large evolution of heat[7] suggests rather complete oxidation to acids.

When the bromo peroxy free radical decomposes according to reaction (8) or reacts with bromine molecules by reaction (10), bromine atoms are regenerated which continue the chain and tend to nullify the effect of oxygen in stopping the bromine-atom chain. The result is to increase the apparent chain length, *i. e.*, the quantum yield. Reaction (8) is favored by raising the temperature and reaction (10) is favored by the addition of bromine. These conclusions are in complete accord with the experimental facts that when oxygen is present the quantum yield is increased both by an increase in temperature and by an increase in the concentration of bromine.

Hydroquinone stops the chain whether or not oxygen is involved, as should any substance capable of combining with bromine atoms.[6]

Although oxygen does not appear to reduce the quantum yield in the photobromination of triphenylmethane, some reaction is nevertheless occurring as shown by the heat effects accompanying the reaction as described in another communication.[7]

The authors are glad to acknowledge the aid of a fellowship of the Procter and Gamble Company during a part of this investigation.

Summary

1. Approximate quantum yields have been determined for the photobromination of cinnamic acid, stilbene, triphenylethylene and triphenylmethane under conditions in which oxygen was practically excluded. The bromine concentration was determined by colorimetric analyses in sealed-off glass vessels.

2. The inhibitory action of oxygen on these reactions has been studied.

3. In the absence of oxygen the photobromination is rapid and independent of temperature.

4. The quantum yield is greatly reduced by the addition of hydroquinone.

5. Photobromination in the presence of oxygen causes the consumption of the oxygen.

6. The results in the absence of oxygen are explained on the basis of chains propagated by bromocinnamic acid free radicals.

7. The results in the presence of oxygen are explained on the basis of competing reactions involving bromo-peroxy-cinnamic acid free radicals.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Heat of Photobromination of the Phenyl Methanes and Cinnamic Acid, and the Influence of Oxygen

BY JOHN L. MAGEE AND FARRINGTON DANIELS

Direct measurements of the heats of photochemical reactions[1] make possible the study of reactions, such as the bromination of hydrocarbons, which are too slow to measure in the dark. Calorimetric measurements of this type are useful in studies of molecular structure and chemical kinetics. For example, oxygen is known to have an effect on photohalogenations[2a,b,c,d] and the amount of heat produced during the reaction gives valuable information concerning the mechanism. If the oxygen acts only as a catalyst and is not consumed in any of the reactions, the heat evolved should be practically the same in the presence and absence of oxygen, but if it promotes or inhibits the reaction by taking part in a competing oxidation process, the heat of reaction should be larger when oxygen is present. The heats of oxidation are so large that evidence of oxidation can be found even when chemical detection of the oxidation products would be difficult. The results of this investigation indicate that oxygen reacts during the photobromination of the phenyl methanes and of cinnamic acid. Thus it is necessary to remove most of the oxygen in order to obtain the heat of the actual bromination reaction.

It is impossible to check the experimental results of this work by means of calculations based on heats of combustion because the combustion data on the bromides are inaccurate. This fact

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[1] Magee, DeWitt, Smith and Daniels, THIS JOURNAL, **61**, 3529 (1939).

[2] (a) Bauer and Daniels, *ibid.*, **56**, 2014 (1934); (b) Deanesly, *ibid.*, **56**, 2501 (1934); (c) Willard and Daniels, *ibid.*, **57**, 2240 (1935); (d) Brown and Daniels, *ibid.*, **62**, 2820 (1940).

indicates the importance of direct thermal measurements on these reactions.

Experimental Procedure

The photocalorimeter with its quartz cell of 2.9 cc. capacity and fifty thermocouple junctions has been described.[1] The source of light for these experiments on photobromination was a commercial capillary mercury lamp (G. E. H-3, 85-watt) with a lens and filter system restricting the light fairly well to 4360 Å. and giving 200 to 700 ergs per second, incident on the calorimeter cell. The calorimeter was calibrated as before by filling with a chemically inert solution and measuring the deflections when radiation of different intensities was being absorbed. A trace of glycerol was added to the glass stoppers to prevent any evaporation.

The carbon tetrachloride (Mallinckrodt) of low sulfur content was further purified[3] by saturating with chlorine and chlorine dioxide and subjecting to illumination of a 500-watt lamp for twenty-four hours. It was then washed with potassium hydroxide solution and dried over phosphorus pentoxide. It was distilled without a drying agent because it was found that phosgene is produced when carbon tetrachloride is heated with phosphorus pentoxide in the presence of air. The test of purity was the absence of any detectable reaction when a solution of bromine was illuminated. Furthermore, there was practically no absorption of light at 3130 Å.

Bromine of reagent quality was distilled from anhydrous calcium bromide and sealed off in small glass reservoirs in the absence of air.

Triphenylmethane melting at 93° was prepared from chloroform and benzene. Diphenylmethane melting at 26° was prepared by hydrogenating benzophenone. The authors are indebted to Dr. R. F. Brown and to Mr. R. C. Franklin for these materials. The toluene was purified with sulfuric acid and with mercury. Kahlbaum's cinnamic acid was used, which after recrystallization from alcohol melted at 133°.

The bromine solutions in carbon tetrachloride were kept in desiccators in the dark and analyzed by titration with thiosulfate after addition of potassium iodide. They were mixed with carbon tetrachloride solutions of the phenyl methane or of cinnamic acid. In some of the experiments designed to remove oxygen the pipet and cell were swept out with purified nitrogen and, after filling, the nitrogen was bubbled through for five to ten minutes. These operations were carried out in a box containing carbon dioxide from the evaporation of dry-ice. A faint red light was used to prevent photochemical reaction.

After the calorimeter cell had come to equilibrium in the double thermostat and the lamp had reached a steady intensity, the shutter was opened and the reaction started. Deflections of the calorimeter–galvanometer were taken every minute for a while and then at longer time intervals. The transmitted light was measured by the thermopile behind the calorimeter and the incident light was measured just after removing the calorimeter. Sometimes the reaction was allowed to go to completion, and sometimes the reaction was stopped and the unreacted bromine titrated.

A given deflection of the calorimeter–galvanometer at time t indicates a definite temperature difference and the loss of a definite quantity of heat per second to the aluminum container. Calibration in the steady state where the rate of absorption of measured radiant energy is exactly offset by the loss of heat to the thermostated aluminum block showed that the deflection in cm. multiplied by 90 gives the evolution of heat in ergs per second when the calorimeter is filled with a solution of bromine in carbon tetrachloride. The calorimeter–galvanometer deflections, x, are plotted against time. Then $\int_0^\infty x\,dt$ gives the total evolution of heat in units determined by the calibration of the apparatus. In simple reactions of known order it is possible to integrate this expression after suitable substitutions but in the reactions studied here the integral was evaluated by plotting galvanometer deflections against time on graph paper and determining the area under the curve with an integraph. The *total* area represents the heat of reaction plus the radiant energy which the calorimeter is absorbing. In rapid reactions the latter is often negligible in comparison with the former.

In order to obtain the *rate* of heat evolution at any time further calculations are necessary. The rate of cooling is given by the formula

$$-dx/dt = k(x - y)$$

where x is the observed deflection and y is the deflection due to the heat evolved by an accompanying reaction at time t. The constant k is evaluated by measuring the rate of cooling when there is no accompanying reaction involved and $y = 0$, *i. e.*, using a bromine solution in carbon tetrachloride which has been heated by the absorption of radiation. Under these conditions a plot of log x against t gave a value of 0.172 for k (when the calorimeter was filled with water, k was 0.088[1]). The rate of evolution of heat, y, due to the chemical reaction at any time is given in cm. deflection by the expression

$$y = \frac{1}{k}\frac{dx}{dt} + x$$

It is evaluated from the observed deflection x and the tangent to the curve, dx/dt.

Since the heats of these reactions have not been measured, the accuracy of the calorimeter was checked by measurements on the heat of inversion of cane sugar. The average of six determinations on the heat of inversion of cane sugar in 0.3

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[3] Bray, *Z. physik. Chem.*, **54**, 592 (1906).

N hydrochloric acid solution was 3450 calories per mole with an average deviation of 90 calories. Sturtevant[4] gives a value of 3563 and Barry[5] gives a value of 3558. The errors in the present determinations are magnified because the measurements were made with only 2.9 cc. of solution.

The quantum yields Φ can be calculated when a single reaction is involved and the heat of reaction per mole, ΔH, is known. Then $y/\Delta H$ is the number of moles reacting per second. If E is the radiant energy absorbed in calories per second, and Q is the number of calories per einstein (6.06×10^{23} quanta), E/Q is the number of einsteins absorbed per second, then

$$\Phi = \frac{y}{\Delta H} \Big/ \frac{E}{Q}$$

The quantity E is obtained from the thermopile readings of incident and transmitted light after a small correction for reflections and for a slight cloudiness of the windows.

The type of data obtained is illustrated in Fig. 1 for experiment 1 on the photobromination of the triphenylmethane, described later. Curve A gives the actual calorimeter–galvanometer deflections and the area under it permits a calculation of the total heat evolved while the 7.05×10^{-6} mole of bromine is reacting. After the fast bromination reaction is practically completed there is still a slight further reaction the heat of which is represented by the area under the extrapolated curve B. The area enclosed between A and B is 424 cm.-minutes and the heat evolved in the corresponding bromination is $424 \times 90 \times 60/4.18 \times 10^7$ or 0.055 calorie. Then for a mole of bromine reacting ΔH is $0.055/7.05 \times 10^{-6}$ or 7750 calories.

One minute after turning on the light, the deflection was 73.5 cm. Then $y_{30} = 1/k(dx/dt)_{30} + x_{30} = 1/0.172 \times 73.5/1 + 73.5/2 = 466$ cm. Heat was being evolved at the rate of $466 \times 90/4.18 \times 10^7$ or 0.001 calorie per second. Light was being introduced at the rate of 460 ergs per second and in this solution of 2.6×10^{-3} mole of bromine per liter, 94% of it was absorbed in the length of the calorimeter. Then E is 433 ergs or 1.04×10^{-5} calorie per second, ΔH is 7750 calories per mole, and Q for 4360 Å. is 65,000 calories per mole. Thus

$$\Phi_{30} = \frac{0.001}{7750} \times \frac{65{,}000}{1.04 \times 10^{-5}} = 810 \text{ molecules per quantum}$$

The quantum yields are only approximate since dx/dt and x cannot be determined accurately at the beginning of the experiment while conditions are changing rapidly. They do, however, check very well with the yields obtained by Brown and Daniels.[6]

It must be remembered also that the quantities measured are very small. The *total* input of radiation throughout the whole experiment is of the order of thousandths of a calorie and the total heat evolved is usually less than 0.1 calorie.

Results

Phenylmethanes.—The measurements on the phenylmethanes are summarized in Table I and Figs. 1 and 2. The volume of the calorimeter cell was 2.9 cc.

TABLE I

PHOTOBROMINATION OF PHENYLMETHANES IN CARBON TETRACHLORIDE AT 25°

Incident light, ergs/sec.	Moles Br_2 $\times 10^6$	Moles phenylmethane $\times 10^6$	ΔH, kcal./mole	y_{30}, ergs/sec. $\times 10^3$	Φ molecules/quantum
		Triphenylmethane (oxygen removed)			Φ_{30}
460	7.4	140	7.75	41	810
223	4.9	2.3	7.85	72	410[a]
310	12.0	168	7.50	62	2200
305	7.6	22.3	8.00	36	1240
335	6.3	39.0	8.40	35	1170
355	3.1	32.4	7.50	12	570
345	3.1	32.4	7.90	11	560
		Diphenylmethane (oxygen removed)			Φ_{30}
645	7.50	137	11.4	19	170
400	0.75	70	12.2	1.1	70[b]
280	7.92	22	12.4	13	270
435	8.35	50	12.1	15	210
645	7.50	137	11.4	19	170
		Toluene (oxygen removed)			$\Phi_{max.}$
610	9.0	143	14.9	0.5	40
345	8.4	23	14.2	.2	60
420	8.6	53	14.8	.1	50
		Triphenylmethane (oxygen from air saturation)			Φ_{30}
355	9.6	19.5	7.75	23	950
267	15.7	22.8	7.70	29	970

[a] Triphenylmethane concentration low. [b] Bromine concentration low.

The light striking the calorimeter, as given in the first column, is nearly the same as the intensity per square cm. The number of moles originally present in the calorimeter is given in the second and third columns. These values can be converted into moles per liter through multiplication by 1000/2.9. Usually the phenylmethane was in

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(4) J. M. Sturtevant, THIS JOURNAL, **59**, 1528 (1937).

(5) Barry, *ibid.*, **42**, 1911 (1920).

(6) Brown and Daniels, THIS JOURNAL, **62**, 2820 (1940).

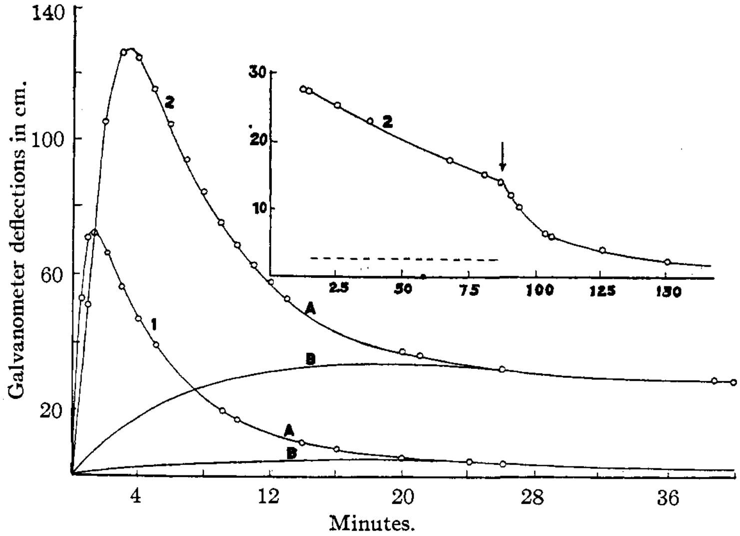

Fig. 1.—Heat of photobromination of triphenylmethane: curve 1, oxygen swept out with nitrogen; 2, saturated with oxygen from air. The concentration of bromine in 2 is twice that in 1.

excess and the reaction was continued until the bromine was nearly used up. In all except the last two experiments at the bottom of the table nitrogen was bubbled through the solution in the small cell in the calorimeter to remove oxygen. Obviously it was not possible to remove the last traces of oxygen in this way.

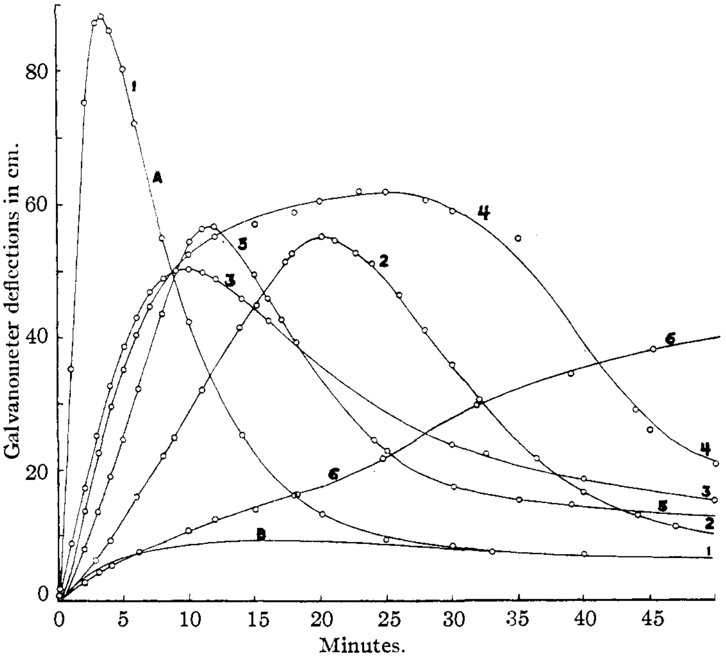

Fig. 2.—Heat of photobromination of diphenylmethane and toluene: curve 1, diphenylmethane with oxygen removed; 2, toluene with oxygen removed; 3, diphenylmethane with air; 4, diphenylmethane and bromination products with air; 5, diphenylmethane and hydrobromic acid; 6, toluene with air.

The experimental data for the first determination on triphenylmethane given in the table are shown in curve 1 of Fig. 1. They have been used already in illustrating the method of calculation. In Fig. 2, curve 1 gives the data for the first determination in the table on diphenylmethane and curve 2 gives the data for the first determination on toluene.

In the second determination on triphenylmethane shown in Table I the bromine was in excess. Since bromine was left over, the calculation of heat evolved per mole was based on the number of moles of triphenylmethane, giving 0.018 cal./2.3 $\times$ 10^{-6} or 7850 calories. It is gratifying that this value agrees with the value obtained in the other experiments by calculating on the basis of the bromine concentration. These facts show that the reaction involves a 1 to 1 relation between the two reactants.

Examination of the table shows that the average heat of bromination for triphenylmethane is 7.84, for diphenylmethane it is 12.0 and for toluene it is 14.6. Under the conditions of these experiments it is seen that when bromine is in excess roughly a thousand molecules of bromine disappear for each quantum of light absorbed in the triphenylmethane solution. The quantum yield for diphenylmethane is about two hundred and for monomethylmethane approximately fifty. The quantum yields for tri- and di-phenylmethane are taken thirty seconds after turning on the light but since the bromination of toluene shows a distinct induction period, the quantum yield is calculated for the time at which the deflection is a maximum.

The quantum yield for the bromination increases with the concentration of bromine and is independent of the phenylmethane when the latter is in sufficient excess.

Reactions with Oxygen.—The straight bromination is a rapid reaction which is quickly finished as shown in curve 1 of Fig. 1. However, if oxygen is present and triphenylmethane is not in excess the reaction is complicated by another and slower reaction as shown in curve 2 of Fig. 1, which corresponds to the last determination shown at the bottom of Table I. The heat being absorbed from the beam of light is shown by the dotted line and the long continuing evolution of heat as shown at the right must involve a chemical reaction. The rapid brominations are practically over in about ten minutes. This longer reaction is probably a bromine-sensitized photo-oxidation. That it is photochemical is shown by the rapid cooling which ensues when the light is turned off as indicated by the arrow in the curve at ninety minutes. The extrapolation of the slow oxidation reaction B back to zero time is not accurate and the area between curves A and B, on which the calculation of the heat of bromination (7700 calories) depends, is subject to some uncertainty.

The heat of this second reaction, obtained by plotting the data after thirty minutes and extrapolating, gives a heat evolution of 0.49 calorie. If it is a reaction of a product of bromination, the heat evolved per mole would be $0.49/1.57 \times 10^{-5}$ or 31,000 calories. A reaction heat as large as this must be due to an oxidation. The oxidation of hydrobromic acid is exothermic by 21,700 calories but this reaction does not take place with light of 4360 Å. even in the presence of bromine, a fact which was verified experimentally in this work. The oxygen dissolved in the cell was about 5×10^{-6} mole which corresponds to saturation of pure carbon tetrachloride with air at atmospheric pressure. Assuming that it is the limiting factor and calculating on the basis of heat per mole of oxygen, ΔH would be $0.49/5 \times 10^{-6}$ or 98,000 a value which is about right for the reaction

$$(C_6H_5)_3CH + O_2 \longrightarrow (C_6H_5)_2C{=}O + C_6H_5OH$$

as determined from heats of combustion.

In the photobromination of diphenylmethane the quantum yield is smaller and the reaction is slower so that it is more difficult to separate the bromination reaction from the bromine-sensitized photo-oxidation; in fact it cannot be done at all unless some of the oxygen dissolved from the air is removed. Typical data for the photobromination of diphenylmethane when saturated with air are shown in curve 3 of Fig. 2. Taking the heat of bromination to be 12 kcal. as determined in the absence of oxygen the initial quantum yields (Φ_{30}) estimated from this curve is 30. The average of eight such determinations is 30 ± 10 molecules of bromine reacting per quantum absorbed. This is to be contrasted with a value of about 200 obtained when most of the oxygen is removed. In curve 4 of Fig. 2 is shown an experiment in which some products of a previous bromination were added. The initial quantum yields were not appreciably affected but the oxidation was greatly increased as shown by the large evolution of heat over a long period of time. The increased oxidation must be due to the diphenyl bromide rather than to hydrobromic acid because the latter substance alone was added in another experiment shown by curve 5. There was a slight inhibition and a slight reduction in Φ_{30} but no increased heat evolution nor oxidation.

The oxygen-effect on the bromination of toluene is still more pronounced than on diphenylmethane. A curve resembling that of curve 3 of Fig. 2 was obtained with a solution through which nitrogen had been bubbled. The same solution was then allowed to stand for a day in contact with air and curve 6 of Fig. 2 was obtained. It was impossible to separate the oxidation from the bromination reactions in order to make calculations. Even after an hour very little of the bromine had been consumed and the quantum yield for bromination must be quite low in the presence of oxygen. The evolution of heat was large but the calculations are subject to large errors.

In an experiment on toluene, not shown in the figures, hydrobromic acid was added. The initial reaction was accelerated, suggesting that the induction period may involve the accumulation of hydrogen bromide as a product of the photobromination. Swenson[7] found that the hydrobromic acid formed in the reaction with toluene is consumed in a second reaction which is slower than the bromination. His work showed also that the bromination is stopped in the presence of atmospheric oxygen, before the reaction is complete.

It is interesting to note that the presence of oxygen has little or no effect on the photochemical disappearance of bromine with triphenylmethane, that it greatly reduces the rate of disappearance with diphenylmethane, and that it practically stops the bromination reaction with monophenylmethane. In all three cases the presence of oxygen results in a large increase in the evolution of heat but only in the case of triphenylmethane, where the photobromination is rapid, is it possible to

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(7) Swenson, *Z. wiss., Phot.*, **20**, 206 (1920).

separate the normal heat of bromination from the bromine-sensitized photo-oxidation.

Triphenylmethane forms a peroxide in contact with oxygen. Since peroxides are known to affect halogenations,[8] some experiments (not shown in Table I) on photobromination were carried out in the presence of peroxides. A sample of triphenylmethane which had been in contact with air for two years gave a heat of photobromination of about 24,000 calories, nearly three times as much as a pure sample of triphenylmethane. The quantum yield, however, was about the same, namely, a few hundred molecules of bromine consumed per quantum absorbed. A freshly crystallized sample gave a greater heat of reaction after it had stood in contact with air for two months. The extra heat evolved for a given consumption of bromine in the presence of peroxide is probably due to the exothermic decomposition of peroxide, photosensitized by bromine, or to subsequent oxidation reactions.

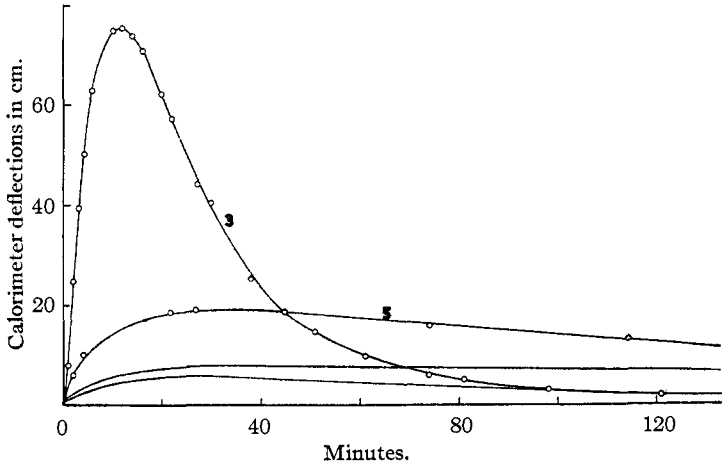

Fig. 3.—Heat of photobromination of cinnamic acid: curve 3, oxygen removed; 5, saturated with oxygen.

Another observation should be recorded with reference to the thermal bromination in the absence of light. In stock solutions of triphenylmethane from which air was not removed the bromine concentration remained practically unchanged for days. In stock solutions from which the air was partially removed all the bromine disappeared when kept in the dark even for less than a day. Oxygen then inhibits the thermal bromination of triphenylmethane, although it has only a slight effect on the photochemical reactions. The different behavior in the photochemical reaction suggests that the mechanisms in the dark and light are different.

Cinnamic Acid.—In cinnamic acid the addition of bromine to the double bond is involved rather than substitution of hydrogen by bromine. The results are summarized in Table II and Fig. 3.

In expt. 1 the solution was saturated with air and in expts. 2, 3 and 4, varying amounts of oxygen were present, as produced by passing nitrogen through the solution for different periods of time.

Expt. 3 is plotted in Fig. 3 and the lowest curve shows the correction which was necessary to allow for the radiant heat absorbed by the bromine. The quantum yield is sensitive to the presence of oxygen but when the oxygen is less than that corresponding to air saturation the heat of reaction is not seriously affected. The value is probably more reliable than the values for the bromination of the phenylmethanes. The averaged value is 16.3 kcal., which is in excellent agreement with the value of 16 calculated[9] from combustion data using the rules of Kharasch. It is also in agreement with the value obtained from bond energy values.

Expt. 5, also shown in Fig. 3, was carried out after first bubbling pure oxygen from a tank through the solution in the calorimeter. It has been found[6] that the quantum yield for the disappearance of bromine varies almost inversely with the oxygen content. The present work is in agreement with this relation as well as can be determined. In expt. 5, the dissolved oxygen was five times as much as in expt. 1 and the initial quantum yield is one-fifth as large.[9]

The heat of reaction in expt. 5 is very large, in-

TABLE II

PHOTOBROMINATION OF CINNAMIC ACID IN CARBON TETRACHLORIDE AT 25°

Expt.	Intensity, ergs/sec.	Moles Br_2 reacting $\times 10^6$	Moles cinnamic acid $\times 10^6$	ΔH, kcal./mole	y_{30}	Φ_{30}
1	645	15.4	49.8	16.4	2.4	15
2	625	15.6	49.8	16.4	3.3	22
3	665	18.1	56.0	15.6	5.6	34
4	665	16.9	56.0	16.8	3.6	22
5	700	5.9	56.0	26	0.5	3
6	750	18.6	59.0	25	2.4	13

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(8) Kharasch, THIS JOURNAL, **59**, 1405 (1937).

(9) Bauer and Daniels, *ibid.*, **56**, 381 (1934).

dicating an oxidation process when oxygen is present in large quantities.

In expt. 6, hydrogen bromide was added. The large heat of reaction suggests a bromine-sensitized photochemical addition of hydrobromic acid to the double bond.

The quantum yield, 15, of experiment 1 with air-saturation agrees with former work of this Laboratory obtained by different methods in so far as comparison can be made with different concentrations and different light intensities. At comparable concentrations but with a light intensity of 20,000 ergs per second a quantum yield of 10 was obtained[3] and at one-third the concentration and 170 ergs per second a yield of 14 molecules per quantum was obtained.[6]

The largest quantum yield for cinnamic acid shown in Table II is 34, but in the accompanying contribution[6] values up to 215 are reported under conditions where the oxygen was more effectively removed in a closed system.

Discussion

From the experimental facts recorded, it is clear that the brominations of the phenylmethanes are chain reactions, triphenylmethane having the longest chain and toluene the shortest. The quantum yield increases with bromine concentration, but is independent of the hydrocarbon concentration as long as the hydrocarbon is in reasonable excess. The reactions are affected by oxygen which inhibits the direct bromination (most in the case of toluene, and least in the case of triphenylmethane) and complicates the reaction by introducing a competing photo-oxidation.

The addition of hydrobromic acid accelerates the photobromination of toluene, inhibits the reaction with diphenylmethane and has no effect on the photobromination of triphenylmethane.

Induction periods are observed in the bromination of toluene and diphenylmethane.

It is assumed that the reaction chain is carried by radicals $(C_6H_5)_3C$, $(C_6H_5)_2HC$, or $(C_6H_5)H_2C$. The oxygen effect can be explained as a competing reaction of oxygen with the free radicals leading to a bromine-sensitized photo-oxidation. The importance of the oxygen effect depends on the ratio of the two rates, as given by the expression

$$\frac{k_{\text{oxidation}} c_{O_2} c_{(C_6H_5)_3C}}{k_{\text{bromination}} c_{Br_2} c_{(C_6H_5)_3C}}$$

The bromination is the faster of the two and is more important at the beginning of the reaction. In general, the first part of the reaction represents bromination and the latter part bromine-sensitized photo-oxidation. In some reactions it is difficult to separate the two but in the case of triphenylmethane, the separation can be accomplished readily. Anything which accelerates bromination will tend to minimize the photo-oxidation effect and anything which inhibits the bromination will increase the relative amount of bromine-sensitized photo-oxidation.

The reaction is supposed to take place by means of the following chain

$$Br_2 + h\nu \xrightarrow{I} 2Br \qquad (1)$$

$$R_3CH + Br \xrightarrow{k_2} R_3C + HBr \qquad (2)$$

$$R_3C + Br_2 \xrightarrow{k_3} R_3CBr + Br \qquad (3)$$

The chain may be stopped in any one of three ways

$$R_3C + R_3C \xrightarrow{k_4} R_3C{-}CR_3 \qquad (4)$$

$$Br + Br \xrightarrow{k_5} Br_2 \qquad (5)$$

$$R_3C + Br \xrightarrow{k_6} R_3CBr \qquad (6)$$

Here R_3C refers to the free radicals $(C_6H_5)_3C$, $(C_6H_5)_2CH$ or $(C_6H_5)CH_2$, and I refers to the quantity of light in einsteins absorbed per liter per second. The stationary state for this reaction is quickly reached in which the rate of change of concentration of Br and of R_3C is negligible. Setting $\mathrm{d}c_{Br}/\mathrm{d}t = \mathrm{d}c_{R_3C}/\mathrm{d}t = 0$ in the kinetic equations where c represents concentration in moles per liter, it follows[10] that the quantum

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(10) At the stationary state

$$\mathrm{d}c_{Br}/\mathrm{d}t = 0 = 2I - k_2c_{R_3CH}c_{Br} + k_3c_{R_3C}c_{Br_2} - 2k_5c^2_{Br} - k_6c_{Br}c_{R_3C} \qquad (a)$$

$$\mathrm{d}c_{R_3C}/\mathrm{d}t = 0 = k_2c_{R_3CH}c_{Br} - k_3c_{R_3C}c_{Br_2} - 2k_4c^2_{R_3C} - k_6c_{Br}c_{R_3C} \qquad (b)$$

Solving equation (b) and realizing that reactions (4) and (6) are slow in comparison with (2) and (3)

$$c_{Br} = \frac{k_3c_{Br_2}c_{R_3C} + 2k_4c^2_{R_3C}}{k_2c_{R_3CH} - k_6c_{R_3C}} \cong \frac{k_3c_{Br_2}}{k_2c_{R_3CH}}\, c_{R_3C} \qquad (c)$$

Adding (a) and (b)

$$2I = 2k_4c^2_{R_3C} + 2k_5c^2_{Br} + 2k_6c_{Br}c_{R_3C} \qquad (d)$$

Substituting in (d) the value of c_{Br} from (c)

$$c_{R_3C} = \sqrt{\frac{I}{X}} \qquad (e)$$

where

$$X = k_4 + k_6\left(\frac{k_3}{k_2}\,\frac{c_{Br_2}}{c_{R_3CH}}\right) + k_5\left(\frac{k_3}{k_2}\,\frac{c_{Br}}{c_{R_3CH}}\right)^2$$

But

$$-\mathrm{d}c_{Br_2}/\mathrm{d}t = I + k_3\,c_{Br_2}c_{R_3C} - k_5c^2_{Br} \qquad (f)$$

and substituting (c) and (e) into (f)

$$\frac{-\mathrm{d}c_{Br_2}}{I\,\mathrm{d}t} = k_3c_{Br_2}\sqrt{\frac{1}{IX}} + \frac{k_4 + k_6\left(\dfrac{k_3}{k_2}\,\dfrac{c_{Br_2}}{c_{R_3CH}}\right)}{X}$$

Since the last term must be less than unity it can be dropped out in comparison with Φ.

yield, Φ, is given approximately by the expression

$$\Phi \cong k_3 c_{\mathrm{Br}_2} \sqrt{\frac{1}{IX}}$$

If reaction (4) is the most important chain-breaking step, k_4 is the predominating term in X and the quantum yield should be directly proportional to the concentration of bromine. The experimental results are in agreement with this relation. Again referring to X it is seen that if the recombination of bromine atoms (5) is the most important step in breaking the chain Φ should be independent of c_{Br_2} while if reaction (6) is the most important the quantum yield should be proportional to the square root of the bromine concentration.

The effect of oxygen in reducing the rate of bromination can be explained on the basis of the formation of a peroxy free radical, R_3COO, in the chain-breaking mechanism

$$R_3C + O_2 \xrightarrow{k_7} R_3COO \qquad (7)$$

$$R_3COO + R_3C \xrightarrow{k_8} R_3COOCR_3 \qquad (8)$$

At the stationary state corresponding to this chain-breaking mechanism it is evident that

$$\frac{\mathrm{d}c_{\mathrm{R_3COO}}}{\mathrm{d}t} = 0$$

as well as

$$\frac{\mathrm{d}c_{\mathrm{R_3C}}}{\mathrm{d}t} = \frac{\mathrm{d}c_{\mathrm{Br}}}{\mathrm{d}t} = 0$$

and it is easy to show[11] that under these conditions

$$\Phi = \frac{-\mathrm{d}c_{\mathrm{Br}_2}}{I\,\mathrm{d}t} = 1 + \frac{k_3 c_{\mathrm{Br}_2}}{k_7 c_{\mathrm{O}_2}}$$

This mechanism leads to the conclusion that the quantum yield is proportional to c_{Br_2} and is inversely proportional to c_{O_2} in agreement with experiment.[2,6]

There is ample evidence for the formation of a peroxide[12a,b] when oxygen comes in contact with a solution of triphenylmethane but the situation is probably complicated by the presence of bromine. The completion of reaction (7) followed by the formation of a peroxide (8) or oxidation products such as benzophenone and phenol, or acids is responsible for most of the extra heat evolved in the presence of oxygen.

The greater oxidation noted when the bromination products were added to a reaction mixture as shown in curve 4 of Fig. 2 is explained on the basis of a bromine sensitized photo-oxidation of the bromide. Bromine atoms can react with the bromide to form free radicals which in turn can react with oxygen, as represented by the reversal of reaction (3). It is known that bromides are more susceptible to oxidation than the corresponding hydrocarbons,[13] as would be expected from the fact that a C–Br bond is more easily broken than a C–H bond and the free radicals are more easily formed.

Thermochemical Data

The heats of reaction obtained are rendered somewhat uncertain by the difficulty of removing all the oxygen from the photocalorimeter. The large heat of the bromine-sensitized photo-oxidation is not entirely eliminated and the graphical correction is subject to error when the effect is large. The approximate heats of bromination are given in Table III. These values are the true heats of reaction only in so far as there is no complication due to solvation effects. There is little reason in this case to believe that the heats of solution of the reactants and products should be essentially different.

TABLE III

HEATS OF BROMINATION IN KCAL.

Toluene	Diphenylmethane	Triphenylmethane	Cinnamic acid
15	12	8	16

The heat of addition of bromine to the double bond in cinnamic acid is in exact agreement with that estimated by Bauer and Daniels[9] from combustion data and the rules of Kharasch.

The heat of bromination of methane is 6.5 kcal. The increase of 8.5 kcal. for toluene is undoubtedly due to increased resonance in benzyl bromide over that present in methyl bromide. In diphenyl- and triphenylmethane there is also an increased resonance but a steric effect is introduced which reduces the heat of reaction. The large bromine

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(11) $$\frac{\mathrm{d}c_{\mathrm{Br}}}{\mathrm{d}t} = 0 = 2I - k_2 c_{\mathrm{Br}} c_{\mathrm{R_3CH}} + k_3 c_{\mathrm{R_3C}} c_{\mathrm{Br}_2} \qquad \text{(a)}$$

$$\frac{\mathrm{d}c_{\mathrm{R_3C}}}{\mathrm{d}t} = 0 = k_2 c_{\mathrm{Br}} c_{\mathrm{R_3CH}} - k_3 c_{\mathrm{R_3C}} c_{\mathrm{Br}_2} - k_7 c_{\mathrm{R_3C}} c_{\mathrm{O}_2} - k_8 c_{\mathrm{R_3C}} c_{\mathrm{R_3COO}} \qquad \text{(b)}$$

$$-\mathrm{d}c_{\mathrm{R_3COO}}/\mathrm{d}t = 0 = -k_7 c_{\mathrm{R_3C}} c_{\mathrm{O}_2} + k_8 c_{\mathrm{R_3C}} c_{\mathrm{R_3COO}} \qquad \text{(c)}$$

Adding together (a), (b) and (c)

$$2I = 2k_7 c_{\mathrm{R_3C}} c_{\mathrm{O}_2}$$

from which

$$c_{\mathrm{R_3C}} = I/k_7 c_{\mathrm{O}_2}$$

but

$$-\mathrm{d}c_{\mathrm{Br}_2}/\mathrm{d}t = I + k_3 c_{\mathrm{R_3C}} c_{\mathrm{Br}_2}$$

Substituting

$$\frac{-\mathrm{d}c_{\mathrm{Br}_2}}{I\,\mathrm{d}t} = 1 + \frac{k_3 c_{\mathrm{Br}_2}}{k_7 c_{\mathrm{O}_2}}$$

(12) (a) Bachmann in Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, 1938, p. 493; (b) Halford and Anderson, *Proc. Nat. Acad. Sci.*, **19**, 759 (1933).

(13) Fisher, THIS JOURNAL, **56**, 2056 (1934).

atom is unable to stay far enough away from all of the phenyl groups.

Whereas these direct calorimetric measurements are inaccurate because of accompanying oxidation, it should be emphasized that indirect calculations obtained from combustion measurements are still less reliable. The latter values are differences of large quantities which are themselves uncertain because it is difficult to be sure of the products of combustion of halogen compounds.

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Summary

1. The photo-kinetics of bromine substitution and addition have been studied for carbon tetrachloride solutions of toluene, diphenylmethane, triphenylmethane and cinnamic acid, making use of calorimetric measurements.
2. All these brominations, carried out in blue light (4360 Å.), are chain reactions and all are inhibited by oxygen.
3. All the quantum yields increase with increasing bromine concentration. After fairly complete removal of the oxygen at a bromine concentration of 0.002 mole per liter and light intensity of 500 ergs per second the quantum yields are approximately as follows: triphenylmethane, 1000; diphenylmethane, 250; toluene, 50; cinnamic acid, 35 molecules per quantum.
4. The heats of bromination in the absence of oxygen are as follows: triphenylmethane, 15 kcal./mole; diphenylmethane, 12; toluene, 8; cinnamic acid, 16.
5. The larger evolution of heat in the presence of oxygen indicates that an oxidation process accompanies the inhibited photochemical reaction.
6. The oxygen inhibition is greatest for toluene and cinnamic acid and least for triphenylmethane.
7. The oxygen inhibition may be explained by a competing reaction between oxygen and the free radicals which propagate the chain.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DARTMOUTH COLLEGE]

Oxygen Exchange between Water and Inorganic Oxy-anions

BY G. ALEXANDER MILLS[1]

Introduction

The importance of heavy oxygen as a means of investigating the mechanism of certain reactions was recognized soon after its discovery. From preliminary studies on the exchange of oxygen between water and certain compounds, a process which depends on chemical reactions normally occurring between water and the oxygen containing solute, certain generalities concerning the molecular structure of the solute can be drawn. These investigations also have shown that the rate of reaction is often determined by the *p*H of the solution not only because some of the reactions are subject to acid or base catalysis but also because of the dependence on *p*H of the concentration of the reacting substrate. It is important to note in this connection that the rate of attainment of elementic equilibrium, in which the numbers of ions and molecules are established, is much more rapid than for isotopic equilibrium since in that case the reaction must occur many times.

Heavy oxygen reactions have been reviewed by Rietz[2] and by Day.[3] Carboxylic acids exchange both oxygen atoms,[4] only the undissociated molecule taking part in the reaction which is acid catalyzed. The rate can be related directly to hydrolysis and esterification.[5] In contrast to the rapid hydroxyl hydrogen exchange no oxygen exchange has been found for alcohols[4a,b,e] with the exception of one tertiary alcohol, trianisylmethanol, with strong polar groups. Aldehydes and ketones[4a,e,6] undergo exchange rather readily

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(1) Present address: Catalytic Development Company, Marcus Hook, Pa.

(2) Rietz, *Z. Elektrochem.*, **45**, 101 (1939).

(3) Day, *Science Progress*, **34**, 47 (1939).

(4) (a) Cohn and Urey, THIS JOURNAL, **60**, 679 (1938); (b) Roberts, *J. Chem. Phys.*, **6**, 294 (1938); (c) Roberts and Urey, THIS JOURNAL, **61**, 2580 (1939); (d) Herbert and Lauder, *Trans. Faraday Soc.*, **34**, 1219 (1938); (e) Senkus and Brown, *J. Org. Chem.*, **2**, 569 (1938).

(5) Roberts and Urey, THIS JOURNAL, **60**, 2391 (1938), *ibid.*, **61**, 2584 (1939); Herbert and Lauder, *Nature*, **142**, 954 (1938); Datta, Day and Ingold, *J. Chem. Soc.*, 838 (1939).

(6) Herbert and Lauder, *Trans. Faraday Soc.*, **34**, 432 (1938).