employed and increases with increasing temperature, as determined by the dioxane precipitation method.

The precipitate formed during the preparation of the Grignard reagent from methyl chloride contains magnesium chloride etherate from the disproportionation of methylmagnesium chloride, so that the reagent contains 20% of dimethylmagnesium in addition to that formed by the disproportionation of the methylmagnesium chloride remaining in solution.

BRYN MAWR, PA. RECEIVED JUNE 4, 1935

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

The Photobromination of Tetrachloroethylene and of Chloroform with Special Reference to the Effects of Oxygen

BY JOHN WILLARD AND FARRINGTON DANIELS

Oxygen, present as an incidental impurity, is known to have a marked effect on the rate of certain chemical reactions,[1] and very likely it is a factor in others where its influence has not yet been suspected. The matter is of interest both from a theoretical and from a practical standpoint.

The photobromination of cinnamic acid has been under investigation in this Laboratory for several years[2] and it seemed desirable to investigate also the photobromination of the very simple molecules, tetrachloroethylene for addition, and chloroform for substitution. These two substances are valuable for investigational purposes not only on account of their simple structure but also on account of the fact that they have high vapor pressures and can be studied in the gas phase as well as in the liquid phase.

All of the photochemical work described here was carried out with a large quartz monochromator and capillary lamps of high intensity,[3] and a large area thermopile.[4]

Photobromination of Tetrachloroethylene

Experimental Procedure

Tetrachloroethylene.—Chlorine was passed into Eastmen tetrachloroethylene and exposed to light.[5] After washing several times with sodium hydroxide and with water the liquid was dried with calcium chloride and twice distilled through a Widmer column in an all-glass still, the middle fraction being retained. It was further purified by freezing in an all-glass reservoir equipped with a dozen taps which could be opened with magnetically operated hammers.

Bromine.—Merck reagent quality bromine was distilled from potassium bromide onto phosphorus pentoxide which had been resublimed in a stream of oxygen. It was then fractionally distilled four times and fractionally crystallized three times, all steps in the purification process being carried out in an all-glass system. After degassing in the manner to be described shortly, it was distilled into a dozen small bulbs.

Oxygen.—Commercial tank oxygen was liquefied in a liquid air trap and the middle-boiling fraction was used to fill a series of bulbs of 1 cc. or less in volume. The pressure of oxygen was determined with a glass manometer.

Degassing Liquids.—Dissolved oxygen was removed from the reservoirs of liquid tetrachloroethylene and bromine by a repeated cycle of freezing with liquid air, evacuation with a mercury vapor pump, melting and brief boiling. When gas from the frozen liquid was no longer able to support a discharge from a Tesla coil, the material was deemed to be sufficiently free from oxygen. It was usually necessary to go through a series of six or seven freezings and evacuations before the oxygen and other permanent gases were sufficiently removed to meet this criterion.

Apparatus.—The experiments were carried out in a fused quartz cell 1 × 2 cm. in cross section and 8 cm. deep. The cell was equipped with a head as illustrated in Fig. 1. Side arm A contains bulbs of reactants which may be shaken into depression C to be broken by the glass-enclosed hammer B. D-E-G is a sealed-in, magnetically-operated stirrer designed to give efficient stirring in the illuminated portion of the cell, without interrupting the beam of light. It consists of the quartz-enclosed iron core D, the quartz landing button E and the quartz rod which terminates in the stirring button G. When an experiment is in progress the circuit through the solenoid M is opened and closed about twice a second by means of a contact operated by a metronome or by a cam on a pulley wheel. This jerks the stirrer up several centimeters and then allows it to fall under its own weight to the point where E is stopped by the quartz platform, F. In falling rapidly the button G sets into motion a body of liquid which travels on into the illuminated region of the cell. The button G has to be 5 mm. or less in diameter, in order to pass through the neck

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[1] See, among others, Deanesly, THIS JOURNAL, **56**, 2501 (1934); Bauer and Daniels, *ibid.*, **56**, 2014 (1934); Dunnicliff and Joshi, *J. Ind. Chem. Soc.*, **6**, 121 (1929); Kistiakowsky, "Photochemical Processes," Chemical Catalog Company, New York City, 1929, pp. 118, 119, 166, 183.

[2] Bauer and Daniels, THIS JOURNAL, **54**, 2564 (1932).

[3] Heidt and Daniels, *ibid.*, **54**, 2381, 2384 (1932).

[4] Damon, Ph.D. Thesis, University of Wisconsin, 1932.

[5] Dickinson and Leermakers, THIS JOURNAL, **54**, 3853 (1932).

of the cell and its shape makes little difference in the effectiveness of stirring.

Part H of the cell-head is a quartz-to-Pyrex graded seal which allows the cell to be sealed to Pyrex systems.

To fill the cell it was first sealed through the outlet K to the glass tap M of a reservoir of purified and degassed tetrachloroethylene. It was then evacuated by a mercury vapor pump through J and protected by a liquid air trap. While evacuation was taking place all portions of the cell except that containing the bulbs of reactants were flamed. The pump was then sealed off at J, the tap M was broken by the hammer L and tetrachloroethylene was distilled into the cell and sealed off at P and at K. The glass tap I allowed the cell to be opened without contamination of air, for addition of materials or removal of the reaction mixture for analysis. When the cell had been filled with tetrachloroethylene and sealed, its light transmission was compared with that of a similar blank cell. A bromine bulb was then broken in C. The bromine vaporized and was quickly absorbed by the tetrachloroethylene. The solution was then illuminated and readings of the light transmitted by the reaction cell and by the blank were taken at frequent intervals in order that the reaction might be followed by Beer's law. When a sufficient number of readings had been taken to show the course of the reaction in the absence of oxygen a bulb of oxygen was broken in C and the readings were continued. At the end of each experiment three graphs were made in which light absorption, concentration and quantum yield were plotted against time.

Measurements were confined to 4360 Å. because liquid tetrachloroethylene itself showed absorption for the ultraviolet lines of the mercury spectrum. The absorption at 3650 Å. was very slight. It was determined qualitatively, that light of 3650 and 5780 Å. causes the addition of bromine when oxygen is absent. It was shown experimentally that absorption of light at 4360 Å. by the product is negligible.

Calculations

A straight line was obtained when the logarithm of the transmission of light of 4360 Å. was plotted against the concentration of bromine used in the solutions. The averaged value of E, defined by the relation $E = 1/lc \log I_0/I$, was 197 ± 3 where l is the length of the light path in cm. and c is the concentration of bromine in moles per liter. This value is the same as that obtained by Bauer and Daniels[6] for the extinction coefficient of bromine dissolved in carbon tetrachloride, namely, 195 ± 3.

From the transmission of light by the reaction mixture the concentration of bromine at any time was determined by reference to the logarithmic plot. Transmissions were determined by readings of the galvanometer deflections when the light passed through the reaction cell, when it passed through a blank cell and when it was cut off by a shutter. All readings were corrected for reflection losses at the several windows. The same galvanometer readings, calibrated in terms of a U. S. Bureau of Standards standard radiation lamp, permitted a calculation of the number of ergs and the number of quanta absorbed.

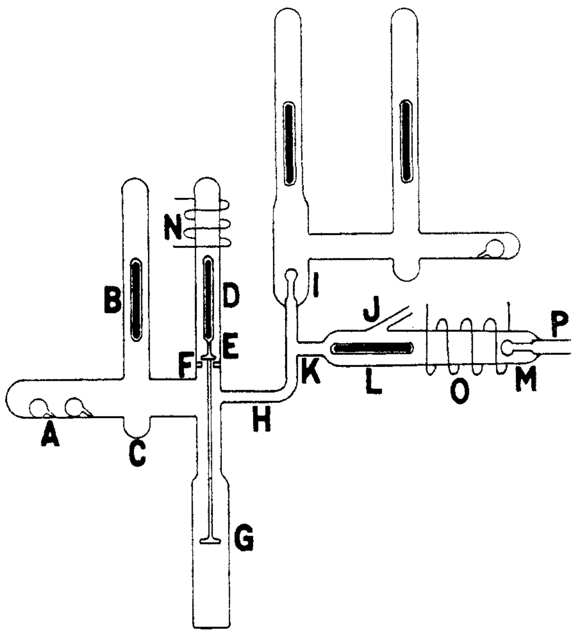

Fig. 1.—Reaction cell.

The concentration of bromine was plotted against time of illumination and the slope of the smooth curve, determined with a Richards–Roope tangent meter, gave the rate of the reaction at any time. The quantum yield at any time was determined by expressing this rate of reaction in terms of the number of molecules reacting per second and dividing by the number of quanta absorbed per second.

Results

Effect of Oxygen.—When reaction mixtures of bromine and tetrachloroethylene, which had been treated to free them from oxygen, were illuminated bromine was consumed at a readily measurable rate. When a bulb of oxygen was broken in the reaction chamber, giving a partial pressure of 20 to 50 mm. of the gas, the rate showed a sharp increase, indicating that small amounts of oxygen accelerate this reaction. Curves E and H of Fig. 2 illustrate this fact. Curves for other experiments indicate that the accelerating oxygen is gradually used up during the exposure to light. When oxygen at one atmosphere pressure was admitted to the cell the reaction was almost com-

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(6) Bauer and Daniels, THIS JOURNAL, **56**, 380 (1934).

pletely inhibited as shown in Fig. 3, where the readings which give the curve A were made with a reaction mixture from which oxygen had been removed and those for part B were made with the same mixture after oxygen at one atmosphere pressure had been admitted to the cell. Many experimental measurements were made which cannot be recorded here in detail,[7] but it should be emphasized that the results are all in substantial agreement even though the purification and procedures were considerably altered.

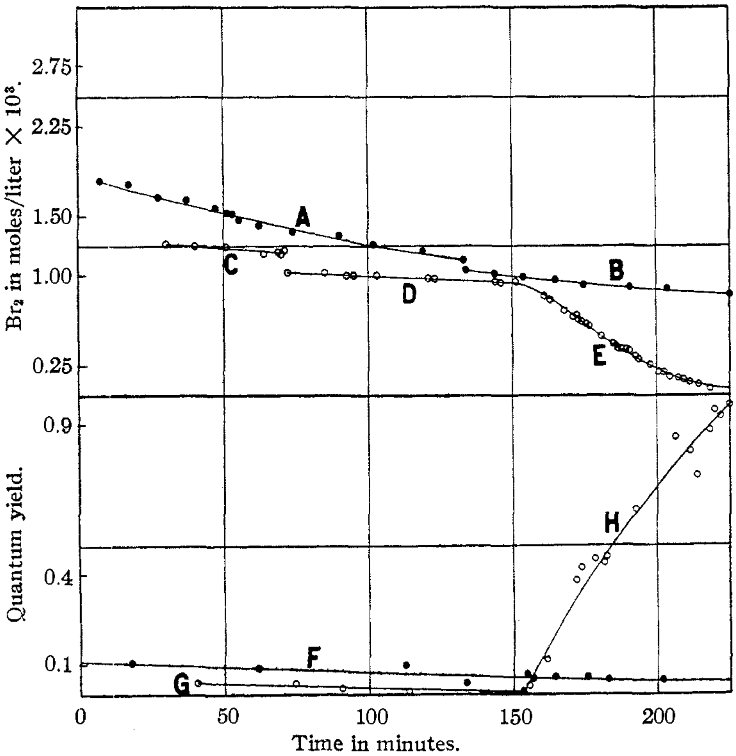

Fig. 2.—A, plot of concentration of bromine against time for reaction mixture in which considerable concentration of product has previously been built up. B, continuation of A after nine hour dark interval. C, continuation of B after breaking a fresh bulb of bromine in the reaction chamber; 225 minutes should be added to the time scale for curves C, D, E, G and H. D, continuation of C after a thirty-seven hour dark interval. E, continuation of D after breaking bulb containing about 1.5 × 10^{-5} mole of oxygen in the cell of 35-cc. capacity. F, plot of quantum yield against concentration corresponding to curves A and B. G, plot of quantum yield against concentration corresponding to curves C and D. H, curve showing increase in quantum yield after breaking oxygen bulb.

Inhibition by Products.—The two curves in each section of Fig. 2 represent the reactions which occurred after the breaking of two different bromine bulbs in the same solution of tetrachloroethylene. Since the concentration of tetrachloroethylene may be considered to remain essentially constant during these experiments, the fact that the slope of curves C and D in Fig. 2 is less than that of curves A and B at points of equal bromine concentration, indicates that the apparent rate of reaction has been decreased by the accumulation of products in the reaction mixture. This inhibition is also shown by the fact that curve G shows lower quantum yield values than does curve F.

Stirring.—If, during the course of an experiment, the stirrer was operated only during alternate intervals of illumination, the plot of concentration against time was of a sawtooth nature, indicating that bromine was consumed in the path of the light much more rapidly than it diffused in from the surrounding solution. If, however, a complete experiment was carried out without stirring, a smooth curve resulted, but such experiments differed from those in which stirring was used, in that the plot of percentage of incident light absorbed against time which they gave was convex to the axes of the plot while that for the stirred solutions was concave. This difference can probably be ascribed to the accumulation of the reaction product in the illuminated region of the unstirred reaction mixtures.

Temperature Effect.—One experiment was made with a deoxygenized system, in which readings were taken first at 0 and then at 25°. The quantum-yield values for the 0° illumination were extrapolated over a seven-minute interval of illumination which occurred between the last 0° reading and the first 25° reading. The value thus obtained divided into the quantum yield corresponding to the first reading of the 25° illumination gave a 25° temperature factor of 1.33. This gives a 10° temperature factor of $\sqrt[2.5]{1.33}$ or 1.12.

Concentration of Tetrachloroethylene.—Two experiments were carried out with carbon tetrachloride solutions of bromine and tetrachloroethylene. The amount of bromine consumed was determined by volumetric analysis after several

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(7) Complete details may be found in part of a Ph.D. thesis filed in the Library of the University of Wisconsin by John Willard in August, 1935.

hours of illumination and quantum yields were calculated. The bromine concentrations, the light intensities and the amounts of bromine consumed were of the same order of magnitude in the two cases. One reaction was carried out at 0° and the other at 25°, and the concentration of tetrachloroethylene was about 0.17 mole/liter in one case and about 5 moles/liter in the other. When the quantum yield for the reaction at 0° was corrected to 25° by means of the temperature factor given above, it was found that the yield for the solution of higher tetrachloroethylene concentration was only about 2.5 times greater than for the solution in which the concentration was one twenty-fifth as great. Both yields were of the same order of magnitude as those obtained with solutions of bromine in tetrachloroethylene which were not diluted with carbon tetrachloride. These facts indicate that the concentration of tetrachloroethylene is not important in determining the rate of the bromination reaction.

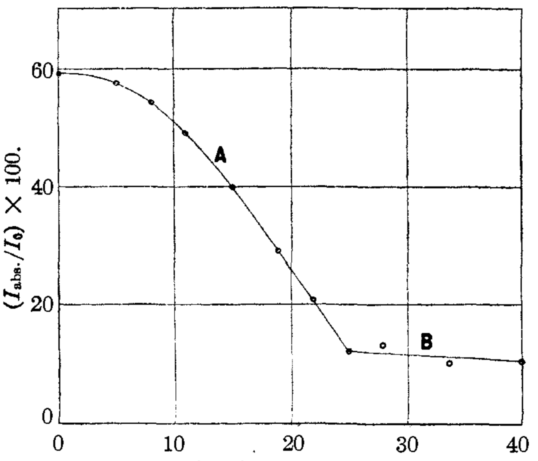


Fig. 3.—Inhibition of the photobromination of tetrachloroethylene by an excess of oxygen.

Dark Reaction.—The vertical drops between curves A and B and between curves C and D in Fig. 2 show that a slight dark reaction occurred over dark intervals of nine and thirty-seven hours. The rate of the dark reaction thus observed and also that observed when mixtures of bromine and tetrachloroethylene were allowed to stand in the dark while exposed to air was very much less than the rate reported by Herz and Rathmann.[8]

Gas Phase.—A few experiments were made on the gas phase reaction of bromine and tetrachloroethylene at temperatures between 50 and 60°. In one case a curve showing decreasing concentration of bromine with time of illumination was observed. In another, crystals of product formed on the windows of the reaction cell. In two others there was no indication of a bromination occurring even after long-continued illumination. These two experiments, however, showed a decrease in light absorption after the contents of the cell had been frozen out and then allowed to return to room temperature. When the cell was illuminated after such a treatment the light absorption increased from its reduced value to a rather definite maximum. This phenomenon is illustrated in Fig. 4 where A, B, C and D represent periods of illumination at 50° separated by dark periods in which the temperature was lowered. A three-hour period intervened between B and C. A bulb of oxygen was broken between C and D at the lower temperature. These facts may be explained by the assumption that during the liquefaction and freezing a small amount of dibromotetrachloroethane is formed and that on illumination of the revaporized mixture it is decomposed through a bromine sensitized photodecomposition of the type shown to exist by the recent work of Carrico and Dickinson,[9] which was published after the present research was completed.

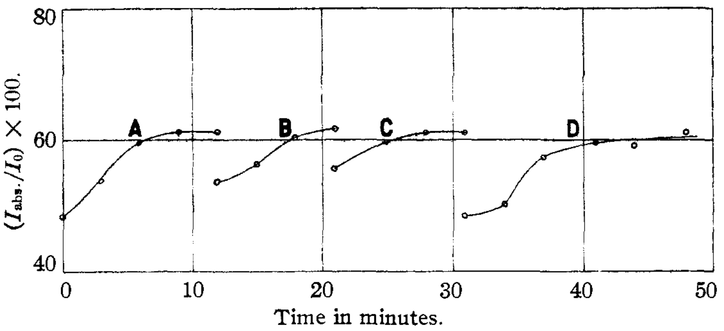


Fig. 4.—Influence of alternate periods of low temperature (dark), and high temperature and light on the concentration of bromine in gaseous mixtures, with tetrachloroethylene.

Quantum Yields.—The quantum yields observed in the liquid phase experiments dropped rapidly during the first periods of illumination of a given reaction mixture. The quantum yield represented by the lowest point of curve G, Fig. 2, is 0.009. This is the lowest observed in any experiment. In the experiments shown in Fig. 2

(8) Herz and Rathmann, *Ber.*, **46**, 2588 (1913).

(9) Carrico and Dickinson, THIS JOURNAL, **57**, 1343 (1935).

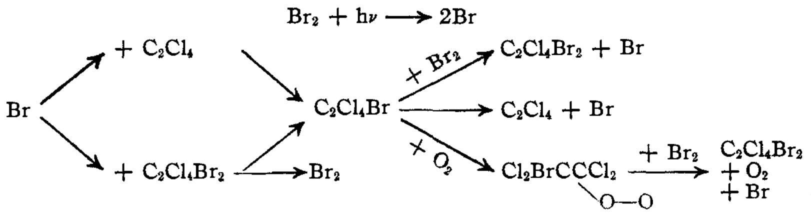
the solution originally contained an excess of bromine which was removed by illumination before the transmission measurements were begun, with the result that a concentration of the reaction product had been built up. This fact accounts for the low values of the quantum yields and for the fact that the yield is decreasing only slowly with time as contrasted to its rapid rate of change when the concentration of product is smaller.

The quantum yields varied with the individual fillings of the cell and with the concentration of products. The highest quantum yield observed was 24 molecules of bromine disappearing for each quantum absorbed; the lowest was 0.009. Under the conditions of most of the experiments with the removal of oxygen but with the accumulation of some dibromotetrachloroethane, quantum yields from one to five were commonly obtained.

It is clear that both the straight addition of bromine to the double bond in tetrachloroethylene, and also the oxygen-accelerated reaction, involve chains. Large quantities of oxygen cause a different reaction to take place, in which the bromine is not consumed.

Mechanism

Carrico and Dickinson have established the fact that in the gas phase at temperatures between 100 and 135° the photobromination of tetrachloroethylene occurs only slightly if at all but that the bromine-sensitized photodecomposition of dibromotetrachloroethane occurs through reaction chains which may be as much as 45 molecules long. This fact may be correlated with the characteristics of the addition reaction in the liquid phase at room temperatures by a mechanism which postulates that a bromine atom may react with either tetrachloroethylene or dibromotetrachloroethane to form a mono-bromo free radical, C_2Cl_4Br. This radical may either undergo a unimolecular decomposition to form tetrachloroethylene and a bromine atom as suggested by Carrico and Dickinson, or it may react with a bromine molecule to form dibromotetrachloroethane and a bromine atom. The first possibility is a step in a dibromotetrachloroethane decomposition chain, the second is a step in a chain causing the addition of bromine to tetrachloroethylene. Decomposition predominates when the life of the radical is short; addition predominates when the life is long enough to give opportunity for radicals to undergo collision and reaction with a bromine molecule. The rate of decomposition of this free radical is assumed to have a high temperature coefficient, an assumption which is in agreement with the value of about 2 for the 10° temperature factor of the decomposition reaction which may be calculated from the data of Carrico and Dickinson. As a result only the decomposition reaction is observed at high temperatures while the addition reaction is the one experimentally apparent at low temperatures. This hypothesis is in accord with a test made since the publication of the results of Carrico and Dickinson, which shows that if a liquid reaction mixture that has been illuminated until it becomes nearly colorless at 25° is then illuminated at 65° a distinct bromine coloration reappears.



The accelerating effect of oxygen on the addition reaction may possibly be accounted for by the formation of a monobromoperoxy free radical which is capable of reacting with a bromine molecule but which is capable of existing longer without decomposition than is the mono-bromo free radical. The formation of peroxy free radicals by the reaction of oxygen with free radicals has been suggested by Haber and Willstätter,[10] and by Ziegler.[11] The latter author conceives these peroxy free radicals to be capable of giving off their oxygen and being regenerated as the original free radical which is then capable of taking on more oxygen.

The inhibition of the photobromination of tetrachloroethylene by large quantities of oxygen and the fact that small accelerating quantities of oxygen are gradually used up in the photochemical reaction may be well explained by the assumption that a bromine-sensitized photo-oxidation takes precedence over the addition of bromine, just as the chlorine-sensitized photo-oxidation takes pre-

(10) Rice and Rice, "The Aliphatic Free Radicals," Johns Hopkins Press, Baltimore, Md., 1935, p. 173.

(11) Ziegler and Ewald, *Ann.*, **504**, 162 (1933).

cedence over the chlorination of tetrachloroethylene as shown by Dickinson and Leermakers.[5]

In a system containing bromine, tetrachloroethylene, dibromotetrachloroethane and oxygen the reactions indicated may occur according to the mechanisms already discussed.

All the reactions at the right are capable of continuing chains which can be stopped by the reaction

$$\mathrm{Br} + \mathrm{Br} + \text{third body} \longrightarrow \mathrm{Br_2}$$

The bromine-sensitized oxidation reaction may be represented by

$$\mathrm{Br}^* + \mathrm{O_2} \longrightarrow \mathrm{Br} + \mathrm{O_2}^*$$
$$\mathrm{O_2}^* + \mathrm{C_2Cl_4} \longrightarrow \text{oxidation products}$$

The asterisk which passes from the bromine atom (or molecule) to the oxygen is used to indicate the fact that the bromine has been made incapable of reacting with tetrachloroethylene while making the oxygen capable of doing so.

Other mechanisms may be developed for this reaction some of which involve the concept of transitory bromine oxide, or of a peroxide formed on the double bond. The one which has been presented seems, however, to be the most serviceable in accounting for the characteristics of both photobromination and bromine sensitized photochemical decomposition.

This hypothesis, that the life period of the free radical $\mathrm{C_2Cl_4Br}$ is the factor which determines the relative amount of decomposition and addition, suggests possibilities for explaining the facts of certain iodination and chlorination reactions.

The Photobromination of Chloroform

The photobromination of liquid chloroform was studied at room temperatures with light of wave length 2650 Å. from the large monochromator using reaction mixtures with concentrations of bromine sufficient to absorb 100% of the light. Bromine was introduced from weighed capillaries which could be sealed in the side-arm of a quartz reaction cell and broken by heating. The bromine consumed was determined by volumetric analysis after several hours of illumination; and quantum yields were calculated.

When it was desired to carry out experiments in the absence of oxygen the reaction cell was filled with chloroform; this was partially boiled away, and the cell was sealed while the boiling continued. In cases where this technique was used practically no bromination occurred during long periods of illumination. In other cases approximately known amounts of oxygen were obtained in the cell by first boiling the chloroform and then allowing a chloroform vapor and air or oxygen equilibrium to be attained in the cell at a temperature at which the vapor pressure of chloroform was known. The outlet from the cell to the air or to an oxygen tank led through a tube of phosphorus pentoxide.

When pressure of oxygen of about 30 mm. was present above the liquid reaction mixture in the cell, quantum yields of about 2 were obtained. When a pressure of 660 mm. of oxygen was present the yields dropped to negative values, indicating that halogen had been liberated by an oxidation of chloroform.

Tests to determine at what wave lengths the bromination would take place in the presence of air showed negative results at 3650 and 3130 Å. but bromine was used up at 2850 and 2650 Å.

Summary

1. It has been found that photobromination of tetrachloroethylene is inhibited by the product of the reaction, that the concentration of the tetrachloroethylene is not an important factor in the rate, and that the temperature effect is small.

2. Small amounts of oxygen accelerate the photobromination of tetrachloroethylene. When large amounts of oxygen are present, the rate of bromination approaches zero, probably on account of a competing bromine-sensitized photooxidation.

3. Mixtures of liquid chloroform and bromine do not react appreciably in the absence of oxygen when illuminated at 25° with light of 2650 Å. Reaction occurs in the presence of oxygen.

4. A mechanism postulating a bromo free radical is suggested to account for the characteristics of the photobromination of tetrachloroethylene and for the fact that the reaction is reversed at higher temperatures. It is assumed that the life period of this radical is dependent on temperature and that the radical is partially stabilized by oxygen.

5. An effective method for degassing liquid systems is described.

6. A magnetically-operated, sealed-in stirrer for use in photochemical work is described.

MADISON, WISCONSIN RECEIVED AUGUST 20, 1935