{-2}$. Those given in the table are on the basis of Br_2 produced.

Gas analyses were made in many of the above experiments. The volume of gas (at 760 mm. and 0°) not condensed by liquid nitrogen, V_n ,

from an original pressure of methyl bromide of about 100 mm. (8.25 cc. at 760 and 25°) exposed for eight hours, was slightly more than 1 cc. at atmospheric pressure. Combustion analysis showed the gas to correspond to a C_1 gas whose hydrogen content was less than that of methane. Mass spectrographic analysis¹⁰ showed the presence of carbon monoxide and methane only. The carbon monoxide was subsequently estimated from the decrease in volume occurring on treatment at $\sim 350^\circ$ with a bead containing potassium hydroxide and copper oxide (potassium cuprate).⁷ The remaining methane could then be estimated by explosion with oxygen followed by drying with phosphorus pentoxide and carbon dioxide absorption in potassium hydroxide. The average carbon monoxide content was 25%; the remaining 75% was methane.

The volume of gas after removal of carbon monoxide and methane and not condensed in *s*-butyl chloride was always very small, much less than 0.1 cc. Analyses of this fraction were similar to those of the liquid nitrogen fraction. It was probably merely a trace of the gas from that fraction.

Several calculations were made of the quantum yield on the basis of methane produced. The order of magnitude was 10^{-2} , somewhat higher than that based on bromine. This is to be expected from analogy with the work of West and Schlessinger with methyl iodide, who found that some of the decomposed iodide appeared as methylene diiodide. The presence of carbon monoxide in the gases in this case, as is discussed later, is perhaps traceable to a reaction with silica with a consequent loss of bromine-containing compounds. Hydrogen bromide, methylene dibromide, and ethyl bromide were sought in the products without success.

It is to be noted that in all these experiments a small pressure increase amounting to less than two per cent. of the initial pressure was always observed.

Methyl Bromide and Nitric Oxide.—Shortly after the commencement of photolysis in the presence of nitric oxide a mist formed in the reaction vessel and later settled as greenish droplets of liquid. The pressure was found to increase at the beginning and then steadily decrease. If, during the increase, the arc was shut

(10) The authors wish to thank Dr. David Rittenburg of Columbia University for these analyses.

off, the pressure fell below its original value. A white solid always remained after these photolyses. It was easily sublimable, and on decomposition by heating gave a test for ammonia using Nessler reagent. These observations point to the formation of CH_3NO probably resulting in the formation of the polymer of formaldoxime.

Analysis of the product gases not condensed in liquid nitrogen showed the presence of carbon monoxide and nitrogen. The condensate in liquid nitrogen was frequently greenish in color. This appears to be due (most probably) to nitrogen tetroxide, indicating that oxidation in the presence of the nitric oxide was occurring. This is further confirmed by the presence of free nitrogen and of carbon monoxide. It is certain that the function of nitric oxide is not alone that of fixing the methyl radicals as CH_3NO and the bromine as nitrosyl bromide. Nevertheless this appears to be its major function, and quantum yields were calculated from the amount of methyl bromide decomposed as measured by the nitrosyl bromide produced. These data are included in Table II.

TABLE II
THE PHOTOLYSIS OF METHYL BROMIDE IN THE PRESENCE OF NITRIC OXIDE

Expt.	Initial [NO]/[CH ₃ Br], mm.	Time, min.	CH ₃ Br moles × 10 ⁻¹⁸		Quan- tum yield	V _n , cc.	% CO
			Initial	Decom- posed			
61	423/39 = 10.8	4.7	72.8	8.15	1.7	0.40	..
62	431.7/32.4 = 13.3	1.5	60.3	1.03	1.1	.37	9.7
63	380/33.1 = 11.5	9.0	61.8	6.27	1.0	.83	..
64	147/43 = 3.4	2.5	80.0	6.72	2.0	.39	35.4
65	122.9/41.5 = 3.0	2.5	77.5	4.43	1.7	.31	45.0
66	62.8/52.1 = 1.2	2.5	97.5	6.39	1.8
67	55.6/55.7 = 1.0	2.0	104.8	4.45	1.4	.46	..
68	32.2/44.2 = 0.73	1.5	82.6	4.32	1.9
71	8.9/41.1 = 0.22	2.0	16.4	1.08	.4
72	7.2/43.6 = 0.17	15.0	13.2	3.98	.02
30	503.6/95.2 = 5.3	7.0	175	21	1.2	.59	19.6
31	439.3/98.5 = 4.5	7.5	184	13	.7	.59	17.5
32	437.1/72.7 = 6.0	8.0	136	27	1.8	.41	16.3
38	424.4/78.3 = 5.4	4.5	145	18	1.9	.29	37.4
45	167.6/81.2 = 2.1	2.2	152	7	1.6	.24	31.3

Experiments 30 to 45 may be less accurate than the others since no allowance for the blank reaction of methyl bromide and nitric oxide was made. This would make the yields high. On the other hand, no correction was made for the depletion of methyl bromide during the run, nor for absorption by nitrosyl bromide. Nitrosyl bromide probably absorbs strongly at 2537 Å. This suggests that the real quantum yields are actually in excess of the values given, assuming no photosensitization by the nitrosyl bromide. It appears probable, however, that nitrosyl bromide does act as a

photosensitizer, in which case the quantum yields are most certainly lower than those given.

Methyl Bromide and Silver.—The most obvious experimental result of the presence of silver on the photolysis of methyl bromide was the rapidity of the decomposition. The pressure change during photolysis was either negligibly small or a slight increase as with methyl bromide alone. The products not condensed at liquid nitrogen temperatures again analyzed as methane and carbon monoxide. Very small volumes could be drawn through *s*-butyl chloride and these too analyzed as C₁ gases. Hydrogen bromide was shown not to be present. The gases coming through an ice-salt-bath at -6° which might contain ethyl bromide were less than 0.1 cc. in volume, and showed no test for ethyl bromide. When silver was present in only a part (the bottom half) of the vessel, instead of throughout, the full length, small amounts of free bromine, equivalent to about one drop of 0.01 *N* sodium thiosulfate were found. This amount is approximately the same as that produced in a similar period when no silver was present, indicating a simple photolysis in the upper part of the vessel.

The absence of ethane in methyl bromide, whereas West and Schlessinger find it to be the chief product with methyl iodide in presence of silver, necessitated a repetition of the latter experiments in the present apparatus as a check. Two such runs were made. In both, the volume of gas through *s*-butyl chloride, that is, essentially ethane and ethylene, was almost twice that through liquid nitrogen, essentially methane, confirming the previous findings. It was found here also that the liquid nitrogen fraction contained upward of 15% carbon monoxide. A further significant observation was that with methyl iodide the decomposition involved a small but definite pressure *decrease* as opposed to the increase with the bromide.

The quantum yield for methyl bromide in presence of silver was calculated on the basis of methane formed. The data are included in Table III.

As will appear in the discussion, for reasons connected with the presence of carbon monoxide, a number of experiments on the photolysis of methylene bromide were made at room temperature. The product gases not condensed in liquid nitrogen analyzed as high as 67% carbon monoxide. The rest was methane. Analysis with the mass spectrograph showed hydrogen to be absent.

TABLE III
PHOTOLYSIS OF METHYL BROMIDE IN THE PRESENCE OF SILVER

Expt.	CH ₃ Br, mm.	Time, min.	ΔP, mm.	Quantum yield	V _n , cc.	CO, %
(A) Temp. 25°						
2	44.9	13.75	0.4	0.8	0.31	17.2
5	117.8	5.00	0.8	1.1	.70	(20) ^b
6	50.5	7.00	1.7	1.2	.39	(20)
8	135.0	6.50	3.3	0.9	.60	(20)
10	81.0	7.00	0.0	.7	.38	(20)
11	97.0	7.00	.4	.7	.42	(20)
13	113.5	7.00	.4	1.0	.80	(20)
14 ^a	106.7	7.25	.8	0.6	.59	(20)
15	89.2	10.25	1.6	.5	.52	21.2
16 ^a	87.4	10.50	0.4	.5	.61	27.3
17	88.3	10.50	0.0	.3	.21	18.8

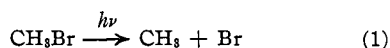
^a Silver present only in lower half of reaction vessel, and bromine detected. ^b Assumed.

(B) At other temperatures				
Temp., °C.	CH ₃ Br, mm.	Time, min.	V _n , cc.	CO, %
100 ^a	104.7	14	0.36	32.4
97.7 ^b	102.6	10	0.46	26.0
257 ^c	279.8	10	2.38	23.4

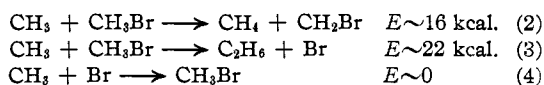
^a CH₃Br alone using 1 *N* sodium chloride solution as bath and light filter. ^b CH₃Br in presence of silver using 1 *N* sodium chloride solution. ^c CH₃Br in presence of silver in air-bath using no filter.

Discussion

From the evidence now available both on the absorption act and on the secondary reactions, the primary step in the photolysis of methyl bromide may be taken as



The following secondary reactions will be considered



The energy of activation for reaction (2) has been taken as 16 kcal. by analogy with the similar methane-producing reaction in acetaldehyde.¹¹ The method suggested by Eyring and co-workers¹² gives an approximate value for the Walden type reaction (3). They have estimated for the inversion reaction of a hydrogen atom with methane an energy of activation of 37 kcal. Since in methyl bromide the bond broken is a C-Br bond instead of the C-H in methane, the energy of activation will be lowered in the ratio of the two

(11) F. O. Rice and Herzfeld, *THIS JOURNAL*, **56**, 284 (1934); Burton, Taylor and Davis, *J. Chem. Phys.*, **7**, 1080 (1939); Haden, Meibohm and O. K. Rice, *ibid.*, **8**, 998 (1940).

(12) Gorin, Kautzman, Walter and Eyring, *J. Chem. Phys.*, **7**, 633 (1939).

bond strengths. This leads to the value 22 kcal. If the energy of activation of reaction (4) is taken as zero, it is easy to understand why in pure methyl bromide this is the principal secondary reaction, and why the quantum yield is so low. Reaction (4) is of the type which is ordinarily assumed to go only as a three-body process. Kimball¹³ has calculated that the half-life of methyl bromide formed by the two-body reaction is only 4.3×10^{-12} sec. However, Kimball assumed symmetrical approach of the particles in his calculations. It is probable that in general most of the collisions are not of this variety (the activation energy of eq. (4) then being increased by 2-3 kcal.), and that a mechanism exists, therefore, for temporary dissipation of the energy among other degrees of freedom until such time as collisional deactivation can occur. It is interesting to point out that this same reasoning would account for the ease of combination of methyl and mercury already reported by Saunders and Taylor.¹⁴

It is to be expected on the basis of the mechanism given that any substance which would remove the methyl radicals or bromine atoms would increase the amount of decomposition by inhibiting reaction (4). Since the energies of activation of the reactions of nitric oxide with methyl radicals and with bromine atoms are small, the introduction of an excess of nitric oxide should almost completely inhibit reaction (4), and the over-all quantum yield should be that of the primary step (1). The average value (1.5) so obtained is actually greater than unity. This might be interpreted as indicating a chain reaction, which is most unlikely with nitric oxide present, or that nitrosyl bromide is acting as a photosensitizer for methyl bromide. In view of the complexity of the products in the presence of nitric oxide already pointed out, it is certain that nitric oxide is functioning in some way as an oxidizing agent, and that significance can be strictly attached only to the order of magnitude of the quantum yield. It is furthermore significant that the quantum yield is low when the ratio of nitric oxide to methyl bromide is small and rises as the ratio increases. It is interesting to note that Iredale¹⁵ obtained a quantum yield of two on the basis of iodine produced in methyl iodide photolysis in the presence of nitric oxide, attributing the high yield to faulty calibration of the light source.

(13) Kimball, *ibid.*, **5**, 310 (1937).

(14) Saunders and Taylor, *ibid.*, **9**, 616 (1941).

(15) Iredale, *Trans. Faraday Soc.*, **35**, 458 (1939).

The introduction of silver removes bromine atoms and thus reduces the reverse reaction (4), and permits the over-all quantum yield to rise to that of the primary act, namely, unity.

The absence of ethane as a product of secondary reactions is to be accounted for on the basis of the estimated 22 kcal. energy of activation of reaction (3), while the production of methane by reaction (2) requires only 16 kcal. The latter reaction should proceed $e^{6000/2 \times 300} = 10^{4.3}$ times as rapidly; hence the lack of ethane. Even if the temperature is raised to 100° or even 250°, the rate of methane production is still $10^{8.5}$ and $10^{2.5}$ times as fast, respectively. At these temperatures no detectable amount of ethane was found. Furthermore, the quantum yield showed no appreciable change, as would be expected.

If this is the correct explanation of the absence of ethane from methyl bromide, the production of ethane from methyl iodide must be accounted for by the difference in the strengths of the C-Br and C-I bonds. Taking the C-I bond as 40 kcal., the energy of activation of ethane production from methyl iodide reacting with a methyl radical, using the Eyring method as before, is only 15 kcal. This is approximately the same as that taken for methane production, and hence comparable amounts of ethane and methane are to be expected, as found. The ethane discrepancy is thus accounted for even if the same value is assumed for the energy of activation of methane production from both the bromide and the iodide. It is, however, to be expected that precisely because the C-Br bond is stronger than the C-I bond, a difference in energy of activation of methane production would exist, and methane production might be easier from the bromide.¹⁶ On both counts then, the absence of ethane from methyl bromide is easily explicable. At the same time, it is clearly demonstrated that the combination of methyl radicals as the source of the ethane found in many decompositions is not as important as heretofore believed. It is possible that this is merely a question of the concentration of methyl radicals, competing reactions with favorable activation energies being so efficient as never to permit a sufficient concentration to make recombination probable.

Since in the photolysis of pure methyl bromide

(16) Saunders and Taylor¹⁴ have shown a similar difference in the energy of activation of methane production from acetone and mercury dimethyl on reaction with methyl radicals, which at about 200° amounts to 2-3 kcal.

the fate of the methyl radicals produced in the absorption act is either methyl bromide by combination with bromine, or methane by reaction with methyl bromide, it seems justifiable to assume that the methyl radical and bromine atom concentrations are not markedly temperature dependent. Hence the temperature coefficient of methane production should give the energy of activation of reaction (2). At 30° (116 mm.) methyl bromide gave 1.16 cc. of methane in 512 minutes, while at 100° (104.5 mm.) methyl bromide gave 0.255 cc. of methane in fourteen minutes. This corresponds to an energy of activation of 6.6 kcal., a value quite close to those found by Smith and H. S. Taylor¹⁷ for methane production by methyl radicals produced by photolysis of mercury dimethyl. The discrepancy between these values and those associated with the corresponding purely thermal reactions must be traced to the excess energy of the radicals produced by photolysis. Thus in the experiments reported here, the light absorbed is equivalent to 112 kcal. per mole, while only 59 kcal. is required to break the C-Br bond, leaving an excess of 53 to be divided between the methyl and bromine. The situation in the mercury dimethyl reactions is closely similar since the Hg-C bond has been estimated as about 50 kcal.

The reaction which produces carbon monoxide has been taken to be one between a free radical and silica to give a silicon compound, carbon monoxide and water. This is supported by the appearance, after photolysis, of a slight brown deposit in the reaction vessel, which disappears on heating in air. It is felt that the radical is probably CH_2Br or CH_2 , since in the photolysis of methylene dibromide in presence of silver, up to 70% of the gas passing through liquid nitrogen is carbon monoxide. If the brown deposit was a carbon-containing compound such as a polymethylene, the pressure increase observed during photolysis would be difficult to explain on the basis of the products found. The postulation of a reaction of chlorine atoms with silica has previously been made by Bodenstein¹⁸ with the production of silicon tetrachloride. Furthermore, it is well known that halogens react with silica only in presence of some carbonaceous matter as a reducing agent. Since the carbon monoxide amounts to only about a quarter of the liquid ni-

(17) Smith and H. S. Taylor, *J. Chem. Phys.*, **7**, 390 (1939).

(18) Bodenstein and Unger, *Z. physik. Chem.*, **B11**, 276 (1930).

trogen fraction, and not one-half as would be expected if every CH_2Br radical reacted with silica (the remainder of the fraction being methane), CH_2Br radicals must also clean up in some additional way. West and Schlessinger found rather more than one third of the methyl iodide decomposed appearing as methylene diiodide. It is possible that methylene dibromide is formed in this case but relatively less than with the iodide, and hence its identification was not possible. Alternatively, reaction of CH_2Br with a methyl radical might produce ethyl bromide, which was also looked for without success. In the absence of more experimental evidence, it is of no advantage to speculate further on the fate of the remaining CH_2Br radicals.

The authors wish to thank Dr. M. Burton for his help in this work.

Summary

1. The photolysis of methyl bromide chiefly by light of wave length 2537 Å. gives a quantum yield based on bromine produced of 4×10^{-3} . The principal products other than bromine are methane and carbon monoxide.

2. In the presence of nitric oxide, the quantum yield based on nitrosyl bromide produced is about unity. The presence of free nitrogen, other oxides

of nitrogen, and carbon monoxide show the reaction to be complex. It is, however, necessary to conclude that the low yield in pure methyl bromide photolysis is due to the back reaction.

3. In presence of silver, the quantum yield based on methane production is again about unity. Methane and carbon monoxide are the sole products.

4. The absence of ethane, denying the possibility of recombination of methyl radicals, is accounted for on the basis of about 6 kcal. difference in the energy of activation of ethane and methane production. It is shown that if ethane results from reaction of a methyl radical with methyl halide, approximately equivalent amounts of methane and ethane are to be expected from methyl iodide as found, but no ethane from methyl bromide.

5. Increase of temperature up to 250° does not change the above findings qualitatively. From the data at room temperature and at 100° , the energy of activation of methane production under the prevailing experimental conditions is found to be 6.6 kcal.

6. The presence of carbon monoxide is shown probably to be due to reaction of CH_2Br radicals with silica.

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The Influence of Hydroxyl Ion Concentration on the Autoxidation of Hydroquinone

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Confusion exists in the literature regarding the exact kinetic expression for the rate of oxidation of hydroquinone by oxygen in alkaline solutions. LaMer and Rideal¹ measured the rate of absorption of oxygen in borate buffer solutions. Their experiments indicated that the rate was proportional to the first power of the hydroquinone concentration, to the first power of the oxygen pressure, and to the three-halves power of the hydroxyl ion concentration. Later, Reinders and Dingemans² repeated the investigation with both phosphate and borate buffers. Their results differed from those of LaMer and Rideal in that their experimentally deduced rate law contained the sec-

(1) Victor K. LaMer and Eric K. Rideal, *THIS JOURNAL*, **46**, 223 (1924).

(2) W. Reinders and P. Dingemans, *Rec. trav. chim.*, **53**, 209 (1934).

ond power of the hydroxyl ion concentration, instead of the three-halves power. It was with the object of deciding which of the laws is correct or whether either is correct that the present investigation was undertaken.

Experimental

The apparatus consisted of a gas buret and a water-jacketed reaction vessel attached to a shaker. These parts were connected by a pair of ground glass joints and a set of spiralled tubes. The latter permitted our shaking the reaction vessel to keep the contents in a froth without disturbing the buret. The temperature in the reaction vessel was kept constant by a flow of water from a thermostat through the jacket.