and hydrochloric acid present, to their mixing with the coagulating electrolyte, and to the changes in the adsorption equilibria taking place.

Summary

1. The heat of coagulation of ferric oxide hydrosol of widely varying purity with 0.2 N sodium sulfate solution has been investigated, using sols prepared by three very dissimilar methods; (*1*) oxidation of ferrous chloride solution with hydrogen peroxide and dialysis, (*2*) peptization of precipitated ferric oxide in ferric chloride solution, (*3*) addition of various amounts of hydrochloric acid to a sol of high purity made by the first method.

2. The same value for the heat of coagulation at a given purity and total iron concentration is obtained with sols prepared by all three methods, indicating that ferric oxide sols represent an equilibrium which is defined by the temperature, pressure, concentration and purity.

3. The change in dispersity of ferric oxide during coagulation does not involve a measurable heat effect.

4. The heat effects observed during the coagulation of sols of low purity are due to (*1*) dilution of the ferric chloride and hydrochloric acid in the sols, (*2*) mixing of these electrolytes with the coagulating electrolyte, (*3*) changes in the adsorption equilibria.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA]

THE HYDROLYSIS OF METHYL ORTHO-NITROBENZOATE IN ACID SOLUTION

BY GERALD E. K. BRANCH AND DONALD S. MCKITTRICK

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Introduction

The mono-*ortho* substituted benzoic acids, in the presence of hydrogen ion, esterify much more slowly than does the unsubstituted acid. The difference is particularly noticeable when the substituent is a nitro group. The velocity constants as written by Goldschmidt[1] are: benzoic acid, 0.0428; *o*-nitrobenzoic acid, 0.0028; *o*-methylbenzoic acid, 0.011. On the other hand, Kellas[2] found that methyl *o*-nitrobenzoate in alcoholic potash hydrolyzes considerably faster than does methyl benzoate; but he also found that the introduction of a methyl group in the *ortho* position caused a greater slowing up of the alkaline hydrolysis than of the esterification in acid. These results may point to an actual difference in the phenomenon of steric hindrance, in the esterification and hydrolysis reac-

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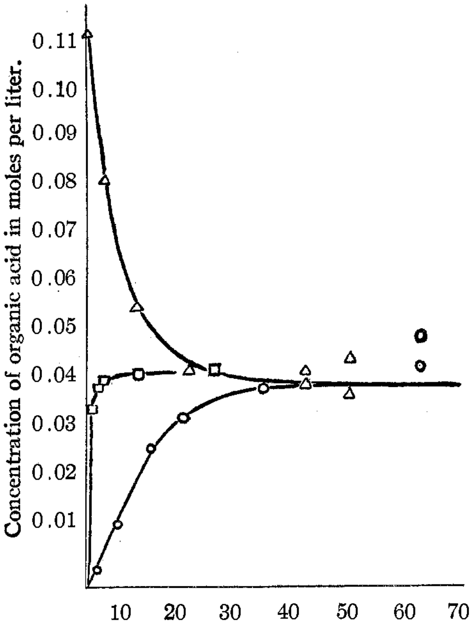
[1] Goldschmidt, *Ber.*, **28**, 3218 (1895).

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

tions, or to an influence of the substituent on the relative catalysis by hydrogen and hydroxyl ions. If it is assumed that the mechanism of catalysis involves the formation of addition products between the acid or ester and the ions, we should expect the introduction of a negative group to increase the catalysis in alkali and decrease it in acid. To settle this point we measured the rates of hydrolysis of methyl benzoate and methyl *o*-nitrobenzoate and the rate of esterification of *o*-nitrobenzoic acid in acid solution. It was found that the influence of a nitro group in the *ortho* position was the same in sign and order of magnitude for both hydrolysis and esterification. The similarity of the steric influence of a single nitro group upon both hydrolysis and esterification was further shown by finding that the equilibrium was practically the same for both the substituted and unsubstituted substances.



⊙, methyl *o*-nitrobenzoate; △, *o*-nitrobenzoic acid; □, methyl benzoate.

Method

The reactions were carried on in sealed tubes which were heated for different lengths of time in boiling chlorobenzene (b. p., 133°) then removed and rapidly cooled under water; two 10cc. portions were thereupon titrated with 0.0991 *N* sodium hydroxide solution. The tubes contained methyl alcohol, and the acid or ester under investigation at a concentration of 0.1104 moles per liter, together with sufficient sulfuric acid to make the acidity of the catalyst 0.25 *N*, and water to reduce the methyl alcohol content to 60%.

With each of these tubes was heated a duplicate containing the same concentration of methyl alcohol and sulfuric acid, but no organic acid or ester, and slightly more water to make up for the deficiency in volume thus produced. These "blanks" were heated, cooled, and titrated in the same manner as were the "reacting" tubes. The difference in titer of corresponding pairs of tubes, with a slight correction, gave the concentration of organic acid at the different times.

The correction to be applied is necessary because of the slight difference in the equilibrium point of the reaction, $H_2SO_4 + CH_3OH = CH_3HSO_4 + H_2O$, caused by the difference in concentration of water in the 2 tubes. It may be easily calculated by assuming that the equilibrium constant is the same in both solutions. This results in the expression, $AB/CD = A'B'/C'D'$, where A, B, C, and D represent the concentrations of methyl alcohol, sulfuric acid, methyl hydrogen sulfate, and water, respectively, in the blank, and the accented letters the corresponding values for the reaction mixtures.

This reduces to the following approximate equation,[3] $\frac{2T-t}{T-t} = \frac{2x-T}{T-x} \cdot \frac{V+v}{V-v}$, where T is the original titer of the blank, t the titer after the reaction has reached equilibrium, V the volume of water in the blank, v the volume of organic acid or ester introduced, and x the corrected value for the titer of the blank. Regarding the justification for the use of v it was found that the volume change of the acid or ester on solution was negligible. In all three cases the correction was approximately 0.1 cc.

The procedure outlined was found to give consistent titrations checking to within 0.1 cc. equivalent to 0.001 moles per liter when the time of heating was short. We think that the measurements taken during the first 20 hours and the entire curves are accurate to within 0.002 moles per liter; but owing to a peculiar side reaction between the sulfuric acid and the methyl alcohol the results for long heating are not reliable. This side reaction was evident after the equilibrium between sulfuric acid and methyl alcohol had been reached by the formation of pressure, as a slow increase in the acid titer, and as a discrepancy in the titrations of duplicate tubes. The equilibrium for the esterification of *o*-nitrobenzoic acid has, therefore, to be determined by extrapolation.

The results obtained for the hydrolysis of methyl *o*-nitrobenzoate and methyl benzoate are given in Tables I and III. The values for the esterification of *o*-nitrobenzoic acid are given in Table II. In these tables Col. 1 gives the time, Col. 2 the concentrations of the organic acid in moles per liter, determined as the mean of 2 measurements; when duplicates did not check to within 0.002 moles per liter both figures are given. These results are also shown graphically. In drawing these curves experiments which did not check to within 0.002 moles per liter were neglected, although they are indicated by points on the figure.

TABLE I

HYDROLYSIS OF METHYL ORTHO-NITROBENZOATE

Initial conc. of ester = 0.1104 moles/liter; conc. of acid at equil. = 0.040 moles/liter

Time Hours	Conc. of acid = x	K_1 = Veloc. const. of hydrolysis in moles/liter/hour
0.00	0.0000	....
2.00	0.0031	0.0142
6.00	0.0124	0.0204
12.67	0.0275	0.0266
19.08	0.0331	0.0256
35.42	0.0391	0.0270
..	0.0439	....
66.17	....	....
..	0.0498	....

K from initial slope of the curve = about 0.020 Mean K = 0.0230

The progress of the esterification of the sulfuric acid by methyl alcohol, and that of the side reaction of methyl alcohol when heated with dil.

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[3] This equation neglects the changes of water and alcohol concentrations due to the esterifications and hydrolyses which are being measured, and the formation of methyl sulfate. Of these only the last mentioned can be of the same order of magnitude as the correction.

sulfuric acid are shown in Table IV, which gives the titers of the blanks and their discrepancies.

TABLE II

ESTERIFICATION OF ORTHO-NITROBENZOIC ACID

Initial conc. of ester = 0.1104 moles/liter; conc. of acid at equil. = 0.040 moles/liter

Time Hours	Conc. of acid = x	K_1 = veloc. const. of hydrolysis in moles/liter/hour
0.00	0.1104	....
3.50	0.0813	0.0221
10.00	0.0565	0.0238
20.33	0.0441	0.0256
..	0.0412	....
43.83	....	....
..	0.0442	....
..	0.0396	....
52.25	....	....
..	0.0465	....

K from initial slope of curve = about 0.019   Mean K = 0.0238

TABLE III

HYDROLYSIS OF METHYL BENZOATE

Time Hours	Conc. of acid = x in moles/liter	K_1 = veloc. const. of hydrolysis in moles/liter/hour, calculated for mono-molecular hydrolysis For dimolecular esterification	 For monomolecular esterification
0.00	0.0000	...	...
1.00	0.0352	0.506	0.671
2.10	0.0395	0.348	0.476
3.00	0.0407	0.282	0.384
10.17	0.0421	...	...
25.17	0.0433	...	...

K from initial slope of curve = about 0.36

TABLE IV

TITER OF THE BLANKS

Time Hours	Mean titer Cc.	Discrepancy in duplicate titrations Cc.
0.00	25.10	0.04
1.00	20.01	0.06
2.00	19.95	only one tube
2.10	19.90	0.10
3.00	19.90	0.12
3.50	19.85	0.01
6.00	19.81	only one tube
10.00	20.00	0.17
19.08	20.06	0.12
20.33	20.16	0.24
35.42	20.37	0.29
43.83	20.78	0.31
66.88	21.76	0.82
74.00	21.65	0.70

Order of the Reactions

Inspection of the curves for methyl *o*-nitrobenzoate and *o*-nitrobenzoic acid shows that the initial slope of the former is much the smaller while the equilibrium is not far from the middle point. This indicates that the hydrolysis reaction is of a lower order than the esterification. If the rates are of the first and second orders then the rate of change of the acid concentration in both cases is given by

$$\frac{dx}{dt} = K_1\,(a-x) - K_2x^2 \qquad (1)$$

where x is the concentration of the acid at the time t; K_1 the rate constant for hydrolysis; and K_2 that for esterification.

At equilibrium,

$$(a-x_e)\ K = K_2x^2{}_e,\ \text{or}\ K_2 = \frac{a-x_e}{x_e^2}\,K_1 = bK_1 \qquad (2)$$

where x_e is the acid concentration at equilibrium.

Substituting bK_1 for K_2 in Equation 1 and integrating,

$$K_1t = \frac{1}{\sqrt{1+4ab}}\left[\log\frac{\sqrt{1+4ab}-1}{\sqrt{1+4ab}+1} - \log\frac{\dfrac{\sqrt{1+4ab}-1}{2b} - x}{\dfrac{\sqrt{1+4ab}+1}{2b} + x}\right]$$

where $x = 0$ when $t = 0$ (for hydrolysis) and

$$K_1t = \frac{1}{\sqrt{1+4ab}}\left[\log\frac{a + \dfrac{1-\sqrt{1+4ab}}{2b}}{a + \dfrac{1+\sqrt{1+4ab}}{2b}} - \log\frac{x + \dfrac{1-\sqrt{1+4ab}}{2b}}{x + \dfrac{1+\sqrt{1+4ab}}{2b}}\right]$$

where $x = a$ when $t = 0$ (for esterification).

Taking $x_e = 0.040$ from the curves, this expression gives fairly constant values for K_1 which are approximately the same for hydrolysis and esterification.

The above equations can only be approximate, for they depend on the assumption that the rates of hydrolysis will be proportional to different powers of the ester and organic acid concentrations even at equilibrium. This is expressed in Equation 2, $K_1\,(a-x_e) = K_2x_e^2$. This would necessitate that simultaneous and proportionally equal changes of the concentrations of ester and acid would alter the equilibrium ratio between these substances. This could be possible only if their fugacites vary with different powers of their respective concentrations. This deviation from the laws of dilute solutions would correspond to a high degree either of dissociation of the acid or of association of the ester. The former alternative is impossible and the latter improbable. It would appear, therefore, that the laws governing these reactions must be more complicated, and that the hydrolysis must take place by a more complex mechanism, as well as by a first order reaction. The values of K, obtained by these equations will, however, give the effective rate of hydrolysis with sufficient accuracy for the comparisons made in this article.

In the case of the hydrolysis of methyl benzoate, the measurements are so near to equilibrium that they are of little or no value in determining the order of reaction. For comparison with the nitro ester, however, we have calculated the velocity constants for this reaction by the above equation, and also upon the assumption that both the direct and reverse reaction are of the first order, taking the equilibrium value of acid as 0.0427 moles per liter, the mean of the last two measurements.

Comparison of the results for the hydrolysis of methyl benzoate and its *o*-nitro derivatives shows that the former reaction is between 15 and 20 times the faster. This is in agreement with the results obtained by Goldschmidt, who found for the esterification of the corresponding acids the ratio 15:1. The equilibrium in the two reactions of the nitro derivatives is practically the same. This would hardly be the case unless the influence of the nitro group were the same in both reactions. Therefore, the difference between the steric hindrance of the *o*-nitro group on esterification in acid and hydrolysis in alkali as found by Kellas was due to the different catalyst used.

Theoretical

If we assume, as is generally done, that the hydrolysis of an ester in acid solution is preceded by the formation by means of a rapid reversible reaction, of a complex with hydrogen ion, then the speed will depend not only on the velocity constant of the hydrolysis of the intermediate to the acid and alcohol, but also on the equilibrium, Ester $H^+ \rightleftarrows$ Ester + H^+. The compound on the left side of this equation is the ion of a weak unstable base; therefore the introduction of a negative group into the ester should decrease the strength of this base, and hence also the concentration of its ion (just as there is less $NO_2C_6H_4NH_3^+$ than $C_6H_5NH_3^+$ in equivalent solutions of the corresponding chlorides), and consequently should lower the rate of hydrolysis of the ester.

In a similar way, the introduction of a negative group should decrease the rate of esterification of an acid in the presence of hydrogen ion as a catalyst. The case of the hydrolysis of an ester in alkaline solution is just the reverse, for the assumed addition product with hydroxyl ion is the ion of a weak acid, so that the introduction of a group which increases the strength of acids should increase the concentration of this ion and hence should increase the rate of hydrolysis.

From this it follows that the introduction of a nitro group should increase the rate of hydrolysis in alkali and decrease it in acid. Obviously, this does not account completely for the effect known as steric hindrance, for the decrease in the rate of hydrolysis in acid caused by the introduction of an *o*-nitro group is much greater than the increase in alkaline solution; but it does show that we cannot compare the steric influence of two groups until we have studied the reaction in both acid and alkali. Thus the greater influence of the nitro than of the methyl group upon the esterification of the *ortho* substituted acids is due to the effect of the acid strength of the intermediate compounds with hydrogen ion, not, as has been often assumed, to a difference in mass; for we find a much greater rate of hydrolysis in alkali of the methyl *o*-nitrobenzoic than of the methyl substituent. Again the steric hindrance of a *meta*-nitro group is entirely explained by the above theory; in fact, the introduction of a nitro group in the *meta* position speeds up the hydrolysis in alkali more than it slows down the esterification in acid.

Summary

The rates and equilibria of the hydrolysis of methyl *o*-nitrobenzoate and methyl benzoate and the esterification of *o*-nitrobenzoic acid were studied under the same conditions: 60% methyl alcohol, 40% water, 0.25 *N* sulfuric acid, and 0.1104 moles per liter of organic acid or ester. It was found that (1) the equilibria for the substituted and unsubstituted bodies were practically the same; (2) the esterification reaction of the nitrobenzoic acid was found to be of a higher order than the corresponding hydrolysis; (3) the rate of hydrolysis of the nitrobenzoic ester was about $^1/_{20}$ as great as that of the benzoic ester. This last is contrary to the results obtained by Kellas working in alkaline solution. The discrepancy is explained by assuming the reaction to be preceded by complex formation between the ester and the hydrogen or hydroxyl ion. As may be expected, the nitro group favors the formation of the complex with hydroxyl ion and the dissociation of that with hydrogen ion, and consequently slows down the reactions in acid and speeds them up in alkaline solutions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY]

A COMPARISON OF THE NORMAL BOILING TEMPERATURES OF UNDESICCATED SULFUR AS MEASURED BY THE DYNAMIC AND THE STATIC METHODS

BY ALAN W. C. MENZIES

Received November 2, 1922

History and Outline of the Problem

Reference has been made elsewhere[1] to the literature of the extended controversy, particularly between Kahlbaum on the one hand and Ramsay and Young on the other, in regard to the identity of the boiling-point values obtained, respectively, by the static and the dynamic methods.

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[1] Compare Ostwald, "Lehrbuch der Allgemeinen Chemie," Engelmann, **1910**, Vol. I, 308.