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Kinetic Studies of the Acid-catalyzed Etherification of Ethyl Acetoacetate with Ethanol

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It has been reported that the facility of the acid-catalyzed etherification of the allelotrope of *p*-nitrosophenol and *p*-benzoquinoneoxime may depend upon a special kind of keto-enol tautomerism.[1] It seemed that another system of keto-enol tautomerism could, therefore, be etherified easily with alcohols in the presence of acid as well. Actually, the acid-catalyzed etherification of ethyl acetoacetate with ethanol took place when well-dried hydrochloric acid was passed through the ethanolic solution for 10 min at −10°C; only the ethyl β-ethoxycrotonate was formed.[2]

Experimental

Materials. The ethyl β-ethoxycrotonate was prepared by refluxing a mixture of ethyl acetoacetate, acetyl chloride, and ethyl orthoformate;[3] it was recrystallized from petroleum ether after the crude product had been obtained by the removal of the other ingredients; yield 40%; mp 31°C (lit., 30°C,[2] 31°C[3]). Ethanol containing 0.16 M water was used as the reactant and solvent. The ethanolic solution of sulfuric acid was prepared from guaranteed sulfuric acid and the ethanol mentioned above.

Ultraviolet Spectrophotometry and Chemical Analysis. The reactions were followed by a Hitachi Perkin-Elmer UV-VIS spectrophotometer, model 139. The reaction product, ethyl β-ethoxycrotonate, has a broad absorption maximum at 235 mμ, while the reactant, ethyl acetoacetate, has only a small absorption in this UV region, as is illustrated in Fig. 1. Mixtures of ethyl acetoacetate, ethyl β-ethoxycrotonate, and sulfuric acid of known concentrations corresponding to 0, 20, 40, 60, 80, and 100% conversions were prepared; a plot of the difference in extinctions, $(E_{235}-E_{270})$ *vs.* $(E_{235}-E_{255})$, gave a straight line, and the calculated conversion from the values of $(E_{235}-E_{255})$ at 0 and 100% conversion agreed well, within about a 1% error, with the conversions calculated from the composition of the mixture.

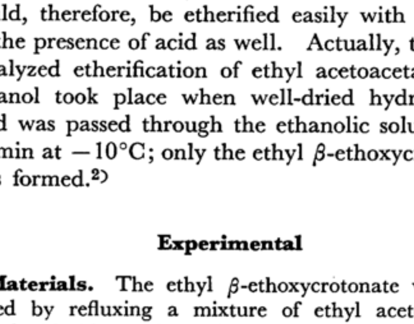

Fig. 1. Ultraviolet spectra of reactant and product in 5×10^{-5} M methanolic solution.
1, ethyl acetoacetate; 2, ethyl β-ethoxycrotonate.

Criterion of the Reaction. As the $(E_{235}-E_{270})$ *vs.* $(E_{235}-E_{255})$ plots of the actual reactions did not deviate at all from the calibration curve, it can be considered that the reaction forming ethyl β-ethoxycrotonate proceeds without any side reaction.

A Typical Run for the Rate Measurements. A solution of 2.5 m*l* of 1 N sulfuric acid in ethanol was poured into a 2.5 m*l* portion of a 1 M ethanolic solution of ethyl acetoacetate to start the reaction after both solutions had attained temperature equilibrium. Aliquots (0.1 m*l* each) were taken out at appropriate time intervals; each one was diluted with methanol to a 5×10^{-5} M total concentration of ethyl acetoacetate and ethyl β-ethoxycrotonate. The conversion percentage was calculated from the observed value of $(E_{235}-E_{255})$, and then the value of the apparent first-order rate constant, *k*, was calculated graphically.

Determination of the Water in the Reaction System. The water present in the reaction system was determined to be 0.20 M by the Karl Fischer method.

Results and Discussion

As the forward and reverse reactions are regarded as pseudo first-order reactions, the reaction will follow the pseudo first-order kinetics for a reversible reaction:

$$\ln[z/(z-x)] = kt, \qquad (1)$$

where *x* and *z* are the concentrations of the consumed reactant at time *t* and at the equilibrium stage respectively. In these studies, the plots of $\log[z/(z-x)]$ *vs.* *t* gave a straight line, and the value of the apparent rate constant, *k*, was obtained graphically. Assuming the pseudo first-order rate constants for the forward and reverse reactions to be k_1 and k_{-1} respectively, the forward rate constant, k_1, can be

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[1] Y. Furuya, D. Morikawa and K. Itoho, This Bulletin, **40**, 1425 (1967).

[2] R. S. Curtiss, *Am. Chem. J.*, **17**, 435 (1895).

[3] F. Arndt, L. Loewe and M. Ozansoy, *Ber.*, **73** 779 (1940).

TABLE 1. THE RATE DATA FOR THE REVERSIBLE REACTION OF ETHYL ACETOACETATE WITH ETHANOL

$[\mathrm{EAA}]_0$ M	$[H_2SO_4]$ N	Temp. °C	$-\log (C_{BH^+}/C_B)$	H_0	$10^5 k_1$ sec^{-1}
0.1	0.5	20	−0.3045	0.996	1.63
0.5	0.5	20	−0.3045	0.996	1.62
1.0	0.5	20	−0.3045	0.996	1.66
0.5	0.1	20	0.4991	1.799	1.45
0.5	1.0	20	−0·6572	0.643	1.79
0.5	0.5	30	−0.3045	0.996	2.84
0.5	0.5	40	−0·3045	0.996	7.20

E_a, 6.53 kcal mol^{-1} $\Delta S^{\ddagger}$, −21.8 e.u.

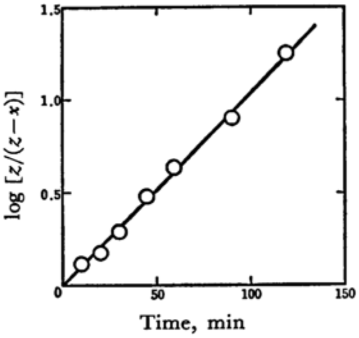


Fig. 2. The rate plots for the reversible first-order reaction at 20°C.
$[\mathrm{EAA}]_0$: 0.5 M, $[H_2SO_4]$: 1 N z: 4.34%

obtained from the following equations[4]:

$$\ln [z/(z-x)] = (k_1+k_{-1})t = kt$$
$$z/(a-z) = k_1/k_{-1}$$

where a is the initial concentration of ethyl acetoacetate. The rate data are shown in the table.

The rate was not affected by the acidity, though the reaction does not occur without acid. The plots of log k_1 *vs.* H_0[5] gave a straight line with a slope of −0.07, as is illustrated in Fig. 3. Therefore, a proton may participate after the rate-determining step.

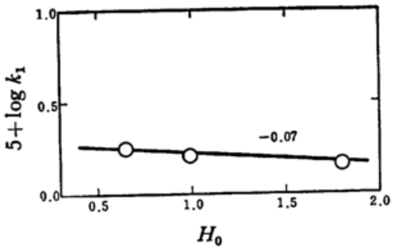
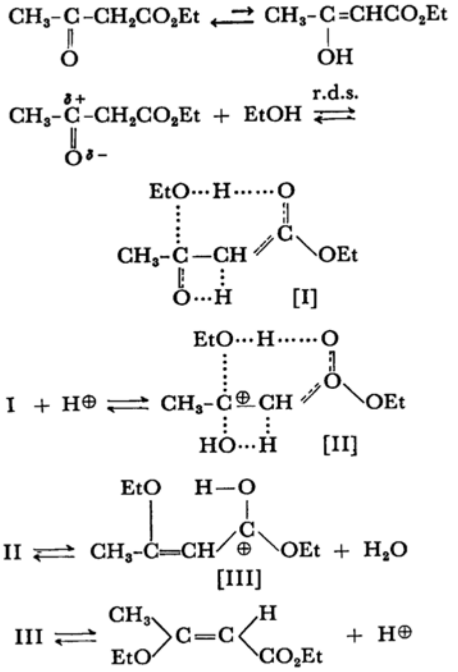


Fig. 3. The plots of log k_1 *vs.* H_0 for the etherification at 20°C.

It is well known that only β-ethoxycrotonic acid is obtained by the reaction of ethanol containing sodium ethoxide with potassium β-chlorocrotonate and/or β-chloroisocrotonate[6] and also with ethyl β-chloroisocrotonate.[7] In the title reaction as well, only ethyl β-ethoxycrotonate was obtained; no ethyl β-ethoxyisocrotonate formed at all, as has been described above. Therefore, a mechanism which involves the rate-determining formation of the hydrogen-bonding complex, I, can be considered.

From these findings, the following over-all mechanism can be suggested:



The autors are grateful to Mr. T. Sonobe for his aid in performing these experiments.

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[4] Y. Ogata, Y. Furuya and K. Aoki, This Bulletin, **38**, 838 (1965).

[5] *p*-Nitroaniline was used as the indicator; its pK_{BH^+} value in ethanol was 1.3. M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

[6] R. Friedrich, *Ann.*, **219**, 322 (1883).

[7] A. Koll, *ibid.*, **249**, 303 (1888).