

CCCLXXI.—*Acid and Salt Effects in Catalysed Reactions. Part XXV. Catalytic Effects in the Intramolecular Transformation of Phorone.*

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OBSERVATIONS on the reaction between phorone and iodine in a suitably buffered reaction medium have shown that the substitution of hydrogen occurs at a rate which is proportional to the concentration of the phorone but is independent of the concentration of the iodine. The relations involved are similar to those associated with the reaction of the halogens on the simple ketones, and suggest that the rate of disappearance of the iodine is determined by the speed of some intramolecular change, probably keto \longrightarrow enol in type, in the phorone molecule.

On account of the limited solubility of phorone in water, the investigation of the conditions which affect the velocity of the reaction cannot be carried out in pure aqueous solution, and for this purpose a mixture of water and ethyl alcohol containing 50 vols. % of the latter has been used as solvent.

Preliminary observations (Battye and Dawson, *Proc. Leeds Phil. Soc.*, 1929, 2, 21) on the reaction rate in presence of buffer mixtures (p_H 2.7—8.8 according to potentiometric measurements) have shown that the plot of the velocity against p_H gives a catenary curve which is symmetrical with respect to the point of minimum velocity characterised by $p_H = 6.0$ or approximately $[H^+]_i = 1.0 \times 10^{-6}$. So far as the general form of the v - p_H curve is concerned, it can be explained on the assumption that the reaction is catalysed by hydrogen and hydroxyl ions, the joint effect of which is expressed by the equation

$$v = v_h + v_{OH} = k_h[H^+] + k_{OH}[OH'].$$

If these ions are the only effective catalysts, the minimum speed of the reaction should be given by $v_i = 2k_h[H^+]_i$, whereas the actually observed minimum velocity is about 50 times this value. The divergence may be regarded as a clear indication of the existence of catalytic effects other than those attributable to the hydrogen and hydroxyl ions.

In the present investigation attention has been directed to the explanation of the above difference, and in particular, to the catalytic effects produced by the solvent medium and by the constituents of acetate buffers.

The measurements were made at 25° with phorone, purified by repeated crystallisation from 50% alcohol, which melted sharply at 27.7°. To remove from the absolute alcohol the impurity which is responsible for the absorption of a small amount of iodine, the alcohol was treated with iodine, then with sodium, and distilled three times. The use of 50% alcohol as solvent interferes with the sharpness of the end-point in the titration of the iodine with 0.01*N*-sodium thiosulphate, but satisfactory conditions were obtained by running the 20-c.c. samples of the reaction mixture into 200 c.c. of ice-cold water, to which 5 c.c. of a saturated solution of sodium chloride were added when the end-point was nearly reached. Furthermore, the difficulties of titration which arise from the separation of phorone on dilution were largely eliminated by the use of phorone solutions of low concentration, usually 0.04*M*. The values recorded for the reaction velocities and the catalytic coefficients are, however, those which refer to a phorone concentration of one mol. per litre.

Hydrochloric Acid as Catalyst.—In the presence of hydrochloric acid (0.005 or 0.01*M*) the catalytic effect is mainly due to the

hydrogen ion, but the influence of the solvent necessitates the introduction of a small correction factor when the data are used for the derivation of k_h . The velocity v is given by $v = k_h[\text{H}^+] + v_s$, where v_s is the velocity due to the solvent, whence $k_h = (v - v_s)/[\text{H}^+]$. The results obtained in typical experiments are summarised below:

Phorone conc.	HCl conc.	$v \cdot 10^3$, obs.	$v_s \cdot 10^3$.	$k_h \cdot 10^3$.
0.04	0.005	0.662	0.013	130
0.02	0.01	1.32	0.013	131
0.02	0.005	0.665	0.013	130

The value thus derived for k_h on the assumption that the hydrochloric acid is completely ionised is 130×10^{-3} .

Autocatalysis.—When iodine is added to a solution of phorone a measurable amount of the halogen is found to have disappeared after a few minutes. The velocity of the change increases continuously, and in its later stages the speed of the reaction is approximately proportional to the concentration of the hydriodic acid formed, as measured by the fall in the concentration of the iodine. There is, however, a very marked departure from this simple relation in the earlier stages of the autocatalysed reaction, and this would seem to be accounted for almost completely by the catalytic activity of the solvent which introduces a factor that remains constant throughout the process.

The fact that the solvent is a mixture of water and alcohol imposes certain limitations on the analysis of the experimental data, but it would seem permissible to assume that the acid and basic functions of the complex solvent are essentially determined by the water as the more readily ionisable constituent. The value of $K_w = [\text{H}^+] \cdot [\text{OH}']$ for the aqueous-alcoholic solvent is, however, unknown, and for this reason it is not possible to determine the magnitude of the coefficient k_{OH} from the equation $[\text{H}^+]_i = \sqrt{k_{\text{OH}} \cdot K_w / k_h}$, in which $[\text{H}^+]_i$ is the hydrogen-ion concentration corresponding with the minimum reaction velocity for a series of dilute buffer solutions of varying p_{H} value. The value of $k_{\text{OH}} \cdot K_w$ is, however, given by $k_h \cdot [\text{H}^+]_i^2 = 1.3 \times 10^{-13}$.

Having regard to the nature of the solvent, the reaction velocity in the initial stages of the autocatalysed reaction should be given by

$$\begin{aligned} v &= v_h + v_{\text{OH}} + v_s = k_h[\text{H}^+] + k_{\text{OH}}[\text{OH}'] + v_s \\ &= k_h[\text{H}^+] + k_{\text{OH}}K_w/[\text{H}^+] + v_s \end{aligned}$$

in reference to which it may be pointed out that if the catalytic effect of the solvent is sufficiently great, the rate of increase of the hydrogen-ion concentration may be such that the influence of the hydroxyl ion is not of any importance so far as the actual course of the reaction is concerned. The experimental data show, indeed, that the hydroxyl term can be left out of account, and in these

circumstances the equation for the velocity of the autocatalysed reaction becomes

$$dx/dt = (k_1x + v_S)(m - x) = k_h(r + x)(m - x)$$

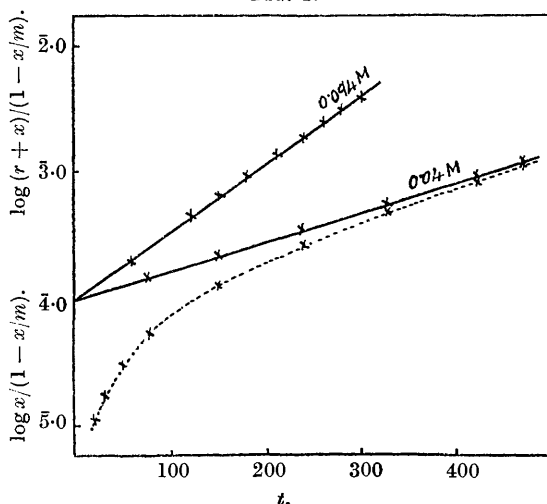
where m is the initial concentration of the phorone, $r = v_S/k_h$, and x is the measured fall in the iodine concentration, and consequently the concentration of the hydrogen ion, after time t .

On integration, the above equation may be written

$$\log(r + x)/(1 - x/m) = (m + r)k_h t + \log r$$

according to which the plot of $\log(r + x)/(1 - x/m)$ against t is a straight line which intercepts the ordinate $t = 0$ at $\log r$. Since r is

FIG. 1.



Autocatalysis of phorone. Continuous lines show plot of $\log_{10}(r + x)/(1 - x/m)$ against t (minutes) for 0.04 and 0.094M-phorone solutions. Dotted curve shows corresponding plot of $\log_{10} x/(1 - x/m)$ for 0.04M-phorone.

small compared with x , in the later stages of the reaction, an approximate value of r may be obtained by plotting $\log x/(1 - x/m)$ against t and extrapolating. The process is then repeated with $\log(r + x)/(1 - x/m)$ and leads thereby to a final value of $r = 0.000100$. The individual values of r given by independent experiments deviate from the mean by less than 3% and, as required by the above equation, the results obtained with 0.04 and 0.1M-phorone solutions show that r is independent of the phorone concentration. Furthermore, since r is very small in comparison with m , the slope of the line obtained when $\log(r + x)/(1 - x/m)$ is plotted against t should be proportional to the phorone concentration, and this is also in agreement with our experiments. The diagram shows the graphs for

0.04 and 0.094*M*-solutions of phorone. The dotted curve shows the plot of $\log x/(1 - x/m)$ against t for the former solution. This should be a straight line if the catalytic effect were solely due to the hydrogen ion. Its divergence from linearity illustrates the effect of the solvent catalysis in the early stages of the autocatalysed reaction. In accordance with the previous equation

$$k_h = \frac{2.30}{(m + r)t} \log_{10} \frac{(r + x)}{(1 - x/m)r}$$

and the values of k_h given by a typical experiment with 0.04*M*-phorone are shown in col. 4 of Table I. Col. 1 gives the values of t , col. 2 the number of c.c. of 0.01*N*-thiosulphate required for titration of the iodine in 25 c.c. of the reaction mixture, and col. 3 the corresponding value of x .

TABLE I.

Autocatalysed reaction with 0.04*M*-phorone and 0.0016*M*-iodine.

t (mins.).	Na ₂ S ₂ O ₃ , c.c.	$x \cdot 10^4$.	$k_h \cdot 10^3$.	t (mins.).	Na ₂ S ₂ O ₃ , c.c.	$x \cdot 10^4$.	$k_h \cdot 10^3$.
0	9.935	—	—	424	4.855	8.26	132
76	9.625	0.52	(137)	474	3.26	10.83	131
151	9.195	1.22	132	513	1.695	13.38	131
240	8.355	2.57	133	524	1.25	14.10	131
330	7.05	4.69	132				

The mean value of k_h from a number of similar experiments is 0.130, which agrees with that afforded by the measurements made with hydrochloric acid as catalyst. Since $r = v_s/k_h$ is 0.00010, it follows that $v_s = 0.013 \times 10^{-3}$. With regard to the hydrogen-ion concentration represented by r , it may be noted that the actual course of the autocatalysed reaction, in which the solvent catalysis plays an important part, is the same as that which would obtain if the only catalytic entity were the hydrogen ion with an initial concentration equal to 0.00010 ($p_H = 4$).

The results thus provided by the study of the autocatalysed phorone reaction are similar to those obtained in the investigation of the corresponding reaction for mesityl oxide by Dawson and Key (J., 1928, 2154). For the latter, the value of $r = v_s/k_h$ is 0.000047, which indicates that the effective action of the solvent (5 vols. % alcohol), expressed in terms of an equivalent initial hydrogen-ion concentration, is rather less than half as large as the solvent action in the phorone reaction.

The data obtained by Dawson and Powis (J., 1912, 101, 1503) in the investigation of the autocatalysed acetone reaction were recently examined (Dawson, J., 1927, 458) on the assumption that the solvent action is negligibly small. The existence of a solvent effect has since been definitely established (Dawson and Key, J., 1928, 543; Dawson and Spivey, J., 1930, 2180), and it would now seem probable that in

this case the initial stages of the reaction are affected, not only by hydroxyl-ion catalysis, but also by the catalytic action of the solvent. In connexion with the elucidation of this question, further experiments are in progress.

Acetic Acid as Catalyst.—In 50% alcoholic solution, acetic acid is ionised to a much smaller extent than in a corresponding pure aqueous solution. For this reason the disturbance caused by the catalytic action of the liberated hydriodic acid is more pronounced, and the accuracy with which the initial velocity of the acetic-acid catalysed reaction can be determined is considerably less than that which is readily attained in the investigation of the catalytic effects produced by acetic acid in pure aqueous solution containing acetone. In the absence of a knowledge of the ionisation constant of acetic acid in 50% alcohol it is, moreover, not possible to calculate the reaction velocities due to its catalytic effects. On the other hand, the observed results may be utilised for the derivation of the ionisation constant. The equation for the reaction velocity is

$$v = k_h[H^*] + k_a[A'] + k_m[HA] + v_s$$

and since k_a is very small compared with k_h , whilst $[H^*] = [A']$, this becomes

$$v = k_h[H^*] + k_m \cdot c + v_s$$

whence

$$[H^*] = (v - k_m c - v_s) / k_h$$

in which c is the concentration of the acetic acid and k_m is the corresponding catalytic coefficient, the value of which ($k_m = 7 \times 10^{-6}$) has been derived from experiments with acetate buffers. For 0.1*M*-acetic acid, $v = 80.0 \times 10^{-6}$, which gives $[H^*] = 5.1 \times 10^{-4}$ and $K = [H^*]^2/c = 2.6 \times 10^{-6}$. The corresponding data for 0.5*M*-acid are $v = 130 \times 10^{-6}$, $[H^*] = 1.18 \times 10^{-3}$, and $K = 2.8 \times 10^{-6}$. The mean value, $K = 2.7 \times 10^{-6}$, for 50% alcoholic solution compares with $K = 1.8 \times 10^{-5}$ in aqueous solution.

Reaction Velocity in Acetate Buffers.—In presence of a mixture of acetic acid and sodium acetate, the reaction is somewhat anomalous in that the velocity diminishes as the reaction proceeds and does not show the normal autocatalytic effect which, however, is obtained with pure acetic acid. For a given concentration of acetic acid, the effect becomes more marked as the proportion of acetate increases. Although the anomalous behaviour cannot yet be explained, it is sufficient to note that the velocity diminishes linearly with the fall in the iodine concentration, and it is therefore possible to determine the initial velocity with the same precision as when the autocatalytic effect is normal.

For a series of buffers represented by $0.1\text{CH}_3\cdot\text{CO}_2\text{H} + x\text{CH}_3\cdot\text{CO}_2\text{Na}$, the initial velocity of the phorone reaction shows a rapid fall on the

addition of small quantities of acetate, passes through a minimum, and subsequently increases linearly with the acetate concentration. The relations are similar to those which have been observed in corresponding experiments with acetone in aqueous solution. In accordance with the previous method of interpretation, the slope of the linear portion of the curve affords a measure of the catalytic activity (k_a) of the acetate ion, and by extrapolation to $x = 0$, a measure of the catalytic effect due to the combined action of the solvent (v_s) and of the undissociated acetic acid ($0.1k_m$) is obtained. The actual $v-x$ plot leads to $k_a = 11 \times 10^{-6}$ and $v_s + 0.1k_m = 13.7 \times 10^{-6}$, whence $k_m = 7 \times 10^{-6}$.

The value thus derived for k_a may be somewhat affected by the incidence of hydroxyl-ion catalysis in the more concentrated acetate buffers, and possibly by inert-salt action. These factors are eliminated in the process of extrapolation by which k_m is determined, but, on the other hand, the extrapolated velocity represents mainly the influence of the solvent, and in consequence the value of k_m can only be approximate.

The initial reaction velocities obtained in our experiments are shown in the last column of Table II. Col. 1 gives x , and col. 2 the

TABLE II.
Catalytic effect of $0.1\text{CH}_3\cdot\text{CO}_2\text{H} + x\text{CH}_3\cdot\text{CO}_2\text{Na}$.

x .	$[\text{H}^+]. 10^6$.	$v_h. 10^6$.	$v_m. 10^6$.	$v_a. 10^6$.	$v_s. 10^6$.	$v_{\text{calc.}}. 10^6$.	$v_{\text{obs.}}. 10^6$.
0	5.10	66.3	0.7	—	13.0	80.0	80.0
0.02	13.5	1.75	0.7	0.22	13.0	15.7	15.3
0.04	6.7	0.87	0.7	0.44	13.0	15.0	14.6
0.06	4.5	0.58	0.7	0.66	13.0	14.9	14.6
0.10	2.7	0.35	0.7	1.10	13.0	15.1	15.0
0.30	0.9	0.12	0.7	3.3	13.0	17.1	17.0
0.50	0.5	0.07	0.7	5.5	13.0	19.3	18.7
0.80	0.3	0.04	0.7	8.8	13.0	22.5	23.0
1.0	0.3	0.04	0.7	11.0	13.0	24.7	25.0

values of $[\text{H}^+]$ calculated from $K = 2.7 \times 10^{-6}$; cols. 3—6 give the partial velocities due respectively to the hydrogen ion (v_h), the acetic acid molecule (v_m), the acetate ion (v_a), and the solvent (v_s), and col. 7 gives the calculated total velocity $v_{\text{calc.}} = v_h + v_m + v_a + v_s$.

The agreement between the observed and calculated velocities for the acetate buffer series affords strong evidence for the multiple character of the observed catalytic effects.

The phorone reaction is thus seen to be similar to the acetone and the mesityl oxide reaction which have been previously examined with reference to the associated catalytic effects. The catalytic coefficients derived from the experiments with acetone (in water), with mesityl oxide (in 5% alcohol), and with phorone (in 50% alcohol) are compared in Table III. The coefficients and the solvent effects

refer in all cases to a ketone concentration of one mol. per litre and 25°.

TABLE III.
Comparison of catalytic coefficients.

	Acetone.	Mesityl oxide.	Phorone.
$k_h \cdot 10^3$	1.72 (100)	420 (100)	130 (100)
$k_{\text{HAc}} \cdot 10^3$	0.0055 (0.33)	0.10 (0.025)	0.007 (0.005)
$k_{\text{Ac}'} \cdot 10^3$	0.015 (0.9)	0.20 (0.05)	0.011 (0.008)
$k_{\text{OH}'} \cdot 10^3$	25,000 (15×10^5)	185,000 (0.45×10^5)	—
$v_s \cdot 10^3$	0.000025 (0.0015)	0.02 (0.005)	0.013 (0.01)

Although the comparison of the numbers in the table is restricted by the variation in the reaction medium, it may be noted that all the coefficients are greatest for the mesityl oxide and, in general, least for the acetone reaction. If for each reaction the coefficients are expressed in terms of the corresponding value of k_h ($k_h = 100$), the numbers in parentheses are obtained, and these indicate that the relative catalytic effects of the acetic acid molecule and the acetate ion are much the largest for the acetone reaction and least for the phorone. The relative solvent effects are, however, in the inverse order.

Summary.

The intramolecular transformation of phorone which precedes the substitution of iodine for hydrogen is accelerated by acids and bases. The catalytic effects produced by hydrochloric and acetic acids and by acetate buffers in 50% alcohol have been determined, and a detailed study has been made of the autocatalysed reaction, which shows that the course of this is largely determined in its earlier stages by the catalytic influence of the solvent medium.

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