Catalytic Oxidation of *p*-Cymene in the Liquid Phase

C. E. SENSEMAN AND J. J. STUBBS

Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.

A study has been made of the catalytic effect of manganese dioxide in the liquid-phase oxidation of p-cymene, with oxygen as the oxidizing agent. Particular efforts were made along two lines: the preparation of the oxide in a finely divided form that could be well suspended in the liquid, thus lending itself to the best possible surface action; and the efficient breaking up of the oxygen stream to give a similar effect. A description of the apparatus is given, as well as the detailed method of preparing the catalyst. Runs were made also to determine the accelerating value of a number of other metallic oxides. Tables show relative temperature, time, and catalytic values.

Oxidation products identified were: p-toluic acid, p-tolylmethyl ketone, formaldehyde, formic acid, terephthalic acid, water, and carbon dioxide.

IN HIS research on the liquid-phase oxidations of various aromatic hydrocarbons, with no catalysts, Stephens (*3*) found that 100 grams of *p*-cymene heated to 85° C. for 14 days with oxygen bubbling through it yielded 1.23 grams of cumic aldehyde and 0.81 gram of cumic acid. Also, he found that, when 50 grams were heated to 102–104° C., other conditions remaining the same, 0.96 gram of *p*-tolylmethyl ketone as well as some cumic acid and aldehyde were formed; and finally that 50 grams of *p*-cymene and 25 grams of water, when oxidized at the boiling point for 18 days, yielded 1.8 grams of *p*-tolylmethyl ketone, but no acid or aldehyde. From 50 grams of ethylbenzene oxidizing at a temperature of 110–115° C. for 24 days, he obtained 9.5 grams of acetophenone. None of this ketone was found after passing oxygen for 31 days through 50 grams of ethylbenzene and an equal weight of water at the boiling point.

In studying the catalytic oxidation of ethylbenzene, King, Swann, and Keyes (*1*), operating at a temperature of 102–104° C. for 24 hours and using a high-speed stirrer for bringing about better contact of liquid and gas, found that the yield of acetophenone increased from 1.67 per cent, when no catalyst was used, to 20.6 per cent when 2 per cent of manganese acetate was used as a catalyst. Various oxides and other acetates showed little accelerating value.

In an investigation of the vapor-phase partial oxidation of *p*-cymene, the authors (*2*) observed that, when a finely divided manganese dioxide was used as a catalyst at the relatively low temperature of 300° C., slight explosions occurred. This result, together with the data obtained by the previously mentioned investigators, led to the conclusion that the oxidation of *p*-cymene in the liquid phase probably could be greatly accelerated under the catalytic influence of a manganese compound. Some preliminary runs were made in an apparatus essentially the same as that described later to ascertain the relative catalytic values, if any, of manganese acetate and manganese dioxide. It was found that the passage of oxygen through the heated mixture of *p*-cymene and manganese acetate always resulted in the formation of a sludge by the latter substance on the porous disk, which prevented the steady flow of oxygen. It was observed, also, that the salt turned brown, owing undoubtedly to the formation of an oxide of manganese; to this could probably be attributed any catalytic effect. Since the finely divided manganese dioxide showed definite accelerating value and did not present the difficulty encountered with the acetate, its catalytic value and that of manganese toluate were investigated further; later a less detailed study was made of the effect of the oxides of chromium, iron, nickel, cobalt, and cerium.

EXPERIMENTAL PROCEDURE

PREPARATION OF MANGANESE DIOXIDE. A modification of Witzemann's method (*4*) for preparing this oxide from permanganate and formaldehyde solution was found to give a very active form. Thirty-seven and a half grams of potassium permanganate were dissolved in one liter of hot water and cooled to 15° C. or under. The formaldehyde solution was made up by adding 20 cc. of 40 per cent formaldehyde and 1 gram of sodium carbonate to 100 cc. of water. About 90 cc. of this well-cooled solution, or enough to destroy the permanganate color, were slowly added to the cold permanganate. This gave a very finely divided oxide that remained suspended for a considerable period. After filtering and washing thoroughly, it was dried in the oven at 80° C. Before using, it was ground well in a mortar. Heating over a low flame did not change its effectiveness. The yield of the oxide was approximately quantitative.

MANGANESE *p*-TOLUATE. This substance was prepared by adding a concentrated manganese acetate solution to a concentrated solution of sodium *p*-toluate, filtering and washing the precipitated manganese *p*-toluate, and drying over calcium chloride. The salt is slightly pink in color, and, when added to hot *p*-cymene, a portion of it forms a dark brown suspension which remains as such for a long period. This behavior of the salt in the *p*-cymene indicates the formation of an oxide to which its catalytic value is attributed.

Other metallic oxides shown in Table III had some catalytic value, but of such order that space need not be given to the methods of preparation.

APPARATUS. In order to obtain a finely divided stream of oxygen through the liquid, an alundum disk of approximately 3 cm. diameter was fitted tightly into the base of the Pyrex reaction chamber, as shown in Figure 1. To insure against leakage of gas around the edges of the disk, water glass was used. The cylinder was heated in the oven and later over a free flame.[1] Oxygen measured by a meter was led in from a cylinder as shown. A mercury safety tube was placed in line to denote any back pressure which developed when some catalysts were used that did not disperse well in the *p*-cymene. With any indication of clogging, manual stirring was employed to clean the disk and reëstablish the normal pressure. With

---

[1] At the time this investigation was nearing completion, Keyes and Snow published in the University of Illinois Engineering Experiment Station Bulletin 238 a similar method of bringing about intimate contact of liquid and gas in the partial oxidation of ethyl alcohol.

the manganese dioxide which gave best results, excellent dispersion and stirring were obtained by the well-broken stream of oxygen.

A side-arm delivery tube was sealed into the reaction chamber to carry off water or other volatile products formed in the reaction. Some *p*-cymene escaped with these products but was readily condensed and recovered.

In operating the apparatus, the glycerol bath was brought to the desired temperature, and 42 grams of purified *p*-cymene, together with the catalyst, were poured into the reaction chamber. Oxygen was then passed through the apparatus at a definite rate for the desired period of time. At the end of the run the product in the reaction chamber was weighed and examined as outlined below.

ANALYSIS OF PRODUCTS. When oxidizing at temperatures of 140–160° C. with 100 cc. of oxygen per minute and manganese dioxide as a catalyst, the following products were found in the reaction mixtures taken from the oxidizing chamber:

	IDENTIFICATION METHOD
p-Cymene	B. p., 178° C.
p-Toluic acid	M. p., 180.2° C.; b. p., 274–275° C.; neutralization equivalent, 136
p-Tolylmethyl ketone	B. p., 225–226° C.; m. p. of its oxime, 87.4° C.; m. p. of its semicarbazone, 202–203° C.
Terephthalic acid (small quantities present only after long period of oxidation)	M. p. of methyl ester, 138–139° C.
Dark brown resin	....

Test for aldehydes with the fuchsin reagent was negative.

Tests for alcohols with (1) sodium and (2) 3, 5-dinitrobenzoyl chloride were negative.

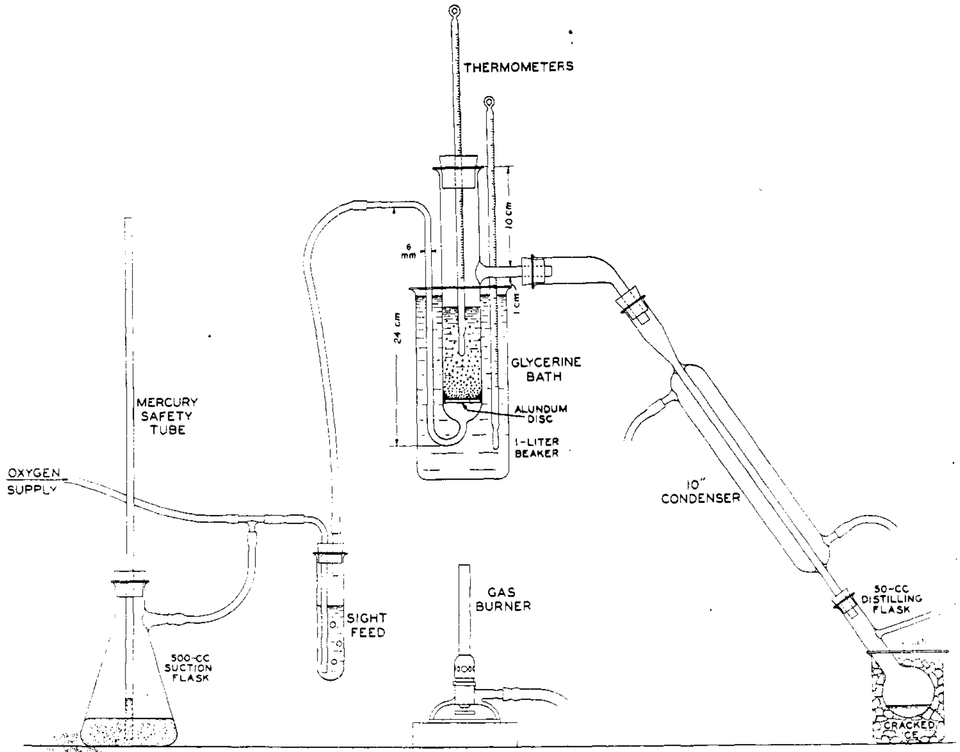


FIGURE 1. APPARATUS FOR LIQUID-PHASE OXIDATION

In the condensates collected in the ice bath, the following were found:

	IDENTIFICATION METHOD
p-Cymene	B. p., 178° C.
Water	B. p., 100° C.; cupric sulfate test
Formaldehyde	Resorcinol test
Formic acid	Mercuric oxide test

Carbon dioxide and formaldehyde were identified in the uncondensed gas.

In the various comparative runs, quantitative data were collected on the amount of *p*-toluic acid formed and the *p*-cymene unattacked. For obtaining these, the following method was used:

The material from the oxidizing chamber was shaken in a separatory funnel with sodium bicarbonate solution to take up the acid products. Following this separation, dilute sulfuric acid was added to the water solution, the liberated organic acid was extracted with ether, and this solution was washed with small amounts of water until free of sulfuric acid. It was then made up to a definite volume, an aliquot was removed, the ether was evaporated, and a small quantity of alcohol and several volumes of water were added. It was titrated with 0.1 *N* sodium hydroxide solution, phenolphthalein being used as an indicator. From this titration the quantity of acid was calculated. For determining the *p*-cymene unattacked, the residue remaining after the acid was extracted with sodium bicarbonate was distilled in several fractions. That boiling above *p*-cymene was treated in the cold with concentrated sulfuric acid, a separation was made, and the portion insoluble in the sulfuric acid was again distilled. Some *p*-cymene was recovered in this manner. To these quantities was added that obtained from the condensate in the ice bath.

DISCUSSION OF RESULTS

In the four tables showing the effects of different variables, the percentage of *p*-cymene recovered from each run has been calculated from distillation results. These data in turn have been used in calculating the percentage of acid obtained from the *p*-cymene attacked. Inasmuch as more or less loss is always inherent in a distillation method, the same degree of accuracy cannot be claimed for them as for the other data given. However, they give an approximation of the efficiency and extent of the oxidation, and it is believed that a more accurate analytical procedure would have indicated greater efficiency of the process.

In Table I are given the results obtained through variation in temperature with 100 cc. of oxygen per minute over a period of 5 hours. In the experiment made at a temperature of 170° C., much *p*-cymene was carried over and collected in the

TABLE I. TEMPERATURE EFFECT[a]

TEMP.	*p*-CYMENE Recovered	*p*-CYMENE Attacked	*p*-TOLUIC ACID YIELD	Based upon *p*-cymene attacked	Based upon *p*-cymene in charge
° *C.*	%	*Grams*	*Grams*	%	%
140	36.9	26.5	10.1	38.1	24.0
150	38.1	26.0	12.0	46.1	28.6
160	21.4	33.0	13.7	41.5	32.6
170	25.0	31.5	13.9	44.1	33.1[b]

[a] All runs made with 42 grams *p*-cymene, 1 gram manganese dioxide, 100 cc. oxygen per minute, and an oxidizing period of 5 hours.

[b] *p*-Cymene distilling over was returned to reaction chamber at end of second, third, and fourth hours.

TABLE II. TIME EFFECT[a]

TIME	*p*-CYMENE Recovered	*p*-CYMENE Attacked	*p*-TOLUIC ACID YIELD	Based upon *p*-cymene attacked	Based upon *p*-cymene in charge
Hours	%	*Grams*	*Grams*	%	%
2	50.0	21.0	6.6	31.4	15.7
4	28.6	30.0	10.6	35.3	25.2
5	21.4	33.0	13.7	41.5	32.6

[a] Conditions of runs: 42 grams *p*-cymene and 1 gram manganese dioxide in charge, and 100 cc. of oxygen per minute, at 160° C.

TABLE III. VARIATION IN FORM AND QUANTITY OF MANGANESE CATALYST[a]

CATALYST	*p*-CYMENE Recovered	*p*-CYMENE Attacked	*p*-TOLUIC ACID YIELD	Based upon *p*-cymene attacked	Based upon *p*-cymene in charge
	%	*Grams*	*Grams*	%	%
1 gram MnO_2	21.4	33.0	13.7	41.5	32.6
0.21 gram MnO_2	20.2	33.5	13.4	40.0	31.9[b]
0.8 gram manganese *p*-toluate[c]	29.8	29.5	12.5	42.4	29.8
0.8 gram manganese *p*-toluate[c]	25.2	31.4	15.7	50.0	37.4[d]
0.247 gram commercial 85% MnO_2[c]	25.0	31.5	4.45	14.1	10.6[e]

[a] Conditions: 42 grams *p*-cymene in charge, and 100 cc. of oxygen for 5 hours at 160° C.

[b] Obtained 10 grams of resin.

[c] Manganese dioxide equivalent, 0.21 gram.

[d] Oxygen used, 100 to 120 cc. per minute.

[e] Obtained by distillation 10.5 grams *p*-tolylmethylketone (33$^1/_3$ per cent weight yield based upon *p*-cymene attacked).

receiver in the ice bath. This was returned to the reaction chamber at the end of the second, third, and fourth hours. Otherwise the increasing viscosity of the reacting mass, due to acid and resin formation, would not have permitted the continued and ready passage of oxygen. For the same reason, runs at temperatures of 160° C. could not be consistently carried beyond the 5-hour period. Under the conditions of the experiment, *p*-tolylmethyl ketone, which is an intermediate product in the oxidation of *p*-cymene to *p*-toluic acid, is apparently easily oxidized to the acid. At the end of 2 and 4 hours, when the acid found was 31.4 and 35.3 per cent, respectively, of the *p*-cymene attacked, as shown in Table II, only small quantities of the ketone were found. In only one case was much of this compound observed to be present—that in which a commercial precipitated 85 per cent manganese dioxide was used. In recovering the *p*-cymene from this 5-hour run, it was observed that much more than the usual amount of the ketone was present. A double distillation yielded 10.5 grams, or 33$^1/_3$ per cent, of the *p*-cymene attacked. The reaction during this run seemed as vigorous as when the specially prepared oxide was used. The formation of water, carbon dioxide, and formaldehyde was observed almost immediately after starting the oxygen. The *p*-toluic acid yield, however, was only 4.45 grams, or 14.1 per cent, of the *p*-cymene attacked. These results are given in the last line of Table III. Other data in this table reveal that 0.21 gram of the specially prepared oxide, or 0.5 per cent of the *p*-cymene used, checks closely the results obtained when 1 gram, or 2.3 per cent, of catalyst was used; also, that manganese *p*-toluate, whose behavior in *p*-cymene is described under the preparation of the salt, accelerated the reaction in a similar manner, and, that by increasing the flow of oxygen from 100 cc. per minute to 100–120 cc., the yield of acid was greater than that for any other run. (Partial clogging of the alundum disk caused the slowing of the flow of oxygen during the run.)

In Table IV are given comparative data on the accelerating values of different oxides for acid production. Attention is called to the fact that, although the yields obtained when using other oxides did not approach those obtained when using manganese dioxide, methods were not available for producing them under the more favorable conditions of low temperature and semi-colloidal state.

TABLE IV. EFFECT OF VARIOUS CATALYSTS[a]

CATALYST	*p*-CYMENE Recovered	*p*-CYMENE Attacked	*p*-TOLUIC ACID YIELD	Based upon *p*-cymene attacked	Based upon *p*-cymene in charge
	%	*Grams*	*Grams*	%	%
None	73.8	11.0	0.38	3.5	0.9
MnO_2	21.4	33.0	13.70	41.5	32.6
Cr_2O_3	36.9	26.5	4.50	17.0	10.7
Co_2O_3	28.6	30.0	3.06	10.2	7.3
CeO_2	42.4	24.2	2.76	11.4	6.6
Fe_2O_3	35.7	27.0	2.70	10.0	6.4
Ni_2O_3	41.9	24.4	2.62	10.7	6.2
CuO	32.1	28.5	2.45	8.6	5.8

[a] Conditions: 42 grams *p*-cymene and 1 gram oxide in charge, and 100 cc. of oxygen per minute for 5 hours at 160° C.

CONCLUSIONS

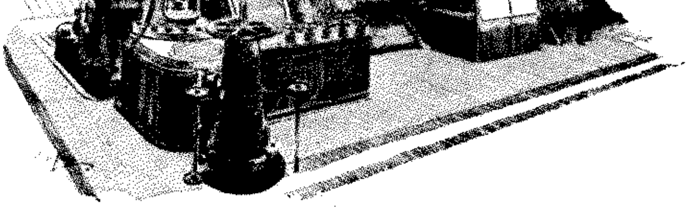
The oxidation of *p*-cymene, at elevated temperatures, to *p*-toluic acid by means of well-dispersed oxygen is greatly accelerated by the use of a specially prepared manganese dioxide catalyst which suspends well in the *p*-cymene. Similar results are obtained when manganese *p*-toluate is used. Under the conditions of the experiment a commercial grade of manganese dioxide gave a much lower yield of *p*-toluic acid but yielded 33$^1/_3$ per cent of *p*-tolylmethyl ketone.

Other metallic oxides of much less accelerating value are: chromium, cobalt, cerium, iron, nickel, and copper.

LITERATURE CITED

(1) King, Swann, and Keyes, IND. ENG. CHEM., **21**, 1227 (1929).
(2) Senseman and Stubbs, *Ibid.*, **23**, 119 (1931).
(3) Stephens, *J. Am. Chem. Soc.*, **48**, 1824, 2920 (1926).
(4) Witzemann, *Ibid.*, 37, 1079 (1915).

RECEIVED June 9, 1932. Contribution 211 from the Color and Farm Waste Division, Bureau of Chemistry and Soils



Courtesy Bromborough Port Estate