[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

Kinetics of the Esterification of Substituted Benzoic Acids

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The esterification of substituted benzoic acids has been studied by Hartman and Borders,[2] and by Hartman, Storms and Gassmann,[3] and others.[4,5] These investigations showed that in hydrion catalyzed esterifications, the reaction is facilitated by recession of electrons from the seat of the reaction and is therefore, according to Williams,[6] a Class B reaction. Both E and P of the Arrhenius equation

$$k = PZe^{-E/RT}$$

have been found to affect the reaction velocity. The effect of a meta or para substituent on the benzene nucleus on the reaction velocity is expressed by the equation[7]

$$\log k = \log k_0 + \rho\sigma$$

where k is the velocity constant of the substituted reactant, k_0 is the velocity constant of the unsubstituted reactant; ρ is a constant depending on the reaction, medium and temperature, and σ is a constant depending upon the substituent. Good agreement between observed and calculated values was found for the acids studied.

The object of this investigation was to determine the velocity constants of esterification of each of the three monosubstituted iodo-, fluoro-, methoxy-, and ethoxybenzoic acids with methyl alcohol and catalyzed by hydrions. Because *p*-iodobenzoic acid is only slightly soluble in methyl alcohol, its reaction rate was not studied. Using the data thus obtained, the energies of activation were determined in order to analyze the results in the light of the Arrhenius equation.

Experimental

Materials.—Absolute methanol was purified by the method of Bjerrum and Lund.[8] Water, aldehyde and ketone tests were negative. The acids were obtained either from Eastman Kodak Company or from Professor C. S. Marvel of the University of Illinois. The melting points of the purified acids agreed with those recorded in the literature. The acids were dried over phosphorus pentoxide, preceded in certain instances by drying in an oven at 105–110°.

Procedure.—The procedure followed was similar to that of Hartman and Borders.[2] The total acid concentration was determined at the beginning and at intervals throughout the course of the reaction by titrating 5-ml. samples against barium hydroxide solution using phenolphthalein as indicator. Correction was made for the expansion of solvent. The thermostats were maintained at 25.00, 40.00, 50.00 and 60.00 ± 0.02°.

Results and Discussions

The value of the velocity constant which accounts for the retardation of the reaction due to the water formed is given by the equation[9]

$$k = \frac{(r + a)\ln\left[\dfrac{a}{a - x}\right] - x}{crt}$$

where r is a constant which compensates for the water formed, a is the initial organic acid concentration, x is the quantity of acid esterified in time t, c is the concentration of the hydrion catalyst, and k is the velocity constant in g. moles/liter/sec. The values of r used were[2,10]

Temp., °C.	25	40	50	60
r	0.22	0.36	0.50	0.65

Table I shows a typical esterification reaction. The individual figures for $(a - x)$ and for k represent averages of several runs.

TABLE I

ESTERIFICATION OF *m*-FC_6H_4COOH AND CH_3OH AT 25°

$a = 0.1034$, $c = 0.0197$

Time, min.	$a - x$	$10^4\ k$
1560	0.0820	1.32
2940	.0675	1.33
4320	.0572	1.29
5760	.0471	1.32
7200	.0410	1.28

No values of k were used which represent less than 20% or more than 80% reaction. This eliminates anomalies that might result from experimental errors and hydrolysis effect at the beginning and end of a reaction. Table II gives the velocity constants and energy of activation for benzoic acid and the eleven substituted benzoic acids studied in this investigation.

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[1] This paper represents a part of a thesis to be presented by Albert George Gassmann to the Faculty of the Graduate School of Indiana University in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Hartman and Borders, THIS JOURNAL, **59**, 2107 (1937).

[3] Hartman, Storms and Gassmann, *ibid.*, **61**, 2167 (1939).

[4] Kellas, *Z. physik. Chem.*, **24**, 221 (1897).

[5] Sudborough and Turner, *J. Chem. Soc.*, **101**, 237 (1912).

[6] Williams, *ibid.*, 37 (1930).

[7] Hammett, THIS JOURNAL, **59**, 96 (1937).

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

[9] Goldschmidt, *ibid.*, **39**, 711 (1906).

[10] Williamson and Hinshelwood, *Trans. Faraday Soc.*, **30**, 1145 (1934).

TABLE II

VELOCITY CONSTANTS AND ENERGIES OF ACTIVATION FOR HYDRION CATALYZED ESTERIFICATION OF AROMATIC ACIDS WITH METHYL ALCOHOL

Acid	$10^4 k$				Energy of activation
	25°	40°	50°	60°	E
o-Iodobenzoic	0.331	1.13	2.27	4.21	14,300
p-Fluorobenzoic	.756	2.45	5.04	9.02	14,400
p-Methoxybenzoic	1.04	3.34	6.73	13.07	14,300
p-Ethoxybenzoic	1.13	3.22	6.52	14.25	13,400
m-Fluorobenzoic	1.31	3.90	8.63	16.51	14,300
m-Iodobenzoic	1.37	3.89	8.62	16.65	14,400
m-Methoxybenzoic	1.91	5.68	13.03	25.32	14,600
Benzoic	1.94	6.57	15.24	28.69	15,500
o-Fluorobenzoic	1.99	5.62	12.54	23.84	14,000
m-Ethoxybenzoic	2.11	6.50	13.61	26.55	14,300
o-Ethoxybenzoic	6.61	24.88	38.28	74.58	13,700
o-Methoxybenzoic	8.30	25.76	51.96	89.15	13,900

The values of E were obtained graphically from the slope of the line obtained by plotting log k against the reciprocal of the absolute temperatures. The energy of activation of benzoic acid was found to be 15,500 cal. The same value was reported by Hartman and Borders.[2] Hinshelwood and Legard[11] report 15,700 calories.

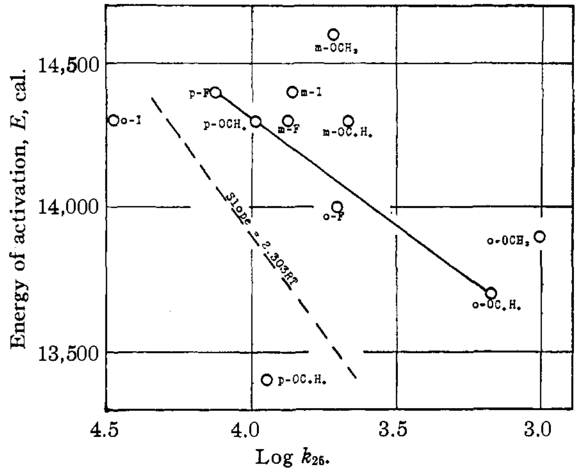

Fig. 1.—Relationship between speed of reaction and activation energy.

Table III gives the observed values of log k_{25} for meta and para substituted acids and the corresponding values as calculated from Hammett's equation.[7] The value of ρ was -0.54[2] and the values of σ were taken from Hammett.[7] The average error of log k is greater than the mean value of probable error by Hammett.[7] It is noticed in Table III that the error is greater for the *p*-methoxy-, *p*-ethoxy-, and *p*-fluorobenzoic acids than for the corresponding meta substituted acids. The average error of log k for the meta substituted acids is 0.056, which compares very favorably with that of Hartman and Borders[2] and Hammett.[7]

TABLE III

COMPARISON OF LOG k_{25} OBSERVED WITH LOG k CALCULATED FROM THE EQUATION: LOG $k = -3.712 + \sigma(-0.54)$

Acid	Log k, obsd.	Log k, calcd.	Error
m-Ethoxybenzoic	−3.676	−3.793	0.117
m-Methoxybenzoic	−3.719	−3.774	.055
m-Iodobenzoic	−3.863	−3.902	.039
m-Fluorobenzoic	−3.883	−3.894	.011
p-Ethoxybenzoic	−3.947	−3.577	.370
p-Methoxybenzoic	−3.983	−3.568	.415
p-Fluorobenzoic	−4.121	−3.745	.376
		Av.	.198

Because of the lack of close agreement between the observed and calculated values of log k for the *p*-methoxy-, *p*-ethoxy-, and *p*-fluorobenzoic acids, it appears that the Hammett equation fails in these instances.

To determine whether changes in velocity are due to changes in E or to changes in P of the equation $k = PZe^{-E/RT}$, log k was plotted against the measured value of E. Changes of E would be responsible alone if the resulting slope of the line were 2.303 RT. Figure 1 shows such a plot where the broken line represents the theoretical line having a slope of 2.303 RT and the solid line represents an approximate graphical average obtained from the data of this investigation. It is apparent that the two lines do not have the same slope and it may therefore be concluded that changes in E are not alone responsible for changes in reaction velocities. That the P term changes has been found to be true in the investigations of Hartman and Borders[2] and those of Hinshelwood and Legard.[11]

Summary

1. The study of the effect of polar groups has shown that the velocity of hydrion-catalyzed esterification of substituted benzoic acids is increased by displacement of electrons toward the carboxyl groups.

2. Comparison of experimental log k with that calculated from the Hammett equation shows good agreement for the meta substituted acids. Good agreement was not found, however, for the *p*-ethoxy-, *p*-methoxy-, and the *p*-fluorobenzoic acids.

3. Both the P factor and energy of activation have an effect on the velocity of esterification.

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[11] Hinshelwood and Legard, *J. Chem. Soc.*, 587 (1935).