entropies obtained from the temperature coefficient of these rate constants apply to this reaction.

Discussion

The results show, with one exception, an increase in activation energy when α- or β-hydrogens are replaced by methyl groups. The activation energy of the ethyl bromide reaction is 2.9 kcal. greater than that of the methyl bromide reaction. As would be expected, the effect of the introduction of a second methyl group on the α-carbon, 1.6 kcal., is not as great as that caused by the introduction of the first group. Entropy differences for the reactions of the members of the α-methylated series are small. The exact value of the isopropyl bromide reaction is uncertain. The value for the methyl bromide reaction is just on the border line of significance since it is only 0.2 cal. greater than the probable error.

The one exception is found on the introduction of the first methyl group on a β-carbon. As one goes from the ethyl to the *n*-propyl reaction the activation energy drops slightly, yet the reaction rate is halved due to a 3 cal./deg. drop in the entropy of activation. However, upon introduction of a second methyl group, *i. e.*, the reaction of isobutyl bromide, the drop in reaction rate is again primarily due to a 1.7 kcal. rise in the activation energy. The entropy has not decreased significantly. This result is in close agreement with the calculations of Dostrovsky, Hughes and Ingold[6] which predict a rise of 1.4 kcal. in the activation energy because of increased steric hindrance.

The data are consistent and, with exception of the reaction of *n*-propyl bromide, they are in agreement with explanations of the decrease in reactivity accompanying α- or β-methylation which are based on increased energy barriers to the activated complex caused by significantly increased polar and steric effects.

Summary

The rates of reaction of methyl bromide with thiosulfate ion in 50% water–alcohol solvent were measured at 0, 10 and 20° and those of isobutyl bromide with thiosulfate ion at 12.5, 25, 37.5 and 50°. From the rates of reaction the energies and relative heats and entropies of activation of the reactions were computed.

The amount of thiosulfate ion used up in the methyl bromide reaction corresponds to only 90 mole % of that required to react with all of the methyl bromide added. This has been investigated and it has been shown that this incompleteness of reaction does not interfere with the kinetics.

(6) Dostrovsky, Hughes and Ingold, *J. Chem. Soc.*, 173 (1946).

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[CONTRIBUTION NO. 75 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Kinetics of Acid-catalyzed Esterification of Dimethylsubstituted Benzoic Acids

BY HILTON A. SMITH* AND RUPERT B. HURLEY[1]

The rates of acid-catalyzed esterification of the monomethyl substituted benzoic acids have been previously reported.[2] It was found that substitution of a methyl group in the meta or para position of benzoic acid did not greatly alter the rate constant, while similar substitution in the ortho position caused the esterification rate to drop to one-third of that of benzoic acid. Hartman and Borders also reported that for each of the toluic acids, the activation energies were considerably lower (1100 to 1700 calories per mole) than for benzoic acid.

Since little work has been done on the dimethyl substituted benzoic acids, it seemed of interest to prepare the various isomers, and to measure their esterification rates. In addition, benzoic acid was also studied for comparison purposes.

Experimental

Merck reagent grade, primary standard **benzoic acid** was used without further purification. The dimethylbenzoic acids were prepared and recrystallized in the manner previously described.[3] Table I shows the melting points and neutral equivalents of the materials used.

TABLE I

MELTING POINTS AND NEUTRAL EQUIVALENTS OF ACIDS ESTERIFIED

Acid	Cor.[a] m. p., °C.	Neutral equivalent Found	Neutral equivalent Theoretical
Benzoic	121.0–121.6	122.3	122.0
2,3-Dimethylbenzoic	144.5–145.5	150.4	150.2
2,4-Dimethylbenzoic	125.2–125.8	150.0	150.2
2,5-Dimethylbenzoic	133.9–134.6	150.2	150.2
2,6-Dimethylbenzoic	115.5–116.2	150.5	150.2
3,4-Dimethylbenzoic	168.6–169.2	151.0	150.2
3,5-Dimethylbenzoic	173.2–173.8	150.8	150.2

[a] All melting points have been corrected for emergent thermometer stem and were determined in an aluminum melting-point block.

Methanol was obtained in a pure, dry state, as in previously reported work, by careful fractionation of methyl alcohol through a 5-ft. helix-packed column. The method used to ob-

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* Harvard University Ph.D. 1934.

(1) Tennessee Eastman Fellow, 1947–1948.

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

(3) Smith and Stanfield, *ibid.*, **71**, 81 (1949).

tain rate constants was essentially that previously described,[4] except that the concentration of the hydrogen chloride catalyst was increased to 0.01 *M*. Corrections were made for solvent expansion.

Experimental Results and Calculations

The rate constants were calculated from Goldschmidt's equation

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

where a is the original concentration of organic acid, x is the concentration of ester formed after time t, and the catalyst is hydrogen chloride. The values of the constant, r, used were those obtained in earlier work.[5]

Since the reaction of methanol with hydrogen chloride is appreciable under the conditions used, it was necessary to correct the concentration of catalyst accordingly. The rates of reaction between solvent and hydrogen chloride were determined experimentally. The results are shown in Table II.

TABLE II

RATE OF REACTION OF HYDROGEN CHLORIDE WITH METHANOL IN 0.01 *M* SOLUTION

Temp., °C.	Reaction rate %/minute
25	0.000215
35	.000525
45	.00197
55	.0100

These rates are approximately twice those obtained for 0.005 *M* solutions.[6] Corrections for change in catalyst concentration were made in the same manner as previously described.[5]

The results for a typical run are shown in Table III, while the rate constants and activation energies for all of the reactions studied are given in Table IV. The activation energies were obtained from the Arrhenius equation by application of the method of least squares. A plot of log k against the reciprocal of absolute temperature is shown in Fig. 1.

TABLE III

ESTERIFICATION DATA FOR 3,4-DIMETHYLBENZOIC ACID AT 45°

t, min.	$(a - x)$	(HCl)	k (liters moles^{-1} sec.$^{-1}$)
720	0.367	0.00986	0.000858
975	.336	.00981	.000865
1395	.391	.00973	.000874
2230	.231	.00956	.000860
2860	.200	.00944	.000839
4005	.152	.00921	.000849
			Av. 0.000858 ± 0.000009

TABLE IV

REACTION RATE CONSTANTS AND ACTIVATION ENERGIES FOR THE ESTERIFICATION OF BENZOIC ACID AND THE SIX DIMETHYLBENZOIC ACIDS USING 0.01 *M* HYDROGEN CHLORIDE CATALYST

Acid	$k \times 10^5$ liters moles^{-1} sec.$^{-1}$ 25°	35°	45°	55°	*E* cal. mole^{-1}
Benzoic	20.4	44.6	96.4	195	
	20.5	43.7	96.6	194	14,600
Av.	20.4	44.2	96.5	195	
2,3-Dimethylbenzoic	7.26	15.8	33.7	71.5	
	7.27	16.1	36.0	71.2	14,800
Av.	7.27	16.0	34.9	71.4	
2,4-Dimethylbenzoic	5.87	13.5	28.7	63.7	
	5.88	13.5	29.5	64.3	15,400
Av.	5.87	13.5	29.1	64.0	
2,5-Dimethylbenzoic	5.65	13.1	29.3	61.6	
	5.73	13.0	29.2	63.4	15,500
Av.	5.69	13.0	29.3	62.5	
2,6-Dimethylbenzoic	Would not react				....
3,4-Dimethylbenzoic	17.1	38.1	85.8	175	
	17.8	38.4	84.9	177	15,000
Av.	17.4	38.2	85.4	176	
3,5-Dimethylbenzoic	20.9	47.9	101	212	
	21.2	48.0	102	213	14,900
Av.	21.0	48.0	102	213	

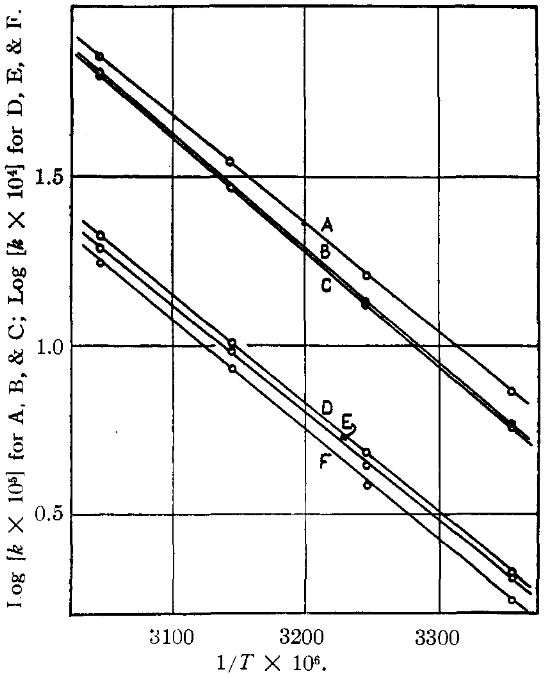

Fig. 1.—Temperature coefficients for esterification of benzoic and the dimethylbenzoic acids: A, 2,3-acid; B, 2,4-acid; C, 2,5-acid; D, 3,5-acid; E, benzoic acid; F, 3,4-acid.

Discussion

For convenience the data of Hartman and Borders[2] are given in Table V, together with data from this research. The reacting acids are arranged in the order of those with none, one, and

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[4] Smith, THIS JOURNAL, **61**, 254 (1939).

[5] Smith and Reichardt, *ibid.*, **63**, 605 (1941).

[6] Smith, *ibid.*, **62**, 1136 (1940).

two methyl substituents in the position ortho to the carboxyl group.

TABLE V

EFFECT OF METHYL SUBSTITUENTS ON THE RATE OF ESTERIFICATION OF BENZOIC ACID IN METHANOL

Acid	$k_{25} \times 10_5$, liters moles^{-1} sec.$^{-1}$	E, cal. mole^{-1}
Benzoic	21.7	14,600
Benzoic[a]	19.2	15,500
p-Toluic[a]	19.7	13,800
m-Toluic[a]	21.7	14,200
3,5-Dimethylbenzoic	21.0	14,900
3,4-Dimethylbenzoic	17.4	15,000
o-Toluic[a]	6.41	14,400
2,4-Dimethylbenzoic	5.87	15,500
2,5-Dimethylbenzoic	5.69	15,400
2,6-Dimethylbenzoic	No reaction	....

[a] Data of Hartman and Borders, ref. 2.

It is quite obvious that the acids fall into three groups, depending on the number of substituents in the ortho position, and that the rate of reaction is decreased with increasing number of such substituents. The results for benzoic acid reported here give an activation energy for the esterification of benzoic acid which is 900 calories lower than that reported by Hartman and Borders. With this revision, there seems to be little evidence for lowering of the activation energy by methyl substituents. On the contrary, there seems to be a slight increase when a methyl group is substituted in the ortho position. One would estimate that the activation energy for the 2,6-substituted acid is much greater than any value recorded in Table V.

It seems probable that the retarding influence of the 2-methyl groups is primarily steric in nature, and is much the same as that of β-methyl substituents in aliphatic acids.

Summary

The kinetics of the acid-catalyzed esterification in methanol of benzoic acid and of the dimethyl-substituted benzoic acids have been studied. Velocity constants and activation energies for these reactions have been compared with similar values for the toluic acids. It has been shown that the relative rates of esterification are influenced by substitution in the ortho, but not in the meta and para position.

KNOXVILLE, TENNESSEE RECEIVED OCTOBER 10, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE JOHNS HOPKINS UNIVERSITY]

The Electrolytic Reduction of *p*-Aminoacetophenone[1]

BY MILTON J. ALLEN[2a,b] AND ALSOPH H. CORWIN*

Numerous studies have been undertaken in the past to determine the effects of electrolytic reduction on ketones. Usually the reduction proceeds to a pinacol, an alcohol, a hydrocarbon or a mixture of both pinacol and alcohol. Of these reactions, the formation of a hydrocarbon is not usually a continuation of the secondary alcohol formation, as secondary alcohols are not easily reduced by electrolytic methods.[3] There is no doubt that the reaction which takes place depends upon the electrode material and the type of electrolyte used. Elbs and Brand[4] found that in alkaline solution, using a lead cathode, the aliphatic and aromatic ketones are reduced to the corresponding secondary alcohol, whereas in acid solution, a mixture of pinacol and alcohol is obtained.

Escherich and Moest[5] found that Michler ketone yields the pinacol with a copper cathode, while both pinacol and alcohol are formed in almost equal amounts at a nickel cathode.

The prime purpose of this investigation was to study the change in products resulting from a change in experimental conditions, using a single type of cathode material, in an attempt to find the conditions which would give a maximum yield of 2,3-bis-(*p*-aminophenyl)-2,3-butanediol.

Experimental

The apparatus used in this work was similar to that described by Lingane,[6] with the exception that cathode potentials as high as six volts and currents as high as 20 amperes were provided for. Essentially, this apparatus will give automatically controlled impressed voltage to secure constant cathode potential. Two cells were developed for both small (25–50-ml.) and larger (400–800-ml.) quantities of material (Fig. 1a and 1b).

In the experiments to be discussed, the *p*-aminoacetophenone was dissolved in the desired solution and placed in the cathode chamber. A blank solution which excluded the ketone was placed in the anode compartment. The two compartments were separated by a cellophane membrane.[7] Table I gives some experimental results using a carbon anode and a mercury cathode.[8] A smooth platinum anode and a mercury cathode were used in the experiments listed in Table II. Most of the experiments were performed with diluted hydrochloric acid as the electrolyte, as the pinacol dihydrochloride was the desired product.

The alcohol was isolated from the mother liquor after filtering off the pinacol. The solvent was removed, the

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* Harvard University Ph.D. 1932.

(1) This investigation was supported, in part, by a research grant awarded M. J. A., by the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service.

(2) (a) Research Fellow, National Cancer Institute, 1947–1949; (b) from the Ph.D. dissertation of Milton J. Allen, The Johns Hopkins University, June, 1949.

(3) Tafel, *Z. Elektrochem.*, **17**, 972 (1911).

(4) Elbs and Brand, *ibid.*, **8**, 783 (1902).

(5) Escherich and Moest, *ibid.*, **8**, 849 (1902).

(6) Lingane, *Ind. Eng. Chem.*, ***Anal. Ed.***, **17**, **332** (**1945**).

(7) Purchased from the Visking Corp., Chicago, Ill.

(8) Mercury was found more desirable as higher overvoltages were obtainable, and also because mercury is readily purified.