- (15) Makowwiecki, J. Russ. Phys. Chem. Soc., 40, 752 (1908).
- (16) Mason and Wheeler, J. Chem. Soc., 121, 2079 (1922).
- (17) Masson and Hamilton, IND. ENG. CHEM., 19, 1335 (1927). Ibid., 20, 813 (1928).
 Moore, J. Soc. Chem. Ind., 36, 109 (1917)
- (20) Paterno and Spallino, Atti acad. Lincei, [5] 16, I 87 (1906).
- (21) Reid and Hoffman, IND. ENG. CHEM., 21, 695 (1929).
- (22) Taffanel and Le Floch, Compt. rend., 157, 469 (1913). (23) Tanaka and Nagai, Proc. Imp. Acad. (Tokyo), 2, 219 (1926).
- Tanaka and Nagai, J. Soc. Chem. Ind. Japan, 29, 266 (1926). (24)
- (25) Thompson, IND. ENG. CHEM., 21, 134 (1929).

(26) Wurtz, Ann. chim., [3] 69, 323 (1863).

RECEIVED May 23, 1933. Published by permission of the Director, U. S

Bureau of Mines. (Not subject to copyright.)

Catalytic Oxidation of Ethylbenzene in the Liquid Phase

C. E. SENSEMAN AND J. J. STUBBS, Bureau of Chemistry and Soils, Washington, D. C.

N A PREVIOUS article (4) the authors presented data - on the liquid-phase oxidation of p-cymene in which a finely divided manganese dioxide prepared by reducing potassium permanganate with formaldehyde was used as a catalyst. It was shown that this oxide had a decidedly accelerating effect upon the reaction.

After that investigation it was decided to make a similar study of the catalytic value of this same oxide in the oxidation

of ethylbenzene, looking particularly toward the production of acetophenone, an organic chemical of increasing importance. In studying the mechanism of the oxidation reactions of a number of hydrocarbons, Stephens (5) found that acetophenone is produced in considerable quantity when oxygen is passed through ethylbenzene over a long period of time and no catalyst is used. King, Swann, and Keyes (3) found that manganese acetate catalyzed this reaction to the extent that 20.6 per cent of the ketone, based upon the initial material, was formed during a period of 24 hours, the reaction being carried out at a temperature of 102° to 104° C. Neither of these investigations showed the formation of the alcohol, phenylmethylcarbinol, or the further oxidation of acetophenone to benzoic acid. Binapfl and Krey (1) claim that, after passing oxygen through ethylbenzene for 7 hours at a temperature of 130° to 140° C., using as an oxygen carrier manganous hydroxide precipitated on marble powder, 59 per cent of the ethylbenzene is recovered and a residue (quantity not stated) is obtained consisting of 80 per cent acetophenone and 20 per cent phenylmethylcarbinol.

EXPERIMENTAL PROCEDURE

A technical grade of ethylbenzene was distilled, and the fraction boiling at 135° to 137° C. was used. The catalyst, manganese dioxide, was prepared according to the method described in a former article (4). Except for the changes noted, the apparatus was also the same as described therein. For greater convenience in operation, an accurately calibrated flowmeter was substituted for the mechanical dry meter, and a sintered disk made of powdered Pyrex glass was sealed into the bottom of the reaction chamber as a substitute for the alundum disk. This glass disk gave better dispersion of the oxygen gas, resulting in better contact of gas, liquid, and catalyst, and better agitation.

In conducting the experiments, 50 grams of ethylbenzene and 0.5 gram of catalyst were poured into the reaction cham-

The catalytic action of manganese dioxide in the liquid-phase oxidation of ethylbenzene has been studied, with particular emphasis on the formation of acetophenone. Phenylmethylcarbinol is found as a reaction product in almost constant quantities after oxidation periods of 5.75 hours or more. An explanation is advanced for this constancy of yield. Reaction products identified were: water, carbon dioxide, formaldehyde, phenylmethylcarbinol, acetophenone, and benzoic acid.

ber, which was then placed in a glycerol bath previously heated to approximately the desired temperature, and the flow of oxygen was started. After the oxidizing period, the weight of the material in the reaction chamber was obtained, as well as that of the products which had distilled off during the course of the run and had been condensed and collected in a flask immersed in an ice bath.

ANALYSIS OF PRODUCTS. Oxidation products detected qualitatively were:

	IDENTIFICATION METHOD				
Phenylmethylcarbinol	M. p. of the acid phthalic ester, 108-108.5° C. (cor.); neutralization equivalent of this ester, 267				
Acetophenone Benzoic acid	 M. p. of the phenylhydrazone, 102-103° C. (cor.) M. p., 121.2° C. (cor.); neutralization equivalent, 123 				
Formaldehyde Carbon dioxide Water	Resorcinol test Barium hydroxide test Cupric sulfate test				

The phenylmethylcarbinol, acetophenone, and benzoic acid were determined quantitatively as follows:

The solution of these three in ethylbenzene as taken from the reaction chamber was thoroughly extracted with aqueous sodium bicarbonate solution which reacted with any uncombined acid. The aqueous solution was then treated with dilute sulfuric acid and the liberated organic acid extracted with ether. After washing the ether solution free of all sulfuric acid, it was made up to a definite volume, an aliquot was removed, the ether was evapo-rated, alcohol and water were added, and the acid was titrated with 0.1 N sodium hydroxide solution, phenolphthalein being used as an indicator. From this titration result, the total quantity of acid was calculated. From the material insoluble in the bicarbonate solution, ethyl-

benzene was removed by distilling at atmospheric pressure from a long-neck distilling flask, after which the residue was distilled long-neck distilling flask, after which the residue was distilled under reduced pressure to avoid possible decomposition of the alcohol. The alcohol fraction contained also the acetophenone. The weights of both fractions were obtained. To a one-gram sample of the mixture of ketone and alcohol, acetic acid was added. The acetophenone was precipitated as the phenylhydra-zone, which was filtered off, washed with 50 per cent alcohol, dried, and weighed. From this weight the total acetophenone was calculated. The alcohol in the mixture was determined by the acetylation method of Gildemeister and Hoffmann (2). the acetylation method of Gildemeister and Hoffmann (2).

DISCUSSION OF RESULTS

Table I has been compiled primarily to show the effect of the temperature variable. By the inclusion of the first and last runs given, comparison is also made between results obtained when using no oxide, a finely divided commercial manTABLE I. TEMPERATURE EFFECT

(50 grams ethylbenzene; 0.5 gram catalyst; length of run, 5.75 hours; 125 cc. of oxygen per minute)

			ETHYLBENZENE		YIELDS OF OXIDATION PRODUCTS ^a					
Run	TEMP	CATALYST	Re- covered	Unre- covered	Acetophenone		Benzoic acid		Phenylmethyl- carbinol	
	° C.		Grams	Grams	Grams	%	Grams	%	Grams	%
1	115	None	46.0	4.0	0.6	High-boiling fraction	Trace	•••	Not determined	
2	110	MnO_2	38.0	12.0	3.8	31.7	Trace		1.4	11.7
3	115	MnO_2	32.3	17.7	9.7	54.8	Trace		2.9	16.3
4	120	MnO_2	28.1	21.9	5.7	26.0	8.0	36.5	2.8	12.8
5	130, 1150	MnO_2	25.0	25.0	15.8	63.2	1.24	5.0	3.1	12.4
6	130, 1155	Commercial MnO ₂	45.0	5.0	0.9	18.0	Trace	••	Not de	termined

All percentage yields are weight yields based upon ethylbenzene unrecovered; yields of oxidation products are calculated from analytical data.
 A temperature of 130° C. was maintained for approximately 45 minutes, then lowered to 115° C.

ganese dioxide, and the specially prepared dioxide. That the latter has a decidedly accelerating effect is conclusive.

Table I further shows that the rate of attack upon the ethylbenzene molecule, as well as the relative amounts of acetophenone and benzoic acid formed, is greatly influenced by small temperature variations.

In both Tables I and II the amount of ethylbenzene unrecovered in each run was arrived at by subtracting from the weight of the charge (50 grams) the weight recovered by distillation after acid extraction, plus the weight of the hydrocarbon distilling over during the run and collected in the flask in the ice bath. The inherent losses of this procedure account for the relatively high amounts of ethylbenzene designated as unrecovered, as compared with the total oxidation products recovered. The percentage yield of each oxidation product was calculated as a weight yield based upon the weight of ethylbenzene unrecovered.

TABLE II. TIME EFFECT

(50 grams ethylbenzene; 0.5 gram catalyst; 125 cc. of oxygen per minute; temperature, 130° C. for approximately 45 minutes and 115° for remainder of the time)

					IELDS (of Oxid/	TION	PRODUCT	's	
		Ethylbenzene						Phenyl-		
-	-	Re-	Unre-	Aceto- phenone		Benz	zoic	methyl- carbinol		
Run	TIME	covered	covered			aci	d			
	Hours	Grams	Grams	Grams	%	Grams	%	Grams	%	
1	4.5	42.0	8.0	2.2	27.5	Trace		1.2	15.0	
2	5.75	25.0	25.0	15.8	63.2	1.24	5.0	3.0	12.4	
3	8	25.5	24.5	11.8	48.1	4.10	16.7	3.0	12.2	
4	10ª	23.8	26.2	14.4	55.0	6.44	24.5	2.5	9.5	
a '	The tem	perature	was 115°	for the	entire 1	period.				

While making various runs at a given temperature for the entire period, it became evident that an appreciable induction period was necessary, after which the reaction proceeded much more rapidly, this being indicated by less heat requirements and greatly increased production of carbon dioxide. In order to lessen this period, runs were then made with an initial temperature of 130° C. until such time as the reaction became more vigorous, usually 45 minutes or more. The temperature was then lowered as indicated in Tables I and II and continued thus for the remainder of the period in an effort to keep down the production of acid which would have resulted at the higher temperature. Comparison of runs 3 and 5, Table I, shows an increased production of acetophenone as a result of this procedure. A 10-hour run made at 130° C. gave a yield of 16.6 grams of acid and 1.2 grams of acetophenone, 55.3 and 3.9 per cent, respectively, based upon the ethylbenzene unrecovered.

The results obtained by increasing the oxidation periods are

shown in Table II. While it is obvious in comparing runs 2 and 3 that oxidation progressed at different rates, it is also evident that acetophenone production is not increased by extending the oxidation period beyond 5.75 hours.

In all runs listed in the two tables, 125 cc. of oxygen per minute were used. Other experiments showed that considerable variations in this volume affected the yields very little; there was always an excess of oxygen over that absorbed which aided in the agitation.

In both tables, when experiments were run at 115° C. for 5.75 hours or longer, the quantities of phenylmethylcarbinol formed were quite uniform. Stephens (5) in his work on oxidation without catalysts found that when 21 grams of ethylbenzene were subjected to oxidation for 11 days at 122° to 124° C., 6.3 grams of acetophenone were produced but no alcohol was formed. When 25 grams of phenylmethylcarbinol were similarly oxidized, only 0.85 gram of acetophenone was formed. He concluded from this, and from his results from other oxidations, that any alcohol formed is not an intermediate product but rather a by-product with formation due to some "exceptional conditions." If we assume that the catalytic oxidation is one of alternate oxidation and reduction of the metallic oxide, giving rise to momentary atomic oxygen, a very different condition exists from that which he had, and one which might produce the alcohol as a by-product. If the alcohol, being in low concentration in the reaction mixture and having, as Stephens found, a slow oxidation rate when not diluted, is very slowly oxidized to the ketone, it can be readily understood that the concentration of the alcohol might reach a point where its oxidation to the ketone would approximate its rate of formation from ethylbenzene. The concentration of the alcohol would then change but little through the remainder of the oxidation period. An explanation is thus given for the uniformity of alcohol yields, which tends toward a confirmation of Stephens' theory.

LITERATURE CITED

- Binapfl and Krey, U. S. Patent 1,813,606 (July 7, 1931).
 Gildemeister and Hoffmann, "Volatile Oils," tr. by Kremers, 2nd ed., Vol. 1, p. 575, Wiley, 1920. tr. by Edward
- (3) King, Swann, and Keyes, IND. ENG. CHEM., 21, 1227 (1929).
- (4) Senseman and Stubbs, Ibid., 24, 1184 (1932)
- (5) Stephens, J. Am. Chem. Soc., 48, 1824, 2920 (1926); 50, 2523 (1928).

RECEIVED June 20, 1933. Contribution 227 from the Color and Farm Waste Division, Bureau of Chemistry and Soils.

for the control of insects and plant diseases. In addition to general educational activities, the Mexican Department of Agricul-ture has also established a large fumigation plant at Guadalajara, and is understood to be contemplating the establishment of others in different parts of the country.

AGRICULTURAL INSECTICIDES IN MEXICO. The use of agricultural insecticides in Mexico is not extensive, and the develop-ment of the market lies in further educating the Mexican agriculturist in the importance of attempting to control insects and diseases affecting plant life. Considerable educational material is being disseminated by the

Mexican Department of Agriculture with a view to increasing the use of insecticides and fungicides, this department being thoroughly cognizant of the importance of spraying and dusting

Perhaps the principal factors to be overcome in the development of the market are the low purchasing power of the great majority of Mexican farmers and the conservative methods employed in the cultivation of their fields.