

## A STUDY OF THE CONVERSION OF *p*-TOLUIC ACID TO TEREPHTHALIC ACID WITH HIGH PRESSURE OXYGEN

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*Received July 12, 1951*

The preparation of aromatic monobasic acids by the oxidation of dialkylbenzenes is a well known and easily effected reaction. However, the further oxidation of such acids in the liquid phase to dibasic acids is much more difficult to achieve.

This paper describes the oxidation of *p*-toluic acid to terephthalic acid by the application of techniques similar to those utilized for the oxidation of coal (1). The *p*-toluic acid was dissolved in aqueous sodium hydroxide and oxidized with oxygen gas. Preliminary experiments were made in a gas-agitated autoclave at 240° with an applied oxygen pressure of 700 lb. In later work an American Instrument Company autoclave equipped with a stirrer was found to be more suitable, since as much oxidation could be effected in it in one hour at 260–275° with an applied oxygen pressure of 1000 lb. as in six hours in the gas-agitated autoclave.

In six hours in the gas-agitated autoclave the best results (35–40% conversion and 56–68% yield) were obtained with a potassium metavanadate catalyst in the presence of such promoters as *p*-tolualdehyde or ascaridole. A ferric oxide catalyst was slightly less effective—29% conversion and 55% yield. These results are in contrast to a 4% conversion and 33% yield of terephthalic acid from *p*-toluic acid obtained in the absence of a catalyst. Conversions of 17% and yields of 46–57% were obtained with such catalysts as potassium permanganate, selenium dioxide, lead dioxide, and potassium bichromate.

In one hour in the American Instrument Company autoclave, using sodium hydroxide as the alkali, the best catalyst proved to be an iron oxide-aluminum oxide catalyst. The conversion of *p*-toluic acid to terephthalic acid was 49% and the yield 66%. The aluminum oxide component in this catalyst could be replaced by the oxides of zinc, cerium, titanium, zirconium, or germanium with very little diminution in activity. On the other hand replacement of the iron oxide component with the oxides of cobalt, copper, manganese, nickel, or lead gave a catalyst which actually produced lower conversions and yields than were obtained with no catalyst at all where the conversion was 33% and the yield 64%. Catalytic activity (39–48% conversions and 57–68% yields) also was exhibited by cobalt chromate, iron vanadate, lead chromate, ferric oxide, potassium metavanadate, and silver hydroxide.

Substitution of a mixture of potassium hydroxide and potassium carbonate for the sodium hydroxide in the presence of the iron oxide-aluminum oxide catalyst produced the best oxidation, a 77% conversion and yield. The crude terephthalic acid thus produced assayed 98%. With potassium hydroxide alone

the conversion was 66% and the yield 77%. A similar improvement was observed when potassium hydroxide was used in the presence of a ferric oxide catalyst.

The use of sodium carbonate as the alkali also speeded up the oxidation, but did not improve the yield. In one hour's time 98% terephthalic acid was obtained in 56% conversion and 57% yield.

Air could be used as well as oxygen as the oxidizing gas, although the conversions were much lower. Thus in the presence of sodium hydroxide the conversion fell from 51% to 25% and the yield from 65% to 59%. In the presence of potassium hydroxide the conversion fell from 54% to 21% and the yield from 66% to 64%.

A number of other alkylaromatic acids were oxidized with oxygen in aqueous sodium hydroxide solution to dibasic acids. While the conditions were not identical in every case, they were roughly comparable. These oxidations are summarized in Tables IV and V.

The authors are grateful to Mr. Leroy Jackson for the preparation of the toluic acids and to Dr. George F. Deebel for the *p*-ethylbenzoic acid. Mr. Ira F. Phelps and Mr. Paul L. Weintritt designed the gas-agitated autoclave and adapted the stirred autoclave for this application.

#### EXPERIMENTAL

*Apparatus.* The gas-agitated stainless steel bomb measured 14 $\frac{3}{4}$ " by 3 $\frac{3}{8}$ " I.D. and had a capacity of about 1.8 l. It was made of 304 stainless steel and had been hydrostatically tested for a pressure of 1000 psi. A 1000 lb. explosion disk was attached to the off gas line and the inlet line was equipped with a check valve. The oxygen, which was passed into the bottom of the bomb through a ring disperser (2 $\frac{1}{2}$ " circle) drilled with thirty-three  $\frac{1}{32}$ " holes, provided the agitation. The bomb was heated electrically. It had a flange type head equipped with a thermowell extending to the bottom of the bomb. The spent gas and vapors passed through a line leading to the top of a coil condenser, through the condenser, and into a separator. The spent gas then passed out of the top of the trap and the condensate returned to the bomb through a U-leg.

The American Instrument Company autoclave was a top stirred, 316 stainless steel bomb which measured 7" by 4 $\frac{1}{8}$ " I.D. It had a capacity of 1.5 l. and had been cold tested at 5000 psi. It was equipped with a paddle type stirrer (3" by  $\frac{3}{4}$ " blade) which could be operated at 300-435 rpm. Sufficient strip heaters were used to achieve a temperature of 300° within an hour's heating time. The packing was removed and the stuffing box washed thoroughly to remove all traces of oil. It was repacked with Teflon rings which were lubricated with 5% aqueous Santomerse (a sodium dodecylbenzene sulfonate). The oxygen was introduced through an open tube pointed into the stirrer. The off gas removal was the same as for the exploratory bomb.

*Raw materials.* The *o*-, *m*-, and *p*-toluic acids and the 3,5-dimethylbenzoic acid were prepared by the air-oxidation of *o*-, *m*-, and *p*-xylene and mesitylene, respectively. The conditions were similar to those used in Germany (2) except that 1% of cobalt hydrate was used as the catalyst rather than cobalt naphthenate. The xylene oxidations were carried to about 30-40% conversion, so that only a small amount of dibasic acid was produced. The amount of dibasic acid present in these products which were used as starting materials is shown in the various tables. The 3,5-dimethylbenzoic acid was obtained in 11% conversion and 29% yield, m.p. 164-165°<sup>1</sup> (170°) (3). Tar formation was appreciable. The methyl-

<sup>1</sup> All of the melting points are uncorrected.

phenoxyacetic acids were prepared by the method described by Higginbotham and Stephan (4). The *m*-methylphenoxyacetic acid was obtained in 64% yield, m.p. 100–101° (102°) (4) and the *p*-methylphenoxyacetic acid in 61% yield comprising two crops, m.p. 133.5–134.5° and 130–132° (135°) (4).

*Oxidations.* Unless otherwise indicated the charge for the gas-agitated autoclave comprised 100 g. of *p*-toluic acid, 73.5 g. of sodium hydroxide, 450 g. of water, and the catalyst in question. The oxygen flow was started at 700 psi. and the bomb was heated to 240° and held there for six hours. A substantial excess of oxygen was used and its rate of flow was controlled by the exhaust valves at between 31 l. and 45 l. per hour. At 240° and 700 psi. the oxygen partial pressure was about 210 psi. The oxygen then was turned off and the

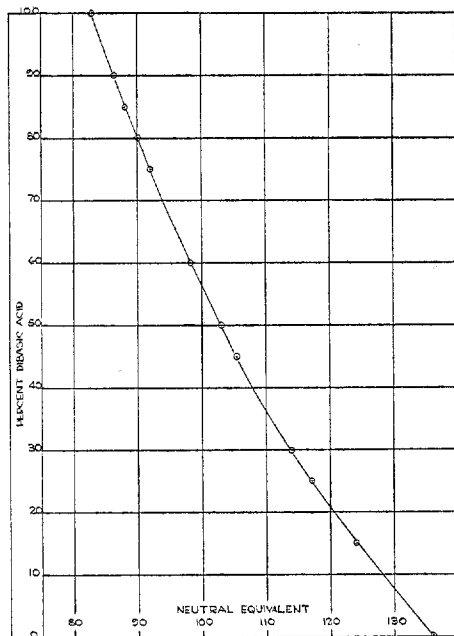


FIGURE 1. CONVERSION OF NEUTRAL EQUIVALENTS TO PERCENT DIBASIC ACID IN TOLUIC ACID-TEREPHTHALIC ACID MIXTURES

bomb allowed to cool to room temperature. It was emptied and rinsed with water. After the combined reaction mixture and washings had been filtered free of catalyst, they were heated to 50–70° with vigorous stirring and acidified with 10% sulfuric acid. The slurry was cooled to 15° and centrifuged. The product was washed twice by stirring with 1 l. of water and then centrifuging. It was dried to constant weight in a 50°-oven. The neutral equivalent of the product<sup>2</sup> was used to read the weight percent of terephthalic acid from the accompanying graph (Fig. 1). Since no products other than this acid ever were isolated, the remainder of the starting material evidently was burned to carbon dioxide.

In summarizing all of these oxidations two values are given: Percent conversion and percent yield. The percent conversion is the mole-percent of *p*-toluic acid charge, which is converted to terephthalic acid and the percent yield is the same figure corrected for recovered *p*-toluic acid.

For the American Instrument Company autoclave the charge comprised 150 g. of *p*-

<sup>2</sup> These neutral equivalents were determined by the analytical staff of this laboratory.

TABLE I  
CATALYST STUDY IN GAS-AGITATED AUTOCLAVE

| RUN NO. | CATALYST                                      | PROMOTER               | N.E. OF CHARGE | N.E. OF PRODUCT | PROD-UCT, G. | CONVER-SION, % | YIELD % |
|---------|---|------------------------|----------------|-----------------|--------------|----------------|---------|
| 1       | None  | None                   | 133.0          | 127.5           | 93           | 4.2            | 33      |
| 2       | KMnO <sub>4</sub>                             | None                   | 126.5          | 111.2           | 86           | 17.0           | 46      |
| 3       | SeO <sub>2</sub>                              | None                   | 126.5          | 110.9           | 86           | 17.0           | 46      |
| 4       | PbO <sub>2</sub>                              | None                   | 132.0          | 116.0           | 90           | 17.3           | 55      |
| 5       | K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> | None                   | 132.0          | 115.0           | 88           | 17.1           | 50      |
| 6       | KVO <sub>3</sub>                              | None                   | 132.0          | 116.0           | 90           | 17.1           | 57      |
| 7       | Fe <sub>2</sub> O <sub>3</sub>                | None                   | 123.9          | 101.7           | 85           | 28.6           | 55      |
| 8       | KVO <sub>3</sub>                              | Tetraethyl lead        | 130.4          | 112.2           | 89           | 20.3           | 56      |
| 9       | KVO <sub>3</sub>                              | Cobalt acetylacetonate | 130.4          | 112.4           | 89           | 20.6           | 58      |
| 10      | KVO <sub>3</sub>                              | <i>p</i> -Tolualdehyde | 130.4          | 99.3            | 90           | 39.7           | 68      |
| 11      | KVO <sub>3</sub>                              | Ascaridole             | 123.9          | 97.6            | 83           | 35.0           | 56      |

TABLE II  
CATALYST STUDY IN STIRRED AUTOCLAVE

| RUN NO.         | CATALYST   | N.E. OF CHARGE | N.E. OF PRODUCT | PRODUCT, G. | CONVERSION, % | YIELD, % |
|-----------------|--|----------------|-----------------|-------------|---------------|----------|
| 12              | None   | 129.5          | 103.2           | 134         | 32.7          | 64       |
| 13              | None   | 132.4          | 102.2           | 127         | 34.3          | 60       |
| 14              | Cr <sub>2</sub> O <sub>3</sub>                                 | 132.6          | 102.8           | 133         | 36.0          | 63       |
| 15              | Cobalt acetylacetonate   | 132.6          | 113.8           | 134         | 19.8          | 55       |
| 16              | CuCrO <sub>4</sub> ·2CuO·2H <sub>2</sub> O                     | 132.4          | 113.5           | 119         | 16.2          | 38       |
| 17              | CuCr <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O            | 129.5          | 103.2           | 121         | 28.7          | 51       |
| 18              | CoCrO <sub>4</sub>   | 129.5          | 97.5            | 126         | 39.6          | 61       |
| 19              | Fe(VO <sub>3</sub> ) <sub>3</sub>                              | 132.4          | 99.3            | 131         | 40.0          | 66       |
| 20              | PbCrO <sub>4</sub>   | 129.5          | 98.4            | 130         | 39.6          | 65       |
| 21              | AgOH   | 132.4          | 94.8            | 130         | 47.6          | 67       |
| 22              | Fe <sub>2</sub> O <sub>3</sub>                                 | 131.2          | 98.5            | 132         | 40.4          | 66       |
| 23              | KVO <sub>3</sub>   | 131.0          | 100.5           | 136         | 38.5          | 68       |
| 24              | KVO <sub>3</sub>   | 131.0          | 99.7            | 135         | 39.5          | 67       |
| 25              | CuO-Al <sub>2</sub> O <sub>3</sub>                             | 129.5          | 110.9           | 116         | 17.8          | 39       |
| 26              | MnO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>               | 129.5          | 115.7           | 129         | 13.9          | 44       |
| 27              | NiO-Al <sub>2</sub> O <sub>3</sub>                             | 129.5          | 112.4           | 129         | 18.8          | 51       |
| 28              | PbO-Al <sub>2</sub> O <sub>3</sub>                             | 129.5          | 103.1           | 130         | 31.6          | 60       |
| 29              | CoO-Al <sub>2</sub> O <sub>3</sub>                             | 124.6          | 92.9            | 119         | 41.2          | 55       |
| 30              | Fe <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> | 132.4          | 93.6            | 129         | 48.5          | 66       |
| 31 <sup>a</sup> | Fe <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> | 129.5          | 86.1            | 107         | 51.5          | 55       |
| 32 <sup>a</sup> | Fe <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> | 129.5          | 86.2            | 113         | 54.5          | 59       |
| 33              | Fe <sub>2</sub> O <sub>3</sub> -ZnO                            | 132.4          | 93.1            | 128         | 49.5          | 66       |
| 34              | Fe <sub>2</sub> O <sub>3</sub> -CeO <sub>2</sub>               | 132.4          | 96.9            | 131         | 43.7          | 66       |
| 35              | Fe <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub>               | 132.4          | 94.0            | 127         | 47.6          | 65       |
| 36              | Fe <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>               | 132.4          | 94.2            | 129         | 47.6          | 65       |
| 37              | Fe <sub>2</sub> O <sub>3</sub> -GeO <sub>2</sub>               | 132.4          | 96.0            | 127         | 43.8          | 64       |
| 38              | Fe <sub>2</sub> O <sub>3</sub> -MgO                            | 120.5          | 90.6            | 118         | 35.0          | 53       |
| 39              | Fe <sub>2</sub> O <sub>3</sub> -BeO                            | 120.5          | 95.4            | 121         | 43.2          | 54       |
| 40 <sup>b</sup> | Fe <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> | 132.6          | 100.7           | 133         | 37.8          | 65       |
| 41 <sup>b</sup> | Fe <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> | 132.6          | 102.0           | 135         | 35.8          | 66       |

<sup>a</sup> Time two hours. <sup>b</sup> Stirring speed 435 rpm.

toluic acid, 110 g. of sodium hydroxide, 675 cc. of water, and the catalyst in question. The operation of the bomb and the work-up of the reaction mixture were similar to those for the gas-agitated autoclave. The oxidations were made at 260–275° with an applied oxygen pressure of 1000 psi. At this temperature the oxygen partial pressure was about 320–120 psi. Off gas flows varied between 34.0 and 76.5 l. per hour. The product was precipitated at

TABLE III  
ALKALI VARIATIONS

| RUN NO.         | ALKALI  | TIME, MIN. | N.E. OF CHARGE | N.E. OF PRODUCT | PRODUCT, G. | CONVERSION, % | YIELD, % |
|-----------------|---|------------|----------------|-----------------|-------------|---------------|----------|
| 22              | 110 g. NaOH   | 60         | 131.2          | 98.5            | 132         | 40.4          | 66       |
| 42              | 180 g. KOH  | 60         | 129.5          | 90.7            | 131         | 54.5          | 69       |
| 43              | 44 g. NaOH + 88 g. Na <sub>2</sub> CO <sub>3</sub>  | 45         | 132.6          | 85.0            | 105         | 51.9          | 55       |
| 44              | 110 g. NaOH   | 60         | 132.6          | 91.7            | 127         | 51.0          | 65       |
| 45              | 146 g. Na <sub>2</sub> CO <sub>3</sub>              | 60         | 132.6          | 83.7            | 107         | 55.6          | 57       |
| 46              | 180 g. KOH  | 45         | 127.9          | 87.6            | 142         | 65.7          | 77       |
| 47              | 61.6 g. KOH + 114 g. K <sub>2</sub> CO <sub>3</sub> | 45         | 132.6          | 83.6            | 143         | 76.5          | 77       |
| 48              | 70 g. KOH + 114 g. K <sub>2</sub> CO <sub>3</sub>   | 37         | 136.1          | 91.0            | 145         | 61.8          | 79       |
| 49              | 75.1 g. KOH + 114 g. K <sub>2</sub> CO <sub>3</sub> | 30         | 127.9          | 86.7            | 131         | 62.7          | 70       |
| 50 <sup>a</sup> | 110 g. NaOH   | 60         | 132.6          | 109.2           | 133         | 25.4          | 59       |
| 51              | 180 g. KOH  | 60         | 132.6          | 90.1            | 126         | 53.7          | 66       |
| 52 <sup>a</sup> | 180 g. KOH  | 60         | 127.9          | 110.7           | 140         | 21.2          | 64       |

<sup>a</sup> Air used as the oxidizing gas.

TABLE IV  
OXIDATION OF OTHER ACIDS

| RUN NO.         | ACID OXIDIZED                 | GRAMS CHARGED | N.E.  | ALKALI      | WATER, G. |
|-----------------|-------------------------------|---------------|-------|-------------|-----------|
| 53 <sup>a</sup> | <i>p</i> -Ethylbenzoic        | 150           | —     | 150 g. NaOH | 825       |
| 54 <sup>b</sup> | <i>m</i> -Toluic              | 150           | 128.9 | 110 g. NaOH | 675       |
| 55 <sup>b</sup> | <i>m</i> -Toluic              | 150           | 128.9 | 180 g. KOH  | 675       |
| 56 <sup>b</sup> | <i>o</i> -Toluic              | 150           | 139   | 110 g. NaOH | 675       |
| 57              | 3,5-Dimethylbenzoic           | 62            | —     | 50 g. NaOH  | 675       |
| 58              | <i>m</i> -Methylphenoxyacetic | 150           | —     | 93 g. NaOH  | 675       |
| 59              | <i>m</i> -Methylphenoxyacetic | 142           | —     | 93 g. NaOH  | 675       |
| 60              | <i>p</i> -Methylphenoxyacetic | 100           | —     | 62 g. NaOH  | 1000      |
| 61              | <i>p</i> -Methylphenoxyacetic | 100           | —     | 62 g. NaOH  | 1000      |

<sup>a</sup> With 1.5 g. of Fe<sub>2</sub>O<sub>3</sub> catalyst. <sup>b</sup> Stirring speed 435 rpm.

80° and filtered in a Buchner funnel rather than centrifuged. The remaining procedure was the same.

*Catalysts and promoters.* In Table I are summarized a series of *p*-toluic acid oxidations in which 1.0-g. samples of various substances were tested as catalysts and promoters. These runs were made in the gas-agitated autoclave.

In Table II are summarized a series of *p*-toluic acid oxidations in which 1.5-g. samples of various substances were tested as catalysts. The catalysts containing alumina were prepared by coprecipitating equimolar quantities of the hydroxides and then roasting the precipitates in a muffle furnace at 500° for one hour. These runs were made in the American Instrument Company autoclave (300 rpm. stirring speed) for one hour. In run 23 1.5 g. of *p*-tolualdehyde also was added as a promoter.

*Alkali variation.* In Table III are summarized a series of *p*-toluic acid oxidations in which other alkaline materials were substituted for the sodium hydroxide. In runs 21 and 37 the catalyst was 1.5 g. of ferric oxide and the stirring speed was 300 rpm. In the other runs the catalyst was 1.5 g. of  $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$  and the stirring speed 435 rpm.

*Oxidation of other acids.* These oxidations were conducted in the American Instrument Company autoclave (300 rpm. stirring speed). The charges used besides the 1.5 g. of  $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$  catalyst are summarized in Table IV.

TABLE V  
CONDITIONS AND PRODUCTS

| RUN NO. | ACID OBTAINED                  | YIELD, G.    | N.E.  | CONVERSION, % | YIELD, % |
|---------|--------------------------------|--------------|-------|---------------|----------|
| 53      | Terephthalic                   | 135          | 104.5 | 52            | 77       |
| 54      | Isophthalic                    | 108          | 86.0  | 50.5          | 54       |
| 55      | Isophthalic                    | 111          | 88.0  | 48.6          | 55       |
| 56      | Phthalic                       | <sup>a</sup> | —     | 21            | 32       |
| 57      | 5-Methylisophthalic            | <sup>b</sup> | —     | 13            | 14       |
|         | Trimesic                       | <sup>b</sup> | —     | 4             | 4        |
| 58      | <i>m</i> -Carboxyphenoxyacetic | <sup>c</sup> | —     | } 4           | } 6      |
| 59      | <i>m</i> -Carboxyphenoxyacetic | <sup>c</sup> | —     |               |          |
| 60      | <i>p</i> -Carboxyphenoxyacetic | <sup>d</sup> | —     |               |          |
| 61      | <i>p</i> -Carboxyphenoxyacetic | <sup>d</sup> | —     | } 4           | } 6      |

<sup>a</sup> The reaction mixture was evaporated to dryness and the acids isolated largely as their ethyl esters. In this way 51.3 g. (38% recovery) of ethyl *o*-toluate, b.p. 100–101°/12 mm. (102.0–102.5°/13 mm.) (5),  $n_D^{25}$  1.5006 ( $n_D^{21.6}$  1.507) (5) and 47 g. of ethyl phthalate,  $n_D^{25}$  1.5040 ( $n_D^{14}$  1.5049) (6) were obtained. A sample of the latter was saponified to give phthalic acid, N.E. 85.7, 85.6. In addition 3.5 g. of unesterified phthalic acid was isolated, N.E. 83.4, 83.6. <sup>b</sup> The isolation was similar to the preceding using the methyl esters. Distillation of these esters yielded 4 g. (6% recovery) of methyl 3,5-dimethylbenzoate, b.p. 100–112°/12 mm. and crude methyl 5-methylisophthalate, b.p. 155°/12 mm.–175°/11 mm. which was crystallized from aqueous methanol. Two crops were obtained: 9 g., m.p. 94–95° (98°) (7) and 2 g., m.p. 92–94°. Extraction of the distillation residue yielded 4 g. of methyl trimesate, m.p. 145–146° (144°) (8). <sup>c</sup> Product isolation was identical with the preceding except that the two runs were combined. Distillation of the methyl esters yielded 128.4 g. (41% recovery) of methyl *m*-methylphenoxyacetate, b.p. 99°/3 mm.–101°/2 mm. (258°) (9),  $n_D^{25}$  1.5088–1.5105 and 14.3 g. of methyl *m*-carbomethoxyphenoxyacetate, b.p. 148–153°/3 mm.,  $n_D^{25}$  1.5223. The latter was saponified and the *m*-carboxyphenoxyacetic acid was crystallized from methanol, m.p. 202–206° (206–207°) (10). <sup>d</sup> Distillation of the product methyl esters yielded 65.8 g. (30% recovery) of methyl *p*-methylphenoxyacetate, b.p. 101–105°/2 mm. (257°/760 mm.) (9),  $n_D^{25}$  1.5091 and 11.6 g. of methyl *p*-carbomethoxyphenoxyacetate, b.p. 147–151°/2 mm., which was crystallized twice from aqueous methanol, m.p. 92.0–93.5° (92.0–92.7°) (11).

The oxidations were for one hour at 255–275°. Off gas flows varied between 26 and 54 l. per hour. The products obtained are summarized in Table V.

#### SUMMARY

*p*-Toluic acid has been oxidized to terephthalic acid in 77% conversion and yield in the presence of ferric oxide and potassium carbonate in potassium hydroxide solution with high pressure oxygen.

A new oxidation catalyst, comprising a mixture of iron and aluminum, zinc, cerium, titanium, zirconium, or germanium oxides, has been developed for use at high temperatures in the presence of aqueous caustic.

Catalytic activity under these conditions also was exhibited by cobalt chromate, iron vanadate, lead chromate, potassium metavanadate, and silver hydroxide.

Under similar conditions *p*-ethylbenzoic acid gave terephthalic acid, *m*-toluic acid gave isophthalic acid, *o*-toluic acid gave phthalic acid, and 3,5-dimethylbenzoic acid gave a mixture of 5-methylisophthalic and trimesic acids.

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