It is interesting to recall at this point that Ivanov (*12*) reported in 1933 that the condensate obtained by the polymerization of so-called ethylene concentrate in the presence of zinc chloride at 320–360° C. and superatmospheric pressure was made up of a mixture of paraffin, aromatic, naphthene, and olefin hydrocarbons. The amount of the olefins present was stated not to exceed 30 per cent.

Conclusions

The following data were obtained from the fractionation of the liquid products under the various conditions shown in Table I:

Exptl. Temp. ° C.	Chief Constituents Present in Liquid Product						Product Distilling in the Motor Gasoline Range (to 200° C.)
	C_5	C_6	C_7	C_8	C_9	C_{10-12}	
	Per cent by volume						
290–310	5.8	10.1	5.9	12.9	18.7	27.3	74.5
200–210	0.07	7.0	1.6	2.0	47.0	32.0	85.9
150–160	0.3	10.6	1.2	1.7	55.9	24.1	92.0

As the experimental temperature was lowered, a successively higher percentage of the liquid product corresponded to the tripolymer of propylene, represented by the C_9 compounds.

Corresponding to the above data, the distillation curve of the 290–310° C. product showed prominent peaks pointing to C_8, C_9, and C_{10-12} compounds, with somewhat lower peaks for the C_5, C_6, and C_7 compounds. The distillation curves of the 200–210° C. and 150–160° C. products had very pronounced peaks corresponding to C_9 compounds, and somewhat lower peaks for C_{10-12} compounds. The C_5, C_7, and C_8 compounds were present only in small amounts.

From a comparison of the properties of the fractions comprising the peaks of the distillation curves with those of known hydrocarbons of similar boiling point, conclusions were drawn regarding the probable composition of the fractions. No evidence was found of the presence of aromatic hydrocarbons. The data indicated the presence of appreciable amounts of naphthenic hydrocarbons in certain of the fractions, in addition to olefins and paraffins.

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4-CHLOROACETOPHENONE

Catalytic Oxidation in the Liquid Phase

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ACETOPHENONE and its derivatives are easily oxidized by the usual oxidizing agents to the corresponding benzoic acids. Recently VanArendonk and Cupery (*6*) showed that 4-chloroacetophenone and other derivatives can be oxidized in good yields with sodium hypochlorite. The writers (*5*) found that, although under carefully controlled conditions good yields of acetophenone could be obtained by the catalytic oxidation of ethylbenzene in the liquid phase, there was a tendency toward further oxidation of the ketone to benzoic acid; this behavior was especially evident at slightly elevated temperatures. Flemming and Speer (*1*) recently extended the scope of their patented process for the liquid-phase oxidation of aliphatic ketones to include the oxidation of acetophenone. A yield of 25 grams of benzoic acid and 7 grams of formic acid is claimed when 50 grams of acetophenone in acetic acid is oxidized for 12 hours at 105° C. in the presence of a small quantity of manganese acetate by means of air bubbled through a filter plate at the rate of 5 liters per hour.

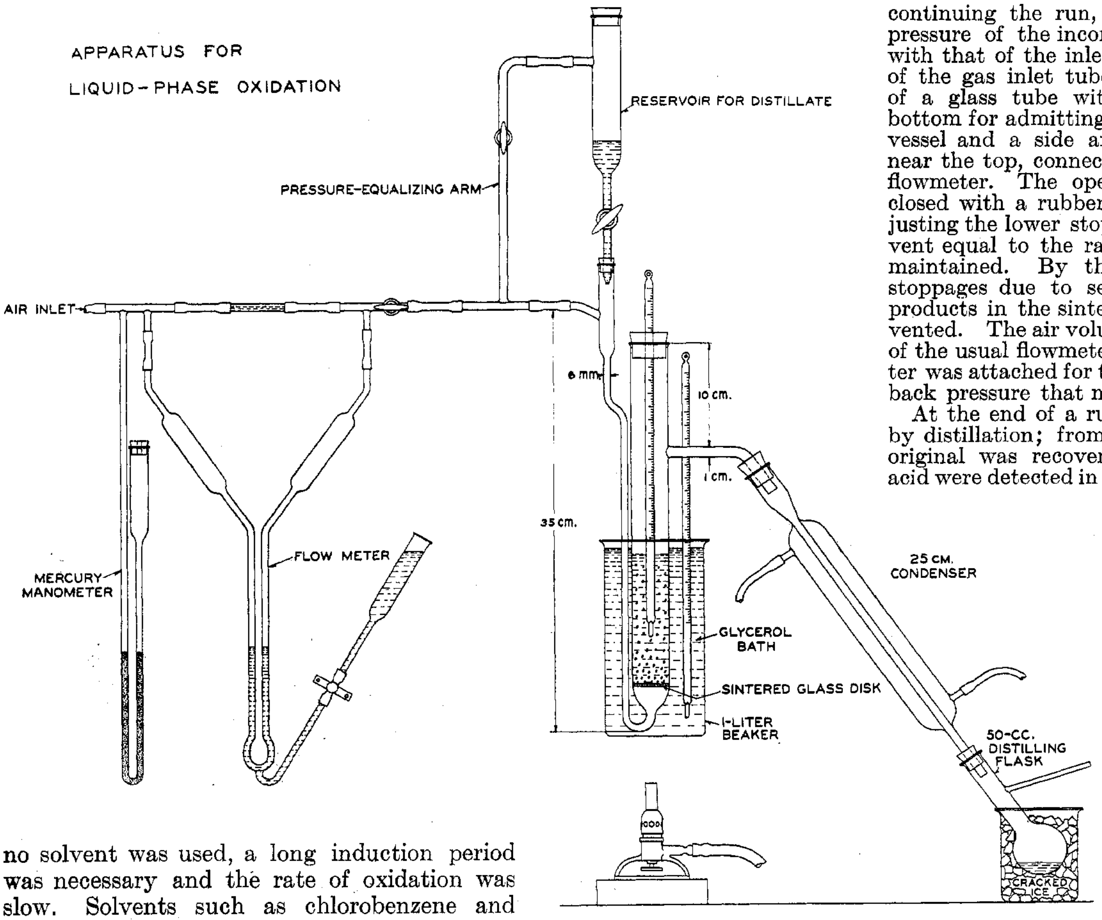
The recent work of Groggins and Nagel (*2*) showing that both acyl groups of acid anhydrides can be made to react with aromatic compounds in the Friedel and Crafts condensation by using increased proportions of aluminum chloride indicates that acetophenones might well be used as a starting material for the production of certain substituted benzoic acids. Thus, Newton and Groggins (*3*) described the preparation of 4-chlorobenzoic acid by the oxidation of 4-chloroacetophenone with chromic anhydride, 95 per cent yields being obtained.

The purpose of the present investigation was to determine the optimum conditions of temperature and of time for the production of 4-chlorobenzoic acid by the liquid-phase catalytic oxidation of 4-chloroacetophenone, using atmospheric oxygen as the oxidizing agent.

Oxidation Experiments

The experiments in general consisted of passing air, dispersed by a sintered glass disk, through a solution of 10 grams of 4-chloroacetophenone in 100 ml. of glacial acetic acid in the presence of 0.5 gram of specially prepared manganese dioxide (*4*). Preliminary experiments had shown that, when

The oxidation of 4-chloroacetophenone in the liquid phase, using manganese dioxide as a catalyst and air as the oxidizing agent, is studied. An apparatus is described, and optimum conditions of temperature and time for the production of 4-chlorobenzoic acid are determined. Yields of the acid in excess of 90 per cent are obtained.



APPARATUS FOR LIQUID-PHASE OXIDATION

no solvent was used, a long induction period was necessary and the rate of oxidation was slow. Solvents such as chlorobenzene and xylene were found unsatisfactory.

Almost immediately after an experiment was started, the color of the reaction mixture changed from brown to dark cherry red. When this color was maintained, the oxidation appeared most vigorous, as evidenced by the evolution of carbon dioxide. At times, especially at the beginning of an experiment when a large excess of ketone was present, there was a tendency for the manganese dioxide to dissolve in the acetic acid, forming a colorless solution. When entirely dissolved, the catalyst showed no activity whatever. The reduction of the catalyst to this inactive state could be prevented by increasing the flow of air, by lowering the temperature, or by adding the ketone in small increments during the reaction. The rate of flow of air was maintained at 250 ml. per minute, since that was the approximate capacity of the apparatus.

Run No.	Temp.	Catalyst	Time	4-Chlorobenzoic Acid	
	° C.		*Hours*	*Grams*	%
1	110–112	None	3	0	0
2	100	Prepared MnO_2[a]	3	8.34	82.3
3	110–112	Same	2	8.10	80.0
4	110–112	Same	2.5	8.80	86.9
5	110–112	Same	3	9.29	91.7
6	110–112	Same	3	9.20	90.8
7	125[b]	Same	3	9.20	90.8
8	110–112	Same	5	9.00	88.8
9	110–112	Manganese acetate	3	8.84	87.2
10	110–112	Commercial MnO_2[c]	3	4.40	43.4

[a] The preparation of this catalyst was described in a former paper (*4*).
[b] Propionic acid used as solvent.
[c] Pulverized 85 per cent MnO_2.

The figure shows diagrammatically the apparatus used in the experiments:

The reaction vessel consisted of a Pyrex glass cylinder, with a diameter of 31 mm. and a capacity of 175 ml.; a sintered glass disk was fused in near the bottom, and a small-bore glass inlet tube was sealed on below for admitting air. In order to return any solvent which distilled over during the reaction without discontinuing the run, a reservoir in which the pressure of the incoming air could be equalized with that of the inlet tube was placed at the top of the gas inlet tube. This reservoir consisted of a glass tube with a glass stopcock at the bottom for admitting the solvent to the reaction vessel and a side arm with a glass stopcock, near the top, connected to the air line from the flowmeter. The opening of the reservoir was closed with a rubber stopper. By properly adjusting the lower stopcock, a steady flow of solvent equal to the rate of evaporation could be maintained. By thus returning the solvent, stoppages due to separation of solid reaction products in the sintered glass disk could be prevented. The air volume was measured by means of the usual flowmeter, and a mercury manometer was attached for the purpose of detecting any back pressure that might develop in the system.

At the end of a run the solvent was removed by distillation; from 80 to 90 per cent of the original was recovered. Only traces of formic acid were detected in the distillate. The 4-chlorobenzoic acid was then dissolved in 10 per cent sodium hydroxide solution, filtered to remove manganese hydroxide, and subsequently extracted with ether to remove any unreacted ketone. The aromatic acid was then precipitated with dilute hydrochloric acid, filtered, washed with water, and dried in the oven. In the experiments in which maximum yields were obtained, the aromatic acid was recovered by distilling off the solvent, during which process the manganese dioxide was converted to manganous acetate. The residue was washed with approximately 600 ml. of water, filtered, and dried. This treatment gave a product with a neutralization equivalent of 156 and a melting point of 238° to 240° C.; the melting point of 4-chlorobenzoic acid is 242.5° to 243.4° C. When this product was dissolved in sodium hydroxide, filtered, extracted with ether, and precipitated with hydrochloric acid as in the first method, the melting point was 240° to 242° C.; the neutralization equivalent remained the same.

The table includes data on temperature and time variations with a specially prepared manganese dioxide catalyst (*4*). The highest yields were obtained at 110° to 112° C. during 3 hours. Since this temperature was the maximum that could be obtained when acetic acid was used as a solvent, a run was made with propionic acid at 125° C., and approximately the same yield was obtained. The yield of acid was not raised by increasing the duration of the run from 3 to 5 hours.

A comparison of the catalytic efficiency of manganese acetate and of commercial precipitated manganese dioxide (85 per cent) with the specially prepared manganese dioxide indicates that the latter is a superior catalyst.

Acknowledgment

The writers are indebted to H. P. Newton of this division for suggesting the possibility of preparing 4-chlorobenzoic acid from 4-chloroacetophenone by this method of oxidation.

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