796. *The Oxidation of Alkylaromatic Compounds in Aqueous Hydrogen Bromide.*

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Dilute aqueous hydrogen bromide catalyses the oxidation of water-soluble methyl-aromatic compounds to the corresponding carboxylic acids. The reaction requires a high pressure of oxygen and a temperature of 180—200°. The presence of a vanadium compound improves the oxidation of water-soluble isopropyl-aromatic compounds and also permits the oxidation of water-insoluble compounds.

The main product of the oxidation of a polymethylbenzene by oxygen in the presence of a catalytic metal ion is normally a monocarboxylic acid, which undergoes further oxidation only with difficulty. *p*-Xylene, for example, is readily converted into *p*-toluic acid, which can thus be made in high yield, but only a little terephthalic acid is formed. The commercial importance of terephthalic acid stimulated work on this topic. Direct liquid-phase oxidation[1] at 240°, oxidation in acetic acid in the presence of a catalytic metal ion[2] at 180°, and oxidation in alkaline solution in the presence of a catalytic metal ion[3] at 240°, although they produced terephthalic acid or its salts, gave low conversions or insufficient yields; more recently oxidation in aqueous hydrogen bromide[4] at 180—200° and oxidation in acetic or propionic acid in the presence of a catalytic metal ion and a bromide[4,5] at 130° have proved more satisfactory. This paper describes the use of aqueous hydrogen bromide as a medium for oxidation, particularly of alkylaromatic carboxylic acids and alkylaromatic hydrocarbons.

When an aqueous solution of *p*-toluic acid was heated with oxygen under pressure at 180—200° in the presence of hydrogen bromide oxygen was absorbed steadily at a slowly diminishing rate until the *p*-toluic acid was almost entirely oxidised. The reaction occurred readily at 180—200° with a hydrogen bromide concentration of 0·5—2% and an initial oxygen pressure of 30—50 atm. (measured at room temperature). Terephthalic acid was produced in yields of up to 99% based on the *p*-toluic acid consumed.

The scope and limitations of the method are indicated by the results shown in Table 1. Methyl groups attached to aromatic nuclei which possessed other substituents conferring both a degree of water-solubility and resistance to nuclear oxidation were readily oxidised to carboxyl groups in high yield. Partially brominated or oxidised methyl groups were similarly oxidised. Isopropyl groups were oxidised to carboxyl groups only with difficulty, and t-butyl groups were unaffected. Compounds which are insoluble in water were also unaffected.

The scope of the method can be extended by introduction of vanadium pentoxide or ammonium vanadate in catalytic amount. In the case of *p*-toluic acid this slightly reduced the yield of terephthalic acid, but it promoted the oxidation of isopropyl and 1-hydroxy-1-methylethyl groups and of water-insoluble compounds (Table 2). In the case of hydrocarbons containing one or more methyl group, however, much nuclear bromination occurred and the major products were bromo-carboxylic acids.

The oxidation of *p*-toluic acid in aqueous hydrogen bromide was studied in more detail. Oxygen absorption was faster the higher the temperature, the hydrogen bromide concentration, and the oxygen pressure, but temperature control became difficult under the more favourable conditions owing to the exothermic nature of the reaction. The rate of oxygen absorption diminished slowly until the *p*-toluic acid had been completely oxidised, then absorption ceased abruptly. Such behaviour indicated that the order of reaction with respect to *p*-toluic acid was zero or negative. Bromide ion (as sodium bromide) was inactive as a catalyst in the absence of acid.

Since direct reaction between hydrogen bromide and oxygen to produce bromine is unknown under these conditions in the absence of an organic material or other promoter, it is probable that the reaction involves formation of an organic peroxide, and that the mechanism is similar in its initial stages to that suggested by Rust and Vaughan[6] for the vapour-phase oxidation of tertiary aliphatic hydrocarbons in the presence of hydrogen bromide. The strong positive dependence of the rate on oxygen pressure and hydrogen bromide concentration, and the lack of positive dependence on *p*-toluic acid concentration, indicate that chain termination is not by a reaction involving a bromine atom.

Side-chain bromination is an important reaction in the vapour-phase oxidation of toluene in the presence of hydrogen bromide,[7] and therefore a likely reaction here. The

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[1] B.P. 666,709.

[2] U.S.P. 2,479,067.

[3] Emerson, Shafer, and Heimsch, *J. Org. Chem.*, 1951, **16**, 1839.

[4] B.P. 833,438.

[5] Ravens, *Trans. Faraday Soc.*, 1959, **55**, 1768.

[6] Rust and Vaughan, *Ind. Eng. Chem.*, 1949, **41**, 2595.

[7] Barnett, Bell, Dickey, Rust, and Vaughan, *Ind. Eng. Chem.*, 1949, **41**, 2612.

product, *p*-bromomethylbenzoic acid, is rapidly hydrolysed under the conditions of the reaction to the corresponding hydroxy-compound.

EXPERIMENTAL

The identity of each oxidation product was checked by comparison of the infrared spectrum with that of authentic material.

Apparatus and Methods.—Three different autoclaves were used. The key letter attached to each is used to refer to it throughout.

(A) A mild-steel autoclave of capacity 1-litre was equipped with an anchor-type agitator, thermocouple pocket, pressure gauge, and bursting disc. The inside of the autoclave body and the thermocouple pocket were lined with enamel. The roof of the autoclave was protected by a plate of Langalloy 4R. Interchangeable agitators were used, one enamel-lined, the other constructed of poly(tetrafluoroethylene). All the measurements of oxidation rates were obtained by using this vessel.

(B) A mild-steel autoclave of capacity 250 ml. was similar to autoclave (A) but lacked means of agitation.

(C) A stainless-steel Bergius rotating autoclave of capacity 2 litres was equipped with a thermocouple pocket, pressure gauge, and bursting disc. A removable glass lining was fitted to reduce corrosion. The space between the glass and the autoclave was packed with asbestos. Agitation was provided by rotating the entire autoclave on its longitudinal (horizontal) axis.

The following general procedure was used with the above autoclaves:

The liquid and solid reactants were charged into the autoclave, which was then sealed, and oxygen was added to the desired pressure from a cylinder. Agitation was begun (A and C), the autoclave was heated electrically to the desired temperature (recorded by a recorder-controller), and the pressure was recorded at intervals. After a given time the autoclave was allowed to cool to room temperature and the contents were discharged.

Sealed glass tubes were also used, as follows: the liquid and solid reactants were added to a glass tube of diameter 2·2 cm., then a smaller glass tube of internal diameter 1 cm., sealed at one end and containing 100-vol. hydrogen peroxide (10 ml.), was introduced. The larger tube (capacity 150 ml.) was sealed and heated in an electric furnace, first for 30 min. at 80—100° to decompose the hydrogen peroxide, then at the temperature and for the time required to conduct the oxidation. Except where otherwise specified, 5% aqueous hydrogen bromide (10 ml.) was used as the reaction medium, and the reaction was conducted at 200° for 4 hr.

Paper Chromatography.—Chromatograms were developed by using the equilibrated organic layer from butan-1-ol–water–triethanolamine (45 : 45 : 10). Spots were detected by contact photography of the developed strip against bromide paper under ultraviolet light.

In the water-soluble product from the oxidation of *p*-toluic acid were detected terephthalic acid, small amounts of *p*-toluic acid and *p*-formylbenzoic acid, and a trace of an acid which ran at the same rate as *p*-hydroxymethylbenzoic acid. For this information we are indebted to Dr. B. F. Nesbitt.

Oxidations.—Table 1 gives the results of oxidations carried out in the presence of aqueous hydrogen bromide, including the appropriate reaction conditions. Table 2 gives the results of oxidations carried out in the presence of aqueous hydrogen bromide and a vanadium compound; the oxidation was always carried out in a sealed glass tube, as already described, with 2% of the compound to be oxidised and addition of 1% of ammonium vanadate based on the aqueous phase.

Hydrolysis of p-*Bromoethylbenzoic Acid.*—The acid (2·0 g.) was heated with 2% aqueous hydrogen bromide (20 ml.) in a sealed tube at 180° for 2 hr. *p*-Hydroxymethylbenzoic acid (1·28 g.; m. p. and mixed m. p. 179—181°) was isolated by filtration.

2,5-*Dibromoterephthalic Acid.*—*p*-Xylene (4·0 g.), water (30 ml.), and bromine (35 g.) were heated together in a sealed tube at 180° for 2 hr. The insoluble product was extracted with boiling acetone. The acetone-soluble material, on extraction with boiling chloroform, left a crude acid which after dissolution in alkali, treatment with carbon, reprecipitation, and recrystallisation from acetone and then water gave 2,5-dibromoterephthalic acid, m. p. 318° [dimethyl ester, m. p. 137° (Found: C, 34·3; H, 2·3; Br, 45·8. Calc. for $C_{10}H_8Br_2O_4$: C, 34·1; H, 2·3; Br, 45·4)].

Bromoterephthalic Acid.—*p*-Toluic acid (2·0 g.), water (20 ml.), and bromine (7 g.) were heated together in a sealed tube at 180° for 2 hr. The water-insoluble product was free from terephthalic acid and entirely soluble in acetone. Extraction with chloroform left bromoterephthalic acid, m. p. 292—296°, raised to 300° by recrystallisation from water (dimethyl ester, m. p. 52°). The chloroform extract on recrystallisation from water provided 3-bromo-4-methylbenzoic acid, m. p. 202°.

TABLE 1.

Oxidation of aromatic compounds in aqueous hydrogen bromide.

Compound oxidised	Acid sought or isolated	Yield (%) & equipment ^{b} †	Concns. (%)		Conditions	
			Compound oxidised	HBr	Temp.	Time (hr.)
p-Toluic acid	Terephthalic	92 A	10	1	200°	2
		90 G	5	5	200	4
m-Toluic acid	Isophthalic	97 C	10	2	180	2
o-Toluic acid	Phthalic	86 C	10	2	180	2
p-Bromomethylbenzoic acid	Terephthalic	82 C	7·5	0	180	2
p-Dibromomethylbenzoic acid	Terephthalic	89 G	4	0	180	2
p-Hydroxymethylbenzoic acid	Terephthalic	91 G	5	5	180	4
p-Formylbenzoic acid	Terephthalic	79 G	3	1·5	180	2
p-Nitrotoluene	*p*-Nitrobenzoic	84 G	5	5	200	2
p-Toluenesulphonic acid	*p*-Sulphobenzoic	49 G	5	5	200	2
γ-Picoline	Isonicotinic	84 * B	10	10	180	5
p-Isopropylbenzoic acid	Terephthalic	24 C	10	2	180	2
p-(1-Hydroxy-1-methylethyl)-benzoic acid	Terephthalic	3 G	2	5	200	4
p-t-Butylbenzoic acid	Terephthalic	0 G	10	2	200	2
Toluene	Carboxylic acids	0 G	20	5	200	4
Ethylbenzene		0 G	20	5	200	4
Cumene		0 G	20	5	200	4
Acetophenone		0 G	20	5	200	4

* After allowance for recovered γ-picoline. † Autoclave A, B, or C; or G = glass.

TABLE 2.

Oxidations in the presence of a vanadium compound and aqueous hydrogen bromide.

Compound oxidised	Product sought or isolated	Yield (%)
p-Isopropylbenzoic acid	Terephthalic acid	82
p-(1-Hydroxy-1-methyl ethyl)-benzoic acid	Terephthalic acid	56
p-Di-(1-hydroxy-1-methylethyl)-benzene	Terephthalic acid	44
Toluene	*p*-Bromobenzoic acid	54
Ethylbenzene	Benzoic acid	40
Cumene	Benzoic acid	59
Acetophenone	Benzoic acid	58
p-Xylene	Terephthalic acid	13
	Bromoterephthalic acid	21
	2,5-Dibromoterephthalic acid	36
p-Cymene	Terephthalic acid	11
p-t-Butyltoluene	Terephthalic acid	0
p-Di-isopropylbenzene	Terephthalic acid	63

Action of Aqueous Bromine on Terephthalic Acid.—Terephthalic acid (2·0 g.), water (20 ml.), and bromine (1·3 g.) were heated in a sealed tube at 180° for 2 hr. Terephthalic acid (2·0 g.) was recovered.

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