BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 654—664 (1966)

Single Stage Oxidation of *p*-Xylene with Ozonized Air

By Tsuguo TAKAYA, Tadashi KOGA and Tadashi HARA

Department of Chemical Engineering, Faculty of Engineering, Doshisha University, Kamikyo-ku, Kyoto

(Received May 22, 1965)

A new method has been found by which terephthalic acid can easily be obtained by a single-stage oxidation of *p*-xylene in glacial acetic acid. *p*-Xylene was oxidized with ozonized oxygen or air at 90°C in the presence of cobaltous acetate, ammonium bromide and an unsaturated aliphatic compound such as tetrachloroethylene. The effects of various factors on the oxidation rate were examined by measuring the absorption rates of oxygen. The reaction rates were measured for two steps, i. e., *p*-xylene to *p*-toluic acid and *p*-toluic acid to terephthalic acid, in the presence and absence of ozone respectively. The reaction mechanisms for each step have been discussed. It seems that the role of ozone and tetrachloroethylene in the present oxidation reaction can be attributed to the formation of ozonide which is transformed to hydroperoxide and which then participates in the chain reaction.

Many attempts have been made to obtain terephthalic acid by the oxidation of *p*-xylene with nitric acid,1) air,2) or oxygen gas,3) sulfur in ammonium hydroxide4) or ammonium sulfide,5) and their combinations,6) etc. Most of these attempts have been carried out under drastic reaction temperature and pressure conditions. The method developed by Brill3) gives terephthalic acid in a good yield by the single-stage oxidation of *p*-xylene under the following conditions: oxidizing agent: oxygen gas; pressure: 1 atm.; solvent: glacial acetic acid; temperature: 90°C; catalysts: cobaltous acetate tetrahydrate; activator: a ketone containing an α-methylene group; and reaction time: 24 hr. However, the reaction does not proceed with air instead of oxygen. The present experiment was, therefore, carried out with the objectives of finding a catalyst with which the oxidation reaction of *p*-xylene is allowed to proceed under conditions milder than those in the conventional method, and of clarifying the reaction mechanism.

As a result of experiments, a new method was developed, and crude terephthalic acid was obtained in an about 95% yield under the following conditions: temperature: 90°C; pressure: 1 atm.; reaction time: 6 hr.; catalysts: cobaltous acetate, ammonium bromide, and a small amount of unsaturated aliphatic compound; oxidant: ozonized oxygen or air; and solvent: glacial acetic acid.

Though the ozone8) has been reported to be effective as an initiator for the liquid-phase oxidation of *p*-xylene, no method has been reported in detail. According to the present procedure, the methyl groups bonded directly to the benzene ring are easily oxidized to the carboxyl groups, and crude terephthalic acid is obtained in a 83—85% yield by the single-stage oxidation of *p*-xylene using air which contains about 0.5% ozone. Unsaturated aliphatic compounds are effective as the promotor; upon their use the yield of terephthalic acid increases more than 10%.

Though the rate equation in the oxidation stage from *p*-toluic acid to terephthalic acid has been given by Ravens,7) no rate equation has been reported with the *p*-xylene → *p*-toluic acid, and *p*-xylene → *p*-toluic acid and *p*-toluic acid → tetrephhalic acid oxidations using ozonized oxygen. Therefore, the rate equation was studied by measuring the absorption rate of oxygen gas, and the reaction mechanism was considered.

Experimental

Reagents.—*p*-Xylene (98.5% purity) presented by the Maruzen-Sekiyu Co., Ltd., was treated with sulfuric acid, sodium hydroxide, and water in that order,

---

1) U. S. Pat. 2636899 (1953).
2) U. S. Pat. 2833816 (1958).
3) W. F. Brill, *Ind. Eng. Chem.*, **52**, 837 (1960).
4) U. S. Pat. 2762839 (1956).
5) W. A. Pryor, *J. Am. Chem. Soc.*, **80**, 6481 (1958).
6) For example, U. S. Pat. 2653165 (1954).
7) D. A. S. Ravens, *Trans. Faraday Soc.*, **55**, 1768 (1959).

dehydrated, and distilled; the distillate was then purified by fractional crystallization. Acetic acid containing 0.38 wt.% water was used. The cobaltous acetate and ammonium bromide were of the reagent grade. The tetrachloroethylene was treated with sulfuric acid, sodium hydroxide, and water in that order, and distilled. The other reagents were used after purification.

Apparatus.—A Siemens-type ozonizer was built up with Pyrex glass, and about 10 kV. of voltage was applied to it through a transformer. The ozonized air was washed with a 10% sodium hydroxide solution in order to remove the oxides of nitrogen, dehydrated with concentrated sulfuric acid and calcium chloride (anhydride), and introduced into a reaction vessel. A 500 ml. reaction vessel attached with four holes to a thermometer, a stirrer, a condenser, and a gas-inlet was used. The reaction vessel was heated by a mantled heater. The oxidants were introduced into the reaction vessel through the ozonizer from an oxygen bomb or after the compressed air had been dehydrated with concentrated sulfuric acid and silica gel. The reaction rate was measured by the apparatus shown in Fig. 1. F is thermostatted at 90°C in an oil-bath, and A, B, and C at 25°C. *p*-Xylene is made to react with oxygen in the cell, F, and the solution is stirred by a magnetic stirrer. The manostat, B, operates by the absorption of oxygen gas, and then the electrolyzer, D, operates until the oxygen pressure in the system becomes equal to the original. The gas evolved by D is sent to the left-hand side of the gas-burette, A, and the meniscus of the right-hand side is raised. The amount of oxygen gas absorbed is read on the right-hand side of A. To operate this apparatus, all the cocks except the cocks 3, 7, 8, and 12 are opened, and the system is evacuated. Then the cocks 1 and 4 are closed in that order, and more than 1 atm. of oxygen gas is introduced into the balloon through the cock 3. The cock 4 is opened, and the system is filled with oxygen gas. The cocks 4 and 2 are closed in that order, and the cock 1 is opened. The cock 7 is gradually opened. For a measurement, the cock 8 is opened, and the cocks 5, 6, 7, 9, 10, and 11 are closed, followed by the opening of the cock 12. When the meniscus of A on the right-hand side has risen up to the top, the cocks 6, 9, and 11 are opened after the closure of the cock 12 and the opening of the cocks 10 and 7, and the measurement is continued as before. F is dipped into the oil-bath when the cock 15 is opened, and the cock is closed just before the measurement. Since the vapor pressure of acetic acid at 90°C is 300 mmHg, the vapor pressure of air at the same temperature is given by $760-300=460$ mmHg. By assuming the composition of the air to be $O_2:N_2=1:4$, the partial pressure of oxygen gas at 90°C is found to be approximately 92 mmHg through all the experiments.

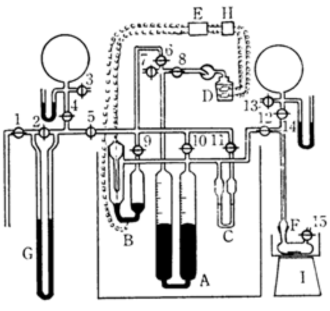


Fig. 1. An apparatus for the measurement of oxidation rate.
A: Gas burette B: Manostat
C: Manometer (charged with dibutyl phthalate)
D: Electrolyzer E: Relay
F: Reaction cell
G: Manometer (charged with mercury)
H: Stabileizr I: Magnetic stirrer

The Analysis of the Oxidation Products.—After the reaction had finished, the products were filtered, washed with glacial acetic acid and water, dried, and weighed, and the yields of crude terephthalic acid were calculated. When an aliquot amount of crude terephthalic acid was esterified with methanol and sulfuric acid, the ester showed a m. p. of 140.2—140.9°C. The aldehyde content was determined by dissolving a sample in an excess silver nitrate/ammonium hydroxide solution, by filtering the deposits off, and by estimating the remaining silver by the Volhard method. The carboxyl group content was also determined conductometrically by dissolving an aliquot amount of the sample in ammonium hydroxide and by titrating it with a standard lithium hydroxide solution. According to this procedure, each acid is determined graphically, since the mixture consisting of mono- and di-basic acids gives two inflection points on the titration curve.

The Determination of the Ozone.—The apparatus shown in Fig. 2 was devised. In Fig. 2, I is the inlet for the sample gas, and II, the outlet. In order to determine the ozone content, the gas sample is passed through the flask, III, and then the cock, IV, and the flask are turned to take a definite volume of the sample. The vessel, V, is filled with an excess potassium iodide solution, and most of the solution is dropped into III by compressed air, after which IV is closed. Then the apparatus is shaken for a minute, and the flask is taken off. The inside of the upper part is washed down with water, and the combined solution is titrated with a standard sodium thiosulfate solution. The results obtained by this procedure agreed with those obtained by the conventional method; the ozone contents in the ozonized oxygen gas and air used in this experiments were approximately 1.0 and 0.5 vol.% respectively.

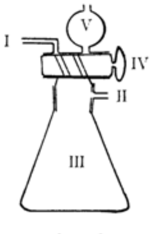


Fig. 2. An apparatus for determination of ozone in ozonized gases.
I: Gas inlet IV: Cock
II: Gas outlet V: KI tank
III: Flask

The Measurement of the Reaction Rate and Order.—The sample is put in the reaction cell, and the cell is heated at 90°C for 5 min. After exactly 5 min., or after 10 minutes' passage of the ozonized oxygen containing approximately 0.8 vol.% ozone, the measurement is started, and the oxygen amount absorbed is read at definte intervals. The reaction rate was expressed as the mean value obtained by dividing the total oxygen amount absorbed by the reaction time.

In order to determine the reaction order of a certain component, the oxygen amount absorbed was measured under conditions in which the concentration of the component was varied, and the reaction rate was plotted against the concentration of the component. The reaction order of the component was found from the slope of a straight line on the graph.

Results and Discussion

The Oxidation of *p*-Xylene with Ozonized Oxygen.—In order to examine the effect of ozone on the oxidation of *p*-xylene, the reaction was carried out under the following conditions: acetic acid: 200 ml.; *p*-xylene: 25.0 ml.; cobaltous acetate tetrahydrate: 4.982 g.; ammonium bromide: 0.1 g.; tetrachloroethylene: 1.0 ml.; reaction temp.: 90°C; ozone content: 1.0 vol.%; gas flow rate: 140 l./hr.; and reaction time: 6 hr. The results obtained are shown in Table I.

TABLE I. THE EFFECT OF OZONE ON THE YIELDS OF TEREPHTHALIC ACID

No.	Yield %	No.	Yield %
1	77.1	4	82.4
2	68.7	5	93.5
3	72.1	6	95.6

No. 1: Ozonized oxygen until the deposit of terephthalic acid, and then oxygen alone
No. 2: Oxygen alone until the deposit of terephthalic acid, and then ozonized oxygen
No. 3: Oxygen alone
No. 4: Ozonized oxygen for 2 hr., and then oxygen for 4 hr.
No. 5: Ozonized oxygen for 3 hr., and then oxygen for 3 hr.
No. 6: Ozonized oxygen for 6 hr.

It has been reported that ozone is effective as an initiator,[8] but it is not always necessary after the solution has become dark green. However, it may be seen from Table I that ozone is effective not only as an initiator but also as an activator during the reaction. In order to examine the effect of aliphatic unsaturated compounds on the yields of terephthalic acid, the oxidation was carried out under the same conditions as before except in the presence of various unsaturated compounds. The results obtained are shown in Table II. As can be seen from Table II, the yields increase in the presence of aliphatic unsaturated compounds. This seems to be because of the interaction between the ozone and the double bond.

TABLE II. THE EFFECT OF ALIPHATIC UNSATURATED COMPOUNDS ON THE YIELDS

Compound	Added	NH_4Br g.	Yield %
Maleic anhydride	7.845 g.	0.1	94.5
Allyl bromide	4.6 ml.	—	84.6
Tetrachloroethylene	1.0 ml.	0.1	95.0
Hexachloro-1,3-butadiene	10.43 g.	0.1	92.5
None	—	0.1	75.0

It has been also reported[9] that *p*-xylene could be oxidized into terephthalic acid under these conditions: catalysts: Co^{2+}, Mn^{2+}, Cl^-, and Br^-; solvent: propionic acid; reaction temp.: 137°C; and reaction time: 5.1 hr. It may, however, be supposed from Table II and the data that the double bond may affect the yields of terephthalic acid more than chloride ions. The product is white in the presence of chloride ions, while yellow in their absence. Therefore, tetrachloroethylene was used as the aliphatic unsaturated compound in the experiments below. The experiments were also designed to examine the effects of cobaltous acetate, bromide, and tetrachloroethylene on the yields of terephthalic acid; the results obtained are shown in Tables III and IV.

Judging from the results shown in Tables III and IV, the following conditions are recommended for the oxidation of *p*-xylene: acetic acid: 200 ml.; *p*-xylene: 25.0 ml.; cobaltous acetate tetrahydrate: 4.982 g.; ammonium bromide: 0.1 g.; tetrachloroethylene: 1.0 ml.

Cobaltous acetate and ammonium bromide had the main effects on the yields. In the case of the oxidation with ozonized oxygen, no interaction was found among cobaltous acetate, ammonium bromide, and tetrachloroethylene, while the reverse was true in the case of the oxidation with oxygen alone. It may, therefore, be supposed that cobalt, bromide, and tetrachloroethylene may be separately activated with ozone to take part in the oxidation reaction. The relationships between the reaction time, or the reaction temperature, or the water content, and the yields were also examined by carrying out the oxidation under the optimum conditions mentioned above; the yields were 35.2, 64.9, 89.6, 94.7 95.6, 96.8, and 97.3% for 2, 3, 4, 5, 6, 8, and 10 hours' reactions respectively; 0, 56.3, 63.3, 69.2, 96.1, and 83.5% at 50, 60, 70, 80, 90, and 100°C respectively; and 92.4, 89.8, 90.1, 90.6, 87.0, 81.2, 78.2, and 22.9% in 0, 1.0, 2.0, 3.0, 4.0, 10.0, 15.0, and 20.0 ml. of waters respectively.

The oxidation products were analyzed by the above mentioned procedures; the results are

---

[8] Brit. Pat. 798619 (1958); A. S. Hay and J. W. Eustance, *J. Org. Chem.*, **25**, 616 (1960).

[9] Japanese Pat. 5472 (1960).

TABLE III. THE EFFECTS OF CATALYSTS ON THE YIELDS OF TEREPHTHALIC ACID

No.	$Co(OAc)_2 4H_2O$ g.	NH_4Br g.	Tetrachloro-ethylene g.	Recovery, % Series I	Recovery, % Series II
1	4.982	0.1	1.0	96.1	88.0
2	4.982	0.5	3.0	92.1	93.5
3	4.982	0.5	1.0	96.5	90.5
4	4.982	0.1	2.0	83.3	86.2
5	2.491	0.1	2.0	76.6	78.3
6	4.982	0.1	3.0	89.9	83.4
7	2.491	0.5	3.0	77.5	86.5
8	2.491	0.5	1.0	84.2	88.9
9	2.491	0.5	2.0	89.9	79.8
10	2.491	0.1	1.0	80.3	74.3
11	4.982	0.5	2.0	92.3	89.8
12	2.491	0.1	3.0	75.0	77.5

TABLE IV. ANALYSIS OF VARIANCE

SS: variation, ϕ: degree of freedom,
V: unbiased variation

Factor	SS	ϕ	V	F_0	F 0.01	F 0.05
A	522	1	522	30	9.33	4.75
B	241	1	241	13.9	9.33	4.75
C	42	2	21	1.2	6.93	3.89
A × B	11	1	11	—		
A × C	26	2	13	—		
B × C	1	2	0.5	—		
A × B × C	18	2	9	—		
E (error)	209	12	17.4			
Total	1070	23				

A: Cobaltous acetate, B: Ammonium bromide, C: Tetrachloroethylene

TABLE V. ANALYSIS OF THE OXIDATION PRODUCTS

Sample No.	Terephthalic acid, %	*p*-Toluic acid, %	*p*-Formylbenzoic acid, %
1	85.0	4.6	9.3
2	88.6	2.9	8.6
3	87.2	5.8	6.8

TABLE VI. THE EFFECTS OF AMMONIUM BROMIDE ON THE YIELDS

(Reaction temp.: 90°C)

NH_4Br added, g. First	NH_4Br added, g. Second	Yield %	Product
0.1960	0.1960	67.5	White*
0.0490	0.0490	70.5	White
0.0980	0.0980	82.4	White
0.0980	0.1960	83.9	White
0.0980	0.2940	84.3	White
0.0980	0.4900	83.2	Slightly yellow

* Reaction temp.: 80°C

shown in Table V. *p*-Toluic acid and *p*-formylbenzoic acid were found as the impurities. *p*-Formylbenzoic acid was easily oxidized into terephthalic acid with Tollen's reagent, and terephthalic acid was recovered with a purity of ca. 99%. Since the contamination with *p*-formylbenzoic acid as an impurity is a serious obstacle to obtaining highly-pure terephthalic acid, an effort is being made to prepare the terephthalic acid free from *p*-formylbenzoic acid.

The present method was further applied to the oxidation of alkylbenzenes; the yields of benzoic acid from toluene, isophthalic acid from *m*-xylene, and phthalic acid from *o*-xylene in 6 hours' reaction were 97.4, 93.3, and 48.8% respectively. However, the yield of phthalic acid increased to 95.2% in 10 hours' oxidation.

The oxidation rate of *o*-xylene is smaller than those of *m*- and *p*-xylene; this shows a close relation with the average reaction rate,[10] $o < m \fallingdotseq p$, in the xylene isomers. It has been reported that the smaller reaction rate of *o*-xylene seems to be based on the chelation between cobaltous ions and phthalic acid, and on the fact that the acidity[10] of phthalic acid is stronger than that of the others.

The Oxidation of *p*-Xylene with Ozonized Air.—The oxidation procedure with ozonized air differs from that with ozonized oxygen in the following points; 1) Ozonized air is blown into the solution; 2) The ozone content is

---

[10] N. Ohta, E. Takahashi and H. Kinase, *Yuki Gosei Kagaku*, **21**, 536 (1963).

TABLE VII. ORIGINAL DATA FOR THE ANALYSIS OF VARIANCE

HOAc: 25.0 ml., *p*-xylene: 1.0 ml., reaction time: 100 min.

Exp. No.	$Co(OAc)_2 4H_2O$ g.	NH_4Br g.	$Cl_2C{=}CCl_2$ ml.	O_2 absorbed, cc.	
				1st	2nd
1	0.20	0.01	0	49.70	47.40
2	0.20	0.02	0.20	9.90	6.60
3	0.20	0.02	0	30.80	30.20
4	0.20	0.01	0.10	23.90	30.20
5	0.10	0.01	0.10	27.20	31.60
6	0.20	0.01	0.20	37.90	39.00
7	0.10	0.02	0.20	50.80	54.00
8	0.10	0.02	0	46.10	52.40
9	0.10	0.02	0.10	40.40	43.30
10	0.10	0.01	0	39.50	37.40
11	0.20	0.02	0.10	16.80	18.30
12	0.10	0.01	0.10	29.20	30.80

TABLE VIII. ANALYSIS OF VARIANCE

Factor	SS	ϕ	V	F_0	F		
					0.01	0.05	0.10
K	828	1	828	135.7	9.33	4.75	3.13
L	26	1	26	4.3	9.33	4.75	3.13
M	694	2	347	56.9	6.93	3.89	2.81
K×L	1752	1	1752	287.1	9.33	4.75	3.13
K×M	190	2	95	15.6	6.93	3.89	2.81
L×M	34	2	17	2.8	6.93	3.89	2.81
K×L×M	263	2	132	21.6	6.93	3.89	2.81
E (error)	74	12	6.1				
Total	3861	23					

K: Cobaltous acetate, L: Ammonium bromide, M: Tetrachloroethylene

about 0.5%; 3) The flow rate is about 300 l. per hour; 4) Two portions of ammonium bromides are added, one at the beginning of the reaction and the other at just one-half the time from the deposit of terephthalic acid to the end, and 5) Chloroacetic acid is added as a co-catalyst.

The effects of ammonium bromide on the yields are shown in Table VI.

It was found that the yields in the presence of tetrachloroethylene increase by 10—13%. The yields were 70.9, 74.5, 75.6, 81.3, 81.1, 79.0, and 57.1%, respectively in the presence of each 0.1, 0.2, 0.3, 0.5, 0.8, 0.9, and 0 g. of chloroacetic acids. Since terephthalic acid was obtained in a high yield in the case of ozonized oxygen, the effects of chloroacetic acid could not be discriminated from its yield. Chloroacetic acid has been reported[11] to be effective for the oxidation of *p*-xylene; this coincides well with the present results. In the coming experiments, chloroacetic acid is always added in 0.5 g. portions until otherwise stated.

The yields were 58.9, 69.3, 81.3, 70.0, 67.9, and 63.6%, respectively, with each 2.491, 4.982, 7.473, 9.964, 12.455, and 14.946 g. of cobaltous acetate tetrahydrate. As may be seen from these results, up to a definite concentration Co^{2+} behaves positively, while it behaves negatively with a greater concentration. Since it has been established that the metal ions showing reversibly changeable valencies often behave as inhibitors in the radical chain reaction,[12,13] the negative behavior of cobaltous ions seems to be based on a similar mechanism.

The yields were 84.3, 87.6, 87.8, and 90.3%, respectively, in 6, 7, 8, and 10 hours' reactions. Since some *p*-xylene was lost, together with some air, it was difficult to raise the yields higher, even by making the reactions last more than 10 hr. When the oxidation products were analyzed, they were found to be composed of 76.9—79.6% terephthalic acid, 10.5—11.97% *p*-toluic acid, and 10—14.8% *p*-formylbenzoic acid. It was also noted that the contents of *p*-toluic acid and *p*-formylbenzoic acid are larger than those in the ozonized oxygen.

The Reaction Rate from *p*-Xylene to *p*-Toluic Acid.—At first, the reaction rate was measured under an oxygen pressure of 92 mmHg without allowing the solution to come in contact

---

[11] N. Ohta, K. Sunaoka and N. Nitanai, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **63**, 768 (1960).

[12] N. Ohta and S. Maruge, ibid., **58**, 798 (1955).

[13] K. Kagami, *Yuki Gosei Kagaku*, **20**, 284 (1962).

with the ozone. The amounts of the oxygen absorbed were measured on the basis of the design of the experiments in which cobaltous acetate, ammonium bromide, and tetrachloroethylene are looked upon as factors; duplicate experiments are planned at the level of $2\times2\times3$. Tables VII and VIII show the original data and the analysis of the variance respectively.

When the significant level is adopted as 10% by taking the reproducibility and the error in measurement into account, the effects are found in all the factors. However, the main effect of cobalt, and the interaction between cobaltous ions and bromide, are predominant among them. The reaction shows an independence of the concentration of *p*-xylene. The reaction also shows a first-order dependence on the concentration of cobaltous acetate at $[\mathrm{Co}^{2+}]\leqq0.024$ mol./l.; thereafter the rate decreases with an increase in $[\mathrm{Co}^{2+}]$. The reaction shows a one-fourth-order dependence on the concentration of ammonium bromide at $\mathrm{NH_4Br}\leqq10.0$ mg., and a negative one-half-order dependence on the concentration of tetrachloroethylene. The negative effect of tetrachloroethylene in the absence of ozone seems to be based on the facts that tetrachloroethylene can be only activated with difficulty and that it consumes the radical in the radical chain reaction. Because 1) the reaction mixture does not become dark green at all, just as in the presence of a considerable amount of bromide, and 2) the interactions among cobalt, bromide, and tetrachloroethylene are found in the design of experiments, it may be supposed that tetrachloroethylene not only consumes the radical but also accelerates the reaction from cobaltic to cobaltous ions in accordance with the following mechanism:

$$\mathrm{Co}^{3+} + \mathrm{HBr} \rightleftharpoons \mathrm{Co}^{2+} + \mathrm{Br}\cdot + \mathrm{H}^{+}$$

$$\mathrm{Cl_2C{=}CCl_2} + \mathrm{Br}\cdot \cdots\rightarrow \text{inactives}$$

The reaction shows a first-order dependence on the concentration of chloroacetic acid at $[\mathrm{ClCH_2COOH}]\leqq0.13$ mol./l.

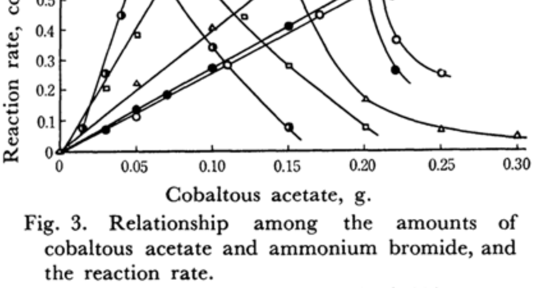


Fig. 3. Relationship among the amounts of cobaltous acetate and ammonium bromide, and the reaction rate.

I: $\mathrm{NH_4Br}$ 0.005 g. IV: $\mathrm{NH_4Br}$ 0.030 g.
II: $\mathrm{NH_4Br}$ 0.010 g. V: $\mathrm{NH_4Br}$ 0.040 g.
III: $\mathrm{NH_4Br}$ 0.020 g.

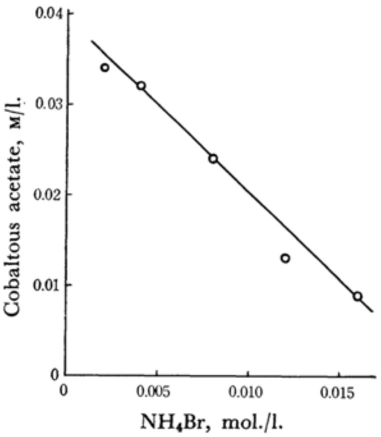


Fig. 4. Relationship between the amounts of cobaltous acetate and ammonium bromide at the maximum reaction rates.

The relationship among the reaction rate and the concentrations of cobaltous acetate and ammonium bromide is given in Fig. 3. The relationship between the concentrations of cobaltous acetate and ammonium bromide at the maximum absorption rate is further shown in Fig. 4, where it is given by a straight line. On the basis of Fig. 4, the relationship is expressed as follows:

$$[\mathrm{Co}^{2+}] + 2[\mathrm{NH_4Br}] \leqq 0.04 \text{ mol./l.}$$

By combining the above results, the reaction rate at $[\mathrm{Co}^{2+}] + 2[\mathrm{NH_4Br}] \leqq 0.04$ mol./l. and $[\mathrm{ClCH_2COOH}]\leqq0.13$ mol./l. is expressed by the following equation:

$$R_1 = k_1[\mathrm{Co}^{2+}][\mathrm{NH_4Br}]^{1/4}\cdot [\mathrm{ClCH_2COOH}][\mathrm{Cl_2C{=}CCl_2}]^{-1/2}$$

With the objective of examining the effect of ozone on the initial reaction, the absorption rate of oxygen after 10 minutes' passage of ozonized oxygen was measured. Though the reaction rates in the above experiments were measured under an oxygen pressure of 92 mmHg, those after the passage of the ozonized oxygen were measured under an oxygen pressure of 460 mmHg. The reaction shows one-half-order, three-second-order, one-half-order at $[\mathrm{NH_4Br}]/[\mathrm{Co}^{2+}]\leqq5/4$ or first-order at $[\mathrm{NH_4Br}]/[\mathrm{Co}^{2+}] > 5/4$, zero-order, and zero-order dependences on the concentrations of *p*-xylene, cobaltous acetate, ammonium bromide, tetrachloroethylene, and chloroacetic acid, respectively.

It may be noted that tetrachloroethylene has a negative effect on the progress of the reaction in the absence of ozonized oxygen, while the reaction rate after 10 minutes' passage of ozonized oxygen is independent of the concentration of tetrachloroethylene. Therefore, ozone may be expected to exert a positive effect on the reaction when it is passed through during the experiment.

This is consistent with an increase of the yield of terephthalic acid in the presence of ozone.

To summarize the above results, the initial rates after 10 minutes' passage of ozonized oxygen are as follows:

$$R_2 = k_{\text{II}}[p\text{-xylene}]^{1/2}[\text{Co}^{2+}]^{3/2}[\text{NH}_4\text{Br}]^{1/2} \quad \text{at } [\text{NH}_4\text{Br}]/[\text{Co}^{2+}] \leqq 5/4$$

$$R_3 = k_{\text{III}}[p\text{-xylene}]^{1/2}[\text{Co}^{2+}]^{3/2}[\text{NH}_4\text{Br}] \quad \text{at } [\text{NH}_4\text{Br}]/[\text{Co}^{2+}] > 5/4$$

The Reaction Rate from *p*-Toluic Acid to Terephthalic Acid.—At first, the absorption rate of oxygen in the absence of ozone was measured much as in the above experiment. The reaction shows an independence of the concentration of *p*-toluic acid, and a first-order dependence on that of cobaltous acetate. The reaction shows a one-half-order dependence on the concentration of ammonium bromide at $[\text{NH}_4\text{Br}] \leqq 0.04$ mol./l. and $[\text{NH}_4\text{Br}]/[\text{Co}^{2+}] \leqq 5/4$. The reaction rate increases ca. 12.5% upon the addition of any tetrachloroethylene, while it shows independences of the concentrations of chloroacetic acid and tetrachloroethylene. To summarize the above results, the reaction rate may be given as follows:

$$R_4 = 1.125k_{\text{IV}}[\text{Co}^{2+}][\text{NH}_4\text{Br}]^{1/2} \quad \text{at } [\text{NH}_4\text{Br}] \leqq 0.04 \text{ mol./l. and } [\text{NH}_4\text{Br}]/[\text{Co}^{2+}] \leqq 5/4$$

Then the absorption rate of oxygen after 10 minutes' passage of ozonized oxygen was measured much as before. The reaction shows an independence of the concentration of *p*-xylene, and three-second-order and one-fourth-order dependences on the concentrations of cobaltous acetate at $[\text{Co}^{2+}] \leqq 0.024$ mol./l. and $([\text{Co}^{2+}]+[\text{NH}_4\text{Br}]) \leqq 0.028$ mol./l., and at $[\text{Co}^{2+}] > 0.024$ mol./l. and $([\text{Co}^{2+}]+[\text{NH}_4\text{Br}]) > 0.028$ mol./l., respectively. The reaction also shows a one-half-order or second-order dependence on the concentrations of ammonium bromide at $[\text{NH}_4\text{Br}] \leqq 0.012$ mol./l. and $([\text{Co}^{2+}]+[\text{NH}_4\text{Br}]) \leqq 0.028$ mol./l., and at $[\text{NH}_4\text{Br}] > 0.012$ mol./l. and $([\text{Co}^{2+}]+[\text{NH}_4\text{Br}]) > 0.028$ mol./l. Further, the reaction shows an independence of the concentration of tetrachloroethylene. To summarize the above results, the reaction rate may be given as follows;

$$R_5 = k_{\text{V}}[\text{Co}^{2+}]^{3/2}[\text{NH}_4\text{Br}]^{1/2}$$

at $[\text{NH}_4\text{Br}] \leqq 0.012$ mol./l. and $([\text{Co}^{2+}]+[\text{NH}_4\text{Br}]) \leqq 0.028$ mol./l.

$$R_6 = k_{\text{VI}}[\text{Co}^{2+}]^{1/4}[\text{NH}_4\text{Br}]^{2.0}$$

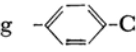
at $[\text{NH}_4\text{Br}] > 0.012$ mol./l. and $([\text{Co}^{2+}]+[\text{NH}_4\text{Br}]) > 0.028$ mol./l.

Reaction Mechanism.—Since no reaction mechanism has been reported with regard to the oxidation of *p*-xylene to *p*-toluic acid, it has been considered first. It is supposed in glacial acetic acid that the following reaction occurs easily, and that [HBr] is directly proportional to $[\text{NH}_4\text{Br}]$, since hydrogen bromide does not dissociate so much.[14]

$$\text{NH}_4\text{Br} + \text{CH}_3\text{COOH} \rightleftharpoons \text{HBr} + \text{CH}_3\text{COONH}_4$$

Thus the reaction rate obtained experimentally may be expressed as a dependence on $[\text{HBr}]^{1/4}$. Hydrogen bromide is thus made to react with oxygen to produce the radical in accordance with the reaction 1:

$$\text{HBr} + \text{O}_2 \xrightarrow{k_1} \text{Br}\cdot + \text{HO}_2\cdot \qquad v_1 \quad (1)$$

By expressing -CH$_3$ with ϕ, reactions 2 and 3 are given as:

$$\phi\text{CH}_3 + \text{Br}\cdot \xrightarrow{k_2} \phi\text{CH}_2\cdot + \text{HBr} \qquad v_2 \quad (2)$$

$$\phi\text{CH}_2\cdot + \text{O}_2 \xrightarrow{k_3} \phi\text{CH}_2\text{O}_2\cdot \qquad v_3 \quad (3)$$

The absence of *p*-xylene from the rate equation establishes that it does not enter into the propagation steps; the reaction 3a, which would involve a first-order dependence on [*p*-xylene], is therefore excluded:

$$\phi\text{CH}_3 + \phi\text{CH}_2\text{O}_2\cdot \rightarrow \phi\text{CH}_2\text{OOH} + \phi\text{CH}_2\cdot \quad (3\text{a})$$

The replacement of 3a by an electron-transfer reaction between a cobaltous ion and a hydroperoxyradical may be suggested; 4 represents the sum of two possible courses, 4a—4b and 4c—4d:

$$\phi\text{CH}_2\text{O}_2\cdot + \text{Co}^{2+} \xrightarrow{k_4} \phi\text{CHO} + \text{OH}^- + \text{Co}^{3+} \qquad v_4 \quad (4)$$

$$\text{(i)} \quad \phi\text{CH}_2\text{O}_2\cdot \rightarrow \phi\text{CHO} + \text{OH}\cdot \quad \text{(thermal)} \quad (4\text{a})$$

$$\text{OH}\cdot + \text{Co}^{2+} \rightarrow \text{Co}^{3+} + \text{OH}^- \quad (4\text{b})$$

$$\text{(ii)} \quad \phi\text{CH}_2\text{O}_2\cdot + \text{Co}^{2+} \rightarrow \phi\text{CH}_2\text{O}_2^- + \text{Co}^{3+} \quad (4\text{c})$$

$$\phi\text{CH}_2\text{O}_2^- \rightarrow \phi\text{CHO} + \text{OH}^- \text{ (very fast)} \quad (4\text{d})$$

Of these mechanisms, it is the more probable, since it is unlikely that the thermal decomposition of a hydroperoxyradical would produce an aldehyde exclusively. The regeneration of the cobaltous ion by the reaction 5 is suggested:

$$\text{Co}^{3+} + \text{HBr} \underset{k_{-5}}{\overset{k_{+5}}{\rightleftharpoons}} \text{Co}^{2+} + \text{Br}\cdot + \text{H}^+ \qquad \begin{matrix} v_{+5} \\ v_{-5} \end{matrix} \quad (5)$$

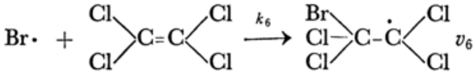
The concentration of Co^{3+} appears to be much smaller than that of Co^{2+}, since the color of the solution during an oxidation shows none of the deep green usually associated with the cobaltic state. The reaction 5 is considered to be reversible and in an equilibrium under a steady state. Since $[\text{Co}^{3+}]$ is much smaller than $[\text{Co}^{2+}]$, v_{+5} is

---

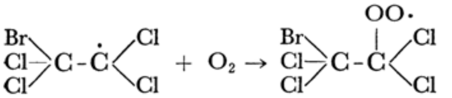
[14] I. M. Kolthoff and A. Willman, *J. Am. Chem. Soc.*, **56**, 1007 (1934).

thought to be very large compared to v_{-5}; therefore, the apparent rate of the reaction 5 may be approximately given by v_{+5}.

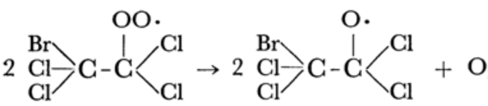
The reaction accompanying tetrachloroethylene is thought to proceed in accordance with the reaction 6, 6a, 6b, and 6c on the basis of the mechanism proposed by Schumacher et al.[15] with regard to the reaction-between Cl· and tetrachloroethylene:



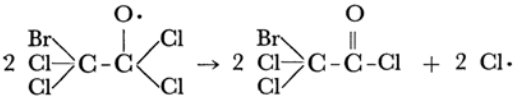
v_6 (6)



(6a)



(6b)



(6c)

On the basis of the data* obtained by the present authors, the Br· in 6 might be replaced by an increasing amount of Cl· in 6c, and there might be a chain reaction consisting of 6—6c. Though a small amount of oxygen is consumed through the reactions 6—6c, the consumption of Br· in 6 would involve a retardation of 2 in the principal chain reaction and would, therefore, allow tetrachloroethylene to behave negatively. By considering further that the velocity of the propagation reaction in the *p*-xylene → *p*-toluic acid reaction is larger than that in the *p*-toluic acid → terephthalic acid reaction, it may be understood that the rate in the former is independent of the concentration of tetrachloroethylene, but that it increases by ca. 12.5%. It is further assumed that the reaction 6 is a rate-determining step in 6—6c, and that, therefore, v_6 is approximately equal to the apparent rate.

By assuming that $v_3 \gg v_4$** even under an oxygen pressure of 92 mmHg, the chain-termination is expressed by the reaction 7:

$$2\ \phi CH_2O_2\cdot \xrightarrow{k_7} \text{inactives} \qquad v_7 \quad (7)$$

When the reaction has reached a steady state, the rate of initiation is equal to the sum of v_6 and v_7.

$$k_1[HBr][O_2] = k_7[\phi CH_2O_2\cdot]^2 + k_6[Cl_2C{=}CCl_2][Br\cdot] \qquad (a)$$

By assuming $v_7 \gg v_6$, since a considerable amount of tetrachloroethylene was recovered after the oxidation of *p*-xylene, Eq. a is given by b and c:

$$k_1[HBr][O_2] = k_7[\phi CH_2O_2\cdot]^2 \qquad (b)$$

hence: $[\phi CH_2O_2\cdot] = \{(k_1/k_7)[HBr][O_2]\}^{1/2}$ (c)

By supposing that v_6 is constant, since $[Br\cdot] \ll$ [tetrachloroethylene] and both are approximately constant at a steady state, Eqs. d and e are obtained:

$$v_6 = k_6[Cl_2C{=}CCl_2][Br\cdot] = K_I \qquad (d)$$

therefore: $[Br\cdot] = (K_I/k_6)[Cl_2C{=}CCl_2]^{-1}$ (e)

Under a steady state, the radical and Co concentrations may be considered stationary; i. e., $d[Co^{3+}]/dt = d[\phi CH_2\cdot]/dt = d[\phi CH_2O_2\cdot]/dt = 0$. The following relations are then obtained:

$$v_3 = v_2 = v_4 + v_7, \qquad v_4 = v_{+5},$$

$$v_1 = v_5 + v_6 \fallingdotseq v_7$$

and $$-d[O_2]/dt = v_1 + v_3 = 2\ v_1 + v_4 = 2k_1[HBr][O_2] + k_4[\phi CH_2O_2\cdot][Co^{2+}]$$

If it is further assumed that the propagation chains are long compared to the initiation reaction, the oxygen absorption by the initiation reaction may be neglected, and Eq. f is obtained:

$$-d[O_2]/dt = k_4[\phi CH_2O_2\cdot][Co^{2+}] \qquad (f)$$

From $v_4 = v_{+5}$, Eq. g is obtained:

$$[\phi CH_2O_2\cdot] = (k_{+5}/k_4)\{[Co^{3+}][HBr]/[Co^{2+}]\} \qquad (g)$$

By introducing v_{+5}/v_{-5} = constant, h is derived:

$$[Co^{3+}] = (k_{-5}K_{II}/k_{+5})\{[Co^{2+}][Br\cdot][H^+]/[HBr]\} \qquad (h)$$

By combining g and h:

$$[\phi CH_2O_2\cdot] = (k_{-5}K_{II}/k_4)[Br\cdot][H^+] \qquad (i)$$

By multiplying c by i, and by taking its square root, j is derived:

$$[\phi CH_2O_2\cdot] = (k_1/k_7)^{1/4}(k_{-5}K_{II}/k_4)^{1/2}\cdot [HBr]^{1/4}[O_2]^{1/4}[Br\cdot]^{1/2}[H^+]^{1/2} \qquad (j)$$

By substituting e for [Br·]:

$$[\phi CH_2O_2\cdot] = (k_1/k_7)^{1/4}(k_{-5}K_{II}/k_4)^{1/2}(K_I/k_6)^{1/2}\cdot [HBr]^{1/4}[O_2]^{1/4}[Cl_2C{=}CCl_2]^{-1/2}[H^+]^{1/2} \qquad (k)$$

By combining f and k, Eqs. l and m are derived:

$$-d[O_2]/dt = (k_4k_{-5}K_IK_{II}/k_6)^{1/2}(k_1/k_7)^{1/4}\cdot [Co^{2+}][HBr]^{1/4}[O_2]^{1/4}\cdot [Cl_2C{=}CCl_2]^{-1/2}[H^+]^{1/2} \qquad (l)$$

---

[15] H. J. Schumacher and W. Thurauf, *Z. Physik. Chem.*, **A189**, 183 (1941).

* Y. Sakuyama and T. Hara, unpublished. The amount of bromide and chloride in the reaction mixtures during the oxidation were investigated potentiometrically by using a glass electrode-silver (silver chloride) electrode combination, and by titrating this with a silver acetate solution in glacial acetic acid. The amount of bromide decreased at the beginning of the reaction, while the amount of chloride increased gradually. There was a considerable amount of chloride at the end of oxidation. These results give an indirect certification for the reactions 6-6c.

** Though this relation generally holds when the oxygen pressure is above ca. 100 mmHg, it is also assumed in the present case, since a similar rate equation, as will be shown later, was obtained at oxygen pressures 92 mmHg or higher pertaining to the oxidation of *p*-toluic acid. Cf. L. Bateman, G. Gee, A. L. Morris and W. F. Watson, *Discussions Faraday Soc.*, **10**, 250 (1951); F. Mashio, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **63**, 699 (1960).

$$-\mathrm{d}[\mathrm{O}_2]/\mathrm{d}t = k_p[\mathrm{Co}^{2+}][\mathrm{HBr}]^{1/4}[\mathrm{Cl}_2\mathrm{C{=}CCl}_2]^{-1/2} \tag{m}$$

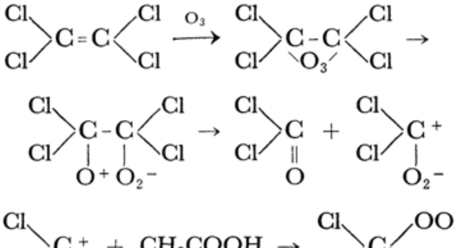
where

$$k_p = (k_4k_{-5}K_{\mathrm{I}}K_{\mathrm{II}}/k_6)^{1/2}(k_1/k_7)^{1/4}[\mathrm{O}_2]^{1/4}[\mathrm{H}^+]^{1/2}$$

Since the present experiment was carried out under a definite oxygen pressure and since the reaction orders of all the factors except chloroacetic acid were examined in the absence of chloroacetic acid, $[\mathrm{H}^+]$ may be considered constant and the term of chloroacetic acid in the experimental rate may be independent. Thus Eq. m agrees in form with the rate equation found by the experiment.

Though chloroacetic acid has been reported to act in three ways:[11] 1) enhancing the reactivity of alkylbenzenes, 2) increasing the activity of catalyst, and 3) offering a radical in itself, its behavior in the present reaction still remains unknown.

Since it seemed to be very difficult technically to oxidize *p*-xylene with oxygen of air containing a definite amount of ozone and to analyze the reaction mechanism, the effect of ozone on the reaction rate was examined by comparing it with one in oxygen alone. The reaction showed a negative one-half-order dependence on the concentration of tetrachloroethylene in the absence of ozone, but a zero-order dependence after 10 minutes' passage of ozone. It is, therefore, supposed in the latter case that the reaction 6 does not occure, but the reactions 8 and 9, which were proposed by Rieche[16] and Criegee,[17] do.



(8)

(9)

Judging from the experimental results, it may further be supposed that the formation of ozonide is not so slow as to consume Br· markedly, and that the hydroperoxide produced in 9 takes part in the propagation reaction, which results in an increase of the yield. By accepting these assumption, it is understandable that the reaction shows an independence of the concentration of tetrachloroethylene. By passing ozonized oxygen into the reaction mixture for 10 min. at 90°C, the cobalt-peroxy-radical shown in the reaction 10 can be produced, as has been proposed by several persons.[18]

$$\mathrm{Co}^{2+} + \mathrm{O}_2 \underset{k_{-10}}{\overset{k_{+10}}{\rightleftharpoons}} \mathrm{Co}^{2+}\cdot\mathrm{O}_2\cdot \qquad \begin{matrix} v_{+10} \\ v_{-10} \end{matrix} \tag{10}$$

The reaction 10 is assumed to be reversible and in an equilibrium. Therefore, Eq. 10-1 and 10-2 are derived:

$$K_{\mathrm{III}} = \frac{k_{+10}[\mathrm{Co}^{2+}][\mathrm{O}_2]}{k_{-10}[\mathrm{Co}^{2+}\cdot\mathrm{O}_2\cdot]} \tag{10-1}$$

$$[\mathrm{Co}^{2+}\cdot\mathrm{O}_2\cdot] = (k_{+10}/K_{\mathrm{III}}\cdot k_{-10})[\mathrm{Co}^{2+}][\mathrm{O}_2] \tag{10-2}$$

The chain reaction is supposed to be initiated by the reactions 11 and 12, followed by the propagation reactions, 13, 14, 15, 16, and the termination reaction, 17.

$$\mathrm{Co}^{2+}\cdot\mathrm{O}_2\cdot + \mathrm{HBr} \xrightarrow{k_{11}} \mathrm{Co}^{3+} + \mathrm{HO}_2\cdot + \mathrm{Br}\cdot \qquad v_{11} \tag{11}$$

$$\mathrm{Co}^{2+}\cdot\mathrm{O}_2\cdot + \phi\mathrm{CH}_3 \xrightarrow{k_{12}} \mathrm{Co}^{2+} + \mathrm{HO}_2\cdot + \phi\mathrm{CH}_2\cdot \qquad v_{12} \tag{12}$$

$$\phi\mathrm{CH}_3 + \mathrm{Br}\cdot \xrightarrow{k_{13}} \phi\mathrm{CH}_2\cdot + \mathrm{HBr} \qquad v_{13} \tag{13}$$

$$\phi\mathrm{CH}_2\cdot + \mathrm{O}_2 \xrightarrow{k_{14}} \phi\mathrm{CH}_2\mathrm{O}_2\cdot \qquad v_{14} \tag{14}$$

$$\phi\mathrm{CH}_2\mathrm{O}_2\cdot + \mathrm{Co}^{2+} \xrightarrow{k_{15}} \phi\mathrm{CHO} + \mathrm{OH}^- + \mathrm{Co}^{3+} \qquad v_{15} \tag{15}$$

$$\mathrm{Co}^{3+} + \mathrm{HBr} \xrightarrow{k_{16}} \mathrm{Co}^{2+} + \mathrm{H}^+ + \mathrm{Br}\cdot \quad v_{16} \tag{16}$$

$$2\ \phi\mathrm{CH}_2\mathrm{O}_2\cdot \xrightarrow{k_{17}} \text{inactives} \qquad v_{17} \tag{17}$$

By introducing a steady state, $v_{17} = v_{11} + v_{12}$, and Eq. n is derived:

$$\begin{aligned} k_{17}[\phi\mathrm{CH}_2\mathrm{O}_2\cdot]^2 &= (k_{+10}k_{11}/K_{\mathrm{III}}k_{-10})[\mathrm{Co}^{2+}][\mathrm{O}_2][\mathrm{HBr}] \\ &\quad + (k_{+10}k_{12}/K_{\mathrm{III}}k_{-10})[\mathrm{Co}^{2+}][\mathrm{O}_2][\phi\mathrm{CH}_3] \end{aligned} \tag{n}$$

By assuming $v_{11}/v_{12} = K_{\mathrm{IV}}$,

$$k_{11}[\mathrm{Co}^{2+}\cdot\mathrm{O}_2\cdot][\mathrm{HBr}]/k_{12}[\mathrm{Co}^{2+}\cdot\mathrm{O}_2\cdot][\phi\mathrm{CH}_3] = K_{\mathrm{IV}}$$

Hence, $k_{11}[\mathrm{HBr}] = K_{\mathrm{IV}}k_{12}[\phi\mathrm{CH}_3]$, and

$$k_{12}[\phi\mathrm{CH}_3] = (k_{11}/K_{\mathrm{IV}})[\mathrm{HBr}]$$

By substituting these values into Eq. n, Eqs. o and o′ are obtained:

$$\begin{aligned} [\phi\mathrm{CH}_2\mathrm{O}_2\cdot] &= (k_{10}k_{12}/K_{\mathrm{III}}k_{-10}k_{17})^{1/2}\cdot \\ &\quad (K_{\mathrm{IV}}+1)^{1/2}[\mathrm{Co}^{2+}]^{1/2}[\mathrm{O}_2]^{1/2}[\phi\mathrm{CH}_3]^{1/2} \end{aligned} \tag{o}$$

or:

$$\begin{aligned} [\phi\mathrm{CH}_2\mathrm{O}_2\cdot] &= (k_{10}k_{11}/K_{\mathrm{III}}k_{-10}k_{17})^{1/2}\cdot \\ &\quad (1+1/K_{\mathrm{IV}})^{1/2}[\mathrm{Co}^{2+}]^{1/2}[\mathrm{O}_2]^{1/2}[\mathrm{HBr}]^{1/2} \end{aligned} \tag{o′}$$

Consequently, Eqs. p and p′ are derived:

$$\begin{aligned} -\mathrm{d}[\mathrm{O}_2]/\mathrm{d}t &= v_{14} + v_{10} = v_{15} + v_{17} + v_{10} \fallingdotseq v_{15} \\ &= k_{15}[\phi\mathrm{CH}_2\mathrm{O}_2\cdot][\mathrm{Co}^{2+}] \end{aligned}$$

---

16) A. Rieche, *Angew. Chem.*, **70**, 251 (1958).

17) R. Criegee and M. Lederer, *Ann.*, **583**, 29 (1953).

18) P. George and A. Robertson, *Trans. Faraday Soc.*, **42**, 217 (1946); G. Wittig, *Angew. Chem.*, **60**, 169 (1948); N. Uri, *Nature*, **177**, 1177 (1956); H. Kropf, *Ann.*, **637**, 73 (1960).

$$=k_{15}(k_{10}k_{12}/K_{\mathrm{III}}k_{-10}k_{17})^{1/2}(K_{\mathrm{IV}}+1)^{1/2}\cdot [\mathrm{Co}^{2+}]^{3/2}[\mathrm{O}_2]^{1/2}[\phi\mathrm{CH}_3]^{1/2} \tag{p}$$

or:

$$-\mathrm{d}[\mathrm{O}_2]/\mathrm{d}t=k_{15}(k_{10}k_{11}/K_{\mathrm{III}}k_{-10}k_{17})^{1/2}\cdot (1+1/K_{\mathrm{IV}})^{1/2}[\mathrm{Co}^{2+}]^{3/2}[\mathrm{O}_2]^{1/2}[\mathrm{HBr}]^{1/2} \tag{p'}$$

Under a definite oxygen pressure, the initial rate is expressed as Eq. q:

$$-\mathrm{d}[\mathrm{O}_2]/\mathrm{d}t=k_{\mathrm{q}}[\mathrm{Co}^{2+}]^{3/2}[\mathrm{HBr}]^{1/2}[\phi\mathrm{CH}_3]^{1/2} \tag{q}$$

Equation q agrees in form with the rate obtained experimentally. Though the reaction showed a first-order dependence on the concentration of hydrogen bromide at $[\mathrm{HBr}]/[\mathrm{Co}^{2+}]>5/4$, this is considered to be due to the increase in v_{11} and to the velocities in the coming reactions.

Though the reaction conditions from *p*-toluic acid to terephthalic acid in the present experiment are different in temperature and oxygen pressure from those used by Ravens, the reaction rate has been obtained in a form similar to that obtained by Ravens. The reaction rate by Ravens is shown by:

$$-\mathrm{d}[\mathrm{O}_2]/\mathrm{d}t=k_{\mathrm{r}}[\mathrm{Co}^{2+}][\mathrm{NaBr}]^{1/2}[\mathrm{O}_2]^{1/2} \tag{r}$$

while that of the present authors is given by:

$$-\mathrm{d}[\mathrm{O}_2]/\mathrm{d}t=1.125k_{\mathrm{s}}[\mathrm{Co}^{2+}][\mathrm{NH}_4\mathrm{Br}]^{1/2} \tag{s}$$

In the latter, the reaction shows independences of the concentrations of both chloroacetic acid and tetrachloroethylene. Therefore, the reaction is considered to proceed by the following mechanism, which is similar to that proposed by Ravens:

$$\mathrm{NH_4Br} + \mathrm{CH_3COOH} \rightleftharpoons \mathrm{HBr} + \mathrm{CH_3COONH_4} \tag{18}$$

$$\mathrm{HBr} + \mathrm{O_2} \rightarrow \mathrm{Br}\cdot + \mathrm{HO_2}\cdot \tag{19}$$

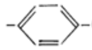
$$\phi'\mathrm{CH_3} + \mathrm{Br}\cdot \rightarrow \phi'\mathrm{CH_2}\cdot + \mathrm{HBr} \tag{20}$$

$$\phi'\mathrm{CH_2}\cdot + \mathrm{O_2} \rightarrow \phi'\mathrm{CH_2O_2}\cdot \tag{21}$$

$$\phi'\mathrm{CH_2O_2}\cdot + \mathrm{Co}^{2+} \rightarrow \phi'\mathrm{CHO} + \mathrm{OH}^- + \mathrm{Co}^{3+} \tag{22}$$

$$\mathrm{Co}^{3+} + \mathrm{HBr} \rightarrow \mathrm{Co}^{2+} + \mathrm{Br}\cdot + \mathrm{H}^+ \tag{23}$$

$$2\,\phi'\mathrm{CH_2O_2}\cdot \rightarrow \text{inactives} \tag{24}$$

where ϕ' means --COOH.

Though the reaction showed an independence of the concentration of tetrachloroethylene, the rate always increased by 12.5% in the presence of any amount of it. This phenomenon has already been explained. Chloroacetic acid was effective in the $\phi\mathrm{CH_3}\rightarrow\phi'\mathrm{CH_3}$ reaction, but not in the $\phi'\mathrm{CH_3}\rightarrow\phi'\mathrm{COOH}$ reaction. The reason for this remains unknown.

By assuming that the reaction mechanism in the oxidation of *p*-toluic acid to terephthalic acid after the passage of ozonized oxygen is similar to that of *p*-xylene to *p*-toluic acid, a rate which is the same as that obtained experimentally is derived; it is shown by Eq. t:

$$-\mathrm{d}[\mathrm{O}_2]/\mathrm{d}t=k_{\mathrm{t}}[\mathrm{Co}^{2+}]^{3/2}[\mathrm{NH}_4\mathrm{Br}]^{1/2} \tag{t}$$

The facts that the reaction shows one-fourth- and second-order dependences on the concentrations of cobaltous ion and ammonium bromide respectively at $([\mathrm{Co}^{2+}]+[\mathrm{NH_4Br}])>0.028$ mol./l. may be attributed to a decrease in the velocity in the reaction corresponding to 12 and to an increase in the concentration of bromide radicals by another reaction, e. g., the direct reaction between oxygen and hydrogen bromide.

Summary

It has been found that terephthalic acid can be obtained by single-stage oxidation in the liquid phase under certain conditions such as the following: *p*-xylene: 25.0 ml.; $\mathrm{Co(OAc)_2\cdot 4H_2O}$: 4.982 g.; $\mathrm{NH_4Br}$: 0.1 g.; tetrachloroethylene: 1.0 ml.; solvent: 200 ml. HOAc; reaction temp.; 90°C; oxidant: ozonized oxygen or air; chloroacetic acid: 0.5 g. (used only in the case of ozonized air); and reaction time: 6 hr.

The yields as crude terephthalic acid were 95% with oxygen and 84% with air. The individuality of the present method consists in the use of the ozonized oxygen or air, together with an aliphatic unsaturated compound.

The reaction rates have been examined by measuring the absorption rate of oxygen; they may be expressed as follows:

1) From *p*-xylene to *p*-toluic acid:

a) Ozone-free (under an oxygen pressure of 92 mmHg)

$$R_1=k_{\mathrm{I}}[\mathrm{Co}^{2+}][\mathrm{NH_4Br}]^{1/4}\cdot[\mathrm{ClCH_2COOH}][\mathrm{Cl_2C{=}CCl_2}]^{-1/2}$$

where $[\mathrm{Co}^{2+}]+2\,[\mathrm{NH_4Br}]\leqq 0.04$ mol./l. and $[\mathrm{ClCH_2COOH}]\leqq 0.13$ mol./l.

b) Ozone present (under an oxygen pressure of 460 mmHg)

$$R_2=k_{\mathrm{II}}[p\text{-xylene}]^{1/2}[\mathrm{Co}^{2+}]^{3/2}[\mathrm{NH_4Br}]^{1/2}$$

at $[\mathrm{NH_4Br}]/[\mathrm{Co}^{2+}]\leqq 5/4$

$$R_3=k_{\mathrm{III}}[p\text{-xylene}]^{1/2}[\mathrm{Co}^{2+}]^{3/2}[\mathrm{NH_4Br}]$$

at $[\mathrm{NH_4Br}]/[\mathrm{Co}^{2+}]>5/4$

2) From *p*-toluic acid to terephthalic acid:

a) Ozone-free (under an oxygen pressure of 92 mmHg)

$$R_4=1.125k_{\mathrm{IV}}[\mathrm{Co}^{2+}][\mathrm{NH_4Br}]^{1/2}$$

at $[\mathrm{NH_4Br}]\leqq 0.04$ mol./l.

and $[\mathrm{NH_4Br}]/[\mathrm{Co}^{2+}]\leqq 5/4$

b) Ozone present (under an oxygen pressure of 460 mmHg)

$$R_5=k_{\mathrm{V}}[\mathrm{Co}^{2+}]^{3/2}[\mathrm{NH_4Br}]^{1/2}$$

at $[NH_4Br] \leqq 0.012$ mol./l.

and $([Co^{2+}]+[NH_4Br]) \leqq 0.028$ mol./l., and

$R_6 = k_{VI}[Co^{2+}]^{1/4}[NH_4Br]^{2.0}$

at $[NH_4Br] > 0.012$ mol./l.

and $([Co^{2+}]+[NH_4Br]) > 0.028$ mol./l.

The reaction mechanism has been further discussed, and the rate equations have been derived by assuming the steady state.

The authors wish to express their hearty thanks to Mr. Sadao Hoshizake, Mr. Yasuo Hayano, Mr. Hiroshi Yamamoto, Mr. Kazuhiro Kashima, Mr. Yasuo Matsumura, Mr. Hitoshi Matsubayashi, and Mr. Ryohei Matsumoto for their help in the experiment. Their thanks are also due to the Maruzen Sekiyu Co., Ltd., which provided the *p*-xylene.