

CCCCXXVIII.—*Acid and Salt Effects in Catalysed Reactions. Part III. Dependence of the Characteristics of the Minimum-Velocity Mixture on the Concentration of the Acid and the Application of Minimum Velocity to the Determination of Catalytic and Ionisation Constants.*

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IN Part II of this series (Dawson and Dean, this vol., p. 2872) it was shown that the curve obtained by plotting reaction velocity against the p_H value of catalysing mixtures of the type $cHA +$

xMA is symmetrical with respect to the point at which the reaction velocity has a minimum value. Denoting the catalytic coefficients for the hydrogen ion, the acid ion, and the undissociated acid molecule by k_h , k_a , and k_m , respectively, and the ionisation constant by K , it was shown that the hydrogen-ion concentration of the minimum-velocity ($M.V.$) mixture is given by

$$[H]_i^+ = \sqrt{k_a K c / (k_h - k_m)} \quad . \quad . \quad . \quad (1)$$

and the corresponding reaction velocity by

$$v_i = 2\sqrt{(k_h - k_m)k_a K c} + k_m c \quad . \quad . \quad . \quad (2)$$

For each series of acid-salt mixtures for which the concentration of the acid is constant, the observed changes in velocity are due entirely to the hydrogen and acid ions, and if the minimum value of this ionic reaction velocity is denoted by $u_i = v_i - k_m c$, it follows from (1) and (2) that

$$u_i/[H]_i^+ = (v_i - k_m c)/[H]_i^+ = 2(k_h - k_m) \quad . \quad . \quad (3)$$

The object of this paper is to show that the experimental data for the acetone-iodine reaction under the catalysing influence of mixtures of acetic acid and sodium acetate are in general agreement with the above equations.

Dependence of $[H]_i^+$ on the Concentration of the Acid.

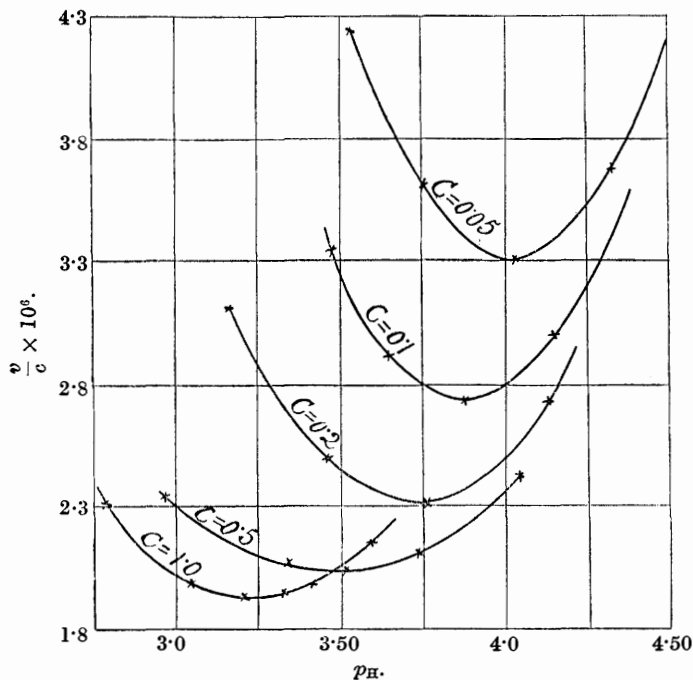
Consideration will be given in the first place to the variation of $[H]_i^+$ with the concentration of the acid. The data available for the testing of equation (1) are those obtained in experiments in which the concentration of the acetic acid was varied from 0.01*N* to 1.0*N*. Below 0.01*N*, the catalytic effect of the hydroxyl ion cannot be ignored, and, as is shown later, disturbing factors come into play when the concentration reaches the upper limit of the series. For the acid-salt mixtures with 0.2 and 0.05*N*-acid, the measurements recorded by Dawson and Carter (this vol., p. 2282) and by Dawson and Dean (*loc. cit.*) have been utilised for the purpose of testing the equation.

In the actual determination of $[H]_i^+$, advantage has been taken of the fact that the $v-p_H$ curves are symmetrical with respect to the $M.V.$ point. It may be noted, however, that $[H]_i^+$ may also be derived from the curves which are obtained by plotting the reaction velocity against the logarithm of the concentration of the salt. Such $v-\log x$ curves give that value of x , namely x_i , for which the reaction velocity is a minimum, and since the value of $[H]_i^+$ may be neglected in comparison with x_i , it follows that the hydrogen-ion

concentration of the *M.V.* mixture may be derived from $[H]_i^+ = Kc/x_i$.

The variation of $(p_H)_i$ with the concentration of the acid is shown in the accompanying diagram. In order to reduce the distortion which shows itself when the velocity- p_H curves are directly compared, the curves which are actually shown in the diagram are those obtained by plotting the specific reaction velocity v/c against p_H

FIG. 1.



*Specific velocity curves for mixtures $cCH_3CO_2H + xCH_3CO_2Na$ showing the dependence of the velocity and the hydrogen-ion concentration of the *M.V.* mixtures on the concentration (c) of the acid.*

for concentrations of acid from 0.05 to 1*N.* The p_H values are those given by the mass-law expression $p_H = \log 1/K + \log (x + [H]^+)/c - [H]^+$.

The $(p_H)_i$ values derived from the curves are in col. 2 of Table I; col. 1 gives the concentration of the acid; and col. 3 the values of $(p_H)_i$ calculated from $(p_H)_i = 3.36 - \frac{1}{2} \log c$ which is the form assumed by the logarithmic equivalent of equation (1) when the values $k_h = 442 \times 10^{-6}$, $k_a = 4.5 \times 10^{-6}$, $k_m = 1.5 \times 10^{-6}$, and $K = 1.85 \times 10^{-5}$ are introduced.

TABLE I.

$(p_H)_i$ values for the *M.V.* mixtures $c\text{CH}_3\cdot\text{CO}_2\text{H} + x\text{CH}_3\cdot\text{CO}_2\text{Na}$.

<i>c.</i>	$(p_H)_i$ (obs.).	$(p_H)_i$ (calc.).	<i>c.</i>	$(p_H)_i$ (obs.).	$(p_H)_i$ (calc.).
0.01	4.33	4.36	0.20	3.72	3.71
0.05	4.03	4.01	0.50	3.50	3.51
0.10	3.88	3.86	1.00	3.23	3.36

For acetic acid concentrations between 0.01 and 0.5*N*, the agreement between the observed and the calculated $(p_H)_i$ values is within the limits of the experimental errors, and it follows that over this range the hydrogen-ion concentration of the *M.V.* mixture is proportional to the square root of the concentration of the acid. At the highest acid concentration, there is an obvious divergence between the observed and calculated $(p_H)_i$ values. The probable cause of this will be referred to later.

Minimum Velocity and Acid Concentration.

The investigation of the relation between the minimum velocity and the concentration of the acid presents greater difficulties than those which are encountered in the study of the connexion between $[\text{H}]_i^+$ and *c*. The speed of the reaction in the region of the minimum velocity is very small for the smaller concentrations of acetic acid, and it is necessary to pay special attention to the danger of loss of iodine by slow interaction of the latter with the catalysing mixture or by leakage. It is probable that the velocities recorded by Dawson and Carter for the 0.1*N*-acid series in the region of the *M.V.* mixture are abnormally large because the acetic acid used was not quite free from impurities which reacted slowly with the iodine.

For the above reason, new measurements have been made of the minimum velocity, carefully purified acetic acid and sodium acetate being used in the preparation of the mixtures. The mixtures actually employed were those which correspond with the $(p_H)_i$ values recorded in col. 2 of Table I.

The results are summarised in Table II, the numbers in col. 2 representing the measured reaction velocities, whilst those in col. 3 are the velocities calculated from equation (2), which takes the form

$$v_i \times 10^6 = 0.383\sqrt{c} + 1.5c$$

when the numerical values of k_h , k_a , k_m , and K are inserted. Col. 4 gives the values of $u_i = v_i - k_m c$, col. 5 those of $[\text{H}]_i^+$ which correspond with the minima on the $v-p_H$ curves, and col. 6 records the values of $u_i/[\text{H}]_i^+$ which, according to equation (3), should be equal to 0.88×10^{-3} . In reference to this ratio, it seems desirable to point out that u_i is not a directly measurable velocity and that

the accuracy with which its value can be obtained depends, not only on the accuracy of the measurement of the minimum velocity v_i , but also on the value assigned to the coefficient k_m . The latter may be derived in various ways, but the methods will not be discussed here. It will suffice to point out that, for the more dilute solutions, the main source of error in u_i lies in the determination of v_i , whilst for the more concentrated solutions the error is in all probability chiefly associated with the value assigned to k_m . In making the comparison between experiment and equation (3), we have actually used the approximate value of $k_m = 1.5 \times 10^{-6}$ obtained by the extrapolation method described by Dawson and Carter (*loc. cit.*).

TABLE II.

Values of v_i and $u_i/[\text{H}]_i^+$ for $c\text{CH}_3\cdot\text{CO}_2\text{H} + x\text{CH}_3\cdot\text{CO}_2\text{Na}$.

c .	$v_i \cdot 10^6$ (obs.).	$v_i \cdot 10^6$ (calc.).	$u_i \cdot 10^6$.	$[\text{H}]_i^+ \cdot 10^4$.	$u_i/[\text{H}]_i^+$ $\times 10^3$.
0.01	0.056	0.053	0.041	0.0468	0.88
0.05	0.164	0.161	0.089	0.933	0.95
0.10	0.273	0.271	0.123	1.32	0.93
0.20	0.464	0.471	0.164	1.90	0.86
0.50	1.020	1.020	0.270	3.06	0.88
1.00	1.94	1.88	0.44	5.89	0.75

Inspection of Table II shows that for the most part the observed minimum velocities and the values of $u_i/[\text{H}]_i^+$ are in satisfactory agreement with the requirements of equations (2) and (3). The data for 1.00*N*-acetic acid afford the only instance for which the divergence may be definitely regarded as greater than that attributable to errors of experiment.

The divergence led us to investigate in a detailed manner the catalytic effect produced by acid-salt mixtures containing 1*N*-acid, and the results of these experiments show clearly that at higher salt concentrations there are very considerable differences between the measured velocities and those calculated from the formula $v = k_h[\text{H}]^+ + k_a[\text{A}]^- + k_m[\text{HA}]$. For additions of salt which are not greater than that required to produce the *M.V.* mixture, the differences in question are, however, comparatively small. The observed velocities and those calculated from the above formula are compared in Table III for salt concentrations varying from 0 to 1 g.-mol. per litre.

With regard to the cause of the divergence between the observed and calculated results for 1*N*-acid solutions, it seems possible that the differences may be connected with the decrease in the ionisation constant of the acid in more concentrated solutions. It is not suggested that the diminution in the ionisation constant is primarily responsible for the observed effects. On the other hand, we are

TABLE III.

Reaction velocities for $1N \cdot CH_3 \cdot CO_2H + xN \cdot CH_3 \cdot CO_2Na$.

x	0	0.0095	0.019	0.0285	0.038	0.0476	0.0762	
$v \cdot 10^6$ (obs.)	3.40	2.31	1.98	1.94	1.95	1.97	2.15	
$v \cdot 10^6$ (calc.)	3.40	2.33	2.00	1.91	1.88	1.88	1.95	
x	0.0952	0.143	0.190	0.286	0.381	0.500	0.660	1.00
$v \cdot 10^6$ (obs.)	2.25	2.54	2.87	3.52	4.20	4.90*	5.90*	8.05*
$v \cdot 10^6$ (calc.)	1.97	2.15	2.36	2.79	3.21	3.77	4.47	6.01

In the experiments indicated by * iodoform was precipitated.

inclined to attribute the divergences to the formation of catalytically active complex acetate ions, the formation of which, in the more concentrated solutions, is rendered very probable by the fact that acid acetates crystallise out from such solutions (Dukelski, *Z. anorg. Chem.*, 1909, **62**, 114).

The results recorded in Tables I and II justify the conclusion that the catalytic behaviour of acetic acid-acetate mixtures over a wide range of concentration can be quantitatively interpreted in terms of the hypothesis that catalytic effects are produced by and are proportional to the concentrations of the hydrogen ion, the acid anion, and the undissociated acid molecule.

It will now be shown that a knowledge of the minimum reaction velocity and of its variation with the concentration of the acid may be made the basis of methods for determining the values of important constants.

Determination of the Catalytic Activity of the Undissociated Acid from Measurements of Minimum Reaction Velocity.

If the minimum reaction velocities corresponding with the acid concentrations c and c' are denoted by v_i and v_i' , then, according to equation (2)

$$v_i - k_m c = 2\sqrt{(k_h - k_m)k_a K c}$$

and

$$v_i' - k_m c' = 2\sqrt{(k_h - k_m)k_a K c'}$$

whence

$$(v_i - k_m c)/(v_i' - k_m c') = \sqrt{c/c'}$$

or

$$k_m = (v_i/\sqrt{c} - v_i'/\sqrt{c'})/(\sqrt{c} - \sqrt{c'}) \dots (4)$$

The important feature of this equation is that it affords a method for determining the value of the catalytic coefficient k_m for the undissociated acid molecule, which is entirely independent of a knowledge of the constants k_h , k_a , and K . It involves nothing more than a determination of the velocities of reaction for two $M.V.$ mixtures the acid concentrations of which are fairly widely separated.

The results obtained for acetic acid by combining the experimental observations for concentrations 0.01 to 0.50N in suitable

pairs are in Table IV. The mean value of k_m thus obtained is 1.43×10^{-6} and this would suggest that the figure adopted by Dawson and

TABLE IV.
Values of k_m from minimum velocities.

Concentration pairs.	$0.1 \& 0.01$	$0.2 \& 0.05$	$0.5 \& 0.1$	$0.2 \& 0.01$	$0.5 \& 0.05$	$0.5 \& 0.01$
$k_m \cdot 10^6$.	1.41	1.37	1.49	1.38	1.48	1.46

Carter is rather high. For the present it is proposed, however, to retain the approximate value $k_m = 1.5 \times 10^{-6}$ as a measure of the catalytic activity of the undissociated acid.

A Kinetic Method for the Determination of Ionisation Constants.

The minimum velocities v_i and v_i' corresponding with acid concentrations c and c' may also be utilised for deriving the value of the dissociation constant of the acid, if this is not too strong. From equation (2) we have

$$(v_i - 2\sqrt{(k_h - k_m)k_a Kc}) / (v_i' - 2\sqrt{(k_h - k_m)k_a Kc'}) = c/c'.$$

Rearranging the terms and squaring, we get

$$(v_i'c - v_i c')^2 = 4(k_h - k_m)k_a K(c\sqrt{c'} - c'\sqrt{c})^2$$

and, since for weak acids, k_m is very small compared with k_h , we obtain

$$K = (v_i'c - v_i c')^2 / 4k_h k_a (1/\sqrt{c'} - 1/\sqrt{c})^2 \quad . \quad (5)$$

an equation which gives K in terms of k_h , k_a , and the minimum reaction velocities for two different concentrations of the acid.

The results obtained from the experimental data for acetic acid by combining the same pairs of experiments as were used in the evaluation of k_m are in Table V. The mean value of K is 2.16×10^{-5} . This is considerably greater than the value indicated by the

TABLE V.
Values of K from minimum velocities.

Concentration pairs.	$0.01 \& 0.1$	$0.05 \& 0.2$	$0.1 \& 0.5$	$0.01 \& 0.2$	$0.05 \& 0.5$	$0.01 \& 0.5$
$K \times 10^5$.	2.22	2.30	1.96	2.25	2.06	2.16

conductivity data for acetic acid. In reference to the discrepancy, it may be pointed out that the kinetic method for determining K involves a knowledge of both k_h and k_a , but not of k_m , which is the most difficult of the three coefficients to determine accurately in

the case of acetic acid. To bring the kinetically determined value of K into agreement with the conductivity value, it would be necessary to increase k_h or k_a by 15%, or to alter both these constants so that their product is increased in this proportion. The accuracy with which k_h and k_a can be determined seems to preclude the possibility of any alteration of this magnitude, and there appears to be no obvious explanation of the difference. Until kinetic data for other acids have been obtained, it would appear to be premature to subject the divergence to further discussion.

EXPERIMENTAL.

The measurements of the reaction velocity were made at 25° by the method previously described. The acetone was purified by treatment with sodium iodide, the acetic acid by the action of chromic acid, and the sodium acetate by repeated crystallisation.

Summary.

The minimum velocities of the acetone-iodine reaction under the catalytic influence of mixtures of acetic acid and sodium acetate have been determined for acid concentrations ranging from 0.01 to 1*N*.

The hydrogen-ion concentration of the minimum-velocity mixture and the magnitude of the minimum reaction velocity vary with the concentration of the acid in accordance with the theoretical predictions.

The ratio of the minimum ionic reaction velocity to the corresponding hydrogen-ion concentration is independent of the concentration of the acid.

It has been shown that minimum velocities may be used for the determination of the catalytic coefficient characteristic of the undissociated acid.

A kinetic method for the determination of dissociation constants of weak acids has been described and applied to the experimental data for acetic acid.

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