

(6) A ratio of 3 parts by weight of sulfuric acid (sp. gr. 1.84) to 1 part of guanidine nitrate will give nitroguanidine in yields of 92 per cent. The temperature should be maintained below 0° during the nitration period, and the guanidine nitrate should be ground to a uniform fineness of 80 mesh.

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Catalytic Oxidation of *p*-Cymene in the Vapor Phase^{1,2}

C. E. Senseman and J. J. Stubbs

BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE, WASHINGTON, D. C.

THE great interest shown in catalytic vapor-phase oxidations of organic compounds during the last decade or more has resulted in a number of well-known successes. Particular reference is made to the oxidation of the aromatic hydrocarbons, naphthalene (1), benzene (2), and anthracene (3).

Gibbs (4) has found that passing a mixture of toluene and air over vanadium pentoxide at temperatures between 200° and 400° C. oxidizes the side chain to benzaldehyde and benzoic acid. Using molybdenum, uranium, and tantalum oxides as catalysts for vapor-phase oxidations, Craver (5) has reported the formation of aldehydes from a number of aromatic hydrocarbons, including *p*-cymene. These achievements led the authors to investigate by a similar process the possibilities of oxidizing *p*-cymene, using vanadium pentoxide as a catalyst. It is well known that this compound is a reactive hydrocarbon and is readily oxidized to a number of compounds in the liquid phase through the use of potassium permanganate, nitric acid, or chromic acid.

Apparatus and Its Operation

The apparatus used is shown in Figure 1.

The carbureter, as well as its inlet and outlet, the reaction chamber, and air and ice condensers were made of Pyrex glass.

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An investigation has been made to determine the possibilities of catalytically oxidizing *p*-cymene, by means of air, to one or more products which would be of commercial interest.

Granular fused vanadium pentoxide and the same oxide from ammonium metavanadate deposited on unglazed porcelain seemed to offer some promise as catalysts. Other catalysts were tried out, but results indicated less efficiency. By using vanadium pentoxide, data were collected primarily on the effect of reaction temperatures and space velocities. Tables are included showing the effects of these variables.

Reaction products qualitatively detected were water, carbon dioxide, formaldehyde, and formic, *p*-toluic, and terephthalic acids. The method used for the separation of *p*-toluic acid from any water-soluble acid and its quantitative determination is given.

The apparatus, of which a drawing and description are included, was much the same as that in general laboratory use for this type of research.

The desired carbureter temperature was maintained by heating its glycerol bath with a gas burner, the temperature being determined by a thermometer immersed in the bath. The reaction chamber had an internal diameter of 2.1 cm. and was heated by means of a properly insulated electric heater. Other dimensions are shown in the drawing. The temperature of the catalyst was determined by a thermometer of 6.1 mm. diameter with its bulb tip situated 2 cm. from the exit end of the catalyst. The thermometer itself was tested for accuracy before and several times during the series of runs. In most cases 20 cc. of the space in the reaction chamber was occupied by the catalyst, the unoccupied portion being sufficient for heating the mixed

gases to the desired temperature before they entered the catalyst zone. That such was the case was shown by inserting a thermocouple in the reaction chamber and measuring the temperatures at various points. The male and female parts of the ground-glass joint at the exit of the reaction chamber were reversed from that generally encountered, the purpose of this being to obviate the necessity either for placing the joint in the furnace or for the scraping of solid reaction products from the end of the reaction tube for analysis.

In the operation of the apparatus, cymene, previously washed with caustic soda solution and distilled from sodium, was placed in the 50-cc. test-tube carbureter to a definite height, and weighings were made before and after each experiment in order to determine the exact quantity used. Air for the vaporization of the hydrocarbon, hereafter referred to as primary air, was taken from the house-pressure line through a needle-valve control, thence to a dry meter and into the heated cymene. The outlet tube of the carbureter had, as indicated, an opening on the side in order that the free passage of gases would not be

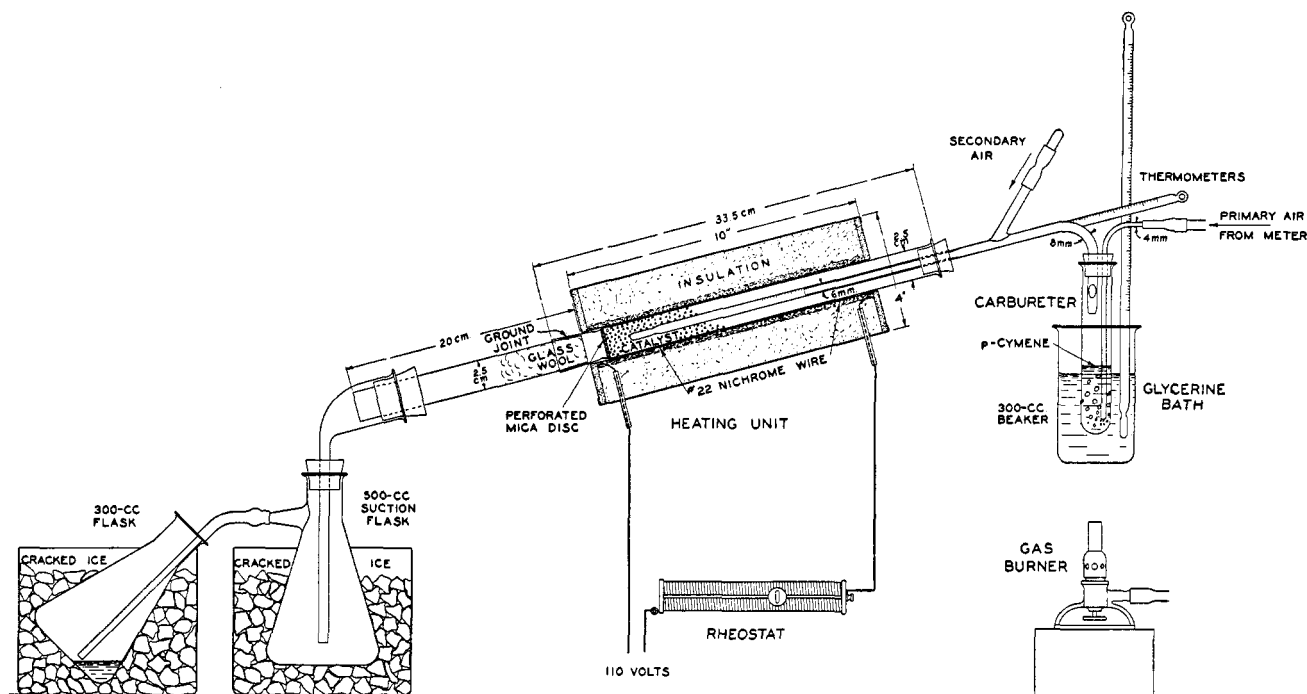


Figure 1—Catalytic Vapor-Phase Oxidation Apparatus

interfered with by the return of any cymene which might condense in the cooler section of the outlet tube.

Provision was made for leaning the mixture of gases by sealing a glass arm into this tube between the carbureter and reaction chamber to permit, if desired, the use of any quantity of metered secondary air. After conditions were somewhat established, this air inlet was seldom used and was kept closed.

At the beginning of each run a small amount of glass wool was placed in the fore part of the air condenser to collect as much as possible of the oxidation products. The uncondensed products carried in the residual air passed on through two flasks immersed in ice baths where further condensation occurred.

Analysis of Products

In the combined condensates there were found water, formaldehyde, formic acid, *p*-toluic acid, terephthalic acid, and unattacked cymene. In the effluent gases, carbon dioxide was present, and there could at times be detected the odors of cuminic and *p*-toluic aldehydes. Formaldehyde was readily identified in the aqueous condensate by its odor, and after distillation its presence was confirmed by the Fuchsine aldehyde reagent. Formic acid was detected by making alkaline the water-soluble portion of the reaction product, evaporating to low volume, acidifying, distilling, and applying the mercuric oxide test. *p*-Toluic acid was identified by a melting point of 178.5° C. after crystallization from 33 per cent alcohol and confirmed by its neutralization equivalent of 135 with 0.1 *N* alkali. Terephthalic acid was identified through the melting point of its dimethyl ester, 139° C. The previous qualitative data were collected through the examination of the oxidation products obtained during a number of preliminary runs only. Tests of this material for other water-soluble acids were negative. However, the possibility of the formation of these under different conditions were recognized, and hence the heading in the tables is given as "Water-soluble acid calculated as formic." Quantitative data were collected on the production of *p*-toluic acid as well as of the water-soluble acid, all of which was calculated as formic acid after making solubility corrections for *p*-toluic acid. The method used was as follows:

The three condensers were well washed out with water at a temperature of approximately 5° C. All these washings carried out some dissolved and some undissolved *p*-toluic acid, as well as all formic acid. While this solution was being maintained for some time at a temperature of 5° C., the condensers were being washed with hot water to dissolve all remaining *p*-toluic acid. To this solution was later added the *p*-toluic acid filtered from the cold-water portion. Both solutions were then titrated with 0.1 *N* sodium hydroxide, phenolphthalein being used as indicator. The solubility of *p*-toluic in water at 5° C. had been previously determined as 0.1938 gram per liter. The presence of small amounts of formic acid did not alter this solubility. The volume of cold water was measured and its titration value determined. The amount of *p*-toluic acid present was then calculated and added to that determined as present in the hot-water portion. After the proper correction for the *p*-toluic acid in the cold water was made, the residual acid was calculated as formic.

Terephthalic acid is very insoluble in both hot and cold water. However, if its presence was indicated by any suspended matter in the hot-water portion it was filtered before being titrated.

Catalysts Used

FUSED VANADIUM PENTOXIDE—For the preparation of this catalyst, a commercial grade of the brown powder was utilized. After fusion the crystalline mass was broken up, and granules averaging about one-half the size of rice grains were utilized. The preliminary passage of air-cymene mixture over this catalyst was necessary in order to bring it to its most active state.

VANADIUM PENTOXIDE ON PORCELAIN—In preparing this material, pieces of unglazed porcelain somewhat larger than the crystals of fused vanadium pentoxide previously described were used. These were well covered with a saturated solution of ammonium metavanadate, the water was evaporated, and the heating continued until the ammonia was driven off and a deposit of the brown pentoxide left on the porcelain. In order to obtain a good deposit on this oxide, the process was repeated six times. This catalyst, after a short preliminary heating in the reaction chamber to insure the absence of all moisture and ammonia, operated at its maximum efficiency.

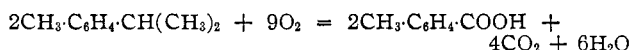
TIN VANADATE—This salt was reported by Maxted (4)

to give a yield of approximately 50 per cent benzoic acid in the oxidation of toluene. In the oxidation of cymene at 290° C. and higher yields of acids in the present experiments were much below that obtained with either form of the oxide. Granular tin vanadate as well as that deposited on porcelain was tried.

MANGANESE DIOXIDE—A finely divided oxide was obtained by the Witzemann method (?) of reducing a concentrated solution of potassium permanganate with formaldehyde. This was well washed, dried, and used in the form of small granules. The passage of air-cymene mixture over this material resulted in a reaction difficult to control. At a temperature of 300° C. mild explosions occurred.

Discussion of Results

Qualitative tests after a number of preliminary runs of wide temperature, space-velocity, and cymene-concentration variations showed the presence of the previously mentioned reaction products. The results obtained lead to the conclusion that in the oxidation of cymene the molecule is most readily attacked at the CH— group. Results to be published later on the liquid phase oxidation point to the same conclusion. As a basis for calculating the amount of air required, the following reaction was assumed as completed:



For this reaction approximately 4.6 liters of air were required to 1 gram of cymene. The various runs throughout the investigation showed the need of using three to six times the calculated amount of air. Within this range comparable yields of the acids could be obtained. Decreasing amounts of air resulted in noticeable increases in the production of aldehydes, particularly at the lower temperatures.

All runs recorded in the tables were made with primary air only, and the average length of run was approximately 4 hours. With each increased air rate, the carbureter temperature was increased in order to give constant air-cymene mixtures as nearly as possible. Notwithstanding this, variations occurred as noted in the tables, but all concentrations are within the above mentioned limits.

Table I—Temperature Effect

RUN	REACTION-CHAMBER TEMP. ° C.	SPACE VELOCITY Liters	CYMENE PER LITER AIR Gram	ACID YIELD ^a		SPACE-TIME YIELD <i>p</i> -TOLUIC ACID Gram
				<i>p</i> -Toluic %	Water-sol. calcd. as formic %	
1	300	246	0.039	7.1	...	0.0007
2	325	237	0.048	8.8	Trace	0.0010
3	350	246	0.051	12.4	2.4	0.0016
4	360	255	0.044	13.7	3.1	0.0016
5	375	225	0.040	14.8	5.3	0.0013
6	400	246	0.046	12.9	6.3	0.0014
7	375	240	0.038	15.2	9.8	0.0014 ^b

^a Weight yield, based upon loss of cymene from carbureter.

^b Catalyst, vanadium pentoxide on porcelain; all others, fused vanadium pentoxide.

In Table I is shown the effect of variation in the temperature of the reaction chamber, while the space velocity is 225 to 255. (Space velocity is defined as the liters of air used per hour per liter of catalyst space.) With fused vanadium pentoxide as catalyst and space velocities as shown, it is seen that a temperature of 375° C. resulted in the highest yield of *p*-toluic acid, whereas a temperature of 400° C. increased the yield of water-soluble acid. The results for run 7, with vanadium pentoxide on porcelain, are given in Table I for the purpose of direct comparison under similar conditions with the results obtained when the fused oxide is used. With this change in the catalyst there was a striking increase in the yield of water-soluble acid.

The space-time yield (grams produced per hour per centimeter, of catalyst space) of *p*-toluic acid are recorded as calculated from the results obtained from each run.

It is believed, however, that, in some instances, these figures do not accurately represent the maximum space-time yields that could be obtained at the temperatures and space velocities given. For example, had the cymene concentration in run 5 been increased to such an amount (approximately 0.06 gram per liter) that the actual percentage of *p*-toluic acid would not have been decreased, the space-time yield would be approximately 0.002 gram.

In Table II are recorded the best results obtained from a large number of runs in studying space-velocity effects at temperatures of 375° and 400° C. with vanadium pentoxide on porcelain at 375° C. and the fused oxide at 400° C. as catalysts. The temperatures given are uncorrected for stem emergent beyond the reaction chamber. While data for necessary corrections could not be obtained for each run when they were so obtained and calculations made thereon, the maximum correction was found to be +7° C. Reference to the tables shows that the increasing corrections for higher temperatures would have but slight effect upon the yields of acid. Highest yields were obtained through the use of the deposited oxide with the added advantage, as previously pointed out, that, after thorough drying, it was in its most active state, whereas the fused oxide did not reach its maximum activity until several runs had been made.

Table II—Space-Velocity Effect

RUN	REACTION-CHAMBER TEMP. ° C.	SPACE VELOCITY Liters	CYMENE PER LITER AIR Gram	ACID YIELD ^a		SPACE-TIME YIELD <i>p</i> -TOLUIC ACID Gram
				<i>p</i> -Toluic %	Water-sol. calcd. as formic %	
CATALYST, VANADIUM PENTOXIDE DEPOSITED ON PORCELAIN						
7	375	240	0.038	15.2	9.8	0.0014
8	375	278	0.042	16.2	9.6	0.0019
9	375	290	0.047	16.7	9.2	0.0023
10	375	300	0.052	16.9	7.7	0.0026
11	375	315	0.061	16.2	7.4	0.0031
12	375	375	0.062	15.9	6.1	0.0032
CATALYST, FUSED VANADIUM PENTOXIDE						
13	400	225	0.052	11.1	6.5	0.0013
6	400	246	0.046	12.9	6.3	0.0015
14	400	285	0.057	15.0	5.7	0.0024
15	400	330	0.054	13.1	5.9	0.0023
16	400	450	0.069	12.2	5.2	0.0036
17	400	600	0.052	10.0	3.5	0.0031

^a Weight yield, based upon loss of cymene from carbureter.

Conclusions

By using vanadium pentoxide as a catalyst and air as an oxidizing medium, it was possible to obtain from *p*-cymene a number of reaction products. Those qualitatively detected were water, carbon dioxide, formaldehyde, formic acid, *p*-toluic acid, and terephthalic acid.

Optimum conditions found for the production of *p*-toluic acid were: reaction temperature, 375° C.; and space velocity, 300, with 3 to 6 times the theoretical amount of air.

Higher yields of acids were obtained through the use of vanadium pentoxide deposited on porcelain than by using the granular fused oxide.

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