tions express the concentration (C) of acid in grams per 100 g. of aqueous solution corresponding to the specific gravity (d) at 20° referred to water at 4°.

Maleic acid $C = 276.78(d - 0.9982)$, for values of d up to 1.071
i-Malic acid $C = 244.55\ (d - 0.9982)$, for values of d less than 1.108, and
$C = 216.17(d - 0.9839)$ for values of d from 1.108 to 1.169

Index of Refraction.—The index of refraction was determined at 20° on aqueous solutions prepared as described under specific gravity and the readings were made with a Zeiss immersion refractometer using the prism which gives a reading of 14.5 with distilled water at 20° ($14.5 = n_D = 1.33301$). The following equations express the concentration of acid in grams per 100 g. of aqueous solution corresponding to the immersion refractometer reading (r).

Fumaric acid g./100 g. of solution $= 0.263r - 3.814$ (for values of r from 14.5 to 16.3)
Maleic acid g./100 g. of solution $= 0.272r - 3.922$ (for values of r from 14.5 to 95)
Malic acid g./100 g. of solution $= 0.323r - 4.68$ (for values of r from 14.5 to 45.5), and
g./100 g. of solution $= 0.289r - 3.132$ (for values of r from 45.5 to 95)

Summary

The solubility, specific gravity and index of refraction of aqueous solutions of fumaric, maleic and i-malic acids have been determined; equations representing these values are given.

CLEVELAND, OHIO

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

THE VELOCITY OF SAPONIFICATION OF ETHYL FORMATE BY AMMONIUM HYDROXIDE IN THE PRESENCE OF AMMONIUM SALTS

BY EDWARD NOEL ROBERTS AND ETHEL M. TERRY

RECEIVED NOVEMBER 4, 1929 PUBLISHED JULY 3, 1930

In early work by Drs. Julius Stieglitz and Edith E. Barnard[1] of this Laboratory, it was found that although ethyl and methyl formates are hydrolyzed at immense speed in dilute solutions of strong bases,[2] the velocity of these reactions may be measured in suitable mixtures of ammonium hydroxide and ammonium salts. The present paper[3] represents a continuation of this work in the case of ethyl formate.

---

[1] The work referred to had been completed before 1911.

[2] Bibliography of published reports on the alkaline hydrolysis of methyl and ethyl formates: (a) Trautz and Volkmann, *Z. physik. Chem.*, **64**, 53 (1908); (b) Nernst, *Ber.*, **42**, 3178 (1909); (c) Handa, *ibid.*, **42**, 3179 (1909); (d) Eucken, *Z. physik. Chem.*, **71**, 550 (1910); (e) Skrabal and Sperk, *Monatsh.*, **38**, 191 (1917). Only the last reference contains data bearing on the present problem. Reference will be made to this later.

[3] The experimental work of this paper was completed in 1918 by Dr. Roberts in partial fulfilment of the requirements for the degree of Doctor of Philosophy at this University. See also Terry and Stieglitz, THIS JOURNAL, **49**, 2216 (1927).

The solutions were always near to 0.08 normal (formula weight per liter of solution) with respect to ester and near to 0.1 normal with respect to ammonium hydroxide. The normality of the salt present at the start of the reaction varied from 0.04 to 0.4. The salts used were ammonium chloride, ammonium nitrate and ammonium formate. The reactions were carried out at 25°.

Experimental Detail

Mixtures of aqueous solutions of ammonium salt, ammonium hydroxide and ethyl formate were made in the container of a special apparatus, described elsewhere,[4] which was designed to permit the rapid removal of accurately measured samples of the mixture for analysis. These samples, which were of volumes close to 99 cc., were discharged at noted times into measured quantities of standard hydrochloric acid which had been kept at 0°. The mixture was then partly frozen and in the course of an hour the excess of acid was determined by titration, care being taken to see that the last of the ice had melted before the titration was completed. The apparatus in which the main reaction occurred was contained in a de Khotinsky thermostat the temperature of which was constant to ±0.01°. The temperature of the reaction mixture was always within 0.15° of that of the bath throughout the major portion of the time during which samples were taken.[5] It was found by experiment that under these conditions the temperature of the reaction mixture could be read by means of a Beckmann thermometer mounted with its bulb in that solution.

As mercury was employed in the special apparatus for displacement of samples of the reaction mixture, it was necessary to be sure that mercury had no effect on the basicity of the mixture. Therefore, solutions containing mixtures of ammonium hydroxide, ammonium chloride and sodium formate were exposed to the action of mercury under conditions to be used in the measurements. No losses of basic strength were found.

The discharge of samples into hydrochloric acid at 0° stopped the reaction provided the quantity of acid used was only slightly in excess of that required to neutralize the ammonium hydroxide present. It will be remembered that Manning[6] has found that the coefficient of autocatalysis of ethyl formate is 4.8 moles per minute per unit concentration of hydrogen ion at 25°. From this it will be appreciated that it was necessary to keep the hydrogen-ion concentration small during the time the neutralized samples were stored. Under the conditions used, samples could be kept for two hours. It was our practice to complete the titrations within an hour of the time the samples were withdrawn.

The titrations were completed using ammonium hydroxide as base and azolitmin as indicator. In order to find the correct color for the end-point, sample solutions of ammonium formate were made from standardized ammonium hydroxide and formic acid solutions and to these sufficient ammonium chloride or nitrate was added to duplicate the composition of samples to be taken from the reaction mixtures. It developed that the same color could be used in all cases[7] provided the titration were carried out at 0°.

---

[4] Gooch and Terry, THIS JOURNAL, **51**, 1959 (1929).

[5] Owing to an oversight this condition of experiment was not mentioned in the earlier papers, see Refs. 3, 4 and 8. It has been faithfully maintained in all our work. [E. M. T.]

[6] Manning, *J. Chem. Soc.*, **119**, 2079 (1921).

[7] Kolthoff, *Rec. trav. chim.*, 41, 54 (1922), has demonstrated that the color of azolitmin in solutions of P_H equal to 7.0–7.1 in a phosphate buffered solution represents a

A 0.15% azolitmin solution was used in the proportion of 0.055 cc. for every 10 cc. of volume of sample at the completion of the titration.

The same precautions were taken to prevent the solutions from taking up carbon dioxide that had been employed in earlier work.[8]

Three or more samples of the reaction mixture were used for the determination of the concentration of ammonia, free and combined, in the solutions. Each sample was first neutralized with hydrochloric acid, and then transferred to a suitable apparatus; concentrated sodium hydroxide was then run in and the freed ammonia distilled into a known quantity of hydrochloric acid in the well-known manner. These analyses were made on mixtures of known composition with and without the additional presence of formates in them but no difference in result was found. Therefore the method was considered satisfactory. The initial concentration of ammonium hydroxide in a given reaction was calculated from the dilution of the stock solution and the concentration of ammonium salt present was calculated from the difference in concentration of total ammonia, free and combined, and the concentration of the free base. As will be shown later these last terms serve only to show the preparation of the reaction mixture. They are not used in the calculation of the coefficient of the reaction.

The ammonium hydroxide was made by allowing gas from a tank to be absorbed in water of high purity, as shown by its conductivity. Ammonium nitrate and chloride were of C. P. grade dissolved in water and the solution filtered in contact with air free from carbon dioxide.

Freshly distilled ester was used for all solutions. Most of the material was from Kahlbaum but some was made in this Laboratory from the reaction of ethyl alcohol and formic acid catalyzed by hydrogen chloride. No difference in rate of reaction was shown by the two products.

Calculation of Results

It seemed probable that for intervals of the reaction for which the activity coefficient of the ammonium salt present might be considered constant, the activity coefficient of ionized ammonium hydroxide might likewise be constant and that under these conditions the rate of the reaction would be equal to a coefficient times the product of the respective molalities (formula weight per 1000 g. of water) of ammonium hydroxide and of ester divided by the molality of the ammonium salts present at the moment in question. Therefore, as a preliminary step, a series of reaction coefficients was calculated as shown below for the intervals in which the activity coefficient of the ammonium salt might be considered constant to 0.5%. It was assumed that the activity coefficient of the ammonium salts would be the same as that characteristic of potassium chloride at like molality, and Scatchard's values were used.[9]

Let B, E and S be the initial molalities of ammonium hydroxide, ester and

---

*P*H of 6.6 in a 0.5 normal potassium chloride solution likewise buffered. It is doubtless this salt effect that accounts for the fact that the same color could be used for all end-points in spite of the fact that with increasing ammonium salt content of the solution the apparent basicity of ammonium hydroxide decreased so that the *P*H of the correct end-point decreased. However, the validity of our use of the indicator does not rest on Kolthoff's observation but on experimental tests.

[8] Wilson and Terry, THIS JOURNAL, **50**, 1250 (1928).

[9] Scatchard, *ibid.*, **47**, 654 (1925).

salt, respectively; let X be the molality of ester or base which has been transformed by the reaction up to the time t; let K_1 be the reaction coefficient; then at the moment t

$$dX/dt = K_1(B - X)(E - X)/(S + X) \tag{1}$$

The integrated form of this expression for the interval $t_2 - t_1$ is

$$K_1(t_2 - t_1) = [2.303/(B - E)][(E + S) \log (E - X_1)/(E - X_2) - (B + S) \log (B - X_1)/(B - X_2)] \tag{2}$$

Certain short cuts were used in the application of this equation. In place of $(E + S)$, $(B + S)$ and $(B - E)$, the same data in terms of normality were used since the factor for conversion of normality to molality would have canceled. The ratio $(B - X_1)/(B - X_2)$ was calculated as $(b - x_1)/(b - x_2)$, the ratio of the number of cc. of standard acid required to neutralize unit volume of the reaction mixture in the respective samples. The number of cc. of standard acid equivalent to the ester present in the sample was found from the difference $(b - x) - (b - e) = (e - x)$, the term $(b - e)$ being the number of cc. of standard acid used to neutralize the base in a sample taken at the end of the reaction. The ratio $(e - x_1)/(e - x_2)$ gave the value of $(E - X_1)/(E - X_2)$.

In Table I will be found details of three representative experiments. Column headings will be understood from the above. In place of $(b - x)$ and $(e - x)$, values one hundred times greater are given to avoid printing decimals.

In Table II will be found a summary of all experiments.

An average temperature per minute[10] was calculated for each experiment and the value of the coefficient corrected by 0.66% for each tenth degree difference in temperature from 25.00°. This correction is the same as that found for the hydrolysis of ethyl acetate.[11] In Expt. 1 of Table I the correction has been applied to each value of K_1, since the temperature correction was sufficiently large to make difficult the observation of the constancy of the uncorrected coefficient. In other experiments the correction was applied to the average of the coefficients, since the temperature change was relatively small.

Although the total error of volume measurements was not over 0.10 cc. per sample and the error in reading the end-point of a titration ranged

---

[10] Since temperature readings were taken at noted times and at frequent intervals, the average temperature of each small interval could be considered as the mean of the two readings, taken at the beginning and at the end. The average temperature for the time $(t_2 - t_1)$ was taken as equal to the sum of the products of the average temperature of each small interval by the duration of the interval, divided by $(t_2 - t_1)$. This manner of finding the average temperature was satisfactory since the temperature readings were taken at such intervals that the change of reading was a matter of three or four hundredths at most. All the temperature readings taken are not shown in the experiments of Table I.

[11] Skrabal and Sperk, Ref. 2e, have shown that the temperature coefficient of alkaline hydrolysis of methyl and ethyl formates is close to 2, as is the case for ethyl acetate.

from 0.03 to 0.06 cc. according to the molality of salt present, the effect on the value of the coefficient was large because the calculation, as appears in Equation 2, depends on the difference of two values which are not far apart. The difference is larger and the effect of the error smaller the greater the value of $(B - E)$ and the nearer the experiment is to completion. Errors from timing are insignificant except where short time intervals were used, as for example in Expt. 1 of Table I. The net effect of all errors was never greater than 3.5% of the value of the average coefficient of each experiment.

TABLE I

DETAILS OF THREE REPRESENTATIVE MEASUREMENTS OF THE RATE OF HYDROLYSIS OF ETHYL FORMATE BY AMMONIUM HYDROXIDE IN AQUEOUS SALT SOLUTION

Part I. Composition of the solution at the start of the reaction in terms of normality: ester, 0.1142; NH_4OH, 0.1358; salt, zero. Normality of acid used in titration, 0.1003; volume of each sample 98.95 cc.; temperature of thermostat, 25.50°.

No.	Temp., °C.	Time, minutes	$(b-x) \times 100$	$(e-x) \times 100$	Molality of salt	Data used in calcn. (Col. I)	γ_{NH_4Cl} at t_1 and t_2	$K_1 \times 100$	$K_1 \times 100$ at 25.00°
1	25.435	4.20	8193	6068	0.050				
2	25.525	6.03	7502	5377	.059				
3	25.565	7.13	7157	5032	.063	1,3	0.807–0.790	4.84	4.68
4	25.585	8.18	6967	4742	.066	2,4	.795– .787	5.09	4.90
5	25.605	9.30	6620	4495	.068	3,5	.790– .785	4.96	4.77
6	25.615	10.52	6368	4243	.071	4,6	.787– .782	4.89	4.70
7	25.620	11.52	6191	4066	.073	5,7	.785– .780	4.94	4.74
8	25.625	12.70	5994	3869	.075	6,8	.782– .778	4.90	4.70
9	25.625	13.82	5828	3703	.077	7,9	.780– .776	5.01	4.81
10	25.625	15.00	5659	3534	.078	8,10	.778– .775	5.11	4.90
								Average	4.78

Part II. Composition of the solution at the start of the reaction in terms of normality: ester, 0.0751; NH_4OH, 0.1119; NH_4Cl, 0.1241. Normality of acid used in titration, 0.09765; volume of each sample, 98.86 cc.; temperature of thermostat, 25.00°.

No.	Temp., °C.	Time, minutes	$(b-x) \times 100$	$(e-x) \times 100$	Molality of salt	Data used in calcn. (Col. I)	γ_{NH_4Cl} at t_1 and t_2	K_1
1	25.02	2.27	9924	6193	0.14			
2	25.06	3.60	9616	5885	.14			
3	25.12	9.40	8538	4807	.15	1,3	0.740–0.735	0.0571
4	25.12	10.70	8348	4617	.15	2,4	.740– .735	.0569
5	25.12	16.83	7586	3855	.16	3,5	.735– .730	.0583
6	25.11	24.97	6873	3142	.17	4,5	.735– .730	.0586
7	25.08	26.40	6770	3039	.17	5,6	.730– .725	.0586
8	25.07	41.70	5922	2191	.18	5,7	.730– .725	.0584
9	25.06	43.17	5864	2133	.18	7,8	.725– .721	.0593
10						7,9	.725– .721	.0593
							Average	.0583
							Value at 25.00°	.0579

TABLE I (*Concluded*)

Part III. Composition of the solution at the start of the reaction in terms of normality: ester, 0.0787; NH_4OH, 0.1038; NH_4Cl, 0.3902. Normality of acid used in titration, 0.09765; volume of each sample, 98.83 cc.; temperature of thermostat, 25.00°.

No.	Temp., °C.	Time, minutes	$(b-x)$	$(e-x)$	Molality of salt	Data used in calcn. (Col. I)	γ_{NH_4Cl} at t_1 and t_2	K_1
1	25.02	2.33	9365	6824	0.41			
2	25.04	3.85	9186	6642	.41			
3	25.07	11.98	8338	5797	.42	1,3	0.667−0.665	0.0789
4	25.09	14.35	8134	5593	.42	2,4	.667− .665	.0779
5	25.10	22.00	7538	4997	.43	3,5	.665− .664	.0788
6	25.09	23.23	7445	4904	.43	4,6	.665− .664	.0807
7	25.07	49.03	6105	3564	.44	5,7	.664− .662	.0800
8	25.06	50.40	6053	3512	.44	6,8	.664− .662	.0796
9	25.05	90.73	4920	2379	.46	7,9	.662− .660	.0790
10	25.04	92.13	4889	2348	.46	8,10	.662− .660	.0794
							Average	.0793

Average temperature per minute, 25.08. K_1 at 25.00 0.789

TABLE II

SUMMARY OF EXPERIMENTS ON THE HYDROLYSIS OF ETHYL FORMATE BY AQUEOUS AMMONIUM HYDROXIDE

No.	Normality at zero time (a) ester	of (b) NH_4OH	(c) salt (NH_4Cl)	Average molality of salt	Average K_1	Average temp., °C.	K_1 at 25.00°
				Part I			
1	0.0784	0.1038	0.3912	0.430	0.0818	25.12	0.0812
2	.0787	.1038	.2902	.435	.0793	25.08	.0789
3	.0859	.1038	.3912	.435	.0803	25.07	.0799
4	.0769	.1038	.3960	.435	.0825	25.29	.0809
5	.0751	.1119	.1241	.16	.0583	25.10	.0579
6	.0796	.1119	.1214	.16	.0563	25.10	.0559
7	.0792	.1123	.0390	.075	.0524	25.05	.0522
8	.0758	.1123	.0838	.109	.0524	25.03	.0523
				Part II			
			(NH_4NO_3)				
1	0.0717	0.1312	0.1085	0.16	0.0559	25.07	0.0555
2	.0766	.1125	.456	.50	.0825	25.06	.0823
				Part III			
1	0.1075	0.1320	0.0	0.060	0.0460	24.81	0.0466
2	.1123	.1322	.0	.064	.0468	25.10	.0465
3	.1142	.1358	.0	.069	.0497	25.56	.0479

Values of K_1 given in Table II will be seen to vary greatly with the molality of the salt present. Thus for 0.109 molal salt solution K_1 equals 0.054 and for 0.43 molal salt K_1 is 0.0818, an increase of 56%.

Significance of the Results

In searching for an explanation of the variations of K_1 it is obviously necessary to consider the possibility not only of catalysis by ionized ammonium hydroxide, but also of two other parallel reactions, the one, the decomposition of the ester brought about by water, and the other, an ammonia catalyzed change.[12a]

The second of these reactions may be eliminated since Manning[6] found no evidence of it in his study of the autocatalyzed hydrolysis of ethyl formate at 25° and the reactions reported on were much slower than those here considered.

For the evaluation of factors of the remaining reaction, the activity coefficients of ammonium hydroxide in ammonium salt solution are needed and these have not yet been determined. Therefore a final analysis of the significance of the results of the present work may not now be made. Since some time must elapse before either of the authors can continue work in this field, it has seemed best to put the present data on record without waiting for the missing data.

It will occur to the reader that since the solutions are dilute it is probable that for our experiments the corresponding thermodynamic data for ammonium hydroxide, 0.5 molal, in potassium chloride solutions at 25°, reported by Harned and Robinson[13] may be used as approximate activity coefficients of ammonium hydroxide in the present instance. The point of uncertainty is, of course, the possibility that ammonium ion has some specific effect on the activity of ammonia (and *vice versa*).

It may, therefore, be of interest that if equations are set up to represent the rate of the reactions as dependent on two reactions, one an hydrolysis of ester by ionized ammonium hydroxide and the other an ammonia catalyzed change, and the data of Harned and Robinson above referred to are used in evaluating the molality of ionized base and of ammonia (the ionization constant of ammonia being taken as 1.81×10^{-5}), it will be found that the coefficient of the first reaction may be taken as 1350 and that of the second reaction as 0.78 gram molecular weights per 1000 g. of water per minute.

Skrabal and Sperk[2e] estimate the coefficient of hydrolysis of ethyl formate by hydroxide ion to be 1400 gram molecular weights per liter of water per minute. Although no great weight may be attached to the close agreement of their value with the one obtained as described above, since the ionization constant of water appears as a factor in the Skrabal and Sperk calculation, it is worthy of note that the two values are of the same magnitude.

[12] (a) Early in his work on the substituted ammonia compounds, Professor Stieglitz (see Refs. 1 and 2) foresaw the possibility that ammonia might function as a basic catalyst. Although Professor Stieglitz has published no account of his views, it seems proper to mention them here since we had the benefit of them at the time the experiments were made. More recently Professor Brönsted, Ref. 12b, has developed the same idea independently and has been the first to publish a quantitative statement of the theory. (b) Brönsted and Guggenheim, THIS JOURNAL, **49**, 2554 (1927). (c) Brönsted, *Rec. trav. chim.*, **42**, 718 (1923); *J. Phys. Chem.*, **30**, 777 (1926).

[13] Harned and Robinson, THIS JOURNAL, **50**, 3157 (1928).

The ratio of 1350/0.78 or 1730/1 is within 11% of the ratio of the corresponding coefficients for the mutarotation of glucose as calculated by Brönsted and Guggenheim.[12b] (These coefficients are 6200 and 3.2 formula weights of glucose per liter per minute.) According to the Brönsted theory a fairly close agreement is to be expected, with some exceptions, between the ratio of the coefficients of catalysis by hydroxide ion and by ammonia.

Thus the results gained by using the Harned and Robinson coefficients are in harmony with expectations based on independent evidence. Since the details of the calculations follow conventional lines and since no proof can be given that the Harned and Robinson data must apply exactly, the above material is given in abstract simply as an answer to an obvious question.

Whether the assumptions made in writing Equation 1 are valid need not be argued at the present time since the coefficients calculated by means of this equation and presented in Tables I and II represent a convenient epitome of our results and that is the first purpose of this paper.

Summary

Measurements are described of the rate of the reaction of ethyl formate at 25° at molalities near 0.08 with aqueous ammonium hydroxide at molalities near 0.10 in various solutions containing either ammonium chloride, nitrate or formate. Coefficients of the rate of the reaction are reported for intervals of the reaction in which the activity coefficient of the ammonium salt may be considered constant. These coefficients have been calculated on the assumption that the rate of the reaction at any moment of time is directly proportional to the coefficient times the product of the respective molalities of base and ester and is inversely portional to the molality of salt present. The data are presented primarily to record new experiments on the reaction of an ester in ammonium hydroxide–ammonium salt solutions. Owing to the lack of thermodynamic data no final interpretation is possible at present. A tentative interpretation is given in abstract.

Chicago, Illinois