Treatment of this substance with sodium carbonate under the conditions which yielded 2-methyl-6-aminopyrimidine-5-aldehyde gave reaction products from which no trace of an aldehyde could be obtained.

The sulfonhydrazide of 4-methylthiazole-5-acetic acid (VIII) was also prepared according to essentially the same procedure as that used for the preceding compound, m. p. 122°.

Anal. Calcd. for $C_{12}H_{13}O_3N_3S_2\cdot H_2O$: C, 43.77; H, 4.56. Found: C, 43.83; H, 4.83.

This substance likewise failed to give any trace of an aldehyde when treated with sodium carbonate under the conditions previously used.

Summary

1. The McFadyen and Stevens aldehyde synthesis has been applied to pyrimidines.

2. In two cases the reaction has been shown to fail where the carboxyl group is not directly attached to the ring.

HARRISON, NEW JERSEY RECEIVED AUGUST 19, 1940

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

Oxygen Inhibition in the Photobromination of Cinnamic Acid

BY ROBERT F. BROWN AND FARRINGTON DANIELS

Several halogenations are inhibited by oxygen[1a-g] but the reactions are not fully understood. The experiments described here were designed to study further this inhibiting effect of oxygen, as reported previously in the photobromination of cinnamic acid.[2] In order to follow the course of the reaction without exposure to atmospheric oxygen an all-glass technique was followed in which the concentration of bromine at any time was determined by the absorption of light as measured with a photoelectric cell. The intensity of light was low (170 ergs per second) so that the concentration would not be changed appreciably by photochemical reaction during the few seconds required to take a reading.

Apparatus.—A monochromator with liquid ethyl cinnamate for the refracting prism[3] was used with an 85-watt General Electric mercury vapor lamp (Type H-3). The parallel beam of light at 4360 Å. passed through a water thermostat and the cylindrical absorption cell. It then struck a photoelectric cell (Westinghouse S.R. 51) connected with an amplifying circuit containing a type no. 76 tube. The galvanometer (2.5 mm. per microvolt) was adjusted to zero by changing a shunt resistance and a resistance in series with the 90-volt batteries. An identical cell filled with carbon tetrachloride was used for the zero reading.

A multiple reaction cell was fused to the vessel in which the reaction mixture was deoxygenated, and to other chambers used for filling with the solution and adding definite quantities of oxygen. Five cylindrical cells 1.7 cm. in inside diameter with fused Pyrex windows 2.5 cm. apart permitted different measurements to be made, all with the same concentration of bromine and oxygen. The solutions of cinnamic acid and bromine in carbon tetrachloride were frozen and evacuated, then melted, frozen and evacuated again. This cycle was repeated three to five times until the emission spectrum of oxygen could no longer be obtained with a Tesla coil. Oxygen was then admitted to a predetermined pressure as read on a manometer and the concentration of dissolved oxygen was calculated from the volumes of the liquid and the gas space of the apparatus, using the distribution coefficients of Horiuti.[4] In some of the experiments the oxygen was admitted with magnetic hammers and sealed-off tubes.

It was found that a rapid diffusion of bromine occurred when there was a marked difference in concentration in the adjacent compartments of the multiple cell. The diffusion apparently took place along a surface film of solution rather than through the gas phase. Consequently it was necessary to use single absorption cells in some of the experiments.

Known solutions of purified bromine in carbon tetrachloride, ranging in concentration from 2.7 to 30.4 $\times 10^{-4}$ mole per liter, gave a straight line when the logarithm of the light transmission was plotted against concentration. The transmission was obtained by dividing the galvanometer deflection with bromine solution in the cell by the deflection with pure carbon tetrachloride in the cell. The constant k in Beer's law, $I = I_0e^{-klc}$ was found to be 458 when l is expressed in cm. and c in moles per liter. Using a thermopile and much more intense light Bauer and Daniels[3] obtained a value of 448.

Solutions of purified carbon tetrachloride and bromine were prepared in an atmosphere of nitrogen and kept in a large storage vessel using a tightly fitting, unlubricated stopcock. Kahlbaum cinnamic acid, recrystallized several times from alcohol, gave a melting point of 133°. The stilbene and triphenylethylene were prepared by Zartman.[5] They melted at 124.4 and 69.8,° respectively. The triphenylmethane was prepared from benzene and chloroform in the presence of aluminum chloride. After

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[1] (a) Luther and Goldberg, *Z. physik. Chem.*, **56**, 43 (1906); (b) Dickinson and Leermakers, THIS JOURNAL, **54**, 3852, 4648 (1932); (c) Willard and Daniels, *ibid.*, **57**, 2240 (1935); (d) Chapman, *ibid.*, **56**, 818 (1934); (e) Pease, *ibid.*, **53**, 3728 (1931); (f) Schultze, *ibid.*, **56**, 1552 (1934); (g) Heisig, *ibid.*, **58**, 1095 (1936).

[2] Bauer and Daniels, *ibid.*, **56**, 2014 (1934).

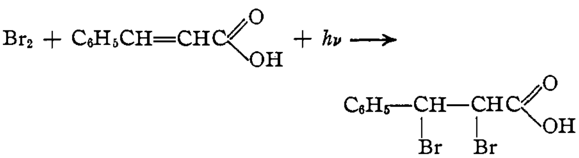
[3] Bauer and Daniels, *ibid.*, **56**, 378 (1934).

[4] Horiuti, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **17**, 125 (1931).

[5] Adkins and Zartman, THIS JOURNAL, **54**, 1668 (1932).

repeated low pressure distillations and crystallizations from alcohol it melted at 93°.

Experimental Results.—In the photobromination of cinnamic acid, the concentration of bromine decreases in accordance with the over-all reaction



The concentration of bromine, colorimetrically determined, was measured at frequent intervals and the smooth concentration–time curves were plotted as shown in Fig. 1. They were nearly straight lines during the first ten minutes of exposure and frequently for nearly an hour. It must be remembered that the light intensity was so low that the concentration was not greatly changed. The input of light was quite constant at 170 ergs per second. The simplest way of recording the effect of the various factors is through a statement of the quantum yield, Φ, *i. e.*, the number of molecules of bromine disappearing per quantum of radiation absorbed. Since it was not practical to stir the solutions, there was a slight concentration gradient between the illuminated and unilluminated portion of the cells, but this difficulty was not serious because the light intensity was so weak. The quantum yields can be regarded only as relative values, however, because the intensity of light was so low that a thermopile was unsatisfactory as an intermediate instrument for standardizing the photoelectric cell against a standard radiation lamp. The relative values are sufficient for the present purpose. The quantum yields are calculated from the data of the first ten minutes of each experiment during which time the conditions were not greatly changed.

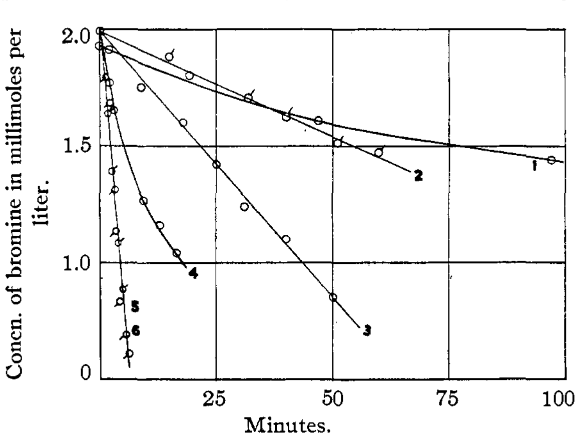


Fig. 1.—Photobromination of cinnamic acid (1–4) and triphenylmethane (5–6); temperature, 35°; concn. of oxygen in millimoles per liter: 1, 5.3; 2, 1.8; 3, 0.8; 4, 0; 5, 3.3; 6, 0.

Quantum Yields with Cinnamic Acid.—The effects of temperature and oxygen concentration on the photobromination of cinnamic acid are summarized in Table I and Fig. 2.

TABLE I

PHOTOBROMINATION OF CINNAMIC ACID

In all experiments the concentration of cinnamic acid was 2.8 to 3.0 millimoles per liter of carbon tetrachloride. All concentrations are expressed in millimoles per liter.

A. Concentration of bromine, 2.0 millimoles per liter; temperature, 35.0°

c_{O_2}	0[a]	0[a]	0.8	1.8	3.4	5.3
Φ	180[b]	155[b]	50	20	20	15

B. Concentration of bromine, 3.8 millimoles per liter; temperature, 35.0°

c_{O_2}	1.1	1.8	3.1
Φ	115	80	68

C. Concentration of bromine, 1 to 3 millimoles per liter; temperature, 25.0°

c_{O_2}	0[a]	0[a]	0[a]	0.8	1.2	1.6	1.6	2.1	3.0
c_{Br_2}	2.5	2.6	0.8	1.4	3.2	1.9	1.2	1.6	1.2
Φ	170	215	50	45	13	14	(24)	11	13

Water added, 4 millimoles per liter; temperature, 25.0°

c_{O_2}	0[a]	3.5
c_{Br_2}	2.0	2.0
Φ	48	16

Hydrobromic acid added, 0.1 millimole per liter; temperature, 25.0°

c_{O_2}	0[a]	3.3
c_{Br_2}	1.4	2.0
Φ	160	25

A trace of hydroquinone added; temperature, 25.0°

$c_{O_2} = 0$. $c_{Br_2} = 1.2$. $\Phi = 5$

[a] Zero concentration of oxygen represents 3 to 5 evacuations. Slight traces may still be present in some cases.

[b] Perbenzoic acid was added to test the effect of peroxides.

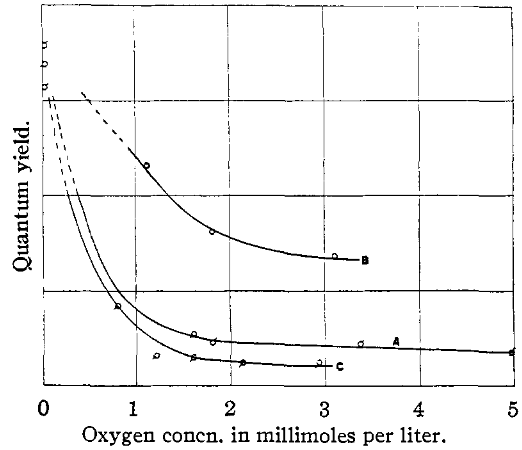


Fig. 2.—Influence of oxygen on the photobromination of cinnamic acid. The concentration of bromine in B is twice that in A and C. The temperature in C is 25°; in A and B it is 35°.

These experiments show that oxygen definitely inhibits the photobromination of cinnamic acid. At low concentrations of oxygen, particularly after evacuating, it is difficult to know with accuracy the amount of oxygen which is present. The experimental results showed in general that the quantum yield varies approximately inversely as the oxygen concentration and that the quantum yield increases almost directly with the bromine concentration. A comparison of curve C with curve A of Fig. 2 shows that a ten-degree decrease in temperature causes a definite decrease in the quantum yield when oxygen is present and other determinations show only a small effect, if any, when it is absent.

Peroxides and water vapor have very little effect on the quantum yield. The small trace of hydroquinone added in the last experiment of Table I practically stopped the chain. This observation is in agreement with the inhibition of the bromination of phenanthrene by hydroquinone as reported by Price.[6]

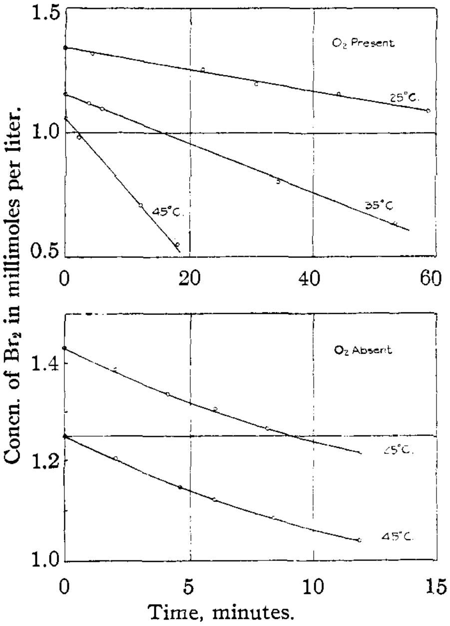


Fig. 3.—Influence of temperature on the rate of photobromination of cinnamic acid in the absence of oxygen (lower curves) and in the presence of oxygen (upper curves).

The quantum yields for the photo-addition of bromine to the double bond in stilbene and triphenylethylene are given in Table II. The pronounced inhibition by oxygen is evident here also. However, oxygen does not produce a large inhibitory effect on the photobromination of triphenylmethane, as shown also in Table II. In the latter case substitution is involved rather than addition, but the substitution involves a chain reaction as shown by the large quantum yield and the strong inhibition by a trace of hydroquinone.

Table II

Photobromination of Stilbene, Triphenylethylene and Triphenylmethane at 35°

	Concn. of oxygen, moles/liter $\times 10^4$	Concn. of bromine, moles/liter $\times 10^4$	Concn. of unsaturated, moles/liter $\times 10^4$	Φ, 0–10 min. approx.
Stilbene	34	18	29	13
	0	15	29	560
Triphenylethylene	33	20	31	4
	0	17	31	105
Triphenylmethane	33	20	31	600
	0	20	31	600
	0	20	31	4[a]

[a] A trace of hydroquinone was added.

Further experiments on oxygen inhibition under similar conditions indicated that the photobromination of tetraphenylethylene is too slow to detect even in the absence of oxygen and that the photobromination of β-amylene is too fast to measure conveniently even in the presence of oxygen.

Temperature Effect.—To test the magnitude of the temperature coefficient for solutions containing oxygen and for those free of oxygen the five-celled vessel previously mentioned was employed. The solutions of cinnamic acid and bromine in carbon tetrachloride were deoxygenated and mixed and separate exposures were taken on three cells at 25, 35 and 45°, respectively.

In Fig. 3 the lower curves are for reactions in the absence of O_2 at 25 and 45° and the upper curves are for reactions in the presence of 2×10^{-3} mole per liter of O_2 at 25, 35 and 45°. The nearly identical slopes of the lower curves establish the fact that the temperature coefficient for a ten-degree interval is practically unity in the absence of oxygen. The variations in slope of the upper curves definitely confirm a temperature coefficient for a ten-degree interval well above unity in the presence of oxygen in agreement with the coefficients obtained by Bauer and Daniels.[3] Their values varied from 1.2 to 2.2 depending on the bromine concentration.

Oxygen Effect.—In order to determine whether the effect of oxygen included the formation of a peroxide, careful tests were carried out

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[6] Price, This Journal, 58, 2101 (1936).

with titanous sulfate and other reagents but no trace of a peroxide was found.

Since oxygen is so effective in stopping the photo-addition of bromine to the double bond it was necessary to determine whether or not it is consumed in the reaction. A series of measurements was made on the rate of oxygen absorption as measured in a gas buret. The oxygen was connected with capillary tubing to a shaking flask in a thermostat at 25.0° containing 0.01 *M* cinnamic acid in carbon tetrachloride. The flask was exposed to the full light of a General Electric H-3 capillary mercury lamp. The results are shown in Fig. 4 where it is seen that oxygen is not consumed until a bulb of bromine is broken at A. A rapid absorption of oxygen then occurred which slowed down as the bromine was consumed, and the light was no longer absorbed. Breaking a second bulb of bromine in the flask at B resulted in a second large uptake of oxygen. This test was repeated three times with the same results. No release of oxygen could be detected when an excess of bromine was added.

A blank was carried out by Dr. John Willard with the illumination of bromine and oxygen and carbon tetrachloride in the absence of cinnamic acid. A slight reaction, much slower than that recorded here, was observed over a period of several hours. This slow bromine-sensitized photo-oxidation of carbon tetrachloride is under further investigation. He showed further that the presence of the reaction products exerts no influence on the rate of photobromination as measured by the disappearance of the bromine, but on the other hand the consumption of oxygen by the photobromination is markedly increased by the addition of the dibromocinnamic acid. As would be expected, the carbon–bromine bond is more easily oxidized than the carbon–hydrogen bond.

In further experiments Dr. Willard confirmed the fact that the removal of oxygen eliminated the temperature effect on the photobromination of cinnamic acid. A degassed solution of carbon tetrachloride containing 0.005 mole of cinnamic acid and 0.0005 mole of bromine per liter was illuminated with weak light for five-minute intervals at 0.5, 25.3 and 48°. The rate of disappearance of bromine under constant conditions of light absorption was of the same order of magnitude at all three temperatures. In the presence of air an increase of 50° in temperature should have produced a large increase under these conditions.

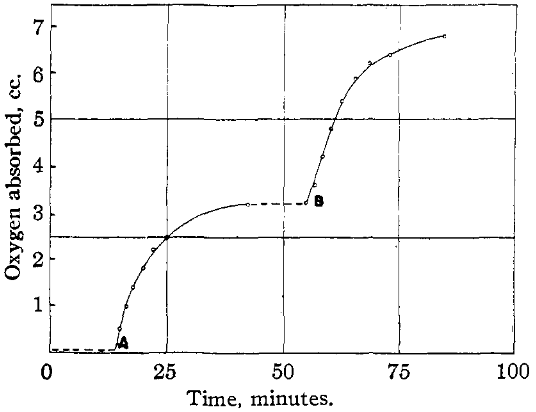

Fig. 4.—Consumption of oxygen during the photobromination of cinnamic acid in carbon tetrachloride solution. Bromine was introduced at A and at B.

Theoretical Discussion.—Under the conditions of this investigation the rate of photobromination and the quantum yield were determined under controlled concentrations of oxygen as well as in the practical absence of oxygen.

In the earlier study[3] it was difficult to reconcile the chain nature of the reaction with the large temperature coefficient. It was realized that a chemical chain of the conventional atom-propagated type could not have the large temperature effect which was observed. An energy chain seemed to be free from this objection but it was discovered[2] that this investigation[3] and most all of the preceding investigations on photobrominations really involved oxygen-inhibited reactions. Since these reactions then were much more complicated than had been supposed, the large temperature coefficient no longer constituted a legitimate objection to the atom-chain. The present investigation shows that when the complication of the dissolved oxygen is eliminated, the temperature effect is indeed eliminated and the atom-chain theory is entirely satisfactory. An explanation is offered in this report, and the one[7] which follows it, for the mechanism of the photobromination both in the presence and absence of oxygen.

In the absence of oxygen the reaction may be represented by the following equations[8] in which cinnamic acid is represented by A:

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(7) Magee and Daniels, THIS JOURNAL, **62**, 2825 (1940).

(8) These equations could be used equally well if an activated bromine molecule were formed as the first step rather than the two bromine atoms. On such an hypothesis the second step would be $Br_2^* + A \longrightarrow ABr + Br$. Reactions (2) and (3) would then follow as given.

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

$$A + Br \xrightarrow{k_2} ABr \qquad (2)$$

$$ABr + Br_2 \xrightarrow{k_3} ABr_2 + Br \qquad (3)$$

The chain is carried by reactions (2) and (3). It is stopped by one or more of the following

$$ABr + ABr \longrightarrow ABr_2 + A \text{ (or } 2A + Br_2) \qquad (4)$$

$$Br + Br \longrightarrow Br_2 \qquad (5)$$

$$ABr + Br \longrightarrow ABr_2 \qquad (6)$$

A stationary state is set up almost immediately, in which the concentration of the bromine atoms and the free radicals, ABr, remain essentially constant. Under these conditions, as shown in the accompanying communication[7]

$$c_{Br} = \frac{k_3 c_{ABr} c_{Br2} + 2k_4 c_{ABr}^2}{k_2 c_A - k_6 c_{ABr}} \cong \frac{k_3 c_{ABr} c_{Br2}}{k_2 c_A}$$

Then it follows that

$$\Phi = -\frac{1}{I}\frac{dC_{Br2}}{dt} = \frac{k_4 + \dfrac{k_6\, k_3 c_{Br2}}{k_2 c_A}}{X} + k_3 c_{Br2}\sqrt{\frac{1}{XI}} \cong k_3 c_{Br2}\sqrt{\frac{1}{XI}}$$

where

$$X = k_4 + k_6\left(\frac{k_3 c_{Br2}}{k_2 c_A}\right) + k_5\left(\frac{k_3 c_{Br2}}{k_2 c_A}\right)^2$$

When the ratio of c_{Br_2}/c_A is small the most efficient chain stopping mechanism is the recombination of the ABr radicals (4); for intermediate values of this ratio, we cannot neglect the reactions of ABr with Br (6); and for large values of this ratio, the recombination of bromine atoms (5) is rate determining.

The inhibiting effect of oxygen must be explained on the basis of some chain stopping mechanism much more efficient than reactions (4), (5) and (6) such for example as the formation of a peroxy-bromo free radical shown in reaction (7)

$$ABr + O_2 \xrightarrow{k_7} ABrO_2 \qquad (7)$$

When the stationary state is reached, the concentration of $ABrO_2$ as well as the concentrations of ABr and of Br remain essentially constant and it can be shown[7] that

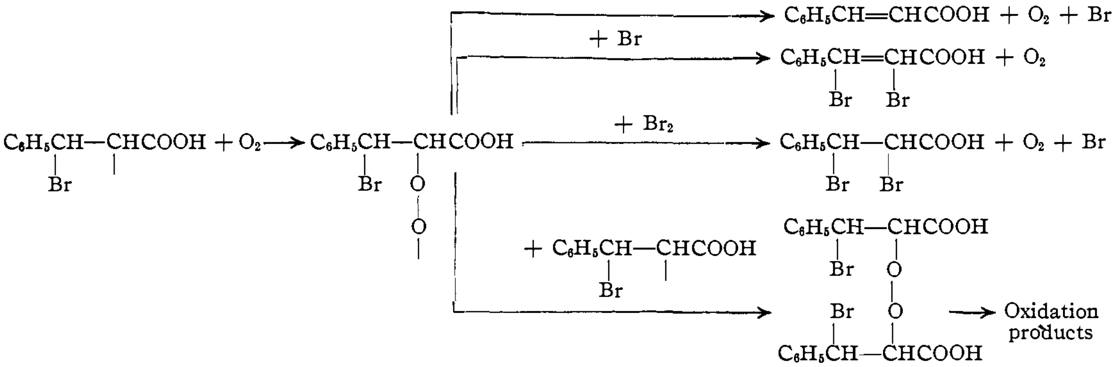
$$c_{ABr} = 2I/k_7 C_{O_2}$$

and

$$\Phi = -\frac{1}{I}\frac{dc_{Br_2}}{dt} = 1 + \frac{2k_3 c_{Br_2}}{k_7 c_{O_2}}$$

Then $(\Phi - 1)\dfrac{c_{O_2}}{c_{Br_2}}$ should give a constant k_3/k_7 which is easily calculated from the data of Table I. It is very roughly constant with an average value of 25 at 25°.

Several conclusions regarding the effect of oxygen can be drawn from the findings of this investigation and the accompanying one,[7] in which it is shown that oxygen causes a large evolution of heat in the photobromination of cinnamic acid. There is no evidence for the existence of an energy chain, nor for a bromine oxide, nor for any particular chemical product which acts as an inhibitor. All the results can be explained readily on the basis of a chemical reaction between the bromo free radical and oxygen to give a bromo-peroxy free radical which can then react in several different ways as shown below.



(8)
(9)
(10)
(11)

Experimental evidence for the existence of a bromo peroxide, similar to that shown in reaction (11), has been reported. Bockmüller and Pfeuffer[9] prepared *bis*-dibromo-isopropyl peroxide by exposing to light a mixture of allyl bromide, bromine and oxygen. They isolated the peroxide and analyzed it. The dibromocinnamic acid peroxide discussed here probably decomposes with the evolution of heat to give other acids such as benzoic acid and oxalic acid. The fact that no chemical test could be obtained with ferrous chloride shows that the peroxide is unstable, and the

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[9] Bockmüller and Pfeuffer, *Ann.*, **537**, 178 (1939).

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.

MADISON, WISCONSIN RECEIVED JULY 1, 1940

[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).