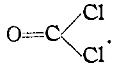
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Photobromination of Acetylene

BY J. E. BOOHER AND G. K. ROLLEFSON

Introduction

Addition reactions have been the subject of many previous investigations both in the gas phase and in solution. Rollefson,[1] Bodenstein,[2] and their co-workers have studied in detail the photochemical addition of Cl_2 to CO and have shown quite conclusively the mechanism of the reaction. This is not, however, a typical reaction as phosgene, the product, is assigned the structure  $O{=}C\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$. From this formula, it is seen, the addition occurs on one atom only, whereas the general case is the reaction of the double or triple bond where the reacting molecule is split into two parts and these parts add to adjacent atoms. Stewart[3] and his co-workers have studied the thermal addition of the gaseous halogens to ethylene. All of the reactions studied were found to be heterogeneous, and therefore the data obtained were not suitable for interpretation in terms of simple mechanisms. In solution a number of reactions of this sort have been studied.[4,5,6,7] The results obtained have been in many ways similar to the phosgene case. The present investigation had as its object an extension of this work to a typical homogeneous gaseous system.

As early as 1884[8] mixtures of pure acetylene and chlorine were observed to be stable in the dark and to react quite smoothly on exposure to diffuse daylight. More recently Peters and Neumann[9] investigated this photochemical reaction in an attempt to determine the conditions under which a maximum yield of dichloroethylene might be obtained. They made no effort, however, to investigate the kinetics of the system. Although this reaction appeared to be suitable for our study, preliminary experiments revealed a number of undesirable properties. First, at the temperature that would be required to keep the products in the gas phase an appreciable dark reaction was observed. Second, unless extreme care was taken as to light intensity and the relative concentrations of acetylene and chlorine, explosions occurred with the formation of carbon and hydrogen chloride. However, if bromine was used instead of chlorine only a small reaction (never more than 3–4% of the light reaction) was observed and under no conditions could explosions be obtained. Therefore the latter reaction was chosen for investigation.

Experimental Methods and Results

The reaction vessel, a Pyrex cylinder 10 cm. long and 6 cm. in diameter, was immersed in an oil thermostat maintained at 150 ± 0.2°. The light source was a Cooper Hewitt 220 volt mercury arc. Zeiss Monochromat light filters A, B and C were used to isolate, respectively, the 5791, 5461 and the 4358 Å. lines of the mercury spectrum. Pressure changes in the system were determined with a sulfuric acid manometer.

The acetylene used in these experiments was obtained from a commercial source and was purified carefully by passing the gas through a series of washing towers which successively contained water, a solution of copper nitrate and nitric acid, a strong potassium hydroxide solution, and concentrated phosphoric acid. The gas was then dried by passing it through a phosphorus pentoxide tube and finally was frozen into a liquid air trap. In order to eliminate all traces of non-condensable gases the acetylene was sublimed and resolidified several times, and each time a high vacuum was pumped on the solid. It was then distilled, the first and last fraction being discarded, and the middle fraction stored in a 3-liter bulb.

The bromine was prepared from Mallinckrodt or Kahlbaum Analytical Reagent. It was kept in contact with C. P. sodium bromide for at least a week, and was then distilled twice *in vacuo* through a phosphorus pentoxide tube at a room temperature to 0° temperature gradient. Each time only the middle fraction was retained. It was stored in a small flask and when not in use was kept solidified in a liquid air bath. All stopcocks through which it passed were of the hollow bore type and were lubricated with Apiezon stopcock grease, which was found to be comparatively inert to the bromine.

The dibromoethylene for these experiments had been specially prepared by Dr. W. Maroney. From measurements of the dielectric constant, which he kindly made, it was shown to be a very pure equilibrium mixture of the cis and trans forms. Once the liquid had been degassed it was kept *in vacuo* and surrounded by a liquid air bath.

The nitrogen used was obtained from the Linde Oxygen

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[1] Lenher and Rollefson, THIS JOURNAL, **52**, 500 (1930).

[2] Bodenstein, Lenher and Wagner, *Z. physik Chem.*, **B3**, 459 (1929).

[3] Stewart and Edlund, THIS JOURNAL, **45**, 1014 (1923).

[4] Berthoud and Beranek, *J. chim. phys.*, **24**, 213 (1927).

[5] Bauer and Daniels, THIS JOURNAL, **56**, 378 (1934).

[6] Leermakers and Dickinson, *ibid.*, **54**, 4648 (1932).

[7] Purkagastha and Ghosh, *Quart. J. Indian Chem. Soc.*, **4**, 409 (1927).

[8] Schlegel, *Ann.*, **23**, 153 (1884).

[9] Peters and Neumann, *Z. angew. Chem.*, **45**, 261 (1932).

Company. In order to remove any trace of oxygen it was purified by bubbling the gas through a washing system containing concentrated ammonium hydroxide and fine copper gauze, and then dried by passing through a liquid air trap filled with glass beads.

The reaction of bromine with acetylene may yield dibromoethylene or tetrabromoethane according to the equations

$$C_2H_2 + Br_2 = C_2H_2Br_2 \qquad (1)$$

$$C_2H_2 + 2Br_2 = C_2H_2Br_4 \qquad (2)$$

There exists the additional possibility of substitution of bromine for the hydrogen either simultaneously with reactions (1) and (2) or as a separate reaction. In order to demonstrate the absence of any substitution reaction in our experiments a three-liter bulb was filled with acetylene and bromine and exposed to visible light while at a temperature of 150°. When the reaction was complete about 100 cc. of water was introduced into the bulb and tested for H^+ and Br^-. No appreciable quantity of either was formed. From an inspection of equations (1) and (2) it is apparent that any pressure change which is observed measures only the amount of bromine reacting and does not distinguish between the two possibilities. It was necessary therefore to determine by analysis, using the apparatus of Fig. 1, the number of moles of bromine reacting per mole of acetylene.

The gas mixture was sampled by allowing part of it to expand into the small trap B which was subsequently cooled to −80° (carbon dioxide and acetone bath), so that only acetylene remained as a gas. The amount of the gas mixture withdrawn was determined from the pressure change in the reaction vessel. The gas was then transferred to the small bulb D and compressed to a standard volume. The pressure of the acetylene in this volume was measured on the manometer E. The relation between the pressures so measured and the acetylene content of the gas sample was determined empirically from analyses of known acetylene and acetylene–bromine mixtures. The presence of bromine did not affect the results. Table I records the results of a number of such analyses at various degrees of completion of the reaction.

TABLE I

RATIO OF BROMINE AND ACETYLENE REACTING

PBr_2	PC_2H_2	ΔBr_2	ΔC_2H_2	$\Delta C_2H_2/\Delta Br_2$
23.95	30.15	11.42	11.45	1.00
24.20	30.00	10.80	10.90	1.01
49.30	30.00	11.50	11.65	1.02
44.82	29.78	11.42	11.08	0.97
53.25	30.15	21.00	22.00	1.05
44.83	30.22	11.95	12.20	1.02
53.32	30.33	21.60	22.12	1.02
55.60	30.35	30.30	28.68	0.95
42.10	50.20	33.30	34.20	1.04

From this it is seen that there is a one to one relationship between the bromine and acetylene reacting until the ratio of the dibromoethylene formed to the acetylene remaining is about five to one. These results were observed at both high and low bromine concentrations. This was checked by adding dibromoethylene to acetylene and bromine gas mixtures, and the rate of this reaction mixture compared to equivalent concentrations of acetylene and bromine alone. Table II gives the results of these experiments.

TABLE II

EXPERIMENTS TO TEST THE EFFECT OF DIBROMOETHYLENE ON THE REACTION RATE

PBr_2 =	39.40		39.3		39.0		38.4
PC_2H_2 =	16.15		15.7		20.1		20.0
PC_2H_2Br =	0		10.5		0		10.7
Δt, min.	ΔP, cm. H_2SO_4						
1/4	2.10	1/4	2.10	1/4	2.60	1/4	2.50
1/4	1.70	1/4	1.60	1/4	2.10	1/4	2.00
1/4	1.40	1/4	1.50	1/4	1.65	1/4	1.65
1/4	1.30	1/4	1.20	1/4	1.45	1/4	1.45
1/2	1.80	1/2	1.75	1/2	2.20	1/2	2.10
1/2	1.40	1/2	1.40	1/2	1.75	1/2	1.70
1	1.95	1	2.00	2	3.95	2	4.10
1	1.45	1	1.40	1	1.20	1	1.30
2	1.50	2	1.70	2	1.40	2	1.60

Here it is seen that even when the reaction mixture initially has approximately equal concentrations of acetylene and dibromoethylene, the reaction rates are identical with those of comparable bromine and acetylene concentrations for the greater part of the reaction. From these experiments it is evident that the first main reaction is that which has been represented in equation 1.

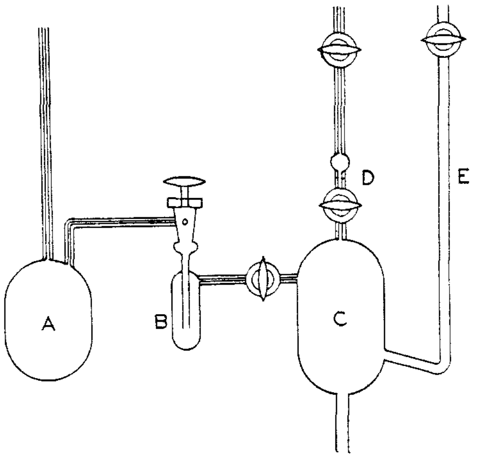

Fig. 1.—Apparatus for the analysis of reaction mixture.

With excess bromine there is the following reaction

$$C_2H_2Br_2 + Br_2 = C_2H_2Br_4$$

This last stage is quite complex. Semi-quantitative experiments with dibromoethylene and bromine showed that this reaction would go photochemically, but relatively slowly. The reaction stopped, however, long before stoichiometric pressure changes could be observed. Table III gives the percentage reaction for dibromoethylene and bromine mixtures, and for acetylene–bromine mixtures which first had been allowed to react to give corresponding amounts of dibromoethylene and then were further illuminated.

In both cases like results were obtained. The fact that only about 50% completion was obtained may mean that a bromine-sensitized decomposition of the product occurred which brought about a photostationary state.

TABLE III

PERCENTAGE REACTION OF DIBROMOETHYLENE WITH BROMINE

$P\mathrm{Br_2}$	$P\mathrm{C_2H_2Br_2}$	ΔP obs.	% reaction
31.7	12.7	6.45	50.8
49.7	16.6	8.30	50.0
32.1[a]	12.55	6.20	49.5
49.3[a]	16.00	8.60	53.5

[a] Original gas mixture contained C_2H_2 and Br_2 which was allowed to react to give the pressures of Br_2 and $C_2H_2Br_2$ listed in the table. This mixture was then further illuminated.

This hypothesis is in part substantiated by the observation that marked changes in light intensity did not greatly affect the rate of the reaction. Due to these complexities attention was focused on the conditions under which the latter reaction could be ignored, and the only rate measured that of the simple addition of bromine to an acetylene molecule to give as a product dibromoethylene.

In several experiments carried out with excess acetylene the illumination was prolonged until bromination ceased. It was observed that the pressure drop was about 3% greater than calculated, due probably to an induced polymerization of the acetylene. This effect, however, is sufficiently small to neglect in the rate measurements.

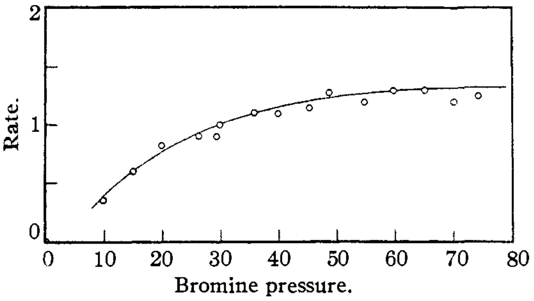

Fig. 2.—Initial rate as a function of bromine pressure, λ = 4358Å.

In determining the quantum yield the reaction vessel used was a cylindrical Pyrex cell, 3.8 cm. in diameter and 4.7 cm. long, which had plane windows sealed in at either end. The volume of this reaction vessel and its various capillary leads was experimentally determined to be 134.5 cc. It was placed in an air thermostat maintained at 150 ± 1°. Plane Pyrex windows were sealed to the ends of the thermostat. A 220-volt mercury arc used in conjunction with the Zeiss monochromat filters gave a source of monochromatic light. The radiation measurements were made using a Moll large surface thermopile and a Leeds and Northrup galvanometer. The thermopile was protected from thermal radiation from the air thermostat by mounting it in a double-walled copper container which had two plane glass windows sealed onto one end. Water at room temperature was circulated between the walls.

The intensity of radiation passing through the empty reaction vessel was determined before and after each measurement. Bromine was added to the cell to a known pressure and the change in the radiation transmitted measured. Acetylene was then added and the reaction mixture illuminated for a definite period. The difference in the radiation passing through the empty cell and the cell filled with bromine was used as the measure of the light absorbed. This introduced but a small error as only a small fraction of the bromine was allowed to react. Another small error which counteracts this one is that the absorption of the bromine is probably slightly greater in the presence of acetylene than in pure bromine. An experimental correction was made for reflection and absorption losses due to the windows between the reaction mixture and the thermopile. Measurements were made at 150 and 21° at the wave lengths 4358, 5461 and 5791 Å. at two different bromine pressures. Typical results are tabulated in Table IV.

TABLE IV

QUANTUM YIELD

$P\mathrm{C_2H_2}$ = 30.0 cm.		$P\mathrm{Br_2}$ = 20.0 cm.	Temp. = 150°
	$\gamma\left(\frac{\text{molecules}}{\text{quantum}}\right)$		
5791	505	524	555
4358	535	520	550
5461	534	502	535
$P\mathrm{C_2H_2}$ = 30.0 cm.		$P\mathrm{Br_2}$ = 30.0 cm.	Temp. = 150°
5461	545	525	
4358	570	564	
$P\mathrm{C_2H_2}$ = 20.8 cm.		$P\mathrm{Br_2}$ = 14.0 cm.	Temp. = 21°
4358	3060	3220	
5461	3400	3250	
5791	2910	3060	

Experimental Results

(a) Dependence of the Rate on Concentration.—Early experiments showed that if two or three clean up reactions were run the rate reached a maximum value and showed no induction period. Hence it was possible to study the effect of concentration by measuring the variation in initial rate with one of the reactions at constant concentration and the other added in various amounts. As we have seen previously the product has no effect on the reaction. Table VA records the initial measurements with bromine variant. Section A is for illumination with the 5791 Å. line and Fig. 2 shows the same relation for insolation with the 4358 Å. line. Table VB records the observed variation in rate with acetylene at constant bromine pressure,

(b) Dependence of the Rate upon Light Intensity.—The intensity of the light incident was varied by the use of a series of fine-mesh screens placed directly in the light path. The transmission factors for the screens were determined before and after these experiments by means of a photronic cell. A given bromine–acetylene mixture was illuminated with and without the screens in place. The data are plotted in Fig. 3.

TABLE V

EFFECT OF BROMINE AND ACETYLENE PRESSURES ON THE INITIAL RATE

A Bromine variant 5791 Å. PC_2H_2 = 50.0 cm.		B C_2H_2 variant PBr_2 = 35.0	
PBr_2	Rate	PC_2H_2	Rate
2.57	0.08	4.5	0.40
5.30	.25	6.7	.60
7.10	.50	10.9	.90
11.35	1.00	16.5	1.25
17.85	1.85	20.7	1.40
25.40	2.80	21.5	1.40
30.30	3.40	31.1	1.70
33.80	3.80	40.3	1.90
37.70	4.25	51.7	2.10
46.00	5.25	60.5	2.10
55.70	6.30	65.2	2.05
70.2	7.6	75.5	2.10

(c) **Dependence of the Rate upon Total Pressure.**—As shown in Table VI, the addition of the inert gas nitrogen produced a definite increase in the reaction rate. A four-fold increase in the total pressure increased the rate by about 22%. An increase of one and one-half fold did not produce a detectable change.

TABLE VI

EFFECT OF INERT GAS

PBr_2	PC_2H_2	PN_2	Rate	Total P
20.2	10.9	..	3.1	31.1
20.4	10.9	90.5	3.8	121.8
20.2	10.9	45.3	3.5	76.4
20.0	11.1	15.1	3.1	46.2

(d) **Temperature Coefficient.**—The measurements of the change of rate with temperature were made with three different reaction vessels. While consistent results could be obtained with any one set up, the absolute magnitude of the temperature coefficient was dependent on the particular vessel used. In every case, however, the calculated heat of activation has a small negative value (*circa* 1500 cal.) which is independent of both the bromine and acetylene pressures.

Discussion of Results

The experimental results which have been presented show that we are dealing with a system in which the light absorption initiates a chain process of considerable length. Any mechanism which is to explain the data must give a high quantum yield, and account for the following facts: the rate of the reaction depends on the first power of the incident light intensity; the acetylene appears in the rate law to a power ranging from zero to one; the bromine appears to a power ranging from zero to one. Furthermore the nature of the reaction is the same at all the wave lengths used although these included radiations of both higher and lower frequencies than the convergence limit of the bromine bands. It is unnecessary to consider any steps leading to the formation of tetrabromoethane as this has been shown to be negligible compared to the formation of dibromoethylene.

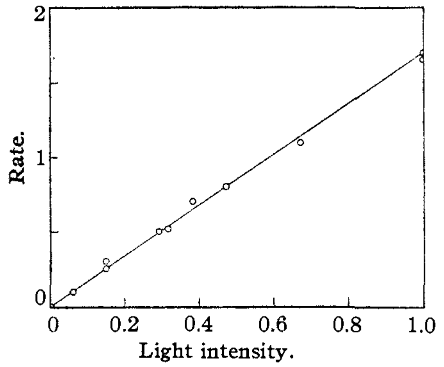

Fig. 3.—Initial rate as a function of light intensity.

The primary action of the light must be settled before any conclusions may be drawn concerning the following reactions. The usual procedure has been to consider that the continuous absorption produced bromine atoms and the band absorption yielded activated molecules although no reaction has been found which showed marked differences in the two regions of the spectrum. Recently Urmston and Badger[10] have presented definite evidence that yellow light produces bromine atoms without the aid of collisions. This may be considered a predissociation process in which the life of the excited molecule with respect to dissociation is sufficiently long to permit the absorption lines to be sharp. It was this type of behavior which led Herzberg[11] to advocate the absence of fluorescence as a better criterion of predissociation than the blurring of the absorption lines. Urmston and Badger performed their experiments at such low pressures that no collision processes needed to be considered. In our experiments the pressures were such that unless we assign a life of less than 10^{-9} seconds to the excited molecule we must consider the effect of collisions. Since the bromine molecules possess sufficient energy to dissociate into normal atoms if the exciting light is of wave length less than

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(10) Urmston and Badger, THIS JOURNAL, **56**, 343 (1934).

(11) Herzberg, *Ergebnisse der exakt. Naturwissenschaften*, **10**, 207 (1931).

6350 Å., the most probable effect of a collision is to favor the dissociation processes.

Experimental evidence for a process of this kind has been presented by Turner,[12] who detected the absorption lines of atomic iodine in iodine vapor which was being illuminated with light of wave length longer than the convergence limit of the bands. Therefore we may represent the primary action of the light at all the wave lengths we have used by

$$Br_2 + h\nu = 2Br$$

A bromine atom formed by this reaction enters into a series of reactions which result in the formation of dibromoethylene and regeneration of the atom until some process occurs which causes the direct or indirect elimination of the bromine atom. The first possibility to be considered is that the bromine atom may react with bromine molecules to form Br_3, which has been shown to be a probable molecule.[13] Then acetylene may react with either the atomic bromine or the Br_3 molecules to yield C_2H_2Br or $C_2H_2Br_3$. These intermediates react to give dibromoethylene and a bromine atom. The chain-terminating process must be first order with respect to one of the four intermediates mentioned above in order to obtain a rate law depending on the first power of the light intensity. Furthermore, it is necessary to have two limiting cases corresponding to the two limiting powers for the acetylene. The following mechanism embodying all these considerations accounts for all the experimental facts.

$$Br_2 + h\nu = 2Br \qquad (1)$$

$$Br + Br_2 = Br_3 \qquad (2)$$

$$Br_3 + C_2H_2 = C_2H_2Br_3 \qquad (3)$$

$$C_2H_2Br_3 = C_2H_2Br + Br_2 \qquad (4)$$

$$C_2H_2Br + Br_2 = C_2H_2Br_2 + Br \qquad (5)$$

$$C_2H_2Br = C_2H_2 + Br \qquad (6)$$

$$Br_3 + W = {}^3/_2Br_2 \qquad (7)$$

$$C_2H_2Br_3 + W = C_2H_2 + {}^3/_2Br_2 \text{ or } C_2H_2Br_2 + {}^1/_2Br_2 \qquad (7')$$

Applying the usual methods of calculation we obtain (with 7′ as the chain terminating step)

$$\frac{-d(Br_2)}{dt} = 2I_{abs.}\frac{k_4}{k_{7'}}\,\frac{k_5(Br_2)}{k_5(Br_2) + k_6} \qquad (A)$$

Using 7 as the chain terminating step

$$\frac{-d(Br_2)}{dt} = 2I_{abs.}\frac{k_3}{k_7}(C_2H_2)\,\frac{k_5(Br_2)}{k_5Br_2 + k_6} \qquad (B)$$

The latter rate law may be derived without the assumption of the existence of an intermediate having formula $C_2H_2Br_3$; in fact it is not even necessary to use Br_3, but both of these are necessary to give law (A). Whether (7) or (7′) is the chain terminating step is determined by the acetylene pressure as may be seen by considering the variation of the concentrations of the intermediates as the acetylene pressure is varied. If we calculate the ratio of the two intermediates involved in 7 and 7′ we obtain

$$\frac{(C_2H_2Br_3)}{(Br_3)} = \frac{k_3(C_2H_2)}{k_4 + k_{7'}} \cong \frac{k_3(C_2H_2)}{k_4}$$

The quantum yield measurements show that $k_{7'}$ is small compared to k_4. From this relationship we see that as the acetylene pressure increases (7′) increases in importance and (7) decreases until in the limit it may be neglected as a chain terminating process. In a sense it may be said that (7′) is a formal method of stating that high pressures of acetylene catalyze the destruction of Br_3 at the walls.

A comparison of the theoretical equations (A) and (B) with the experimental data shows perfect agreement. At any given bromine pressure $I_{abs.}$ is proportional to the intensity of the incident light as is the experimentally determined rate. The limiting powers for the acetylene pressure are zero and one with the range of each dependent upon the relative magnitudes of k_7 and $k_{7'}$. Experimentally some variation was found in the minimum pressure at which the rate was independent of acetylene. This behavior is to be expected if k_7 and $k_{7'}$ do not change exactly the same for any change in the nature of the surface at which these reactions occur.

Bromine affects the rate in two ways: first, it determines the fraction of the incident light which is absorbed and, second, it appears in the fraction $k_5(Br_2)/(k_5(Br_2) + k_6)$. At low bromine pressures the light absorbed is proportional to the bromine concentration, but at high pressures the fraction of the light absorbed may be calculated with the aid of the absorption coefficients given by Style and Gray.[14] The theoretical relationship which we have derived may be tested by plotting the rate, at constant acetylene pressure, against the fraction of the light absorbed multiplied by $k_5\,Br_2/(k_5(Br_2) + k_6)$. If the proper value of k_6/k_5 has been selected a straight line should be obtained. Figure 4 shows a plot of this type in which k_6/k_5 is taken at seven, and it is obvious that the agreement is excellent. It is to be noted

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[12] Turner, *Phys. Rev.*, **41**, 627 (1932).

[13] Rollefson and Eyring, This Journal, **54**, 176 (1932).

[14] Style and Gray, *Proc. Roy. Soc.* (London), **A126**, 603 (1930).

that the rates which appeared to be much too low at low bromine pressures or light absorbed now fall on the line which passes through the origin and the higher pressure data.

The temperature coefficient is a composite effect due to all the specific rate constants which appear in our final rate laws. From the fact that variation of the bromine pressure causes no change in the temperature effect we may conclude that the fraction $k_5(\mathrm{Br_2})/(k_5(\mathrm{Br_2}) + k_6)$ is the same at all temperatures. This means that k_6/k_5 is independent of temperature. The observed effect must, therefore, be due to k_4/k_7' at high acetylene pressures and k_3/k_7 at low pressures. The data which have been presented show that the effects produced by these ratios are the same but they do not permit a separation into effects due to k_4 and $k_{7'}$ or k_3 and k_7. The only conclusion we may draw is that the heat of activation corresponding to $k_{7'}$ is slightly greater than that for k_4 and similarly for k_3 and k_7. Therefore the chain-terminating step has some heat of activation although its magnitude is indeterminate.

The accelerating effect of increasing the total pressure in the reaction vessel may be attributed to a diminution in the rate of diffusion of the intermediates $\mathrm{Br_3}$ and $\mathrm{C_2H_2Br_3}$ to the wall, which causes a decrease in the rates of the chain terminating steps (7) and (7′). It is also possible that the added inert gas may affect the rates of formation of $\mathrm{Br_3}$ and $\mathrm{C_2H_2Br_3}$ in reactions (2) and (3) by furnishing stabilizing collisions. We have not written those reactions as involving a third molecule as these intermediates have sufficient complexity of structure to give the quasi-molecules such long life that they will usually be stabilized even without added gas. A third possibility is that the increase in pressure increases the amount of light absorbed by the bromine and thus affects the observed rate.

Although the mechanism presented in this paper has been derived for the special case of the reaction between bromine and acetylene it is quite probable that the essential features of all photochemical addition reactions involving the halogens are of this form. The action of the light is to produce halogen atoms which then react to form molecules of the form X_3, and these start the chain processes. The use of X_3 molecules in mechanisms for addition reactions has been criticized recently by Sherman and Sun[15] on the basis of some calculations of activation energies by the method of Eyring and Polanyi. They have concluded that for all the halogens the molecules X_2 will add more rapidly than X_3. These calculations involve numerous assumptions which may invalidate the conclusion in some or all cases involving complex systems. In the reactions of the halogens there are so many instances in which the results may be explained by the assumption of a greater reactivity for X_3 than for X_2,[1,6,7,16] we feel the use of such molecules should not be abandoned solely on the basis of the calculations of Sherman and Sun.

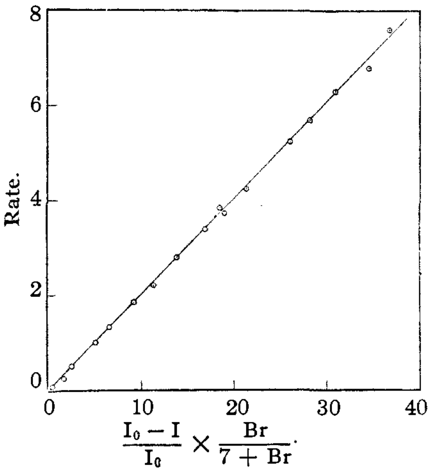

Fig. 4.—Rate *vs.* the fraction of light absorbed × $(\mathrm{Br_2})/(7 + (\mathrm{Br_2}))$.

Summary

A kinetic study has been made of the photochemical reaction between bromine and acetylene at 150°. It was shown that the reaction product was dibromoethylene under the experimental conditions. Measurements of the quantum yield showed that it is a chain reaction with a chain length of approximately 500 at 15° and increasing to about 3000 at 20°. These values were the same, within the experimental error, at all wave lengths used although these included radiations of both higher and lower frequencies than the convergence of the bromine bands.

The kinetics of the reaction were investigated using the Ostwald isolation method. The experimental results were found to conform to the rate law

$$\frac{-\mathrm{d}(\mathrm{Br_2})}{\mathrm{d}t} = 2I_{\mathrm{abs.}} \frac{k_4}{k_7'} \frac{k_5(\mathrm{Br_2})}{k_5(\mathrm{Br_2}) + k_6}$$

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[15] Sherman and Sun, THIS JOURNAL, **56**, 1096 (1934).

[16] Smith, Noyes and Hart, *ibid.*, **55**, 4444 (1933); Vesper and Rollefson, *ibid.*, **56**, 1455 (1934); Dickinson and Carrico, *ibid.*, **56**, 1473 (1934).

at high concentrations of acetylene and to the law

$$\frac{-\mathrm{d}(\mathrm{Br_2})}{\mathrm{d}t} = 2I_{\mathrm{abs.}}\frac{k_3}{k_7}(\mathrm{C_2H_2})\frac{k_5(\mathrm{Br_2})}{k_5(\mathrm{Br_2}) + k_6}$$

at low concentrations of acetylene. A mechanism involving Br, Br_3, $C_2H_2Br_3$ and C_2H_2Br as intermediates, and which would lead to the experimentally observed rate law, was suggested.

Measurement of the relative rates at 150 and at 120° showed the influence of temperature to be very small. Using the integrated form of the Arrhenius equation a value of about −1500 calories was calculated for the heat of activation.

BERKELEY, CALIF. RECEIVED JULY 27, 1934

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

The Quantum Yield in the Photodecomposition of Liquid Ethyl Iodide at 3130, 2654 and 2537 Å.[1]

BY BAYES M. NORTON

The quantum yield in the photodecomposition of liquid ethyl iodide (calculated in terms of the number of atoms of iodine formed per quantum of light energy absorbed) has been measured by Iredale.[2] He used filters to isolate light of wave lengths in the neighborhood of 3660 and 3000 Å., for which he found quantum yields of 1.0 and 1.2, respectively. More recently West and Paul[3] concluded that these yields were too high and reported values, 0.30 and 0,58, for the quantum yields in hexane solutions of several concentrations for wave lengths, isolated by filters, in the neighborhood of 3130 and 2600 Å.

The results given in this paper were obtained with improved technique, and show that the quantum yield for the liquid iodide is 0.315 at 3130 Å., 0.38 at 2654 Å. and 0.41 at 2537 Å.

Materials and Procedures

Ethyl iodide was prepared from ethyl alcohol, iodine and phosphorus according to the directions of Fischer.[4] Also one of the samples used came from the J. T. Baker Chemical Co. Before exposure the iodide was shaken with sodium hydroxide, washed several times with distilled water, dried over calcium chloride and finally freed of oxygen by gentle boiling on a water-bath with a reflux condenser in a current of nitrogen. The reaction cell was connected directly to this system so that it could be flushed with nitrogen before filling.

The cell, which was made of quartz with flat faces of polished quartz fused on, had a capacity of 10 cc. and a depth of 1.5 cm. Stirring was accomplished by a thin glass rod equipped with vanes so that it could be turned by a current of air.

A Hanovia 220-volt advanced research model mercury vapor arc was used as the source of radiation. A quartz lens was used to focus the light on the collimator slit of a D-33 Hilger quartz monochromator. Slit widths of 0.04″ were used in runs A and D of Table II, 0.05″ in runs C, D, F and J of Table III, 0.08″ in runs B and C of Table II and 0.10″ in run E of Table II and in runs A, B, E, G, H and I of Table III. Experiments were thus made with slit widths of either 0.04″ or 0.05″ at all wave lengths used with no appreciable difference in the values of the quantum yields obtained from those using wider slit widths.

The use of the monochromator with a commercial mercury vapor arc meant that the determination of the amount of chemical change by ordinary chemical means of analysis would have necessitated inconveniently long exposures. To overcome this difficulty an optical method of measuring small amounts of iodine was devised. Light from a mazda daylight bulb, filtered by 2.5 cm. of a saturated solution of copper sulfate, entered a thermostat through a window in the wall. The reaction cell was in position behind this and was fixed in a carriage suspended from an overhead track so that it could be run conveniently in and out of the path of light. In back of this there was a copper case with a window through which the light could pass to a thermopile inside. The absorbing solution in the reaction cell and the thermopile were kept at a temperature of 20°.

As comparison standards for this optical method solutions of iodine in ethyl iodide were prepared gravimetrically and diluted with more ethyl iodide until there were present in the cell from 1.5×10^{-6} to 9.5×10^{-6} g. atoms of iodine. The percentage absorption for these amounts ranged from 20 to 60. The absorption values plotted as ordinates against the log of the iodine concentrations as abscissas gave a straight line except for a small decrease in slope at the lower values. By making absorption measurements at intervals on ethyl iodide that was undergoing photolysis and comparing with the graph, it was possible to obtain a number of values for the amount of iodine formed.

The radiometric measurements were made by the integration method[5,6,7] developed by Forbes and his co-

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(1) From the Dissertation presented to the Graduate School of Yale University by the author in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, June, 1934.

(2) Iredale, *J. Phys. Chem.*, **33**, 290 (1927).

(3) West and Paul, *Trans. Faraday Soc.*, **28**, 688 (1932).

(4) Fischer, "Introduction to the Preparation of Organic Compounds," translated by R. V. Stanford, D. Van Nostrand Co., New York, 1928.

(5) Villars, THIS JOURNAL, **49**, 326 (1927).

(6) Leighton and Forbes, *ibid.*, **52**, 3139 (1930).

(7) Leighton and Leighton, *J. Phys. Chem.*, **36**, 1882 (1932)