[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY.]

STUDIES IN ESTERIFICATION, II.

BY W. L. PRAGER.

Received October 7, 1908.

Sec. 1. Introductory.

The preceding communication places the phenomena of Victor Meyer's Esterification Law on a quantitative basis, and does away with the steric hindrance hypothesis which is generally supposed to explain its workings. The present paper gives an account of further experimental investigation along these lines, undertaken at the request of Professor M. A. Rosanoff, but deals with the assumption of steric hindrance in esterification somewhat more generally. The verdict of my new experiments is identical with the conclusion arrived at in the first paper: the hypothesis that the slow rate of esterification observed in the case of many acids is due to the *mechanical* interference of groups or atoms situated near the carboxyl group in the molecule, is untenable.

The acids investigated include the monoethyl ester of α-nitro-phthalic acid, acetic, propionic, isobutyric and trimethyl-acetic acids. The study of the monoethyl ester of α-nitro-phthalic acid corroborated entirely the view of the Esterification Law expressed in the first communication. The derived acetic acids were studied with a view to testing the current idea that "similar influences effect the esterification of both fatty and aromatic acids" and that "the rate of esterification is retarded in proportion to the number and size of the atoms or groups introduced into the acetic acid molecule."[1]

The experimental results given below might be interpreted as showing that a relationship exists between the velocity of esterification constants and the electrolytic dissociation constants of organic acids, rather than between the esterification velocities and the number of methyl groups in the molecule. These results are strengthened by some older observations made by Lichty[2] on the chlorinated acetic acids. I have calculated the esterification velocity constants of these acids from Lichty's experimental data, and the combined results appear to demonstrate clearly the untenability of the steric hindrance hypothesis as applied to the esterification of aliphatic acids.

The experimental method employed was identical with that described in the preceding communication.

Sec. 2. The Monoethyl Ester of α-Nitro-phthalic Acid.

This acid was prepared according to the method of Miller.[3] One part of

---

[1] See Cohen, *Organic Chemistry* (London, 1907), chapter on "The Esterification Law Applied to Fatty Acids," p. 234.

[2] *Am. Chem. J.*, **18**, 590 (1896).

[3] *Ann.*, **208**, 223.

ordinary phthalic acid is heated for two hours on the water bath with 1.5 parts of concentrated nitric acid and the same amount of concentrated sulphuric acid. After allowing the mixture to cool, it is filtered and the precipitate dried, dissolved in absolute alcohol and esterified by the Fisher method. In this way the α-nitro-phthalic acid is changed to $C_6H_3\overset{6}{NO_2}.\overset{1}{CO_2H}.\overset{2}{CO_2}C_2H_5$, whereas the β-nitro-phthalic and any unchanged phthalic acid are transformed into their respective di-ethyl esters. The alcohol is now evaporated, the residue taken up with ether and extracted with aqueous sodium carbonate, from which the acid is set free by hydrochloric acid. The solution is then extracted several times with ether, the ether evaporated, and the residue crystallized from water. My acid melted at 110°. Miller found 110.5°. The results of the esterification are given in Table I.

TABLE I.

t (days).	*v* (liters).	*a*.	*b*.	*x*.	*K*.	*k*.
0.669	0.001738	0.002240	0.01909	0.001746	(0.36)	0.24
0.833	0.001496	0.002036	0.01706	0.001530	(0.30)	0.18
0.9896	0.001320	0.001766	0.01498	0.001430	(0.45)	0.18
1.25	0.001381	0.001583	0.01708	0.001415	(0.76)	0.19
1.646	....	0.001897	0.01512	0.001751	1.57	..
1.792	....	0.002198	0.01785	0.002037	1.62	..
2.669	....	0.002391	0.01915	0.002206	1.55	..

Averages: $K = 1.58$; $k = 0.20$.

Sec. 3. Acetic Acid.

Kahlbaum's best acid was further purified by fractional freezing. The equilibrium constant of acetic acid has been carefully determined at both low and high temperatures (the heat of esterification or saponification in this case is zero). All that had to be done in this case, therefore, was to study the progress of the reaction in time. One mol of acetic acid was mixed with something over five mols of absolute ethyl alcohol, small quantities sealed up in small tubes, and accurately weighed. The reaction was allowed to proceed at the temperature of boiling aniline, the first stage of the reaction being neglected as in all my other work. The electrolytic dissociation constant of this acid at 25° is 0.00180.[1]

TABLE II.

t.	*v*.	*a*.	*b*.	*x*.	*k*.
0.0833	0.0014	0.003565	0.01804	0.002688	1.51
0.0972	0.0011	0.002698	0.01365	0.002122	1.51
0.1042	0.0012	0.003075	0.01556	0.002451	1.48
0.1458	0.00155	0.003203	0.01620	0.002645	1.44

Averages: ($K = 4.0$); $k = 1.48$.

Sec. 4. Propionic Acid.

Kahlbaum's pure acid was further carefully purified by fractional distil-

---

[1] Ostwald, *Z. physik. Chem.*, **3**, 174 (1889).

lation. One mol of this acid was mixed with nearly five mols of absolute ethyl alcohol and the velocity of esterification studied at 183°. The electrolytic dissociation constant at 25° is 0.00134.[1]

TABLE III.

t.	*v*.	*a*.	*b*.	*x*.	*K*.	*k*.
0.0847	0.001125	0.003750	0.01781	0.002616	..	1.01
0.0972	0.001034	0.002910	0.01297	0.001906	..	0.92
0.111	0.001296	0.004004	0.01902	0.002935	..	0.96
0.125	0.001089	0.002867	0.01362	0.002037	..	0.92
0.666	....	0.004272	0.02030	0.003865	2.25	..
0.854	....	0.004519	0.02168	0.004089	2.22	..

Averages: $K = 2.24$; $k = 0.95$.

Sec. 5. Isobutyric Acid.

Again one mol of acid was mixed with nearly 5 mols of absolute ethyl alcohol and the esterification studied at 183°. The electrolytic dissociation constant of this acid at 25° is 0.00144.[1]

TABLE IV.

t.	*v*.	*a*.	*b*.	*x*.	*K*.	*k*.
0.0833	0.001347	0.003339	0.01609	0.001975	(0.20)	1.09
0.0972	0.001276	0.003158	0.01522	0.001972	(0.25)	1.05
0.111	0.001188	0.003102	0.01495	0.002042	(0.30)	1.07
0.125	0.001639	0.004052	0.01952	0.002859	(0.41)	1.07
0.666	....	0.004034	0.01944	0.003646	2.16	..
1.000	....	0.003880	0.01870	0.003487	2.03	..

Averages: $K = 2.10$; $k = 1.07$.

Sec. 6. Trimethyl-acetic Acid.

Kahlbaum's excellent preparation was purified by pressing between folds of filter paper and carefully dried. The esterification was studied as in the cases described above. The electrolytic dissociation constant of this acid at 25° is 0.000978.[2]

TABLE V.

t.	*v*.	*a*.	*b*.	*x*.	*K*.	*k*.
0.633	0.001645	0.003957	0.01999	0.002911	(0.47)	0.19
0.794	0.001732	0.004135	0.02081	0.003193	(0.61)	0.19
1.042	0.001590	0.003509	0.01766	0.002855	(0.84)	0.18
1.250	0.001645	0.003700	0.01862	0.003108	(1.05)	0.18
1.375	0.001667	0.003712	0.01817	0.003130	(1.08)	0.18
1.667	0.001370	0.003118	0.01570	0.002736	(1.51)	0.17
2.000	....	0.003693	0.01853	0.003332	2.01	..
2.628	....	0.003007	0.01513	0.002711	1.99	..

Averages: $K = 2.0$; $k = 0.18$.

Sec. 7. Monochloracetic Acid.

For purposes of comparison with my own results, I have applied the law of mass action to the results of Lichty's experimental study of the esterification of the chlorinated acetic acids. In Lichty's

---

[1] Ostwald, *Loc. cit.*, p. 175.

[2] Cohen, *Organic Chemistry* (London, 1907), p. 234.

paper[1] there is no mention of a determination of the volumes of the reacting mixtures. Accordingly, I have carefully determined the volumes occupied by equimolecular mixtures of the acids with absolute alcohol at the ordinary temperatures and corrected for the expansion to 80°—the temperature at which Lichty conducted his experiments. Following are the results for monochloracetic acid, the first and last stages of the reaction being neglected, as in all my other work. For this acid I obtained $v = 0.13$ liter. The electrolytic dissociation constant is 0.155.[2]

Putting $a = b = 1$ in the general expression for k given in the first paper, and

$$K' = \left(\frac{1-x}{x}\right)^2 = 0.2085,$$

the following equation is obtained:

$$k = \frac{0.3277}{t} \log_{10} \frac{1 - 0.5432x}{1 - 1.4565x}.$$

TABLE VI.

t.	x.	k.
0.0139	0.2223	2.69
0.0174	0.2591	2.64
0.0208	0.2863	2.52
0.0313	0.3596	2.36
0.0416	0.4189	2.34
0.0833	0.5733	2.44

Average, $k = 2.50$.

Sec. 8. Dichloracetic Acid.

Putting in the general formula $a = b = 1$, $v = 0.15$ liter, and $K' = 0.1633$, we get

$$k = \frac{0.4273}{t} \log_{10} \frac{1 - 0.5959x}{1 - 1.4041x}.$$

The electrolytic dissociation constant of this acid at 25° is 5.14.[3]

TABLE VII.

t.	x.	k.
0.01042	0.3553	5.16
0.01388	0.4268	7.30
0.02083	0.4794	6.96
0.02777	0.5179	6.21
0.04166	0.5649	6.25

Average, $k = 6.38$.

Sec. 9. Trichloracetic Acid.

Here $a = b = 1$, $v = 0.16$ liter, and $K' = 0.1633$. The electrolytic dissociation constant at 25° is 121. We get

---

[1] *Am. Chem. J.*, 18, 590ff.

[2] Ostwald, *Loc. cit.*, p. 176.

[3] Ostwald, *Ibid.*, p. 177.

$$k = \frac{0.4558}{t} \log_{10} \frac{1 - 0.5959x}{1 - 1.4041x}.$$

TABLE VIII.

t.	x.	k.
0.00625	0.3230	12.37
0.00764	0.3645	12.23
0.00903	0.3970	11.93
0.01042	0.4298	11.95
0.01180	0.4591	11.99
0.01389	0.4903	11.70

Average, $k = 12.0$.

Sec. 10. Recapitulation of Results for Aliphatic Acids.

The following table reproduces the principal results of experiment and calculation in the case of the substituted acetic acids.

TABLE IX.

Acid.	Elec. diss. const.	k.	Temp.
Acetic	0.00180	1.45	183°
Propionic	0.00134	0.95	183°
Isobutyric	0.00144	1.07	183°
Trimethyl-acetic	0.000978	0.18	183°
Monochloro-acetic	0.155	2.46	80°
Dichloro-acetic	5.14	6.38	80°
Trichloro-acetic	121.0	12.0	80°

The velocity constants in the case of acetic and the three methylated acetic acids can in no way be considered as corroborating the steric hindrance hypothesis. Dimethyl-acetic (isobutyric) acide sterifies more rapidly than monomethyl-acetic (propionic) acid, while if the steric hindrance hypothesis were true the reverse would be the case. The velocity constants of the chlorinated acetic acids even at 80° are greater than that of acetic acid at 183°, and *increase* with the number of chlorine atoms near the carboxyl group, while, again, the reverse would be the case if the steric hindrance hypothesis were true.

On the other hand, in the case of all the acids given in Table IX, increase in the esterification constants runs parallel with an increase in the electrolytic dissociation constants. The two sets of constants are not proportional; but it must be remembered that the electrolytic dissociation constants were determined in aqueous solution and at low temperatures, whereas the esterification constants were obtained at higher temperatures and in alcoholic solutions containing varying amounts of water.

Sec. 11. Separation of Mono-ortho-substituted Aromatic from Other Acids.

The large differences between the esterification constants of mono-ortho-substituted aromatic acids, on the one hand, and of acids with the two ortho positions free, on the other hand (see the preceding communication), suggested the idea that the process of esterification might in many cases be employed for separating mono-ortho-substituted from other acids, just as diortho-substituted acids have been separated from other acids by Martz[1] and others. Three solutions were therefore prepared as follows:

(*a*) Ten grams of benzoic acid were dissolved in 200 cc. of absolute ethyl alcohol containing 3 per cent. of dry hydrochloric acid.

(*b*) Ten grams of anthranilic acid were dissolved in a similar quantity of alcoholic hydrochloric acid.

(*c*) A mixture of 10 grams of benzoic acid and 10 grams of anthranilic acid was dissolved in 400 cc. of the alcoholic hydrochloric acid.

The three solutions were allowed to stand at the ordinary temperature and the changes going on in solutions (*a*) and (*b*) determined from time to time by titration with standard alkali. At the end of 23 days, 86.5 per cent. of the benzoic acid had been changed to ester, while *the anthranilic acid had remained practically unchanged.* The solution containing both benzoic and anthranilic acids was then carefully neutralized with sodium carbonate, most of the alcohol cautiously distilled off, the residue taken up with ether, and the ether distilled off out of a weighed flask. There were thus obtained about 6 grams of pure ethyl benzoic ester. This yield would have been considerably larger if some of the ester had not been lost in the distillation of the alcohol. Plainly, the method, either in the form in which I have employed it, or in some similar form, ought to prove practically useful in separating organic acids which cannot be readily isolated by other means.

Sec. 12. Summary.

The present communication may be summarized as follows:

1. The velocity of esterification of α-nitro-phthalic acid corroborates the conclusions as to the Esterification Law drawn in the preceding communication.

2. The results of a cautious kinetic study of a set of aliphatic acids indicate that the steric hindrance hypothesis is untenable. This is contrary to the opinion held by the majority of investigators in the field. But, if the views expressed in the preceding communication are correct, velocity constants obtained, as usually, by studying esterification as a monomolecular reaction and in the presence of foreign catalytic agents, are by no means always comparable among themselves and can hardly be relied upon for safe guidance in theoretical generalization.

3. By way of a practical application of the results of the preceding communication, it is shown that mono-ortho-substituted aromatic acids can be separated from other acids by esterification.

---

[1] See Victor Meyer and Sudborough, *Ber.*, **27**, 3147 (1894).

In conclusion, I wish to acknowledge my indebtedness to the Director of these Laboratories, Professor M. A. Rosanoff, under whose guidance the above study was carried out.

CLARK UNIVERSITY,
WORCESTER, MASS., June, 1908.

NOTE.

On the "Color Demonstration of the Dissociating Action of Water" of Jones and Allen.—Jones and Allen[1] have published a well known lecture demonstration of the "dissociating action of water," which is repeated by Jones in his text-book, "The Elements of Physical Chemistry."[2] "A few drops of an alcoholic solution of phenolphthalein are placed in a glass cylinder, and diluted to, say, 50 cc. by the addition of alcohol. A few drops of an aqueous solution of ammonia are then added. A red color may appear where the aqueous ammonia first comes in contact with the alcoholic phenolphthalein but this will disappear instantly on shaking the cylinder.....Water is then gradually added to the cylinder, when the red color will appear, at first faint then stronger as the amount of water increases. When the red color has become intense, add a considerable volume of alcohol, and the entire color will disappear." This is given as a demonstration of the dissociating action of water, the explanation being that in the alcoholic solution the ammonia is so little dissociated that there are not enough hydroxyl ions present to color the phenol phthalein. Dilution with water dissociates the ammonia enough to give the red color to the indicator. The further addition of alcohol represses the dissociation and the solution again becomes colorless.

Recent light on the mechanism of the color change in indicators, and a comparison of the relative dissociating power of alcohol with its enormous decolorizing power on slightly alkaline phenolphthalein solutions made it seem highly improbable that the reason for the color change was the one assigned by Jones and Allen. This property of alcohol was noticed by the writer while measuring the dissociation constant of phenolphthalein.[3] It was first remarked by Menschutkin[4] and further observed quantitatively by McCoy.[5]

The effect of the alcohol in this respect is so great as to preclude the possibility of its being due, except in very small proportion, to the smaller dissociating power of the alcohol. Solutions of salts in alcohol show a degree of dissociation about one-third that in water.[6] Mixtures of

---

[1] *Amer. Chem. J.*, **18**, 377 (1896).

[2] Third edition, 1907, p. 295.

[3] *Z. Elektrochem.*, 14, 352 (1908).

[4] *Ber.*, 16, 315 (1883).

[5] *Amer. Chem. J.*, 31, 503 (1904).

[6] Jones, *Z. physik. Chem.*, 14, 701 (1894).