

surface of the mercury cathode. The potential difference between the S.C.E. and the cathode was measured by means of a potentiometer. A gas coulometer³⁰ and a milliammeter were placed in series with the electrolysis cell and a voltmeter was placed in parallel with it. The voltage across the cell was adjusted manually.

In operation the solvent-electrolyte mixture (without hydrocarbon) was pre-electrolyzed by allowing a current of 50 milliamp. to flow through the cell for 15 min. Then a potential difference of 20 v. was maintained across the cell until the cathode had attained the potential desired for the electroreduction. During this time a record of current *vs.* cathode potential was made. When the current had ceased to decrease with time (residual value 2-6 milliamp.), the

initial reading of the coulometer was noted, a sample of 1 ml. of standard 0.1-0.2*M* hydrocarbon substrate in 75% dioxane was added to the cathode compartment, and a timer was started. As the cathode potential immediately became more positive, the overall potential was again raised to 20 v. and the previous procedure of adjusting the voltage was repeated. When the current had reached a steady background value again (1-3 hr.) electrolysis was stopped. The total number of coulombs passed during the electrolysis proper (as calculated from the gas coulometric readings) was corrected for background current-flow (as based both on time of electrolysis and intervening cathode potentials). A sample of the electrolytic solution was withdrawn and tested for unsaturation by means of aqueous permanganate. Results are recorded in Table II.

(30) J. J. Lingane, *J. Am. Chem. Soc.*, **67**, 1916 (1945).

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[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Catalytic Oxidation of Hydrocarbons. Initiation by Ozone

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The isomeric xylenes are readily oxidized to the respective toluic acids with oxygen in acetic acid solvent at reflux temperature. The reaction is catalyzed by cobalt ion and initiated by ozone. *m*-Toluic acid and *p*-toluic acid are oxidized further at a slower rate to the corresponding dibasic acids. When *o*-toluic acid is oxidized the product, *o*-phthalic acid, chelates with cobalt ion and interferes with the chain initiation step, $\text{ROOH} + \text{Co(III)} \longrightarrow \text{ROO}\cdot + \text{Co(II)} + \text{H}^+$, inhibiting the reaction.

Ozone is a powerful oxidant and will oxidize silver (I) ions to silver(II) ions¹ in acid solution. We have found that the characteristic green color of cobalt(III) acetate appears when an ozone-oxygen stream is passed into cobalt(II) acetate solutions in acetic acid. We felt that a more efficient oxidation system might be obtained if the acetaldehyde-oxygen in the Hull oxidation² was replaced by ozone-oxygen. An oxidation of *p*-xylene in acetic acid at reflux temperature was effected by introducing oxygen containing *ca.* 2% ozone into the vigorously stirred system. The reaction rapidly attained the characteristic green color described in the Hull oxidation. However, the product of the reaction is principally terephthalic acid. Furthermore, the ozone can be stopped after the green color is attained and the reaction is self-sustaining, *i.e.* it continues without further addition of ozone. Toluene and some substituted toluenes are also oxidized to the corresponding carboxylic acids. If the water formed is removed continuously then phthalide can be oxidized to phthalic anhydride which does not interfere with the oxidation.

We found that *o*-xylene, unlike the other two isomers, cannot readily be oxidized to the dibasic acid. Initially, we felt that the *o*-phthalic acid formed might be degraded further. Subsequent in-

vestigation showed that *o*-phthalic acid was stable in the reaction mixture. However, when it was present in the reaction in an amount at least equivalent (moles) to the cobalt(II) ion the characteristic green color of cobalt(III) ion could not be obtained even when ozone-oxygen mixtures were passed through continuously. Furthermore, self-sustaining oxidations of any of the xylenes could not be obtained when it was present in appreciable amounts. As a consequence, an *o*-xylene oxidation can be initiated with ozone and the reaction which essentially proceeds stepwise will stop when most of the *o*-xylene is converted to *o*-toluic acid and an amount of phthalic acid equivalent to the cobalt ion in solution is formed. At this point the reaction mixture is no longer green but is the pink color characteristic of cobalt(II) acetate. If the initiator, ozone, is added continuously, more *o*-phthalic acid can be produced at a much reduced rate. The other xylenes are also oxidized to the corresponding dibasic acids in the presence of *o*-phthalic acid at a reduced rate if ozone is added continuously.

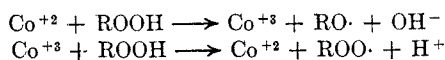
Since the intermediate toluic acids have dissociation constants of the same order of magnitude as the solvent acetic acid, they would be expected to have little effect on the catalyst. Isophthalic and terephthalic acids are relatively insoluble in the reaction mixture and also do not interfere with the catalyst. However, *o*-phthalic acid is not only the strongest acid present in the reaction mixture, but it can also form a chelate with cobalt(II) and co-

(1) A. A. Noyes, S. L. Hoard, and K. S. Pitzer, *J. Am. Chem. Soc.* **57**, 1221-9 (1935).

(2) D. C. Hull, U. S. Patent 2,673,217, March 23, 1954.

balt(III) ions³ and this would change the oxidation potential of the system.⁴ Generally it is found that the higher valence state is stabilized to some degree.

Redox catalysts, such as cobalt ion, function in the following manner:⁵



Since the catalyst in the Hull oxidation must be at least partly in the trivalent state, we can perhaps assume that the reaction of solvated cobalt(III) ion with hydroperoxide is the principal chain initiation step. It is this step that would be interfered with by any material that stabilizes the cobalt ion in the trivalent state. This is in agreement with the experimental data. In the presence of *o*-phthalic acid the oxidation will continue only when the initiator, ozone, is added continuously to the reaction mixture.

EXPERIMENTAL

A round bottom flask was equipped with a gas inlet tube, a thermometer, and a condenser which also served as a gas exit tube. Efficient oxygen-liquid mixing was obtained with a vibromixer stirrer. The ozonizer was the conventional concentric tube type with a brine electrolyte. The phthalic acids and intermediate toluic acids produced in all cases were substantially pure as indicated by melting point or neutral equivalent where the material did not melt below 300°.

Oxidation of m-xylene. To a 2-l. reaction flask was added 130 g. (1.23 moles) of *m*-xylene, 40 g. (0.16 mole) of cobalt(II) acetate tetrahydrate and 1 l. of glacial acetic acid. An ozone (2 g. per hr.)-oxygen stream was passed into the vigorously stirred solution at reflux temperature (115–120°) at a rate of 70 l. per hr. The ozone was stopped after 75 min., at which time the solution was dark green in color. The reaction was continued for a further 15 hr. during which time the reaction mixture remained dark green in color. After cooling to room temperature, the precipitated isophthalic acid was removed by filtration and washed with a small amount of acetic acid to remove cobalt salts. An aliquot of the combined filtrate and washings was evaporated to dryness, then treated with dilute hydrochloric acid to dissolve cobalt salts. Ether extraction separated the *m*-toluic acid from the isophthalic acid. The total yield of isophthalic acid obtained was 136.3 g. (67%) and *m*-toluic acid 35.2 g. (21%).

Similar results are obtained in the oxidation of *p*-xylene.

Oxidation of o-xylene. To a 2-l. reaction flask was added 312 g. of *o*-xylene, 40 g. cobalt(II) acetate tetrahydrate and 750 ml. glacial acetic acid. An ozone (2.2 g. per hr.)-oxygen stream was passed through the vigorously stirred solution at reflux temperature (115–120°) at a rate of 90 l. per hr. The ozone was stopped after 1.5 hr. at which time the solution was dark green in color. At the end of 10 hr., the reaction was pink in color. After cooling, the reaction mixture was flooded with 3.5 l. of water and the precipitated *o*-toluic acid was removed by filtration, washed with water, and air dried to yield 308 g. of *o*-toluic acid (77%). No attempt was made to recover more *o*-toluic acid from the filtrate.

When ozone is passed through the reaction mixture continuously, appreciable amounts of *o*-phthalic acid are

formed. The following oxidations were run containing varying amounts of catalyst. An ozone (1 g. per hr.)-oxygen stream (36 l. per hr.) was passed through a vigorously stirred solution containing the catalyst, and 10.6 g. (0.1 mole) of *o*-xylene in 200 ml. of glacial acetic acid at reflux temperature. After 7.5 hr., the acetic acid was removed by distillation and the residue was treated with enough dilute hydrochloric acid to dissolve the cobalt salts. After filtration the *o*-toluic acid was separated from the *o*-phthalic acid by extraction with chloroform.

Co(OAc) ₂ ·4H ₂ O (moles)	Yield (moles)	
	<i>o</i> -Toluic acid	<i>o</i> -Phthalic acid
1	0.049	0.025
2	0.061	0.019
3	0.061	0.008

Oxidations in the presence of o-phthalic acid. When oxygen containing 1.5% ozone was passed through a glacial acetic acid (250 ml.) solution containing 10 g. of cobalt(II) acetate tetrahydrate (0.04 mole) and 20 g. of *o*-phthalic acid (0.12 mole) at 115° for 2 hr., the solution darkened slightly but did not attain the dark green color characteristic of cobalt(III) acetate that is attained in the absence of *o*-phthalic acid. The oxidation of the xylenes to phthalic acids will proceed in the presence of *o*-phthalic acid only if ozone is passed through the reaction continuously.

Oxidation of p-xylene in the presence of o-phthalic acid. To a solution of 5 g. (0.02 mole) of cobalt(II) acetate tetrahydrate in 200 ml. of glacial acetic acid was added 8.6 g. (0.08 mole) of *p*-xylene and 3.3 g. (0.02 mole) of *o*-phthalic acid. An ozone (2 g. per hr.)-oxygen stream (60 l. per hr.) was passed through the vigorously stirred solution at reflux temperature. After 2.5 hr., the reaction mixture was cooled, filtered, and washed with a small amount of acetic acid to yield 10.2 g. (76%) of terephthalic acid.

In a similar experiment 10 g. (0.06 mole) of *o*-phthalic acid was added to the reaction mixture. After 5 hr., there was obtained 9.8 g. (73%) of terephthalic acid. No attempt was made to isolate the *p*-toluic acid from the filtrates.

Oxidation of p-methoxytoluene. To a solution of 6 g. (0.024 mole) of cobalt(II) acetate tetrahydrate in 200 ml. of glacial acetic acid, was added 12 g. (0.1 mole) of *p*-methoxytoluene. An ozone (1.0 g. per hr.)-oxygen stream (30 l. per hr.) was passed through the vigorously stirred solution at reflux temperature. After 1.9 hr., the ozone was stopped and the reaction was continued for 2.1 hr. further. The reaction mixture was flooded with water and the copious pale yellow precipitate separated by filtration and dried in a vacuum desiccator. There was obtained 12.2 g. (82%) of *p*-anisic acid, which begins to soften at 178°, m.p. 184–187°; neutral equivalent 150, 152 (theory 152).

Oxidation of phthalide. To a solution of 5 g. (0.02 mole) of cobalt(II) acetate in 300 ml. of glacial acetic acid was added 15 g. (0.11 mole) of phthalide. A stream of ozone (1.7 g. per hr.)-oxygen was passed through the vigorously stirred solution at the temperature of reflux. Acetic acid was removed continuously from the reaction mixture through an 8-inch Vigreux column. During a 5-hr. period, a total of 400 ml. of acetic acid was removed from the reaction mixture and a total of 200 ml. of acetic acid was gradually added to the reaction mixture. The ozone was stopped after 4 hr. and after 1 hr. further, the reaction mixture was cooled. There was deposited 13.4 g. (81%) colorless needles, m.p. 132°. There was no depression in a mixed melting point with an authentic sample of phthalic anhydride.

SCHENECTADY, N. Y.

(3) M. Bobtelsky and I. Bar-Gadda, *Bull. soc. chim. France*, 20, 687 (1953).

(4) A. E. Martell and M. Calvin, *Chemistry of the Metal Chelate Compounds*, Prentice Hall, Inc., New York (1953) p. 58–9.

(5) For a discussion of metal-catalyzed autooxidation see C. Walling, *Free Radicals in Solution*, John Wiley & Sons, Inc. (New York) 1957, pp. 427–30.