are of sufficient interest to justify such publication but also because there is little assurance that sufficient funds will be available for further experiments.

The writer wishes to acknowledge the many helpful criticisms made by Dr. L. S. Kassel.

Summary

Data are presented concerning the composition and amounts of products from ethylene polymerization at 377° and 141.5 cm. pressure. These indicate that the primary product is butylene and that propylene formation is secondary. Minute amounts of oxygen accelerate the reaction. There is also a large increase in over-all reaction rate with time of contact. In the temperature range 350–400° the heat of activation was found to be about 42,000 calories.

PITTSBURGH, PA. RECEIVED OCTOBER 27, 1933

[CONTRIBUTION FROM LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

Separation of Photochemical and Thermal Action in the Photobromination of Cinnamic Acid[1]

BY WALTER H. BAUER AND FARRINGTON DANIELS

The addition of bromine to the double bond of cinnamic acid under the influence of light offers a means for studying chain reactions. It has been investigated before,[2,3,4] but in the present work accurate determinations of the quantum yield as a function of the concentration of bromine at different temperatures have been made. Some of the earlier work may now be interpreted differently in view of the concentration effects described here. It has been found that dilution decreases the length of the chain, so that under extreme dilutions the primary photochemical reaction stands alone. Under these conditions the yield of one molecule per quantum is obtained in agreement with the Einstein relation, and the reaction is not affected by temperature.

Experimental Procedure

The monochromator was built around a hollow glass prism of 60°, 12 cm. on an edge, filled with ethyl cinnamate. Light was furnished by a capillary, mercury-vapor lamp[5] of high intensity. The optical train contained two lenses 15 cm. in diameter and 16 cm. in focal length, a series of slits, and a front-silvered mirror in Wadsworth mounting. The prism table was rotated with a machinist's micrometer. At the exit slit, 0.5 mm. wide, the energy intensity was about 20,000 ergs per second for the mercury lines at 436 mμ. Movement of the slit image by 0.5 mm. caused the intensity to drop to 1% of its former value. Entry and exit slits were cut in thin silver foil and mounted on heavy aluminum plates. Adjustable slits of brass were unsatisfactory because the intense radiation caused them to expand and change the width of the slit.

The exit beam, rendered parallel with a convex lens, passed through the reaction cell in a large thermostat of clean water. The reaction cell was of plane, polished quartz, 1 cm. wide, 1.9 cm. thick and 9 cm. high. A long neck permitted the cell to be immersed deep in the thermostat. The 2-mm. stirrer with small vanes of quartz was rotated rapidly just above the region of illumination. The large thermopile, having a receiver area 9 × 33 mm., was constructed in this Laboratory. It was set in a heavy aluminum case, back of the cell in a box immersed in the thermostat. Calibration in absolute units was effected with radiation lamp No. 132 from the U. S. Bureau of Standards.

Kahlbaum's cinnamic acid was recrystallized from alcohol. It melted at 133°.

The bromine, Mallinckrodt analytical quality, was refluxed with potassium bromide and distilled, twice distilled from barium oxide, and further purified by crystallization. Two different preparations gave identical quantum yields.

Carbon tetrachloride was refluxed in 10-liter lots for six hours with alkaline permanganate, washed, and distilled from calcium chloride, and finally distilled from phosphorus pentoxide or metallic sodium. This material showed some slight absorption of the 313 mμ line of mercury. Bovis[6] states that such absorption is probably due to a trace of carbon disulfide, but its presence could not be detected by other tests. Different samples of carbon tetrachloride used over a period of two years showed no difference in the behavior of the reaction.

The extent of the reaction was determined by titrating the decrease in bromine. Stock solutions of bromine and of cinnamic acid in carbon tetrachloride were diluted and mixed in equal portions. The control solution was kept in a blackened quartz flask set deep in the thermostat.

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[1] Presented at the meeting of the American Chemical Society, Chicago, Illinois, September 14, 1933; also THIS JOURNAL, **54**, 2564 (1932). More complete details may be found in the Ph.D. thesis of Walter H. Bauer, filed in the Library of the University of Wisconsin in June, 1933.

[2] Purkayastha and Ghosh, *Quart. J. Indian Chem. Soc.*, **2**, 261 (1926); **4**, 409 (1927); **4**, 553 (1927).

[3] Purkayastha, *ibid.*, **5**, 721 (1928).

[4] Berthoud and Beranek, *J. chim. phys.*, **24**, 213 (1927); *Helv. Chim. Acta*, **10**, 289 (1927); **13**, 385 (1930).

[5] Daniels and Heidt, THIS JOURNAL, **54**, 2381, 2384 (1932).

[6] Bovis, *J. phys. radium*, **10**, 267 (1929).

After the exposure (usually fifteen minutes) samples were withdrawn for titration with a special, small-tipped pipet.

The intensity of the transmitted light was determined with the thermopile and galvanometer at regular intervals and the intensity of the incident light was taken from the readings with the unobstructed beam. It was found that the cell filled with pure carbon tetrachloride alone absorbed less than 1%. The light was very steady, for the lamp was operated with an isolated 500-volt dynamo,[7] but the lamp deteriorated gradually with use. Each centimeter on the scale represented 134.2 ergs per second.

The measurements and calculations may be illustrated with the following typical data. The monochromator was set on the 436 mμ line for an exposure of 900 seconds. The temperature of the thermostat was 30.0°. The galvanometer deflection without the cell was 150 cm. When the light passed through the cell the initial deflection was 0.6 cm. but as the bromine reacted the solution gradually became less absorbing and at the end of the determination the deflection was 9.2 cm. By graphing the incident and transmitted intensities at regular time intervals and taking differences it was found that the average light absorbed corresponded to 143.0 cm. or 19,190 ergs per second. In the 900 seconds, then, 3.83×10^{18} quanta were absorbed. After the absorption of this light, 9.48 cc. of 0.100 *N* sodium thiosulfate was required to titrate the iodine liberated from potassium iodide by 15.6 cc. of the solution. The control solution kept in the dark decreased by 0.16 cc. of thiosulfate in an hour and interpolation to the time of titrating the photochemical solution gave a value of 21.35 cc. The cell contained 16.6 cc. of solution and the titrations showed that bromine equivalent to (16.6/15.6) (21.35–9.48) cc. or 38.3×10^{18} molecules had been consumed in the photochemical reaction. The quantum yield, Φ, then was $(38.3 \times 10^{18})/(3.83 \times 10^{18})$ or 10 molecules of bromine reacting per quantum of light absorbed.

Results

Quantum Yields.—The results are summarized in Tables I–V where $\bar{C}_{Br_2}$ = average concentration of bromine in moles per liter $\times 10^3$, ΔBr_2 = moles of bromine $\times 10^3$ reacting during exposure to light, $\bar{I}_0$ and $\bar{I}_a$ = average intensity of incident and absorbed light in ergs per sec. $\times 10^{-3}$, t = time of exposure in seconds, and Φ = the quantum yield, or molecules of bromine reacting per quantum of light absorbed. In all cases the initial concentration of cinnamic acid was 0.0055 mole per liter, with the exception of those starred, for which the concentration of cinnamic acid was 0.011 mole per liter.

The quantum yield decreases with the length of the exposure as shown in Table III. This phenomenon is explained by the fact that the concentration decreases with the length of the exposure and this decrease in concentration then produces a decrease in the quantum yield. This latter decrease is practically linear (as shown in Fig. 1) and so it is legitimate to take the average concentration of bromine during the exposure for graphing. An exposure of 900 seconds was used most frequently because the amount of bromine changed in this time could be accurately measured at all concentrations.

TABLES I–V

QUANTUM YIELDS FOR PHOTOBROMINATION OF CINNAMIC ACID. WAVE LENGTH, 436 mμ

$\bar{C}_{Br_2}$	ΔBr_2	$\bar{I}_0$	$\bar{I}_a$	t	Φ
Table I. Temperature 30.6°					
7.30	0.0692	14.10	13.96	910	15.0
6.93*	.0756	14.00	13.88	904	16.5
5.00	.0446	11.54	11.22	922	11.8
3.30	.0301	13.26	12.01	911	7.6
1.94	.0168	12.08	9.66	955	5.0
1.77*	.0170	14.20	11.06	897	4.7
1.26	.0088	12.28	7.11	905	3.6
1.08*	.0088	14.60	8.43	908	3.1
Table II. Temperature 20.0°					
8.56	0.0383	14.13	14.10	910	7.9
7.20	.0241	13.67	13.66	900	5.4
5.41	.0193	14.16	13.98	900	4.2
5.37	.0260	18.84	18.57	900	4.2
5.21	.0277	20.09	19.80	900	4.2
5.15	.0253	20.09	19.75	900	3.9
3.44	.0129	14.02	13.28	900	3.0
1.76	.0071	14.28	10.76	900	2.0
1.74	.0074	14.04	10.40	900	2.2
Table III. Temperature 20.0°					
3.37	0.0159	13.88	13.04	1200	2.8
3.44	.0129	14.02	13.28	900	3.0
3.56	.0095	14.02	13.29	600	3.4
3.66	.0052	13.82	13.30	300	3.6
Table IV. Temperature 10.0°					
9.30	0.0166	13.79	13.55	900	3.7
7.59	.0128	13.84	13.78	900	2.9
5.69	.0111	14.10	14.02	900	2.2
3.61	.0077	14.14	13.51	900	1.7
1.86	.0039	14.39	11.47	900	1.0
1.87	.0036	14.17	11.38	900	1.1
Table V. Temperature 0.0°					
8.75	0.0099	14.23	14.23	915	2.1
6.75	.0072	12.53	12.45	886	1.8
4.24	.0054	13.37	12.92	895	1.3
2.49	.0037	12.35	10.48	978	1.0

The marked influence of bromine concentration on the temperature coefficient of the quantum yield is shown in Fig. 2, where the data have been interpolated from the graphs of Fig. 1.

Absorption Measurements.—The intensities of the incident and transmitted light, which must be carefully measured for calculating quantum

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[7] The authors are indebted to the Research Committee of the University of Wisconsin for the purchase of this dynamo.

yields, can be used also for calculating concentrations of bromine, provided Beer's law is applicable. The validity of this law was tested at five concentrations, from 0.0007 molar to 0.0055 molar, using an incident intensity of approximately 15,000 ergs per second per sq. cm., and a cell thickness of 19 mm. When log I_0/I was plotted against bromine concentration, a straight line extrapolating to zero was obtained for solutions ranging in transmission from 1 to 90% transmission. Three widely distributed points taken from actual photochemical determinations, containing the products of the bromination as well as bromine, also fell close to the curve. Hence there occur no serious complications, such as dissociation of bromine or combination with solvent or with products, which change during the reaction. A value for a of $0.448 \times 10^{+3}$ with an average deviation of 0.006 was obtained, using the relation $I = I_0e^{-alc}$, where l is expressed in cm. and c is expressed in moles of bromine per liter.

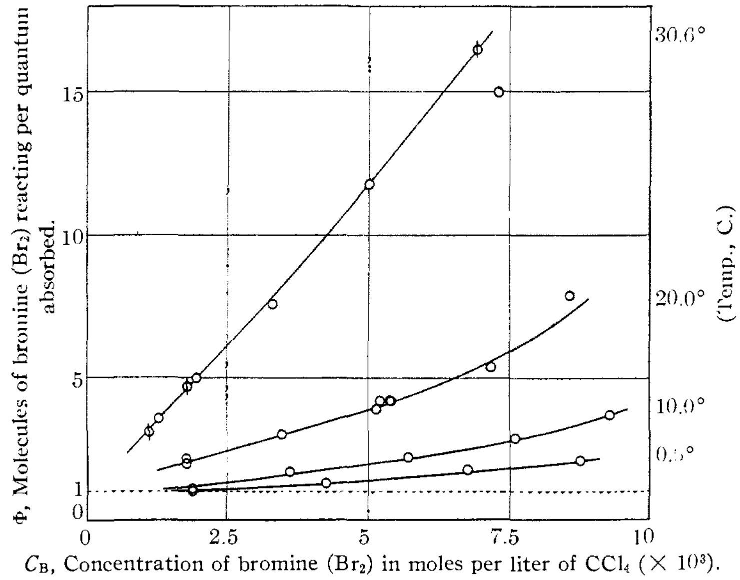

Fig. 1.—Influence of bromine concentration on quantum yield: initial concentration of cinnamic acid 0.0110 for points ϕ; for all others, 0.0055.

A solution of bromine and cinnamic acid, 0.00654 and 0.0054 molar, respectively, was radiated with light of wave length 436 mμ at 20.0°. Frequent readings of the intensity of the incident and transmitted light were made, and by means of Beers' law the concentrations at various times were calculated. From these data k in the first order equation $k = (2.303/t) \log c_0/c$ was obtained. The results are shown in Table VI, where k is the first order constant $\times 10^4$, t is the time in seconds, I_0 and I are the intensities of the incident and transmitted light, and c_B is the concentration of bromine in moles per liter $\times 10^3$. The results of a similar experiment are given in Table VII, where the initial concentrations of bromine and cinnamic acid were 0.00381 and 0.0055 and where the initial and final values of I_0/I were 104/4 and 100/74.

TABLE VI

THE RATE OF PHOTOBROMINATION AS DETERMINED FROM ABSORPTION MEASUREMENTS

t	I_0	I	c_B	k
0	104.3	0.5	6.50	...
600	102.6	.9	5.70	2.2
1200	101.4	1.6	4.90	2.4
1800	100.0	2.8	4.15	2.5
2400	98.5	4.4	3.60	2.5
3600	95.0	10.0	2.65	2.5
4800	92.6	17.2	1.95	2.5
6000	89.7	24.7	1.55	2.4
7200	86.6	27.6	1.40	2.2

TABLE VII

c_B........	3.39	2.46	1.82	1.36	1.06	0.83
k........	2.2	2.5	2.5	2.5	2.4	2.4
c_B........	0.67	0.54	0.44	0.37	0.30	0.28
k........	2.1	2.2	2.1	2.1	2.0	1.9

The first order "constant" obtained here has little theoretical significance as to the reaction mechanism, but it shows the rate of the reaction to be nearly independent of the concentration of cinnamic acid. The rate will be discussed more fully later. To estimate quantum yields at low concentration, Φ was calculated directly from the data used in preparing Table VII, with the help of Beers' law.

The results are given in Table VIII, where c_A and c_B are the concentrations of cinnamic acid and bromine in moles per liter $\times 10^3$, and Φ is the quantum yield at 20.0°.

TABLE VIII

QUANTUM YIELDS AT LOW CONCENTRATIONS AS DETERMINED FROM ABSORPTION MEASUREMENTS

c_B.......	3.37	2.50	1.89	1.39	0.68	0.47	0.31
c_A.......	5.1	4.2	3.6	3.1	2.4	2.2	2.1
Φ........	2.8	2.4	1.8	1.5	1.1	0.8	0.5

If these values of Φ are plotted against c_B a curve is obtained which extrapolates to 1 for the first five points (as do the lines of Fig. 1) but for the last two where the cinnamic acid concentration drops below 0.0025 mole per liter the curve bends and extrapolates to 0 as a limit.

In this connection the one point lying off the curve in Fig. 1 at 30.6° should be noted. In this experiment so much bromination occurred that the concentration of cinnamic acid fell from 0.0055 to 0.0013 molar. From the experiments shown by the barred circles, it is clear that doubling the concentration of cinnamic acid made the points fall on the curve again. When the cinnamic acid is kept sufficiently in excess, apparently above about 0.0025 molar, its concentration has no effect on the reaction rate.

Theory

Chain Reaction.—The system under investigation consists of bromine, cinnamic acid and carbon tetrachloride in the ratios of about 1 to 1 to 2000. Except at great dilution, the photobromination of cinnamic acid is a chain reaction, more than one molecule of bromine reacting per quantum absorbed.

All the results described in this research may be explained on the hypothesis of an energy chain,[8] dividing the reaction, corrected for the dark reaction, into a primary photo process and a secondary, photo-initiated thermal reaction as shown below. The photo process is composed of two steps

$$\mathrm{Br_2} + h\nu = \mathrm{Br_2}^* \qquad (1)$$
$$\mathrm{Br_2}^* + \mathrm{A} = \mathrm{ABr_2}' \qquad (2)$$

where A represents cinnamic acid and where $\mathrm{ABr_2}'$ represents the molecule of reaction product plus its excess energy of $h\nu$ and the heat of reaction, $16{,}000/6 \times 10^{23}$ calories.[9] It is then assumed that the thermal reaction occurs as a result of the lag in reaching the normal Maxwell–Boltzmann distribution of energy at the temperature of the thermostat. This second part can be described by equations 3, 4 and 5 below:

$$\mathrm{ABr_2}' + \mathrm{Br_2} = \mathrm{Br_2}'' + \mathrm{ABr_2} \qquad (3)$$
$$\mathrm{Br_2}'' + \mathrm{A} = \mathrm{ABr_2}''' \qquad (4)$$
$$\mathrm{ABr_2}''' + \mathrm{Br_2} = \mathrm{Br_2}'''' + \mathrm{ABr_2} \qquad (5)$$

where the mark ′ indicates that a molecule has the excess energy E', and where E', E'', E''', . . . $E^{i\prime}$ are the energies in excess of the mean passed on from molecule to molecule. Reactions 3, 4 and 5 compose a chain, which will be stopped when the excess energy, $E^{i\prime}$, falls below a value such that the sum of $E^{i\prime}$ and any energy in excess of the mean already possessed by the bromine molecule is less than the energy of activation. The energy of activation is interpreted here, according to Tolman, as the difference between the mean energy of the molecules able to react and the mean energy of all the molecules. Hence the number of activations of bromine is dependent on the intensity of the radiation absorbed and on the time required after absorption of quantized light energy for the system to reach the statistical equilibrium distribution of energy corresponding to the temperature of the thermostat. This time will depend at least on concentrations, kind of energy transfer between molecules, and rate of transfer of energy to the thermostat. Since the limiting value of Φ is 1, under the conditions described for Fig. 1, deactivation of a photo-activated bromine molecule before reaction must be unlikely. The retarding effect of dilution on the photo-excited thermal reaction may be due to deactivating collisions of the second kind between the activated reaction products $\mathrm{ABr_2}^{i\prime}$, and the solvent; or, it may possibly be due to the increased time given for distribution of the excess energy within the complex molecule $\mathrm{ABr_2}$ itself in such a fashion that it cannot be readily given up in one activating collision with a $\mathrm{Br_2}$ molecule. In a crude sense the latter hypothesis may be considered as a cooling-off with time of the "hot-spots" in the molecules of the newly formed reaction products.

The change with temperature of the photosensitized thermal reaction rate depends on the change in the number of mild thermal excitations, since the number of activations by direct absorption of light is constant for constant light absorption. In all the discussion the assumption is made that the quantum of radiation is large enough to activate a molecule, regardless of its original energy content.

The rate of the total photochemical reaction will depend, then, on the probability, p_r, that reaction 2 will follow reaction 1 above, and the probability, p_{ci}, that if 2 takes place it will be followed by a number of sets, 3, 4, 5, 6. . . i of reactions of the type 3 and 4 depending on the magnitude of p_{ci}.

The dependence of the probabilities p_r and p_{ci} on the temperature, the concentration of bromine, c_B, and the concentration of cinnamic acid, c_A,

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[8] Christiansen and Kramers, *Z. physik Chem.*, **104**, 451 (1923).

[9] Estimated from the methods and tables of Kharasch, *Bur. Standards J. Res.*, **2**, 359 (1929), using the heats of combustion of methane, methyl bromide, cinnamic acid and β-phenylpropionic acid.

can in a general way be predicted and checked with experiment. Briefly, p_r may be taken as unity if the solution is so concentrated in cinnamic acid that a Br_2^* molecule once formed, never is deactivated before it strikes an acid molecule and reacts. Such a critical concentration of cinnamic acid, c^1_A, should be found that

$$p_r = 1 \quad \text{when} \quad c_A > c^1_A \qquad \text{(I)}$$

When c_A is less than the critical value, c^1_A, p_r becomes less than one, and is a function of the number of collisions between bromine and cinnamic acid. The greater the probability of bromine deactivation, the smaller is p_r, the chance that reaction (2) will take place; thus

$$p_r = f_2(c_A, c_B) \text{ when } c_A < c^1_A, \text{ and } p_r < 1 \qquad \text{(II)}$$

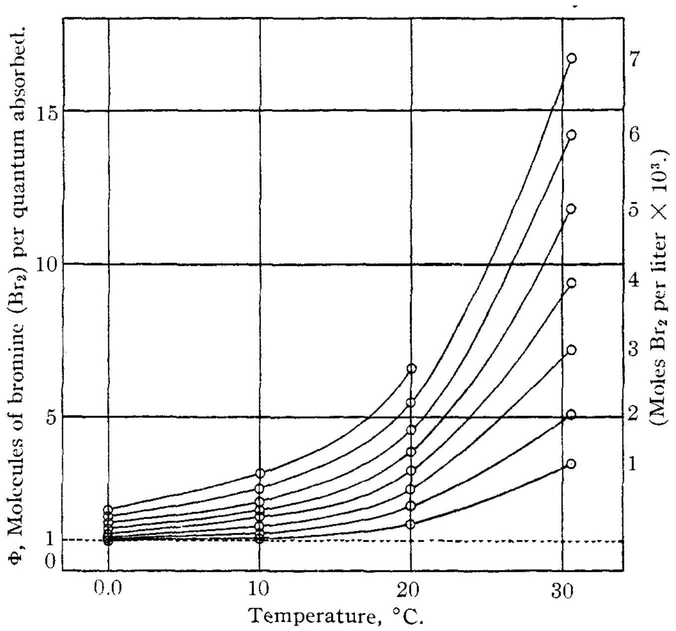

Fig. 2.—Influence of temperature on Φ at various concentrations of bromine.

The probability p_c is a function such that for the critical values c^1_B and T^1, where T is the temperature

$$p_c = 0 \text{ when } c_B < c^1_B \text{ or } T < T^1 \qquad \text{(III)}$$

Above the critical values of c_B and T

$$p_c = f_4(c_B, T) \text{ when } c_B > c^1_B, \text{ and } T > T^1 \qquad \text{(IV)}$$

From these considerations it follows that the quantum yield Φ is given by

$$\Phi = (1 + F_4(c_B, T)) \text{ when } c_A > c^1_A \text{ and where } F_4(c^1_B, T^1) = 0 \qquad \text{(V)}$$

$$\Phi = (F_2(c_A, c_B) + F_4(c_B, T)) \text{ when } c_A < c^1_A \qquad \text{(VI)}$$

It should not be expected that the limits c^1_A, c^1_B, and T^1 are sharply defined; but, for instance, it should be expected that near T^1, and above c^1_A, Φ is nearly one, regardless of c_B.

These relations are in agreement with the experimental facts. In the lines of Fig. 1, where c_A was above 0.0025 molar at all times, at least one reaction per activation was obtained, and I is confirmed. When c_A was allowed to fall below about 0.002 molar, quantum yields of less than one were obtained, as shown by the last two columns of Table VIII. This fact confirms II, showing that here p_r is less than unity, and a function of c_A and c_B. III and IV are confirmed by the data presented in Figs. 1 and 2, for the chain disappears completely at low bromine concentrations or at low temperatures, and is independent of the cinnamic acid concentration in the range of concentrations used. V is confirmed by Figs. 1 and 2, in which c_A was kept above a value of 0.0025 molar, for it is evident that Φ is a function of c_B and T only, and that the limiting value of this function is unity.

The theory thus outlined demands that a part of the photochemical reaction rate be independent of temperature; accordingly an examination of the temperature effects described in the experimental results should be fruitful.

Temperature Effects.—Neglecting the change in the absorption coefficient with temperature, at any specified bromine concentration, c_{B_i}, the variation in Φ_i with temperature is proportional to the variation in the rate constant k; hence, if the Arrhenius equation applies to the total reaction, then

$$\frac{d \ln k}{dT} = \frac{d \ln A_i\Phi_i}{dT} = \frac{E}{RT^2}$$

where A_i is a constant depending only on C_{B_i}. The equation does not apply, for in Fig. 3a the plot of log Φ_i against $1/T$ is not a straight line.

According to the chain mechanism suggested, the part of Φ_i due to the initial activation of molecules by absorption of a quantum of light and the part due to the subsequent photo-excited thermal reaction should be separable. Since the change in the absorption coefficient with temperature is small, at constant light absorption a part of the reaction rate should not change with temperature according to the Arrhenius equation but should remain constant. On taking this part of Φ_i as 1 (from the findings of Fig. 1), there remains that portion of the reaction rate proportional to $\Phi_i - 1$, or Θ_i. The function Θ_i represents the part of the reaction which results from the activation of molecules by means other than the direct absorption of light quanta. The photo-excited thermal reaction may depend for its magnitude on the type of distribution of thermal energy among the molecules. If, then, its variation with temperature is due to factors connected with those which cause ordinary thermal reactions to fit the Arrhenius equation, the following formula should apply.

$$\frac{\mathrm{d}\ln A_i\Theta_i}{\mathrm{d}T} = \frac{W}{RT^2}$$

where W is a constant. In Fig. 3b this equation is confirmed, for a straight line results when log Θ_i is plotted against $1/T$. The average slope is 4580, and thus W expressed in calories is 21,000. Further studies of the purely thermal bromination and comparison with the photo-excited thermal bromination will be of special interest.

Further confirmation of the assumption that the total reaction rate may be divided into two parts, one typically photochemical, and the other resembling in temperature effects a thermal reaction, is gained by a comparison of the values of the temperature coefficients calculated for Φ and for Θ.

Although there is a large error involved in calculating Θ at the lower temperatures (because differences between small numbers are involved),

TABLE IX

TEN-DEGREE TEMPERATURE EFFECTS ON Φ AND ON Θ

Concn. × 10^3, moles per liter	$\Phi_{10°}/\Phi_{0°}$	$\Phi_{20°}/\Phi_{10°}$	$\Phi_{30.6°}/\Phi_{20°}$	$\Theta_{10°}/\Theta_{0°}$	$\Theta_{20°}/\Theta_{10°}$	$\Theta_{30.6°}/\Theta_{20°}$
3	1.4	1.8	2.7	...	3.4	3.6
5	1.4	2.0	3.0	2.5	2.9	3.7
7	1.5	2.1	3.0	2.1	2.7	3.5

it is apparent that Θ_{T+10}/Θ_T has a value approximating 3, in agreement with that of many thermal reactions, while Φ_{T+10}/Φ_T varies from nearly 1 to 3 depending on temperature and concentration. This latter fact confirms the conclusion of Tolman[10] that no significance can be attached to earlier classifications of photochemical reactions based on specific values of their temperature coefficients.

Reaction Rate.—A check on the accuracy of the values for the quantum yield can be obtained by a comparison of the rate calculated from the quantum yield with that obtained in the rate determinations.

The relations between Φ and c as given in Fig. 1 can be represented by an equation of the form

$$\Phi = 1 + Mc_B + f(c_B), \text{ where } f(c_B) \text{ is small, and } M \text{ is a constant} \quad (1)$$

For instance, at 20.0°, $M = 0.56 \times 10^3$ and $f(c_B)$ for the range of concentrations of bromine from 1.6 to 5.0×10^{-3} is less than 0.1. Since Φ is about 2 or greater in this range, $f(c_B)$ may be neglected. Then

$$\Phi = 1 + Mc_B \quad (2)$$

Since this relation gives the dependence of the quantum yield on concentration, c_B, it is possible to calculate the reaction rate.

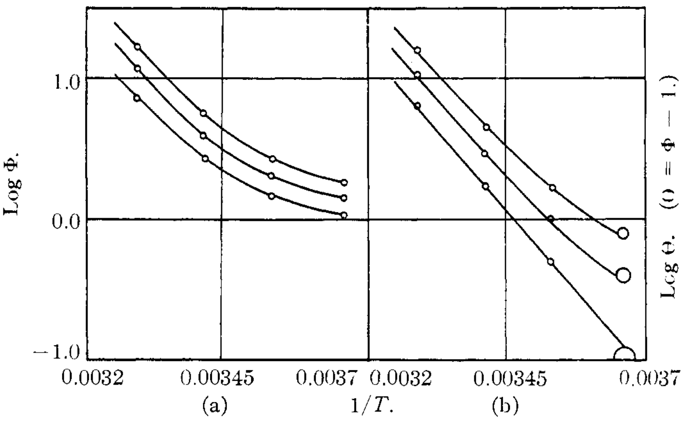

Fig. 3.—(a) Plot of $1/T$ against Φ; (b) $1/T$ against $(\Phi - 1)$.

Assuming that the number of chains, s, started per unit time, is proportional to the light absorbed

$$s = BI_{\text{abs.}} = BI_0\,(1 - e^{-alc_B}) \quad (3)$$

where B is a constant, 1, 2, 3, . . ., depending on the number of activated molecules formed when a bromine molecule absorbs a light quantum, $I_{\text{abs.}}$ is the intensity of the light absorbed, and a the absorption coefficient. Now if Φ/B is the chain length, N Avogadro's number, v the volume in liters of the solution in which the reaction takes place, it is obvious that

$$-\mathrm{d}c/\mathrm{d}t = s\Phi/NvB \quad (4)$$

Substituting the values of s and Φ from above

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{I_0(1 - e^{alc_B})\,(1 + Mc_B)}{Nv} \quad (5)$$

For a region of practically complete absorption, such as (for the cell used) when $c_B > 4 \times 10^{-3}$, $1 - e^{-alc_B}$ may be taken equal to 1. Making this simplification, integrating between the limits c_0 and c, t_0 and t, and setting $t_0 = 0$

$$k' = \frac{I_0M}{Nv} = \frac{2.303}{t}\log\frac{(1 + Mc_B^0)}{(1 + Mc_B)} \quad (6)$$

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[10] Tolman, THIS JOURNAL, **45**, 2285 (1923).

In this equation, I_0, M, N and V are all known. From the data used for Table VI, at time ten minutes, $I_0 = 102.6$; at time 30, 100.0 cm. scale deflection. The average number of quanta incident per second over this interval is thus (101) $(3 \times 10^{13}) = 3 \times 10^{15}$ quanta per second. The time elapsed is 1200 seconds. c°_B is 5.7×10^{-3}, $c_B = 4.15 \times 10^{-3}$ mole per liter. $M = 0.56 \times 10^3$, $N = 6.06 \times 10^{23}$, $v = 0.0166$ liter. Then

$$\frac{I_0 M}{N v} = k' = \frac{(3 \times 10^{15})(0.56)(10^3)}{(6.06)(10^{23})(0.0166)} = 1.7 \times 10^{-4}$$

From the formula

$$k' = \frac{2.303}{t} \log \frac{(1 + Mc^\circ_B)}{(1 + Mc_B)} \qquad (6)$$

it is found that

$$k' = 1.9 \times 10^{-4}$$

The agreement of these two values is close enough to establish the fact that the rate of the reaction can be calculated from a knowledge of the empirical equation for the quantum yield.

For the range of concentrations of bromine of from 0.003 to 0.006 molar, the value of Mc_B is such that the ratio $(1 + Mc^\circ_B)/(1 + Mc_B)$ is nearly equal to c°_B/c_B. Hence equation (6) reduces to a first order equation.

This first order equation holds for the range where the light absorption is constant and practically complete, as is shown by Tables VI and VII.

Discussion

It is evident that this photo-reaction is quite complex and that attempts to express its behavior with standard formulas cannot be successful. Theoretically, there is no reason to expect the reaction to be fundamentally of the first order; it may be zero, first order or approaching second order or any fractional order between, depending on conditions. The rate of reaction does not necessarily vary as the square root of the light intensity; by proper choice of temperature and concentration the relation between reaction rate and light intensity may be made to vary over wide ranges. The temperature coefficient of the whole reaction has no constant value. It may vary with the temperature and concentration from nearly one to three.

The authors have chosen to interpret their data on the basis of an energy chain rather than on the basis of a chemical chain involving bromine atoms. According to the atom chain of Berthoud[4]

$$\begin{aligned} \mathrm{Br_2} + h\nu &= \mathrm{Br} + \mathrm{Br} \\ \mathrm{Br} + \mathrm{A} &= \mathrm{ABr} \\ \mathrm{ABr} + \mathrm{Br_2} &= \mathrm{ABr_2} + \mathrm{Br} \\ \mathrm{Br} + \mathrm{A} &= \mathrm{ABr}, \text{ etc.} \end{aligned}$$

where A represents the cinnamic acid molecule. According to the atom chain of Purkayastha and Ghosh[2]

$$\begin{aligned} \mathrm{Br_2} + h\nu &= \mathrm{Br} + \mathrm{Br} \\ \mathrm{Br} + \mathrm{Br_2} &= \mathrm{Br_3} \\ \mathrm{Br_3} + \mathrm{A} &= \mathrm{ABr_2} + \mathrm{Br} \\ \mathrm{Br} + \mathrm{Br_2} &= \mathrm{Br_3}, \text{ etc.} \end{aligned}$$

These atom chains appear to be less likely for the following reasons. When the chain is stopped at great dilutions the quantum yield approaches one molecule rather than one atom of bromine per quantum. It is possible, however, to devise a somewhat different chain mechanism wherein a molecule of bromine is dissociated into one activated and one normal atom of bromine. If the normal atom of bromine were unable to react with cinnamic acid a quantum yield of one molecule per quantum might then be obtained.

The absorption spectrum of gaseous bromine is continuous below 511 mμ; that of bromine in carbon tetrachloride[11] appears to be continuous throughout the whole visible region. The lack of structure at the longer wave lengths in the solution does not necessarily imply dissociation; it may be due equally well to the broadening of lines by the solvent. If the molecule is dissociated into atoms only below 511 mμ and if atoms are necessary to start chains, then the quantum yield should fall sharply at waves longer than about 511 mμ. If activated molecules are involved in the chain or if the absorption spectrum is without significance in solution, there should be no marked photochemical threshold in the neighborhood of 511 mμ. Additional experiments have shown that light of 546 and 579 mμ gives quantum yields only slightly lower than those obtained with light of 436 mμ.

The experimental results are accurately reproducible and indicate that there are no trace-catalysts nor capricious inhibitors such as frequently accompany sensitive chain reactions of the chemical type.

It is very difficult to decide by direct experimental means between various mechanisms involving transitory compounds. However, it is possible, frequently, to settle such questions with the help of quantum mechanics. Dr. Albert Sherman in this Laboratory has calculated that Berthoud's chain, if it exists, must have a very

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(11) Bovis, *J. phys. radium*, **10**, 267 (1929).

small temperature coefficient, contrary to the experimental findings of this investigation. He will also show in a forthcoming publication that the addition of Br_3 to a double bond requires an energy of activation greater by 10,000 calories than that required for the addition of Br_2. Making the reasonable assumption that the calculations can be applied to cinnamic acid in carbon tetrachloride solution, it is apparent that Purkayastha and Ghosh's chain fails to explain the observed facts because it includes a step which is slower even than the thermal bromination in the dark.

Further experiments are in progress, designed to test the relative merits of the hypotheses of energy and chemical chains.

Summary

1. The photobromination of cinnamic acid in carbon tetrachloride has been measured quantitatively with a monochromator. The influence of concentration, temperature and wave length on the quantum yield has been studied.

2. The reaction is a chain reaction. The quantum yield, Φ, ranged from 1 to 15 or more, depending on the concentration of the bromine and the temperature. The reaction was studied over a range of from 2×10^{-3} to 8×10^{-3} mole of bromine per liter, and at temperatures of 0, 10, 20 and 30°.

3. The photochemical reaction has been shown to consist of two parts; first, a primary photo reaction of one molecule per quantum, and, second, a photo-excited thermal reaction which is measured by $\Phi - 1$, or Θ, and which is suppressed at great dilution of bromine or at low temperatures. Log Θ plotted against $1/T$ gives nearly straight lines whereas log Φ plotted against $1/T$ does not.

4. The experimental facts are in agreement with a theory involving activated bromine molecules and an energy chain.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

The Nature of the Solid Phase in the System Antimony–Bismuth[1]

BY W. F. EHRET AND M. B. ABRAMSON

Although a number of investigations have been made of the antimony–bismuth system, employing practically all of the usual physical methods, there has been no general accord on the nature of the solid phase nor on the position of the solidus in the equilibrium diagram. Studies by Hüttner and Tammann,[2] Gautier,[3] Sapossnikoff,[4] and Parravano and Viviani[5] indicated that the solidus corresponded to an isomorphous series of alloys, the curve dropping sharply from the melting point of antimony to 269° at a composition of 70% antimony and continuing horizontally from that point to the melting point of pure bismuth. Cook,[6] from a careful thermal investigation, obtained the solidus shown in Fig. 1. Ôtani[7] more recently studied the equilibrium diagram by the electrical resistance method. His solidus did not show the horizontal portion but gave the normal curve for a complete series of solid solutions (Fig. 1). After the present investigation had begun, an x-ray analysis of antimony–bismuth alloys was published by Bowen and Morris Jones.[8] They concluded that the lattice parameter varied almost linearly with the weight per cent. of the components, a slight curvature being noticed at the antimony end. There was no evidence of intermetallic phases other than the solid solution. From purely thermodynamic considerations, Yap[9] explained the horizontal solidus by assuming a peritectic reaction between a solid solution $\alpha[Sb_2–Bi_2]$ and the melt, forming solid solution $\beta[Sb_2–Bi_3]$. In this event there should be two solid solutions present between the limits of 35 and 60 mole per cent. bismuth (Fig. 1). The present x-ray investigation was undertaken to see whether any such solutions existed.

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[1] Presented in part before the Physical and Inorganic Division at the 86th meeting of the American Chemical Society, Chicago, Illinois, September 11-15, 1933.

[2] Hüttner and Tammann, *Z. anorg. Chem.*, **44**, 131 (1905).

[3] Gautier, "Contribution à l'étude des alliages," Paris, 1901, p. 114.

[4] Sapossnikoff, *J. Russ. Phys.-Chem. Soc.*, **40**, 665 (1908).

[5] Parravano and Viviani, *Rend. accad. Lincei*, **19**, 835 (1910).

[6] Cook, *J. Inst. Metals*, **28**, 421 (1922).

[7] Ôtani, *Sci. Repts. Tôhoku Imp. Univ.*, **13**, 293 (1924-5).

[8] Bowen and Morris Jones, *Phil. Mag.*, [7] **13**, 1029 (1932).

[9] Yap, Tech. Publication 397, *Trans. Am. Inst. Mining Met. Eng.*, Inst. Metals Division (1931). The authors wish to thank Mr. Yap, Chu-Phay for his interest and aid in the present work.