mary product of the reaction. The validity of the categorical summary of Malkin and Nierenstein's paper is questioned.

2. It is suggested that the formation of ω-chloro-acetophenone is a secondary process and the result of the action of hydrogen chloride on diazo-acetophenone. The special conditions prescribed by Malkin and Nierenstein are such as to favor this secondary process.

3. The interaction of benzoic and succinic anhydrides with diazomethane has been studied. The formation of methyl succinate in the latter case occurs in the presence of water (or methyl alcohol), but, in all probability, succinic acid (or methyl hydrogen succinate) is not an intermediate in the process.

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VAPOR PHASE ESTERIFICATION OF ACETIC ACID BY ETHYL ALCOHOL

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The object of this work was to determine the equilibrium concentration of ethyl acetate in the vapor phase esterification of ethyl alcohol by acetic acid according to the reaction

$$C_2H_5OH + CH_3COOH = CH_3COOC_2H_5 + H_2O$$

Of the various esterification reactions this is the one which has been most frequently studied in the vapor phase, but there does not appear to be any consistency in the values of the equilibrium constant reported in the literature. From experiments with zirconium oxide as the catalyst Mailhe and de Godon[1] concluded that the equilibrium constant was about 6.0 in the temperature range of 280–290°. Mulliken, Chappell and Reid,[2] in studying the formation of ethyl acetate in the presence of silica gel, obtained results which gave an equilibrium constant of 79.3 at 150°, although they believed the actual value to be considerably higher. These experimenters also observed a considerable variation in the equilibrium constant with temperature. By determining the composition of the vapor above a liquid equilibrium mixture of alcohol, acid, ester and water, Edgar and Schuyler[3] obtained values of the equilibrium constant varying between 347 and 559 for the vapor phase in a temperature range of 72.6 to 77.6°, admitting the possibility of a considerable error. Recently

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[1] Mailhe and de Godon, *Bull. soc. chim.*, **29**, 101 (1921).

[2] Mulliken, Chappell and Reid, *J. Phys. Chem.*, **28**, 872 (1924).

[3] Edgar and Schuyler, THIS JOURNAL, **46**, 64 (1924).

Swietoslawski and Poznanski,[4] using the same method but claiming a greater degree of accuracy, reported a value of 59.0. In no case has the equilibrium been approached from the ester–water side, however.

Since these values of the equilibrium constant correspond to conversions of from 71 to 95% for mixtures of ethyl alcohol and acetic acid in equimolal concentrations over a range of 74 to 290° without, however, showing a definite trend in the effect of temperature, an attempt was made to redetermine the equilibrium under carefully controlled conditions. To this end experiments were made in which the equilibrium was approached from both sides over a temperature range of 250 to 300°. On the basis of Mailhe's data zirconium oxide was chosen as the catalyst possessing the highest activity without giving rise to side reactions at the temperatures in question.

Experimental Procedure

The apparatus consisted of two concentric coils of pyrex tubing connected in series and immersed in a fused salt-bath containing equal amounts of sodium and potassium nitrate. The bath was electrically heated and its temperature could be maintained constant within ±0.5°. The inner coil served as a vaporizer and preheater while the outer and larger coil contained 50 cc. of catalyst consisting of 5 g. of zirconium oxide supported on granulated pumice. In the esterification experiments a mixture of glacial acetic acid and anhydrous ethyl alcohol was passed from a buret at a fixed rate into the preheater coil. Since the ester and water were immiscible in the proportions used it was necessary in the hydrolysis experiments to feed the two liquids into the preheater in separate streams. The vapors issuing from the reactor were passed through a condenser and collected in an ice-cooled receiver. The acid content of the product was determined by titration and the equilibrium constant calculated from the percentage conversion. To determine the extent of olefin formation, gas samples were collected at the higher temperatures, *i. e.*, above 300°.

The catalyst was prepared by precipitating zirconium oxide with ammonia from a nitrate solution containing suspended pumice. The resulting material was dried in an electric oven at 90° and subsequently heated in the reactor for several hours at 280° in order to dehydrate the zirconium hydroxide and remove occluded ammonium salts.

Discussion of Results

The results of esterification experiments made with equimolar mixtures of acetic acid and ethyl alcohol at 250, 280 and 300° are listed in Table I. For each temperature the percentage conversion into ethyl acetate is given, together with the feed rate expressed as the number of cc. of liquid entering per hour per 100 cc. of catalyst. In Fig. 1 the conversions at 250 and 280° are plotted against the inverse of this rate. The curve for 280° shows that as the velocity of the vapor over the catalyst decreases, the percentage conversion into ethyl acetate increases rapidly at first, then more and more slowly, until finally it reaches the equilibrium value in the usual asymptotic manner. The average conversion calculated

[4] Swietoslawski and Poznanski, *Roczniki Chem.*, **8**, 527 (1928); *C. A.*, **23**, 2093 (1929).

from the six points on the flat portion of the curve is 87.5%, corresponding to a value of 49.0 for the equilibrium constant of the reaction. At lower temperatures it becomes necessary to correct for the polymerization of acetic acid into double molecules, as pointed out by Edgar and Schuyler.[3] However, extrapolation of Drucker and Ullmann's data[5] gives an equilibrium constant of 0.00437 at 280°, corresponding to only 1% polymerization of the acid. In addition to being somewhat uncertain, the corresponding correction is, therefore, too small to be considered in calculating the equilibrium constant for the esterification reaction at these temperatures.

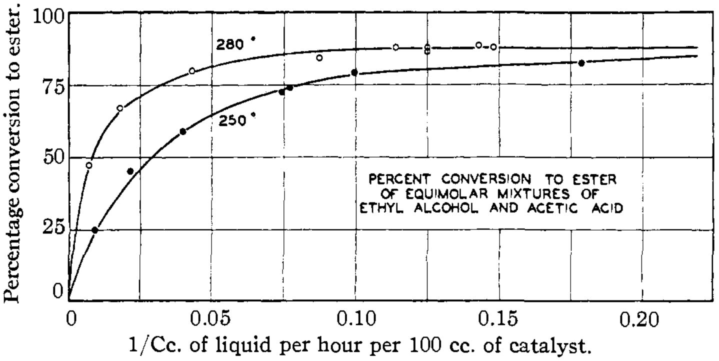

Fig. 1.

At 250° the reaction velocity is so slow that the equilibrium concentration is not reached even at the longest time of contact employed, as seen from the lower curve in Fig. 1. The results obtained at 300°, on the other hand, fall closely along the curve for 280° and for clarity have been omitted from the diagram. The average of the last five experiments at 300°, taken from Table I, give a conversion of 88.8% and an equilibrium constant of 63.0.

TABLE I

ESTERIFICATION EXPERIMENTS

Ratio of ethyl alcohol to acetic acid = 1:1. Temperature, 250°

Cc. of liquid per hour per 100 cc. of catalyst	109.0	46.2	25.0	13.4	13.0	10.0	5.6	4.2
Conversion to ester, %	24.8	44.8	58.5	72.2	74.0	78.8	82.8	85.0

Temperature, 280°

Cc. of liquid per hour per 100 cc. of catalyst	145.0	54.5	23.1	11.4	8.8	8.0	8.0	7.0	7.0	6.8
Conversion to ester, %	46.9	66.8	79.8	84.2	87.6	87.5	86.3	88.2	88.2	87.3

Temperature, 300°

Cc. of liquid per hour per 100 cc. of catalyst	150.0	15.4	14.6	13.6	13.5	12.0	11.1	10.4	8.4	5.0
Conversion to ester, %	47.0	87.2	85.6	85.0	84.5	88.7	87.2	88.9	89.7	89.8

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[5] Drucker and Ullmann, *Z. physik. Chem.*, **74**, 567 (1910).

Experiments made with higher ratios of alcohol to acid gave correspondingly higher values for the percentage of acetic acid converted into ester. However, the results were not accurate enough to serve as a check of the equilibrium determinations since a relatively large error was introduced in analyzing for the small amount of unconverted acid in the condensate. With a 2:1 ratio of alcohol to acid, 98% of the acetic acid should be converted into ester at 280°, and in a qualitative way this was shown to be the case.

Above 300° side reactions began to become noticeable, as evidenced by olefin formation, presumably due to dehydration of the alcohol. Even at 325° the amount of olefin formed was sufficient to disturb the equilibrium determination. Without a catalyst there was no appreciable ester formation at the times of contact employed.

Table II gives the results of a series of hydrolysis experiments made at 280°. Since the ester and water were immiscible in the proportions used and, therefore, had to be introduced in separate streams, it was not possible to duplicate the ratio of the two from run to run. However, the feed rates and, consequently, the molal ratio of ester to water remained constant throughout individual experiments. From the composition of the condensate the equilibrium constant of the esterification reaction was calculated, as shown in the last column of Table II. The average value of the six determinations is 49.0, or exactly the same as that resulting from the esterification experiments. However, in view of the short time of contact employed, the first value cannot be considered representative of equilibrium conditions. By discarding this and the third value, which is out of line with the others and obviously too low, the average becomes 49.3. Even on this basis the agreement with the esterification value of 49.0 is better than the accuracy of the method warrants. Allowing for the errors in analysis and in material balance, the value of the equilibrium constant at 280° may be taken as 49 ± 4.

TABLE II

HYDROLYSIS EXPERIMENTS

Temperature, 280°

Cc. of liquid per hour per 100 cc. of catalyst	Moles in product				
	Ethyl acetate	Water	Acetic acid and ethyl alcohol	K	$1/K$
53.8	0.1125	0.1833	0.0192	0.0179	56.0
34.8	.0716	.0722	.0103	.0205	48.8
27.6	.0522	.0722	.0096	.0244	41.0
25.2	.0522	.0555	.0077	.0205	48.8
19.8	.0379	.0565	.0066	.0204	49.0
11.5	.0502	.0389	.0062	.0197	50.7

In Table III the results obtained in these experiments are compared with those available in the literature. The low figures reported by Mailhe and de Godon are not included, however, since it is apparent that the time of contact was too short for equilibrium to be reached in their experiments. With the exception of Edgar and Schuyler's results, the data in Table III show that the equilibrium concentration of ester is practically constant over a temperature range of 75 to 300°, although the relatively small differences in the conversion figures are magnified in the values for the equilibrium constant. The free energy change accompanying the reaction is not known with sufficient accuracy to permit calculation of the equilibrium constant. In a qualitative way, however, free energy computations give support to the small temperature coefficient indicated by the experiments. Of the writers' constants, the one for 280° is most dependable, considering that it has been determined by approaching the equilibrium from both directions.

TABLE III

COMPARISON OF EQUILIBRIUM DATA

Reaction: $C_2H_5OH + CH_3COOH = CH_3COOC_2H_5 + H_2O$

Basis: Equimolar mixtures of ethyl alcohol and acetic acid

	Temp., °C.	Conversion to ester, %	Equilibrium constant
Edgar and Schuyler	72.6–77.6	About 95	347–559
Swietoslawski and Poznanski	75–76	88.5	59
Mulliken, Chappell and Reid	150	89.9	79.3
Frolich, Carpenter and Knox	280	87.5	49
Frolich, Carpenter and Knox	300	88.8	63

Summary

1. The vapor phase esterification of ethyl alcohol by acetic acid in the presence of a zirconium oxide catalyst has been studied over a temperature range of 250 to 300°.

2. At 250° the reaction proceeded too slowly for equilibrium to be reached in the flow system employed. Above 300° there was a tendency for simultaneous dehydration of the alcohol into ethylene. In the absence of catalyst no appreciable amount of ester was formed.

3. Esterification experiments with equimolar concentrations of ethyl alcohol and acetic acid gave 87.5% of ethyl acetate at 280°, corresponding to an equilibrium constant of 49.0. Hydrolysis of the ester by the reverse reaction gave a value of 49.3. In consideration of the possible error the value of the equilibrium constant at this temperature may be taken as 49 ± 4.

4. At 300° 88.8% conversion was obtained in esterification experiments but was not checked by the reverse reaction. This corresponds to an equilibrium constant of 63.

5. Comparison of these results with others reported in the literature shows that the equilibrium constant changes only slightly with temperature. It may therefore be concluded that the maximum conversion to

ester obtainable in this temperature range from equimolar concentrations of alcohol and acid is about 88 to 90%.

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THE IODINATION OF PHENOL AND CRESOL ETHERS

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The introduction of iodine into aromatic hydrocarbons such as benzene, toluene, cymene, etc., using nitric acid as an oxidizing agent was first described by La Datta and Chatterjee.[1] The method has been studied in detail in this Laboratory and the following paper is an account of the reaction as applied to the phenol ethers. The free phenols are too reactive and the resulting products consist of nitro rather than the desired iodo compounds. When the phenol ethers are used, the reaction proceeds smoothly and in good yields. The interesting fact was also noted that iodine can be introduced into the nitro-anisoles and nitrophenetoles, although nitrobenzene is unaffected under the same conditions. A description of the general procedure is given in one instance; the other results are tabulated.

Experimental

I. **Iodination of Phenetole.**—Phenetole (20 g.) and iodine[2] (15 g.) were placed in a small Kjeldahl flask fitted with a ground in glass condenser and heated in an oil-bath at 180°. For higher temperatures a metal-bath can be used. From time to time 2–3-cc. portions of concentrated nitric acid were added through the condenser. After an hour's heating the iodine had practically disappeared. The residue in the flask was washed with alkali and steam distilled. In the iodination of cresol derivatives the alkali dissolves any substituted benzoic acids formed by oxidation. The oil was separated, dried and fractionated at 11 mm. It came over between 120 and 138° and on cooling part of it solidified. This when freed from oil melted at 28° and proved to be *p*-iodophenetole. The major portion of the oil (b. p. 240° at 730 mm.) corresponded in properties to the known *o*-iodophenetole. Additional evidence of its formation was given by the fact that in one run the main product was 2-iodo-4-nitrophenetole (m. p. 96°).[3]

V. **2-Nitro-4-iodo-anisole** (m. p. 98°).—Reverdin[4] described this ether as melting at 73° but the following proof of structure would seem to confirm the higher melting point.

The nitration of *p*-acetanisidine and subsequent hydrolysis gave the 2-nitro-4-

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[1] Datta and Chatterjee, THIS JOURNAL, **39**, 435 (1917).

[2] The addition of 3–5 cc. of pyridine increases the yield and lowers the temperature at which the reaction occurs.

[3] Reverdin, *Ber.*, **29**, 2596 (1896).

[4] Reverdin, *ibid.*, **29**, 1003, 2595 (1896); *Bull. soc. chim.*, [3] **15**, 639 (1896); Brenans, *Compt. rend.*, **134**, 360 (1902).