$(C_2H_3O_2)Cl\cdot ZnCl_2$, is analogous to the compound $Zn(OH)_2\cdot 3ZnCl_2$, or $Zn(OH)Cl\cdot ZnCl_2$, earlier described by Ephraim.[11] Neither of these aquobasic salts can be dissolved in water without decomposition, but, like their acetic acid analogs, they are stable in contact with solutions containing a large excess of zinc chloride.

Summary

1. A convenient method of preparing anhydrous zinc chloride–acetic acid solutions has been devised, and the freezing points of such solutions, over a wide concentration range, have been determined.

2. Evidence for the presence of an addition compound of zinc chloride and hydrogen chloride, even in dilute solution in acetic acid, has been obtained.

3. The system $ZnCl_2-Zn(C_2H_3O_2)_2-HC_2H_3O_2$ has been studied at 30°. Two new double salts, $Zn(C_2H_3O_2)Cl$ and $Zn(C_2H_3O_2)Cl\cdot ZnCl_2$, have been isolated and analyzed.

(11) Ephraim, Z. anorg. Chem., **59**, 67 (1908).

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Effect of Polar Groups upon Esterification Velocities of Substituted Benzoic Acids with Cyclohexanol

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The effect of substituents on the reaction veolcity of various compounds has long been of interest. There have been attempts made to group the effect of substituents under a single theory. Williams[2] classifies reactions into three groups according to the effect of polar substituents on reaction rates as follows: (A) those favored by accession of electrons to the point of reaction; (B) those favored by recession of electrons from the point of reaction; and (C) those in which the data available are insufficient to classify in either group A or B. Of the three esterification studies cited by Williams, two, those by Goldschmidt[3] and Kailan[4] are in group C. The third, by Michael and Oeschlin[5] is placed in group B, i. e., the esterification reaction was accelerated by a substituent such as the nitro group. Hammett[6] has expressed the effect of a substituent in the meta or para position on the benzene ring upon the rate of a side chain reaction by the equation

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

where k is the velocity constant for the substituted reactant, k_0 the constant for the unsubstituted reactant, σ a constant depending upon the substituent, and ρ a constant depending on the reaction,

medium, and temperature. Hammett found a probable error for $\log k$ of less than 0.1 in thirty-three of thirty-nine reactions, including equilibrium as well as velocity constants. The equation was applied to the esterification work of Goldschmidt.[3] The probable error found was 0.118. Hartman and Borders[7] applied the equation to the esterification of substituted benzoic acids with methanol. They found an average error of 0.058. The values of σ used in the work of Hartman and Borders as well as those used in this work were taken from Hammett[6] and were determined by him from the data of Dippy[8] for the dissociation constants in water of substituted benzoic acids.

The object of this investigation was to determine the velocity constants of hydrion-catalyzed esterification of substituted benzoic acids with cyclohexanol. Using the data thus obtained, the energies of activation are determined in order to analyze the data from the point of view of the Arrhenius equation. Hammett's equation is tested for its applicability to the esterification of the cyclic alcohol, cyclohexanol.

Experimental

Materials.—Pure cyclohexanol was first dried by the method of Bjerrum and Lund[9] and then by refluxing over calcium oxide. The acids were

(1) This paper is constructed from a dissertation presented by Lee B. Storms 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) Williams, J. Chem. Soc., 37 (1930).

(3) Goldschmidt, Ber., **28**, 3220 (1895).

(4) Kailan. Ann., **351**, 186 (1907).

(5) Michael and Oeschlin, Ber., **42**, 317 (1909).

(6) Hammett, THIS JOURNAL, **59**, 97 (1937).

(7) Hartman and Borders, ibid., **59**, 2107 (1937).

(8) Dippy, J. Chem. Soc., 644 (1936).

(9) Bjerrum and Lund, Ber., **64B**, 210 (1931).

purchased from the Eastman Kodak Co. They were dried carefully over phosphorus pentoxide.

Procedure.—The experimental procedure was the same as that followed by Hartman and Borders.[7] The concentration of hydrogen chloride used was 0.1 normal. The thermostats were maintained at 55.00, 60.00, 70.00 and 75.00 ± 0.01°.

Calculations.—The velocity constants were calculated using the formula developed by Goldschmidt[10] which corrects for the retardation of esterification caused by the water formed in the course of the reaction

$$k = \frac{[(a + r) \ln a/a - x] - x}{rct}$$

where a is the original acid concentration, x the amount of acid esterified at time t, and c the H$^+$ concentration. The units are g. mole/liter/sec. The constant r allows for the retardation of the hydrion-catalyzed esterification by water. The values used in this investigation were calculated by the method of Williamson and Hinshelwood,[11] and were

t	55	60	70	75
r	0.10	0.19	0.31	0.40

The average value of k at each temperature is reported for the determination in which k varied the least. The values of the energy of activation were calculated in the usual way by means of the Arrhenius equation.

Results and Discussion

TABLE I

VELOCITY CONSTANTS AND ENERGIES OF ACTIVATION FOR HYDRION-CATALYZED ESTERIFICATION OF AROMATIC ACIDS WITH CYCLOHEXANOL

Acid	55°	60°	70°	75°	Energy of activation, E
		$k \times 10^5$			
o-Nitrobenzoic	...	0.625	1.44	2.20	20,000
o-Toluic	0.889	1.34	2.52	4.26	17,800
o-Bromobenzoic	1.21	1.72	3.92	5.59	17,400
p-Toluic	1.45	2.16	5.03	7.81	19,500
o-Chlorobenzoic	1.61	2.35	5.26	7.31	17,500
m-Toluic	2.03	2.94	6.26	9.08	16,900
Benzoic	2.21	3.25	7.19	10.88	17,700
p-Chlorobenzoic	2.41	3.71	7.60	11.14	17,100
m-Bromobenzoic	2.83	4.26	8.77	12.47	17,000
m-Chlorobenzoic	2.96	4.07	8.55	12.14	15,900
m-Nitrobenzoic	3.05	4.30	10.57	15.91	18,300

Table II gives the values of log k_{55} obtained in this investigation for the esterification of the meta

(10) Goldschmidt, *Ber.*, **39**, 711 (1906).

(11) Williamson and Hinshelwood, *Trans. Faraday Soc.*, **30**, 1145 (1934).

and para substituted benzoic acids and the corresponding values as calculated from Hammett's equation. The value of ρ adopted, 0.262, was obtained by the least squares method (see Hammett[6]).

TABLE II

COMPARISON OF LOG k_{55} OBSERVED WITH LOG k CALCULATED WITH THE EQUATION: LOG $k = -4.656 + \sigma (0.262)$

Acid	Log k, obsd.	Log k, calcd.	Error
m-Toluic	-4.692	-4.674	0.018
p-Toluic	-4.839	-4.701	.138
p-Chlorobenzoic	-4.618	-4.596	.022
m-Bromobenzoic	-4.548	-4.554	.006
m-Chlorobenzoic	-4.529	-4.558	.029
m-Nitrobenzoic	-4.516	-4.470	.046
		Av.	.043

The average error of log k for the work of this investigation was 0.043. This compares favorably with the mean of probable errors of less than 0.1 found by Hammett[6] for a series of thirty-nine reactions, and of 0.122 for the data of Goldschmidt.[3] Hartman and Borders[7] report an average error of 0.054. The authors recalculated the value of ρ from the data of Hartman and Borders and found it to be − 0.53 instead of − 0.58 which they reported. Using this corrected value of ρ together with the values of σ given by Hammett,[6] their average error is found to be 0.049 instead of 0.054 as reported.[7] The results presented here indicate that the equation of Hammett can be applied to the esterification of cyclic alcohols.

Ortho substituted acids are not included in Hammett's theory. Since the effect of a substituent in the ortho position upon the velocity of side chain reactions is of an entirely different mechanism from that of the meta and para substituted acids, the velocity of the ortho substituted acids is not discussed here.

The outstanding difference in the order of the esterification of substituted acids with cyclohexanol and with methanol is that the order is practically reversed. Hartman and Borders[7] found that the order of decreasing speed of esterification with methyl alcohol is m-CH$_3$ > p-CH$_3$ > m-Br > m-Cl > p-Cl > p-NO$_2$. The order found by the authors for cyclohexanol is m-NO$_2$ > m-Cl > m-Br > p-Cl > m-CH$_3$ > p-CH$_3$. It should be noted that the value of ρ for methanol reported by Hartman and Borders is negative, whereas that found in this investigation for cyclohexanol is positive. This change in sign probably accounts for the reversal of the order of the esterification with cyclohexanol

Evans, Morgan, and Watson[12] found in the bromination of substituted acetophenones what they considered to be a significant variation in the non-exponential factor, P, of the Arrhenius equation: $k = PZe^{-E/RT}$. Nathan and Ingold[13] criticized this conclusion because the range of velocities was not sufficient for accurate separation of the factors E and P. This criticism of these factors might also apply to the present work because the ratio of the velocity of the fastest to the slowest acid is only 3.4 to 1.

The change in the various factors of the Arrhenius equation may be analyzed at least qualitatively by plotting the values of E for the various acids against log k_{55}. This relationship is shown in Fig. 1. If the change in the velocity of esterification of the acids produced by the substituents were entirely dependent upon changes in E, a straight line having a slope of $2.303RT$ would be obtained. The solid line in Fig. 1 represents an approximate graphical average obtained from plotting the data of this investigation. The broken line represents the theoretical line having a slope of $2.303RT$. If the experimental line can be considered to be approximately correct, it is apparent that the two lines have nearly identical slopes. The scattered points obtained from the data, however, indicate that such a conclusion cannot be drawn with certainty. If the line can be regarded as nearly true, it could be concluded that the steric factor, P, does not undergo an appreciable change in the Arrhenius equation. As has been pointed out already, however, the small range of velocities studied and the effect of large experimental error at high temperatures

(12) Evans, Morgan and Watson, J. Chem. Soc., 1168 (1935).
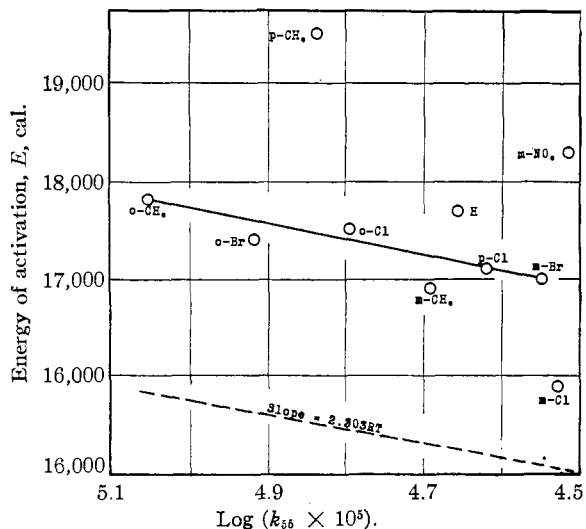(13) Nathan and Ingold, ibid., 222 (1936).

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

upon the values of E, precludes the possibility of a positive statement of this point.

Summary

1. The investigation of the effect of polar substituents on the reaction velocity of hydrion-catalyzed esterification of substituted benzoic acids with cyclohexanol shows that the velocity is decreased by the displacement of electrons toward the carboxyl group.

2. Excellent agreement was found between the experimental values of log k for the esterification reactions and the values calculated from Hammett's equation. This equation is therefore applicable to the esterification of cyclohexanol.

3. It appears that the value of E in the Arrhenius equation is the chief factor in determining the velocity of esterification.

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