The Effect of Oxygen on the Addition of Bromine to Cinnamic Acid in Carbon Tetrachloride.

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The inhibiting effect of oxygen on the addition of bromine to cinnamic acid in carbon tetrachloride was first observed by W. H. Bauer and F. Daniels.(1) They found that bromine and cinnamic acid combine rapidly in the dark at room temperature when dissolved oxygen has been removed from the solution, and when the oxygen has not been removed, the reaction is very slow in the dark, but it proceeds rapidly in the light.

The present paper records the results of somewhat quantitative experiments on the effect of oxygen on the addition of bromine to cinnamic acid in carbon tetrachloride. Special care was taken in purifying the materials, viz. cinnamic acid, bromine, and carbon tetrachloride, and in excluding moisture. A solution of 1 millimol (0.1480 g.) of cinnamic acid in 30 c.c. of carbon tetrachloride was placed in a reaction tube of Pyrex glass with a capacity of 140 c.c. A sealed small glass bulb containing a slight excess of bromine was slipped into the tube. The tube was cooled in liquid air, evacuated, and sealed off with or without admission of oxygen. The contents were melted and mixed well by shaking. The breaking of the bromine bulb usually took place on freezing the contents of the reaction tube in liquid air, otherwise effected by shaking. The tube was then 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. The results are summarized in Table 1.

Each one group of experiments were carried out simultaneously, and thus under the same conditions. According to the measurements of the solubility of oxygen in carbon tetrachloride by J. Horiuti(2) the ratio of the concentration of oxygen dissolved in carbon tetrachloride to that in the gaseous phase is 0.3 at ordinary temperature. The partial pressure of oxygen in the tube at respective temperature, and the amount of oxygen

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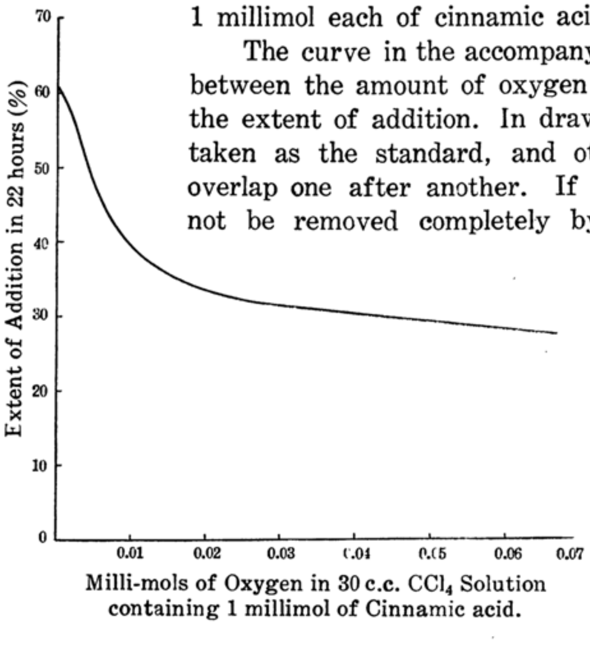
(1) *J. Am. Chem. Soc.*, **56** (1934). 2014.

(2) *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **17** (1931), 213.

Table 1.

Group of exp.	No. of exp.	Bromine (g.)	Oxygen						Extent of addition (%)
			Vol. (c.c.)	Temp. (°C.)	Pres. (mm.)	Vol. n.p.t. (c.c.)	Partial pressure in the tube (mm.)	Amount dissolved in CCl_4 solution (millimol)	
I	1	0.1758	0			0	0	0	60.6
	2	0.1778	0.5	22	757.8	0.46	3.2	0.0016	57.8
	3	0.1800	1.0	22	757.8	0.92	6.4	0.0031	53.4
	4	0.1849	2.0	22	757.8	1.85	13	0.0062	44.9
II	5	0.1854	0			0	0	0	56.6
	6	0.2011	2.0	21	757.0	1.85	13	0.0062	40.7
	7	0.2004	5.0	21	757.0	4.63	32	0.016	31.2
III	8	0.2170	5.0	21	756.7	4.62	32	0.016	32.4
	9	0.2151	10.0	21	756.7	9.25	64	0.031	28.5
IV	10	0.2035	10.0	20	757.3	9.28	64	0.031	33.1
	11	0.2033	20.0	20	757.3	18.57	127	0.063	29.4

dissolved in the carbon tetrachloride solution were calculated on the assumption that this ratio holds in the carbon tetrachloride solution containing 1 millimol each of cinnamic acid and bromine in 30 c.c.



Milli-mols of Oxygen in 30 c.c. CCl_4 Solution containing 1 millimol of Cinnamic acid.

The curve in the accompanying figure shows the relation between the amount of oxygen present in the solution and the extent of addition. In drawing this curve Group I was taken as the standard, and others were shifted so as to overlap one after another. If the dissolved oxygen could not be removed completely by the process of evacuation under cooling in liquid air, as it seems possible from the observation of Bauer and Daniels that the addition was so rapid in absence of oxygen that the rate of reaction could not be measured conveniently, the ordinate must be displaced as much to the left.

In Table 2 addition in vacuum with 1 millimol of cinnamic acid in 30 c.c. of carbon tetrachloride (exp. 12 and 14) is compared with that on a half scale but in a tube of the same dimensions (exp. 13 and 15). There is no significant difference in the extent of addition. The last group of experiments recorded in Table 3 shows that the shaking of the tube during the reaction had practically no influence on the extent of addition. (The greater values of the extent of addition for the last group of experiments were probably caused by the higher room temperature.) These results seem to indicate that the addition of bromine to cinnamic acid in carbon tetrachloride under the conditions as described above is a homogeneous reaction.

Table 2. (Reaction time, 22 hours.)

Group of exp.	No. of exp.	Cinnamic acid (millimol)	CCl_4 (c.c.)	Bromine (g.)	Extent of addition (%)
V	12	1	30	0.1924	61.8
	13	0.5	15	0.0807	56.7
VI	14	1	30	0.1912	62.1
	15	0.5	15	0.0790	65.5

Table 3. (Cinnamic acid, 1 millimol; CCl_4, 30 c.c.; Reaction time, 22 hours.)

Group of exp.	No. of exp.	Bromine	Extent of addition (%)	Remarks
VII	16	0.1779	75.72	The tube was shaken during the reaction.
	17	0.1768	75.28	The tube was not shaken

No detectable peroxide was formed from cinnamic acid and oxygen in carbon tetrachloride even in bright diffused light. This fact makes it very probable that the effect of oxygen on the addition of bromine to cinnamic acid in carbon tetrachloride is caused by the action of molecular oxygen.

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