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Vapor Phase Esterification Over Zirconium Oxide

BY WILLIAM J. KNOX, JR., AND T. N. BURBRIDGE

The equilibrium of the esterification of acetic acid by ethyl alcohol in the vapor phase over various catalysts has been the subject of several recent investigations.[1] The method used in these investigations was a dynamic one involving various degrees of refinement. For temperatures at 150–200° studies have been made only over silica gel which adsorbs appreciably both reactants and products in unknown amounts.[2] For temperatures below 100° the equilibrium constant for this reaction in the vapor phase has been measured by means of a distillation method devised by Edgar and Schuyler[3] and refined by Swietoslawski and Poznanski[4] and Salcewicz.[5] Very recently Halford and Brundage[6] have studied this equilibrium at 40° by an air saturation method. These low temperature data are widely divergent within themselves and are only in general agreement with those obtained from studies conducted with the aid of catalysts. No data obtained from catalytic esterification have been reported for temperatures below 150°.

The purpose of this investigation was to study this equilibrium at 150 and 200° by a static method using zirconium oxide as a catalyst and also to extend the data from catalytic esterification down to 125°.

The results obtained are summarized in Table I. The letters E and H in the second column indicate whether equilibrium was approached from the esterification or hydrolysis side, respectively. The equilibrium position for a 1:1 mole mixture of acid and alcohol or ester and water was found to be between 81.51 and 81.24% of a mole of ethyl acetate at 200° and between 84.70 and 84.35% at 150°. These results are in fair agreement with those obtained over silica gel by Tidwell and Reid and Essex and Clark. For 125° the conversion of acetic acid to ester was found to be between 85.89 and 85.56%.

TABLE I

EQUILIBRIUM DATA FOR EQUIMOLAR MIXTURES OF ACID AND ALCOHOL AND ESTER AND WATER

Temp., °C.	Reaction	Time of run, in hours	Wt. % of acid in products	% of esterification	Average % esterification
200	E	9	10.52	81.40	
200	E	11	10.46	81.51	81.38
200	H	9	10.61	81.24	
150	E	23	8.66	84.70	
150	H	18	8.86	84.35	84.51
150	H	22	8.79	84.47	
125	E	28	8.00	85.86	
125	H	19	7.99	85.89	85.77
125	H	22	8.17	85.56	

Table II contains the average values of the

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EQUILIBRIUM CONSTANTS AND STANDARD FREE ENERGIES FOR VAPOR PHASE ESTERIFICATION

Temp., °C.	200	150	125
K(g)	19.8 ± 0.4	33.3 ± 1.0	45.7 ± 1.4
ΔF^0 (in cal.)	2813 ± 18	2951 ± 24	3029 ± 24

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(1) Frolich, Carpenter and Knox, THIS JOURNAL, **52**, 1565 (1930); Tidwell and Reid, *ibid.*, **53**, 4353 (1931); Essex and Clark, *ibid.*, **54**, 1290 (1932); Jatkar and Gajendragad, *ibid.*, **59**, 798 (1937).

(2) Milligan, Chappell and Reid, *J. Phys. Chem.*, **28**, 872 (1924).

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

(4) Swietoslawski and Poznanski, *Roczniki Chem.*, **8**, 527 (1928).

(5) Salcewicz, *ibid.*, **14**, 702 (1934).

(6) Halford and Brundage, THIS JOURNAL, **64**, 36 (1942).

equilibrium constants and standard free energies of the gaseous reaction calculated from these data. The equilibrium constants were calculated by the method described by Essex and Clark.

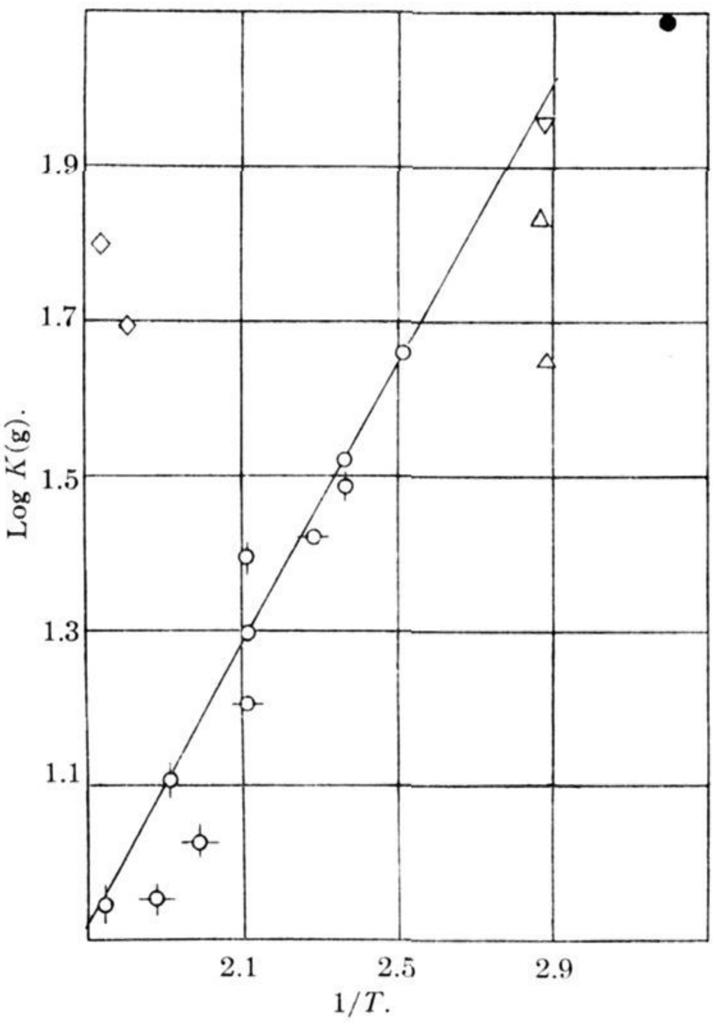

Fig. 1.—Vapor phase esterification equilibrium: ◇, Frolich, Carpenter and Knox; ϕ, Tidwell and Reid; -o-, Essex and Clark (at 150° the point obtained by these authors almost coincides with that of Knox and Burbridge); ⊕, Jatkar and Gajendragad; ▽, Swietoslawski and Poznanski (corrected for association); △, Salcewicz (corrected for association); ●, Halford and Brundage; O, Knox and Burbridge.

In Fig. 1 the log K(g) is plotted against the reciprocal of the absolute temperature. The data here presented yield points which lie almost on a straight line indicating that the heat of the reaction is practically independent of the temperature. This line when extrapolated passes very close to the points obtained from the data of Tidwell and Reid at 250 and 300° and to the point obtained from the data of Swietoslawski and Poznanski at 75° after correcting for the association of acetic acid. When extrapolated to 40° the value of K(g) is found to be 191. This value is in fair agreement with the value of 122 obtained by Halford and Brundage when it is considered that small variations in the conversion data are magnified in values of the equilibrium constant. The slope of this line corresponds to $\Delta H^0 = -4175.6$ cal. and the free energy as a function of the absolute temperature comes out to be $\Delta F^0 = -4175.6 + 2.88\,T$.

The commercial alcohol used in these experiments was dehydrated by treating with fresh quicklime and then with magnesium ethylate according to the procedure described by Lund and Bjerrum.[7] The ethyl acetate used was Merck reagent grade. It was fractionally distilled, that portion boiling over a range of 0.5° being taken. Glacial acetic acid described as having a purity of 99.5% was used without further treatment.

The zirconium oxide catalyst was prepared by dissolving zirconium nitrate in distilled water in which was suspended granulated pumice. Zirconium hydroxide was precipitated by adding an excess of ammonium hydroxide. The water was then evaporated and the residue heated in a furnace at 350° for several hours in order to drive off the ammonium salts and dehydrate the zirconium hydroxide.

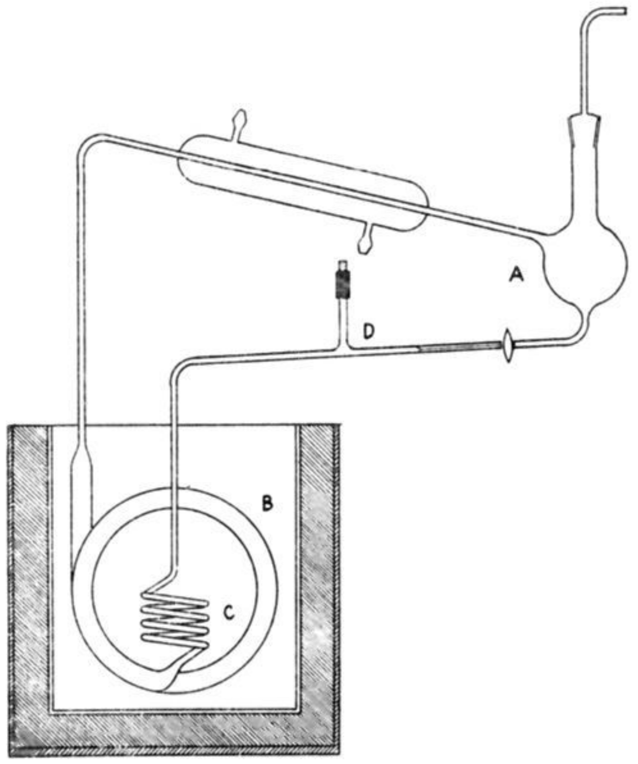

Fig. 2.

A diagram of the apparatus used is shown in Fig. 2. The *oil-bath consisted of a 15-liter galvanized iron container* insulated on the outside and wound with resistance wire. The container was placed in a wooden box and surrounded with kieselguhr. The bath was provided with an electric stirrer and the temperature was thermostatically controlled to within 1.0°.

One mole each of acetic acid and ethyl alcohol or ethyl acetate and water were placed in the bulb "A" which was capped by a ground glass joint. The tube leading from the male part of this joint carried a right angle bend and was tipped by a piece of rubber tubing which could be closed by a Hoffman screw clamp. The reaction mixture was permitted to flow slowly through the stopcock and a short length of capillary tubing into the preheater coil "C" where the liquid was vaporized and brought to the tem-

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[7] Lund and Bjerrum, *Ber.*, **64**, 210 (1931).

perature of the bath. The vapors then passed into the reaction tube "B." This tube was constructed from 2 meters of 18-mm. Pyrex tubing wound into one continuous coil. It contained about 5 g. of zirconium oxide supported on granulated pumice. With such a small amount of catalyst the adsorption effects were found to be relatively small. The original catalyst was used throughout the investigation. The vapors leaving the reaction coil passed into the condenser where they were condensed and carried back into the bulb "A." The side arm at "D" was closed by means of a piece of rubber tubing plugged with glass rod. By applying suction to this tube the apparatus could be emptied of liquid and vapor at the end of a run.

At the beginning of a run as soon as the vapors reached the condenser the rubber tubing on the end of the male part of the ground glass joint was closed and the reaction mixture was refluxed over the catalyst for several days. After a reasonable time had been allowed for equilibrium to be reached the stopcock was closed and the tube leading from the reaction coil to the condenser was heated with a free flame in order to drive over any liquid which might have condensed there after the stopcock was closed. A 10-ml. sample was then pipetted into a 25-ml. weighing flask and weighed. The contents of the weighing flask were carefully washed into a titrating flask and titrated with 0.5 *N* sodium hydroxide. Refluxing was begun again and continued for from one to five days and another sample was removed. Constancy of the acid content was taken to indicate that equilibrium had been reached.

The time allowed for a run depended upon the temperature and varied from nine to eleven days at 200° to from three to four weeks at 125°. For the esterification reaction at the lower temperatures the reaction mixture was refluxed over the catalyst for four or five days at 200° and then the temperature was dropped to 150 or 125° and refluxing continued for from two to three weeks. For hydrolysis at the lower temperatures the same procedure was followed except that the refluxing at 200° was permitted to continue until the two layers had almost disappeared.

The authors wish to express their thanks to Mr. I. J. Terry for his assistance and interest during the progress of this work.

Summary

The equilibrium of the vapor phase esterification of ethyl alcohol by acetic acid over zirconium oxide has been studied by a static method at 200, 150 and 125°. From the data obtained the equilibrium constants and standard free energies for this reaction at these temperatures have been calculated.

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Some Friedel-Crafts Type Alkylations with Boron Trifluoride[1]

BY G. F. HENNION AND R. A. KURTZ

Introduction

While boron trifluoride is now well recognized as a catalyst for the alkylation of aromatic compounds with alcohols,[2] olefins,[3] esters,[4] and ethers,[5] this method has not been applied successfully to similar reactions with the organic halides. Thus boron trifluoride has not served as a substitute for aluminum chloride in Friedel-Crafts alkylations with alkyl halides. Solutions of alkyl halide in anhydrous benzene, for example, do not dissolve boron trifluoride, nor is there evidence of reaction. It has now been found that if a moderate quantity of water, alcohol or other polar compound reactive to boron trifluoride is used also, many active halides alkylate rapidly and in fair yield as shown in Table I.

With benzene and toluene tertiary chlorides and benzyl chloride gave the best yields. Secondary halides gave low yields, which, however, could be increased markedly by the use of sulfuric acid along with water and boron trifluoride. The normal chlorides and bromides were found to be almost wholly unreactive.

An interesting feature of this general method lies in the fact that the lower layers which separate when the reactions are complete may be reused without loss of activity, particularly if resaturated with boron trifluoride to make up for volatilization losses.

Along with the halide one may use the corresponding alcohol, water, methanol or even acetic acid. It therefore cannot be argued that hydrolysis of the halide to the corresponding alcohol with subsequent alkylation by the latter, is necessarily involved in these reactions. The positive fragment mechanism serves well to explain our

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[1] Paper XXVI on organic reactions with boron trifluoride; previous paper, THIS JOURNAL, **63**, 2603 (1941).

[2] McKenna and Sowa, *ibid.*, **59**, 470 (1937); Toussaint and Hennion, *ibid.*, **62**, 1145 (1940); Welch and Hennion, *ibid.*, **63**, 2603 (1941).

[3] Slanina and Sowa, *ibid.*, **57**, 1547 (1935); Wunderly, Sowa and Nieuwland, *ibid.*, **58**, 1007 (1936); Ipatieff and Grosse, *ibid.*, **58**, 2339 (1936).

[4] McKenna and Sowa, *ibid.*, **59**, 1204 (1937).

[5] O'Connor and Sowa, *ibid.*, **60**, 125 (1938); Monacelli and Hennion, *ibid.*, **63**, 1722 (1941).