# The Effects of Oxygen and Peroxides on the Rate of Addition of Bromine to Cinnamic Acid in Carbon Tetrachloride.

By Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI.

(Received October 30th, 1937.)

**I. The Effect of Oxygen.** In the previous paper on the same subject⁽¹⁾ the authors showed the relation between the extent of addition of bromine to cinnamic acid in carbon tetrachloride and the amount of oxygen present. The extent of addition in vacuum, however, was rather too small (about 60%) in view of the observation of W. H. Bauer and F. Daniels⁽²⁾ that the addition was so rapid in absence of oxygen that the rate of reaction could not be measured conveniently. Then it was suspected that dissolved oxygen might not have been removed completely by the process of evacuation under cooling in liquid air. Hence, experiments were repeated by a procedure which differed from the previous method only in that a part of the solvent was evaporated in vacuum in order to remove dissolved oxygen.

Materials used in the experiments were prepared by treating commercial products as follows: Cinnamic acid was recrystallized from alcohol, melting point 133°. Bromine was refluxed with the addition of potassium bromide, distilled, shaken with concentrated sulphuric acid, and redistilled. Carbon tetrachloride was refluxed with an alkaline aqueous solution of potassium permanganate for two days, washed with water, dried over calcium chloride, distilled, and redistilled with the addition of phosphorus pentoxide on the day of use. Oxygen from the bomb was dried with calcium chloride and then with phosphorus pentoxide.

The experimental procedure was as follows: One millimol (0.1481 g.) of cinnamic acid was taken in a reaction tube of Pyrex glass with a capacity of 140 c.c., and dissolved in 40 c.c. of carbon tetrachloride. A sealed small glass bulb containing a slight excess of bromine was slipped into the tube. The tube was evacuated by a vacuum-pump at room temperature until 10 c.c. of carbon tetrachloride distilled over, 30 c.c. being left in the tube, then cooled in liquid air, evacuation being continued, and sealed off with or without admission of oxygen. The contents were melted and mixed well by shaking. The bromine bulb was broken usually

---

(1) This Bulletin, **12** (1937), 356.

(2) *J. Am. Chem. Soc.*, **56** (1934), 2014.

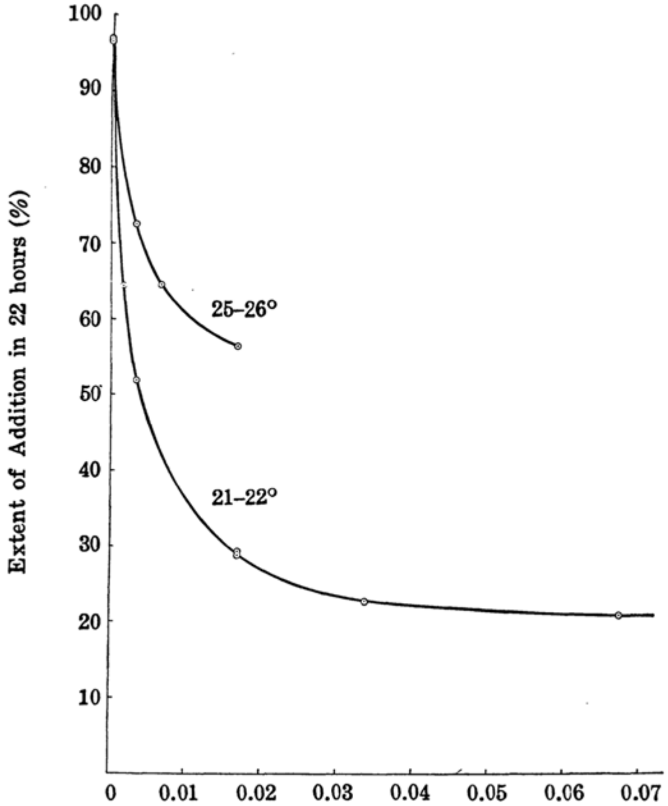
on freezing the contents of the reaction tube in liquid air, otherwise on shaking. The tube was placed in the dark at room temperature for 22 hours. An excess of aqueous potassium iodide was added to the reaction mixture, and the liberated iodine was titrated with N/10 sodium thiosulphate. The extent of addition in percentage to the cinnamic acid used was determined from the amount of bromine consumed. When the extent of addition was greater than 60%, the crystals of cinnamic acid dibromide (melting point 198°, corr.) appeared in the reaction mixture.

The temperatures recorded in all the tables given below are those at the beginning of the experiments. Additions of the same groups were carried out simultaneously, and thus under the same conditions. Only the experiments that belong to the same groups are strictly comparable.

Table 1.

| Group of exp. | No. of exp. | Temp. (°C.) | Bromine (g.) | Amount of oxygen | | Extent of addition (%) |
|---|---|---|---|---|---|---|
| | | | | Admitted (c.c., n.p.t.) | Dissolved in $CCl_4$ solution (millimol) | |
| I | 1 | 26 | 0.1820 | 0 | 0 | 96.9 |
| | 2 | 26 | 0.1798 | 1.0 | 0.0034 | 72.5 |
| II | 4 | 25 | 0.1851 | 2.0 | 0.0067 | 64.3 |
| | 5 | 25 | 0.1885 | 5.0 | 0.017 | 56.3 |
| III | 6 | 22 | 0.2089 | 0 | 0 | 96.6 |
| | 7 | 22 | 0.2002 | 0.5 | 0.0017 | 64.3 |
| | 8 | 22 | 0.1949 | 1.0 | 0.0034 | 51.8 |
| | 9 | 22 | 0.2081 | 5.0 | 0.017 | 28.6 |
| IV | 10 | 21 | 0.2080 | 5.0 | 0.017 | 29.0 |
| | 11 | 21 | 0.2075 | 10.0 | 0.034 | 22.0 |
| | 12 | 21 | 0.2010 | 20.0 | 0.067 | 18.7 |

The results of experiments are shown in Table 1. The amount of oxygen dissolved in the carbon tetrachloride solution was calculated on the same basis as described in the previous paper.(1) The relation between the amount of oxygen and the extent of addition is illustrated in the accompanying figure, the upper curve representing the experiments at 25–26° (Exp. 1, 2, 4, and 5) and the lower those at 21–22° (Exp. 6–12). The addition in vacuum proceeded so rapidly that the extent in 22 hours was nigh upon 100% both at 21–22° and at 25–26°, while in the presence of oxygen a difference of about 4° in the temperature caused a remarkable separation of the two curves.



Millimol of Oxygen in 30 c.c. $CCl_4$ Solution containing 1 millimol of Cinnamic Acid.

II. **The Effect of Peroxides.** Benzoyl peroxide was used. The commercial product was dried in vacuum over sulphuric acid. The purity was found 99.63% by iodometry in acetone solution.(3) Weighed amounts of benzoyl peroxide were dissolved together with cinnamic acid in carbon tetrachloride in the reaction tubes, the experimental procedure in all other respects being the same as described above.

In the iodometric determination of the extent of addition the added peroxide might liberate iodine, thus causing too small values of the extent. However, it was found that benzoyl peroxide liberates only a trace of

---

(3) H. Gelissen and P. H. Hermans, *Ber.*, **59** (1926), 68.

iodine under the conditions as described above: 0.05 g. of benzoyl peroxide was dissolved in 30 c.c. of carbon tetrachloride, and the solution was mixed with 30 c.c. of concentrated aqueous potassium iodide. The mixture, after placed in the dark during such a time (6–7 minutes) as required usually in the iodometric determination of the extent of reaction, was titrated with N/10 sodium thiosulphate. Only 0.05 c.c. was consumed, while 0.05 g. of the peroxide corresponds theoretically to about 4 c.c. of N/10 sodium thiosulphate. The amounts of the peroxide used in the additions ranged from about 0.1 to 0.01 g., and the volumes of N/10 sodium thiosulphate required to titrate the iodine liberated by bromine remaining after the reactions in the presence of the peroxide from 3.7 to 16 c.c. The correction value $-0.05$ c.c. for 0.05 g. of the peroxide was taken into account in all titrations in the presence of the peroxide under the assumption that the peroxide had not been decomposed during the reaction. Although the peroxide seems to be subject to a chemical change with bromine as indicated by the experiments described below, this assumption is valid so long as the peroxidic oxygen remains unchanged.

Benzoyl peroxide is not decomposed by cinnamic acid in carbon tetrachloride, or strictly speaking, the amount of peroxidic oxygen is not changed. Benzoyl peroxide (0.1084 and 0.0108 g. corresponding to 0.1132 and 0.0113 g. of iodine respectively) and cinnamic acid (0.1481 g. each) were dissolved in carbon tetrachloride (30 c.c. each), and the solution was sealed in vacuum in a tube in the same manner as in the experiments of addition. After 22 hours (in the dark at room temperature) the amount of the peroxide was determined by iodometry in acetone solution and found to be unchanged (0.1166 and 0.0117 g. of iodine respectively).

On the other hand, benzoyl peroxide seems to react with bromine in carbon tetrachloride. Just in the same manner as in the experiments of addition, benzoyl peroxide and bromine was dissolved in carbon tetrachloride in absence of air. After 22 hours' standing in the dark at room temperature, the solution was mixed with aqueous potassium iodide, bromine being replaced by iodine, and then, by adding acetone, the peroxide was converted into iodine. The total iodine thus liberated was determined and compared with the value calculated from the initial amounts of benzoyl peroxide (the purity 99.63% being taken into account) and bromine. In Table 2 the change is shown in terms of the corresponding amounts of bromine (designated as g.Br).

The values of decrease shown in Table 2 are less than, and roughly half, the amounts (expressed in g.Br) of benzoyl peroxide used. If this decrease had been caused by the decomposition of the peroxide, matters

Table 2.

| Benzoyl peroxide | | Bromine | Total | Found after reaction | Decrease |
|---|---|---|---|---|---|
| (g.) | (g.Br) | (g.) | (g.Br) | (g.Br) | (g.Br) |
| 0.1084 | 0.0714 | 0.2106 | 0.2820 | 0.2517 | 0.0303 |
| 0.1084 | 0.0714 | 0.1852 | 0.2566 | 0.2079 | 0.0487 |
| 0.2168 | 0.1427 | 0.1813 | 0.3240 | 0.2367 | 0.0873 |

would have been simpler, because the decrease in the amounts of the peroxide would have been no obstacle to qualitative consideration of the results of additions in the presence of the peroxide, and, even if oxygen should have been liberated by the decomposition, its retarding effect on the addition having been well explored, little difficulty would have been encountered in learning the effect of the peroxide from the results of experiments. However, it had to be assumed that a part of bromine was consumed by the peroxide, and that a substitution took place.(4) If so, while the amount of the peroxidic oxygen remains unchanged, bromine will be consumed both by cinnamic acid and by benzoyl peroxide in the reaction of bromine with cinnamic acid in the presence of the peroxide. What might complicate matters more seriously is the formation of hydrogen bromide by the substitution. On this account, it had to be determined what influence is exerted by hydrogen bromide on the addition of bromine to cinnamic acid.

Fortunately enough, it has been found that hydrogen bromide is indifferent to the addition reaction either in presence or in absence of oxygen: As shown in Table 3, in the presence of hydrogen bromide the addition proceeded as rapidly as in vacuum and cinnamic acid dibromide melting at 198° separated in quantity (Exp. 13), while hydrogen bromide exerted no accelerating effect on the reactions retarded by the addition of oxygen (Exp. 15–17).

Now the authors are ready for discussing the results of additions in the presence of benzoyl peroxide, which are summarized in Table 4. The apparent extent of addition corresponds to the total amount of bromine consumed. If the apparent extent is corrected under the assumption that the peroxide consumed half its number of molecules of bromine, the values given in the last column of Table 4 are obtained. However,

---

(4) Compare L. Vanino and E. Uhlfelder, *Ber.*, **33** (1900), 1046.

Table 3.

| Group of exp. | No. of exp. | Temp. (°C.) | Bromine (g.) | Oxygen admitted (c c., n.p.t.) | Hydrogen bromide admitted (c.c., n.p.t.) | Extent of addition (%) |
|---|---|---|---|---|---|---|
| V | 13 | 17 | 0.2043 | 0 | 2.4 | 96.9 |
| VI | 14 | 17 | 0.1910 | 5.0 | 0 | 14.7 |
| | 15 | 17 | 0.1943 | 5.0 | 2.0 | 19.3 |
| VII | 16 | 17 | 0.2144 | 5.0 | 2.0 | 11.6 |
| | 17 | 17 | 0.2167 | 5.0 | 1.0 | 15.2 |

Table 4.

| Group of exp. | No. of exp. | Temp. (°C.) | Bromine (g.) | Benzoyl peroxide | | Extent of addition | |
|---|---|---|---|---|---|---|---|
| | | | | (g.) | (millimol) | Apparent (%) | Corrected (%) |
| I | 1 | 26 | 0.1820 | 0 | 0 | 96.9 | 96.9 |
| | 3 | 26 | 0.1850 | 0.0108 | 0.045 | 96.7 | 94 |
| VIII | 19 | 25 | 0.1976 | 0.0217 | 0.090 | 95.2 | 91 |
| | 20 | 25 | 0.1923 | 0.0434 | 0.179 | 97.2 | 88 |
| | 21 | 25 | 0.1919 | 0.1084 | 0.448 | 99.2 | 77 |

they do not indicate any retarding effect of the peroxide, because the amount of bromine used was only slightly excessive to cinnamic acid alone, and nearly all of it was consumed. On the contrary, the fact that the more benzoyl peroxide was present the sooner the crystals of cinnamic acid dibromide (melting point 198°) appeared indicates qualitatively the accelerating effect of benzoyl peroxide, provided that the presence of the peroxide or the products from the reaction of the peroxide with bromine did not diminish the solubility of the dibromide.

The accelerating effect of benzoyl peroxide is definitely demonstrated by the additions in the presence of both oxygen and the peroxide. The results collected in Table 5 show the effect of the peroxide on the reactions retarded by admitting 5 c.c. of oxygen.

The apparent extent of addition was corrected on the basis of the same assumption as stated above (the last column of Table 5). It can

Table 5.

| Group of exp. | No. of exp. | Temp. (°C.) | Bromine (g.) | Benzoyl peroxide | | Oxygen | | Extent of addition | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | (g.) | (m.mol) | Admitted (c.c., n.p.t.) | Dissolved in $CCl_4$ sol. (m.mol) | Apparent (%) | Corrected (%) |
| VII | 18 | 17 | 0.2164 | 0.0217 | 0.090 | 5.0 | 0.017 | 56.9 | 52 |
| IX | 22 | 19 | 0.1990 | 0.0217 | 0.090 | 0 | 0 | 97.2 | 93 |
| | 23 | 19 | 0.1966 | 0 | 0 | 5.0 | 0.017 | 20.8 | 20.8 |
| | 24 | 19 | 0.1952 | 0.0217 | 0.090 | 5.0 | 0.017 | 77.5 | 73 |
| X | 25 | 20 | 0.2107 | 0 | 0 | 5.0 | 0.017 | 20.1 | 20.1 |
| | 26 | 20 | 0.2106 | 0.0108 | 0.045 | 5.0 | 0.017 | 49.9 | 48 |

be seen from the table that the presence of the peroxide compensated partly the retardation by oxygen. As it can be assumed that there should be no direct interference between the peroxide and oxygen, the effect of the former on the reactions retarded by the latter must be attributed to the inherent accelerating effect of the benzoyl peroxide on the addition of bromine to cinnamic acid.

Although it has been proved that hydrogen bromide is quite indifferent to the reaction, it does not necessarily exclude the possibility that it might be active in cooperation with a peroxide. But this seems improbable from the fact that hydrogen bromide is inactive in the addition of bromine to cinnamic acid even in the presence of oxygen while it is active in the isomerization of isostilbene into stilbene in the presence of either benzoyl peroxide or oxygen.(5)

Some contradictions may be found between the results recorded in the present paper and those published by P. W. Robertson and coworkers.(6) But, no mention being made of air and light there, no comparison can be justified. In this connection, however, it may be emphasized that the addition of bromine to cinnamic acid in carbon tetrachloride under the conditions of the experiments carried out by the present authors is homogeneous(1) and the addition product was always cinnamic acid dibromide melting at 198°.

---

(5) See the following paper, this volume, p. 507.

(6) P. W. Robertson, N. T. Clare, K. J. McNaught, and G. W. Paul, *J. Chem. Soc.*, **1937**, 335.

**Addendum: The Addition in the Presence of Reduced Iron.** The perfect resistance of iron and nickel against hydrogen bromide was essential to the success in the experiments on the addition of hydrogen bromide to allyl bromide in the presence of these metals. If they were resistant also to bromine in carbon tetrachloride, interesting results might be expected from the experiments on the addition of bromine to cinnamic acid in the presence of these metals. However, it has been found that these metals are subject to serious attack by bromine in carbon tetrachloride, and in an addition in the presence of reduced iron the consumption of bromine was more than 100% in reference to cinnamic acid.

## Summary.

(1) The relation between the extent of addition of bromine to cinnamic acid in carbon tetrachloride and the amount of oxygen present has been shown.

(2) It has been indicated that hydrogen bromide is indifferent to the reaction of bromine with cinnamic acid in carbon tetrachloride either in presence or in absence of oxygen.

(3) The accelerating effect of benzoyl peroxide on the addition of bromine to cinnamic acid in carbon tetrachloride has been demonstrated.

(4) In all cases, namely in vacuum and in the presence of any of oxygen, benzoyl peroxide, and hydrogen bromide, the products separating out in crystals were cinnamic acid dibromide melting at 198°.

(5) All the results mentioned above were obtained from the additions in the dark at room temperature.

The authors express their sincere thanks to the Nippon Gakujutsu Shinko-kwai (the Japan Society for the Promotion of Scientific Research) for a grant.

*Chemical Institute, Faculty of Science,*
*Imperial University of Tokyo.*