TABLE III. COMPARISON OF DATA WITH VALUES GIVEN IN THE LITERATURE (*5*)[a]

Weight % Alcohol	15° C. γ (Fig. 2)	15° C. γ (*5*)	25° C. γ (Fig. 2)	25° C. γ (*5*)	30° C. γ (Fig. 2)	30° C. γ (*5*)
2.33	62.0	62.8	60.8	61.2	60.2	60.8
5.94	55.3	54.6	54.0	53.6	53.4	52.3
15.93	43.1	42.4	41.8	41.1	41.2	40.3
29.67	33.8	33.9	33.1	32.6	32.8	32.1
43.64	29.1	29.7	28.5	28.8	28.2	28.2
61.10	27.4	27.2	26.7	26.3	26.3	26.0
75.68	25.8	25.6	25.0	24.9	24.6	24.7
92.72	23.6	24.2	22.9	23.3	22.5	22.5

[a] The values under γ (*5*) were taken (by graphical interpolation) from the data of the International Critical Tables, derived from the measurements of Traube (*11*), Bircumshaw (*1*), and Morgan and Neidle (*7*).

A steel base was attached to the apparatus and a split rubber stopper was placed around the filling tube. The apparatus was supported in the bath by a clamp attached from the stopper to a ring stand and was checked with a plumb line to make sure it was in a truly vertical position. The cylinder, containing the hydrometer and liquid mixture, was also placed in the bath and supported by a clamp attached to the ring stand.

The stirrer was started and the heating coil turned on. At intervals of approximately 15° C. the height of the capillary rise, the hydrometer reading, and the difference in height of the mercury levels were recorded. The temperature range covered was from room temperature to several degrees above the atmospheric boiling point.

The height of the rise of the liquid in the capillary was measured with a cathetometer (by difference). Before each reading the cathetometer was leveled. Three or four readings were taken, and the arithmetical average of the differences was considered the value of h (capillary rise). The difference in level of the mercury in the manometer was also determined with the cathetometer.

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Vapor-Phase Esterification of Benzoic Acid with Ethyl Alcohol

Effect of Oxides on Catalytic Activity of Silica Gel

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REID (*18*) has reviewed the recent work in the field of esterification. His survey cites the progress made in manufacture and indicates the need for research to find the proper catalyst for the reaction and to establish the optimum conditions for a given esterification. In studying ester formation both in the liquid and vapor phase, the system ethyl alcohol–acetic acid has been most commonly used. Other aliphatic or aromatic systems have not been extensively investigated up to the present time.

The formation of ethyl acetate from ethyl alcohol and acetic acid has been the subject of much research. Frolich, Carpenter, and Knox (*8*) and Edgar and Schuyler (*6*) used zirconium oxide as a catalyst; Milligan and Reid (*16*) and Reid (*18*) used silica gel; Sandor (*20*) investigated vanadium pentoxide, cobalt oxide, cesium oxide, and silica gel; Mailhe (*15*) compared thorium oxide, zirconium oxide, and titanium oxide; a patent (*4*) described the use of magnesium oxide and manganese dioxide. Dreyfus (*5*) described the use of alkali and alkali metal compounds as catalysts, and Winkler and Hinshelwood (*22*) used hydrogen chloride to catalyze the formation of ethyl acetate at 450° C.

Esters of ethylene glycol and acetic acid in the vapor phase were prepared catalytically by Turova, Pollack, and Dzioma (*21*), using activated carbon impregnated with phosphoric acid.

Brown and Reid (*2*) passed vapors of ethyl and butyl alcohols over tungstic oxide, alumina, thoria, and silica gel to prepare the respective esters. Lazier (*12, 13*) described the production of several esters by passing alcohols over mixtures of various oxides. He used, among others, oxides of zinc, chromium, manganese, magnesium, cesium, vanadium, tungsten, uranium, copper, cadmium, and lead. Legg and Bogin (*14*) passed butyl alcohol over fused and crushed cupric oxide.

Sabatier (*19*) showed that the reaction velocity for esterification was greater with aliphatic acids than with benzoic acid and its analogs in both the liquid and vapor state. Jaegar (*9*) claims reaction and formation of ethyl benzoate from benzoic acid and ethyl alcohol at 200° to 350° C. when passed in the vapor phase over a mass containing at least

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one "permutogenetic" or base-exchange material. Negative results for the esterification of β-naphthol and salicylic acid with methyl alcohol were reported by Chelberg and Heisig (*3*) using a silica gel catalyst activated by Patrick's method. However, Korolev (*11*) found this reaction to be catalyzed by silica made by precipitating silica with hydrochloric acid and drying at 40° C. for 2 weeks.

The catalytic mechanism is still subject to much discussion, and several investigations have been made to explain the catalysis on the basis of adsorption of vapors. Klosky (*10*), Alvarado and Pearce (*1*), and Ott and Pierce (*17*) investigated the relation of adsorption to the catalytic effect for the formation of ethyl acetate. Information on the vapor-phase catalytic formation of esters of aromatic acids is incomplete. It was therefore decided to study this particular reaction in the vapor phase, using the simplest aromatic acid. Ethyl alcohol was chosen as the esterifying alcohol because the solubility of benzoic acid in it is favorable. The difficultly reducible oxides are good dehydrating agents for vapor-phase work and were therefore used in this investigation.

Experimental

MATERIALS. Benzoic acid of U. S. P. grade was used as obtained. Sublimation was found to be unnecessary since the yields were the same with sublimed and unsublimed acid.

Ethyl alcohol was distilled twice from calcium oxide and once from sodium.

The titanium tetrachloride and the salts used were all of C. P. grade.

The silica gel, 4–8 mesh, was furnished by the Davison Chemical Company.

CATALYSTS. Titanium hydroxide was precipitated on the carrier by hydrolysis of titanium tetrachloride. All other catalysts were prepared by soaking the carrier in a saturated solution of the salt for 30 minutes, adding ammonium hydroxide, filtering, and igniting the catalyst mass.

APPARATUS. A diagram of the apparatus is shown in Figure 1. The solution was displaced by mercury and vaporized in the first part of the quartz tube. The vapors then passed over the catalyst and were condensed in a water-cooled condenser. The reaction temperature was measured by a thermocouple enclosed by a glass shield.

PROCEDURE. The reaction solution was a mixture of 5 moles of alcohol to 1 mole of benzoic acid. At least 20 cc. of vaporized solution were passed through the apparatus before the first sample was taken. After any change during a run at least 10 cc. were displaced before a sample was taken under the new conditions.

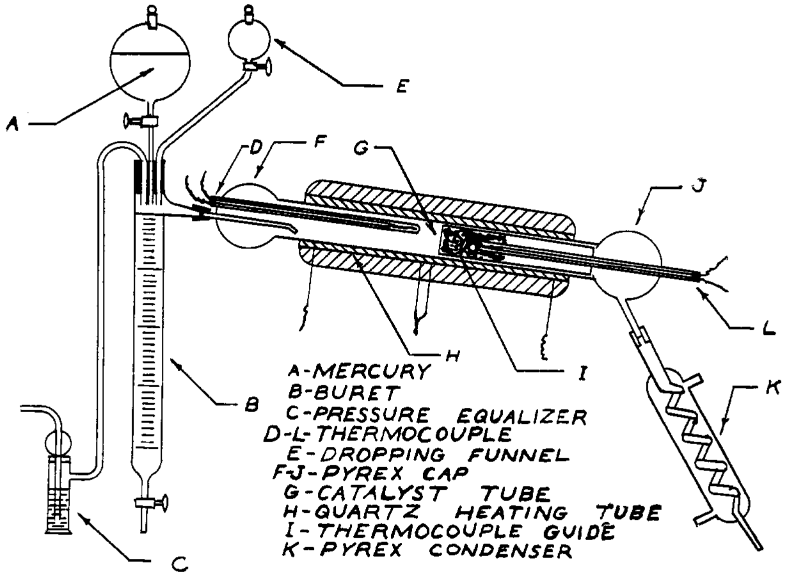

FIGURE 1. APPARATUS FOR VAPOR-PHASE ESTERIFICATION

The vapor-phase esterification of benzoic acid with ethyl alcohol was investigated using as catalysts eleven difficultly reducible oxides suspended on silica gel. The maximum value of the conversion of benzoic acid to ethyl benzoate was 87 per cent with titanium oxide as a catalyst.

A decrease in space velocity resulted in an increase in per cent yield of ester, and a plot of space velocity against per cent conversion of benzoic acid showed a limiting value at zero space velocity which differed for most catalysts.

Each catalyst had a characteristic temperature giving maximum ester formation and minimum carbonization. The reaction temperature was found to be between 370° and 450° C.

The analysis was accomplished by titration for the free acid and hydrolysis for the ester. Some aldehyde resin was formed during hydrolysis, but it was found that these resins did not affect the accuracy of the analysis.

The optimum temperature for each catalyst was determined, and the variation of ester formation with a variation in rate was investigated at the optimum temperature. Since the first sample of the rate run duplicates the conditions under which the sample was taken at that temperature in the temperature run, it was possible to note any change in activity of the catalyst.

Results

A thermal run showed no ester formation in the temperature range used in these tests, but as Table I shows, silica gel does exert considerable catalytic effect. In the tables space velocity is expressed in liters of vapor per hour per liter of catalyst at the reaction temperature. Table I also shows the results of typical measurements made on other catalysts. Table II lists the optimum temperatures for each catalyst tested and percentage conversions at three different space velocities. These space velocities represent the upper and lower limits of flow obtainable with accuracy by this method. The variation from catalyst to catalyst is due to the fact that it was extremely difficult to reproduce the rates exactly. All of these results are from a reaction mixture of 5 moles of alcohol and 1 mole of ethyl alcohol.

All catalysts tried caused esterification, but not all gave conversions better than silica gel itself. Zirconium oxide, barium oxide, manganous oxide, and titanium oxide on silica gel were better than silica gel; magnesium oxide and chromic oxide were about the same; aluminum oxide, strontium oxide, and beryllium oxide were definitely poorer. There was a marked difference in the maximum temperature which could be used for each catalyst. Above 430° C. with silica gel a dense cloud was formed which could not be condensed, and the yield was small. Titanium

Table I. Effect of Four Catalysts

Temp., ° C.	Space Velocity of Acid	% Acid to Ester	% Acid to Side Reactions	Temp., ° C.	Space Velocity of Acid	% Acid to Ester	% Acid to Side Reactions
Silica Gel				Titanium Oxide			
370	123	42	5	370	270	84	..
390	37	59	11	390	278	84	..
390	77	53	8	390	139	75	6
390	137	47	..	390	70	87	10
410	131	49	..				
430	134	48	..				
Magnesium Oxide				Strontium Oxide			
410	295	35	5	390	276	12	7
430	304	39	5	410	284	16	17
450	312	39	8	430	292	16	17
430	304	39	5	410	284	16	16
430	152	49	5	410	142	20	14
430	76	57	10	410	71	26	9

oxide on silica gel gave the same effect at about 400° C.; with calcium oxide on silica gel this difficulty did not appear below 460° C. This cloud formation was also accompanied by a heavy carbonization of the catalyst. In general, the temperature range for the esterification reaction can be placed between 370° and 450° C. for the catalysts tried in these experiments.

Freas and Reid (7) found that, in the liquid phase for an equimolecular mixture of ethyl alcohol and benzoic acid, heating for 96 hours at 200° C. was necessary to reach equilibrium. The equilibrium corresponded to 66.17 per cent conversion of acid, and the equilibrium constant calculated from their data is 3.826. From their data it was estimated that the equilibrium for a 5 to 1 mole mixture of benzoic acid and ethyl alcohol in the liquid phase corresponded to 94.82 per cent conversion of the acid. The nearest approach to this value in our work was a conversion of 87 per cent obtained with titanium oxide as catalyst at 390° C.

Figure 2 shows a graph of space velocity against percentage of benzoic acid esterified for some of the better catalysts. The maximum value of esterification as obtained from these plots is dependent upon the amount of side reactions, and the best value obtained by extrapolation is about 90 per cent esterification.

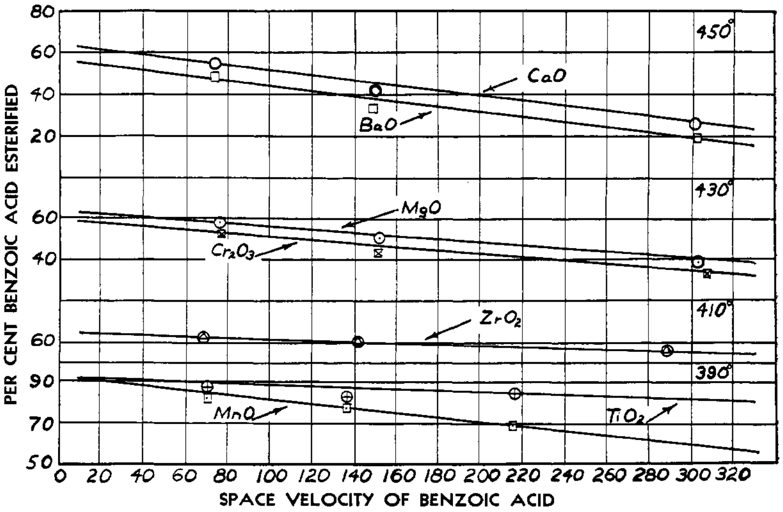

Figure 2. Variation of Esterification with Space Velocity

Table II. Effect of Temperature and Space Velocity on Conversion

Oxide	Optimum Temp., ° C.	Space Velocity of Acid	% Acid to Ester	% Acid to Side Reactions
ZrO_2	410	290	56	..
		145	60	..
		73	62	5
ZnO	430	304	14	..
		152	17	..
		76	24	6
MgO	430	304	39	5
		152	49	5
		76	57	10
Al_2O_3	430	304	25	..
		152	31	..
		76	39	..
Cr_2O_3	430	308	41	2
		154	45	12
		77	53	13
CaO	450	302	27	1
		151	43	4
		75	54	6
BaO	450	302	23	25
		151	32	24
		75	50	23
SrO	410	284	16	16
		142	20	14
		71	26	9
BeO	390	216	30	..
		138	36	..
		69	38	1
MnO	390	278	68	8
		138	79	2
		70	82	8
TiO_2	390	278	84	..
		139	85	6
		70	87	10

Complete tests were not made on all catalysts to determine how the activity changed with use, but the experiments did indicate that there was only a slight decrease in activity if the temperature was below that at which carbonization occurred.

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