# CCLXXXIII.—*Acid and Salt Effects in Catalysed Reactions. Part XVI. Catalytic Effects in the Iodination of Mesityl Oxide.*

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THE experiments now to be described originated in the observation that an old sample of acetone sodium bisulphite reacted abnormally quickly with iodine. It was suspected that the presence of condensation products might be the cause of this enhanced reactivity, and preliminary experiments with mesityl oxide showed that this substance in dilute aqueous solution reacts very rapidly with iodine and that the change is similar to that which occurs with acetone—the reaction is catalysed by acids, and for a given hydrogen-ion concentration the velocity is proportional to the concentration of the mesityl oxide and independent of the concentration of the iodine. It follows that the rate of disappearance of the iodine is determined by a preliminary change in the mesityl oxide, and that the iodine reacts immediately with the product of this transformation.

For the same concentration of ketone, and with dilute hydrochloric acid (*e.g.*, $0{\cdot}01N$) as catalyst, the mesityl oxide reaction takes place more than 200 times as rapidly as the acetone reaction, and this high speed suggested that a study of the autocatalytic change would provide a convenient starting point in the investigation of the factors which determine the velocity of the reaction.

Early experiments of this kind showed that the course of the autocatalysed reaction is similar to the corresponding reaction with acetone. In its later stages, the velocity can be represented fairly satisfactorily by the simple autocatalytic equation $dx/dt = kmx$, in which $m$ represents the concentration of the mesityl oxide, and $x$ the concentration of the catalytically active hydrogen ion in the form of hydriodic acid, which is measured by the fall in the concentration of the iodine in accordance with the equation $C_6H_{10}O + I_2 \longrightarrow C_6H_9IO + HI$. Integration of the differential equation gives $\log x = kmt +$ constant, and in agreement with this it was found that the plot of $\log x$ against $t$ for the later stages of the reaction gave approximately a straight line. Very considerable deviations from the straight line were always found, however, in the initial period, and these deviations were such as to show clearly that the velocity of the reaction in its early stages is much greater than can be accounted for by the above equation. We were at first inclined to seek an interpretation of these oft-repeated observations in the joint catalytic action of the hydrogen and hydroxyl ions, but later experiments showed quite definitely that the combined action of these ions does not account for the facts, which, indeed, can only be explained by the further assumption that catalytic effects of considerable magnitude are to be attributed to the undissociated water molecules.

Attention may first be directed to some of the difficulties which were encountered in the earlier experiments on the autocatalysed reaction. These showed large differences in the behaviour in the initial stages of the reaction when different samples of mesityl oxide were employed. Some of the latter were obtained by repeated fractional distillation of commercial specimens, and others were prepared by us from acetone by conversion into diacetone-alcohol which was separated and subsequently converted into mesityl oxide by distillation with a very small quantity of iodine (Hibbert, *J. Amer. Chem. Soc.*, 1915, **37**, 1748). With such samples of mesityl oxide, which were almost identical in density and refractive index, the times required for the autocatalysed change to proceed to the same point under precisely the same conditions varied very widely. With a concentration of 4 c.c. of mesityl oxide and 0·001 mol. of iodine per litre, the time occupied by the disappearance of the iodine ranged from 40 to 200 minutes, although the course of the reaction in the later stages was the same in each case within narrow limits.

These results directed our attention to observations recorded by Harries (*Ber.*, 1899, **32**, 1329; *Annalen*, 1904, **330**, 189), who found that a specimen of mesityl oxide could not be entirely dissolved in a 40% solution of sodium bisulphite. The insoluble fraction, amounting to 30%, differed but little in density and refractive index from the original and gave the same *cis*- and *trans*-oximes. Since the mesityl oxide recovered from the bisulphite solution dissolved completely on renewed treatment with this reagent, Harries came to the conclusion that mesityl oxide is not chemically homogeneous and that a new type of isomerism is involved. In similar experiments, Morton (J., 1926, 719) failed to detect any such abnormality in the behaviour of mesityl oxide, and inferred that some unrecorded factor was involved in the work of Harries. Our own observations would suggest that the mesityl oxide examined by the latter was impure, for we have found that the miscibility of mesityl oxide with water is very greatly reduced by the impurities which are usually present in the ordinary preparations.

In partial explanation of the inconsistencies in the behaviour of different samples of mesityl oxide in the autocatalysed reaction with iodine, it was found that these contained varying amounts of an acidic substance which is not removed by distillation, but which can be separated by treatment with a dilute solution of alkali, or even by repeated extraction with water. After such treatment, the various samples showed much closer agreement in their behaviour under the conditions afforded by autocatalysis. When, however, these acid-free specimens were examined with reference to the velocity of iodination in acetate buffers of $p_H$ 5—5·5, they exhibited marked differences, and this suggested the presence of a non-acid impurity. The removal of this was eventually effected by crystallising the mesityl oxide from a solution of the acid-free samples in light petroleum. By the use of liquid air to obtain the necessary low temperature, the crystals were separated by filtration and freed from solvent by distillation. The mesityl oxide was then examined by measuring the velocity of iodination in an acetate buffer of $p_H$ 5·2. The results obtained after one, two, and three crystallisations were :

| Mesityl oxide (acid-free). | M. p. | Velocity of iodination. |
|---|---|---|
| Purified by distillation .................. | −44·0° | 2·0 |
| Once crystallised ........................... | −42·5 | 1·2 |
| Twice crystallised........................... | −41·5 | 0·91 |
| Thrice crystallised ........................ | −41·5 | 0·87 |

From the above data it would appear that the product obtained in the second crystallisation is very nearly pure, and this is the material which has been used in our final experiments. These, it may be noted, have not disclosed any factor which was not already indicated in the earlier experiments with less pure samples of mesityl oxide.

Under the conditions of the experiments which we have made with mesityl oxide, there is a close similarity in the behaviour of this substance and of acetone towards iodine, but it should be noted that marked differences are shown in the reactivity of the respective iodo-substitution products. The iodomesityl oxide would appear to undergo hydrolysis very readily, for when the solution in which the reaction has proceeded to completion is titrated with standard alkali and phenolphthalein as indicator, the consumption of alkali is nearly twice that required by the hydriodic acid formed in the primary reaction. The iodomesityl oxide also reacts readily with sodium thiosulphate, and the reactivity disclosed by these observations restricts to some extent the range of the conditions which are suitable for measurements of the velocity of iodination. There are, however, substantial grounds for the belief that the essential factors associated with this reaction have been identified and evaluated. The measurements to be described include observations on the catalytic activity of hydrochloric and acetic acids, on the velocity in buffer solutions, and on the course of the autocatalysed reaction. On account of the limited solubility of (impure) mesityl oxide in water, the solvent used at first contained 5% (vol.) of alcohol, and since this solvent facilitated the addition of small quantities of mesityl oxide in the form of an alcoholic solution, it was employed in all the experiments. The standard concentration of the mesityl oxide was 4·00 c.c. per litre (0·035$M$), and as a rule iodine was added to give a 0·001$M$-solution. The temperature was 25°.

*Hydrochloric Acid as Catalyst.*—In consequence of the high speed of the reaction in dilute hydrochloric acid solution, the progress of the change could not be followed by the customary method of titration with standard thiosulphate, and the following method was therefore adopted. At a given instant the reaction was started by the addition of a measured quantity of iodine to the solution containing the mesityl oxide and hydrochloric acid, and when the reaction was nearly completed a little starch paste was added and the time noted at which the blue colour disappeared. This method has also been used in some of the experiments with acetic acid as catalyst. Such experiments give the mean reaction velocity $\bar{v}$, and from a series in which the quantity of added iodine is varied, it is possible to determine the initial velocity of the reaction. Table I gives the results for such experiments with $0{\cdot}0101N$-hydrochloric and with $0{\cdot}05N$-acetic acid.

TABLE I.

| $0{\cdot}0101N$-HCl. | | | $0{\cdot}05N$-$CH_3{\cdot}CO_2H$. | | |
|---|---|---|---|---|---|
| $I_2$ (mol./l.). | $t$ (mins.). | $v \times 10^4$. | $I_2$ (mol./l.). | $t$ (mins.). | $v \times 10^4$. |
| 0·0005 | 3·20 | 1·56 | 0·0005 | 30·9 | 0·162 |
| 0·0010 | 6·27 | 1·60 | 0·0010 | 54·5 | 0·183 |
| 0·0015 | 9·16 | 1·64 | 0·0015 | 72·8 | 0·206 |

In each series, the mean velocity increases with the iodine concentration. This is connected with the increasing catalytic effect of the hydriodic acid produced, although the influence of the latter is to some extent counteracted by a fall in the concentration of the mesityl oxide. It is sufficient to note that the mean velocity is a linear function of the original iodine concentration and therefore that it is possible to derive the initial velocities for each series. The values so obtained are $1{\cdot}52 \times 10^{-4}$ for $0{\cdot}0101N$-hydrochloric acid and $0{\cdot}141 \times 10^{-4}$ for $0{\cdot}05N$-acetic acid.

From similar series of experiments with hydrochloric acid solutions of varying concentration, it has been found that the initial velocity ($v_0$) is almost exactly proportional to the concentration ($c$). On the assumption that the catalytic effect under these conditions is attributable to the hydrogen ion, these experiments give for $k_h = v_0/c$ the value 0·015. Other observations suggest a somewhat lower value, *viz.*, $k_h = 0{\cdot}0147$.

*Reaction Velocity in Buffer Solutions.*—The possibility that the unexpectedly high speed which had been observed in the early stages of the autocatalysed reaction might be due to the catalytic effect of water molecules led us to investigate the velocity of the reaction in buffer solutions of different $p_H$ and various concentrations. For a buffer solution containing the weak acid HA and the salt MA, the observed reaction velocity may be represented by

$$v = v_h + v_{OH} + v_w + v_a + v_m \quad . \quad . \quad . \quad . \quad (1)$$

in which the successive partial velocities correspond with the catalytic action of the hydrogen ion, the hydroxyl ion, the water molecule, the acid ion $A^-$, and the undissociated acid molecule HA. When the acid–salt ratio of the buffer mixture has a fixed value, the first three partial velocities are constant and the above equation may be written

$$v = v_0 + v_b \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

where $v_0$, which represents the velocity at zero buffer concentration, depends only on the hydrogen-ion concentration, and $v_b$, which represents the catalytic effect of the buffer constituents, is proportional to the concentration of the buffer solution. In other words, the measured velocity $v$ is a linear function of the concentration of the buffer. Velocity measurements for a fixed buffer ratio and varying buffer concentration lead, therefore, by linear extrapolation to the corresponding $v_0$, and such $v_0$ values in their dependence on $p_H$ correspond with points on the water catenary ($H^+$–$H_2O$–$OH^-$).

Acetate buffers were used for the most part, but the higher $p_H$ values were stabilised by means of phosphate buffers. Since the solvent contains 5% of alcohol, the dissociation constants of the acetic and phosphoric acids are appreciably less than for pure water. In the case of acetic acid this reduction is indicated by measurements of conductivity and of hydrogen potential, and comparative observations on the catalytic activity of acetic acid in water and in 5% alcohol suggest that the constant is reduced from $1{\cdot}85 \times 10^{-5}$ to $1{\cdot}7 \times 10^{-5}$. It will be assumed that the proportional reduction in the second-stage constant $K_2$ for phosphoric acid has the same value, *i.e.*, if $K_2 = 1{\cdot}1 \times 10^{-7}$ for aqueous solution, the value for 5% alcoholic solution becomes $1{\cdot}0 \times 10^{-7}$.

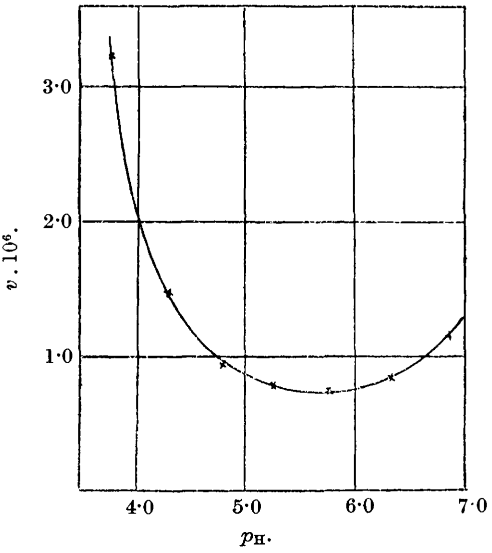
In Table II the results are summarised. The buffer mixtures are indicated in col. 1; col. 2 gives the $p_H$; col. 3 the hydrogen-ion concentrations derived from the ionisation constants of the acids; col. 4 the concentrations of the acid ($c'$) and salt ($s$); col. 5 the observed initial velocities; and col. 6 the values of $v_0$ derived by extrapolation from the straight line which gives the connexion between $v$ and $c'$ (or $s$).

When the values of $v_0$ are plotted against $p_H$ the catenary curve shown in Fig. 1 is obtained. According to this the minimum velocity $v_i$ is $0{\cdot}75 \times 10^{-6}$, and the $p_H$ of the isocatalytic point 5·68 or $[H^+]_i = 2{\cdot}1 \times 10^{-6}$. This minimum velocity is about twelve times the magnitude of the velocity due to the joint action of the hydrogen and hydroxyl ions, for the latter is given by $u_i = 2k_h[H^+]_i = 2 \times 0{\cdot}0147 \times 2{\cdot}1 \times 10^{-6} = 0{\cdot}062 \times 10^{-6}$. The difference between $v_i$ and $u_i$ must be due to the catalytic action of the

TABLE II.

| Buffer mixture. | $p_H$. | $[H^+] . 10^5$. | Buffer concentration, $c'$. | $s$. | $v . 10^6$. | $v_0 . 10^6$. |
|---|---|---|---|---|---|---|
| 10HAc + 1NaAc | 3·77 | 17·0 | 0·05 | 0·005 | 3·42 | 3·22 |
| | | | 0·1 | 0·01 | 3·65 | |
| | | | 0·15 | 0·015 | 3·84 | |
| 3HAc + 1NaAc | 4·29 | 5·1 | 0·015 | 0·005 | 1·55 | 1·46 |
| | | | 0·03 | 0·01 | 1·64 | |
| | | | 0·045 | 0·015 | 1·74 | |
| 1HAc + 1NaAc | 4·77 | 1·7 | 0·005 | 0·005 | 1·00 | 0·94 |
| | | | 0·01 | 0·01 | 1·05 | |
| | | | 0·015 | 0·015 | 1·12 | |
| 1HAc + 3NaAc | 5·24 | 0·57 | 0·005 | 0·015 | 0·91 | 0·79 |
| | | | 0·01 | 0·03 | 1·03 | |
| | | | 0·015 | 0·045 | 1·14 | |
| 1HAc + 10NaAc | 5·77 | 0·17 | 0·002 | 0·02 | 0·89 | 0·75 |
| | | | 0·004 | 0·04 | 1·04 | |
| | | | 0·006 | 0·06 | 1·18 | |
| $4{\cdot}81NaH_2PO_4$ + $1Na_2HPO_4$ | 6·32 | 0·048 | $c' + s =$ | 0·01 | 0·90 | 0·82 |
| | | | = | 0·02 | 0·97 | |
| | | | = | 0·03 | 1·06 | |
| $1{\cdot}41NaH_2PO_4$ + $1Na_2HPO_4$ | 6·85 | 0·014 | $c' + s =$ | 0·01 | 1·29 | 1·15 |
| | | | = | 0·02 | 1·43 | |
| | | | = | 0·03 | 1·56 | |

FIG. 1.



*The water catenary ($v_0$–$p_H$) for the mesityl oxide–iodine reaction.*

water molecules; in other words, $v_w = 0{\cdot}69 \times 10^{-6}$. Furthermore, if $K_w = 10^{-14}$, we derive from $[H^+]_i = k_{OH}K_w/k_h$ the value $k_{OH} = 6{\cdot}5$ for the catalytic coefficient which characterises the hydroxyl ion. From $k_h = 0{\cdot}0147$, $k_{OH} = 6{\cdot}5$, and $v_w = 0{\cdot}69 \times 10^{-6}$, the reaction velocities corresponding with the water catenary may now be calculated by use of the equation

$$v_0 = 0{\cdot}0147[\mathrm{H}^+] + 6{\cdot}5[\mathrm{OH}^-] + 0{\cdot}69 \times 10^{-6}$$

and in Table III these are compared with the velocities derived from the buffer solution experiments. Col. 2 shows the hydrogen-ion concentration; cols. 3, 4, and 5 the partial velocities $v_h$, $v_{\mathrm{OH}}$, and $v_w$, respectively; col. 6 the calculated velocity $v_o$; and col. 7 the observed velocity.

TABLE III.

| Buffer. | $[\mathrm{H}^+] . 10^5$. | $v_h . 10^6$. | $v_{\mathrm{OH}} . 10^6$. | $v_w . 10^6$. | $v_0 . 10^6$. (calc.). | (obs.). |
|---|---|---|---|---|---|---|
| 10HAc + 1NaAc | 17·0 | 2·50 | — | 0·69 | 3·19 | 3·22 |
| 3HAc + 1NaAc | 5·1 | 0·75 | — | 0·69 | 1·44 | 1·46 |
| 1HAc + 1NaAc | 1·7 | 0·25 | — | 0·69 | 0·94 | 0·94 |
| 1HAc + 3NaAc | 0·57 | 0·084 | 0·01 | 0·69 | 0·785 | 0·79 |
| 1HAc + 10NaAc | 0·17 | 0·025 | 0·04 | 0·69 | 0·755 | 0·75 |
| $4{\cdot}81\mathrm{NaH_2PO_4} + 1\mathrm{Na_2HPO_4}$ | 0·048 | 0·01 | 0·135 | 0·69 | 0·835 | 0·82 |
| $1{\cdot}41\mathrm{NaH_2PO_4} + 1\mathrm{Na_2HPO_4}$ | 0·014 | — | 0·465 | 0·69 | 1·155 | 1·15 |

From the reaction-velocity data for the buffer solutions, it is possible to derive the values of $k_m$ and $k_a$ for the buffer constituents HA and $\mathrm{A}^-$. If $q = c'/s$ is the ratio of acid to salt in the buffer mixture, the equation for the velocity may be written

$$\begin{aligned} v &= v_0 + (k_a + k_m q)s \\ &= v_0 + ls \end{aligned}$$

where $l = k_a + k_m q$ is the slope of the curve which is obtained when the velocity for a given buffer ratio is plotted against the buffer concentration of the salt. If $q'$ and $l'$ are corresponding values for a second series of buffers, we obtain

$$k_m = (l - l')/(q - q') \quad . \; . \; . \quad (2) \qquad k_a = (ql' - q'l)/(q - q') \quad . \; . \; . \quad (3)$$

The values derived in this way are $k_m = 3{\cdot}5 \times 10^{-6}$ for the acetic acid molecule, $k_a = 7 \times 10^{-6}$ for the acetic ion, $k = 3 \times 10^{-6}$ for the $\mathrm{H_2PO_4}'$ ion, and $k = 30 \times 10^{-6}$ for the $\mathrm{HPO_4}''$ ion. The much greater activity of the $\mathrm{HPO_4}''$ ion compared with the $\mathrm{H_2PO_4}'$ ion is consistent with the general relation that the activity of the anion increases as the ionisation constant of the corresponding acid diminishes.

*Acetic Acid as Catalyst.*—Under the conditions of these experiments, the reaction velocity is determined by the joint action of the hydrogen ion, the acetic acid molecule, and the water molecule, for the general equation may be written

$$\begin{aligned} v &= (k_h + k_a - k_m)[\mathrm{H}^+] + k_m c_1 + v_w \quad . \quad . \quad . \quad (1b) \\ &= 0{\cdot}0147\,[\mathrm{H}^+] + 3{\cdot}5 \times 10^{-6} c_1 + 0{\cdot}69 \times 10^{-6} \end{aligned}$$

where $c_1$ is the concentration of the acetic acid. The velocity may be measured by titration of the residual iodine with thiosulphate or by the colour-disappearance method used in the case of hydrochloric acid. Both methods have been applied with concordant results.

In Table IV, col. 1 gives the method of observation, col. 2 the concentration of the acetic acid, col. 3 the hydrogen-ion concentration calculated from $K = 1{\cdot}7 \times 10^{-5}$, col. 4 the velocity calculated from equation (1*b*), and col. 5 the observed initial velocity. It is apparent that the observations made with acetic acid are satisfactorily interpreted in terms of (1*b*).

TABLE IV.

| Method. | $c_1$. | $[H^+] . 10^3$. | $v . 10^6$ (calc.). | $v . 10^6$ (obs.). |
|---|---|---|---|---|
| Titration | 0·02 | 0·58 | 9·3 | 9·2 |
| Colour | 0·05 | 0·92 | 14·4 | 14·1 |
| Colour | 0·1 | 1·30 | 20·1 | 20·0 |
| Titration | 0·1 | 1·30 | 20·1 | 20·2 |
| Colour | 0·2 | 1·84 | 28·4 | 27·7 |

*The Autocatalysed Reaction.*—When the mesityl oxide and iodine are dissolved in " conductivity " water, the only catalysts would appear to be the hydrogen ion, the hydroxyl ion, and the water molecule. When the reaction has proceeded far enough to permit of a measurement of the fall in the iodine concentration, the hydrogen-ion concentration of the solution is controlled by the hydriodic acid formed, and the equation for the velocity may be written

$$v = dx/dt = k_h x + k_{OH}K_w/x + v_w \quad . \quad . \quad . \quad (4)$$

If the numerical values of $k_h$, $k_{OH}$, $K_w$, and $v_w$ are introduced in this equation, it is at once apparent that the partial velocity due to the hydroxyl ion may be entirely neglected when the reaction has reached the stage of measurable $x$ values. The equation then becomes

$$dx/dt = k_h x + v_w \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

which by integration yields

$$k_h t = 2{\cdot}30 \log_{10}(x + v_w/k_h) + \text{constant} \quad . \quad . \quad . \quad (4b)$$

Since $v_w/k_h = 0{\cdot}000047$, it follows that $\log(x + 0{\cdot}000047)$ should be a linear function of $t$.

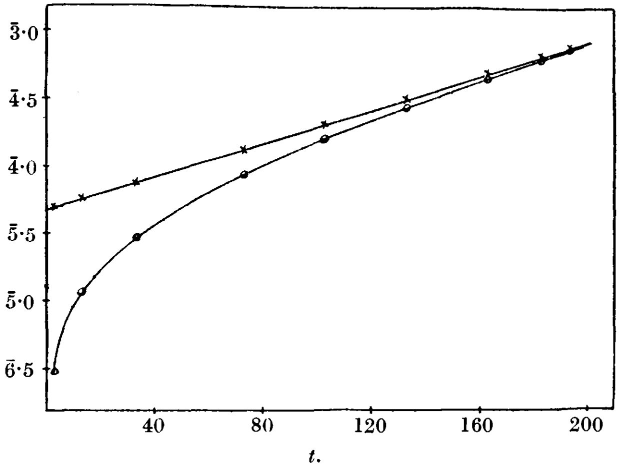
In the determination of $x$, the samples to be titrated were run into a dilute acetate buffer $p_H$ 5·7, which corresponds with the minimum velocity on the water catenary. The experimental data for such an experiment under autocatalytic conditions were :

| $t$ (mins.) | 3 | 13 | 33 | 73 | 103 | 133 | 163 | 183 | 193 |
|---|---|---|---|---|---|---|---|---|---|
| $x . 10^4$ | 0·030 | 0·115 | 0·30 | 0·875 | 1·585 | 2·71 | 4·41 | 6·03 | 7·04 |

The graphs of log $(x + 0{\cdot}000047)$ and of log $x$ against $t$ are shown in Fig. 2. If the reaction velocity were entirely controlled by the hydrogen-ion concentration, the latter should be a straight line. The fact that the slope of the curve increases as we approach the beginning of the reaction is a clear indication of the intervention of some other catalytic effect, whilst the linearity of the first graph would seem to show that this catalytic effect is represented by the action of the water molecules.

Since this line intersects the ordinate for $t = 0$ at $\bar{5}{\cdot}67$, which is $\log_{10} 0{\cdot}000047$, it follows that $x = 0$ when $t = 0$. Interpreted in the light of the relations shown by the autocatalysed reaction between acetone and iodine (Dawson, J., 1927, 458), the conclusion to be drawn from this is that the catalytic action of the hydroxyl ion, as represented by the second term in (4), has no appreciable influence on the course of the autocatalysed mesityl oxide reaction. This accords with the relatively low value of $k_{\text{OH}}/k_h = 440$ for this reaction, whereas the corresponding ratio for the acetone reaction is 15,000. In the former case the hydrogen-ion concentration of the minimum velocity (*M.V.*) point is $2{\cdot}1 \times 10^{-6}$, whilst for the acetone reaction it is $12{\cdot}5 \times 10^{-6}$ (compare Dawson and Key, this vol., p. 543).

FIG. 2.



*Autocatalysis of the mesityl oxide–iodine reaction. Plots of log* $(x + 0{\cdot}000047)$ *(curve ×) and of log x (curve ⊙) against time.*

Although, therefore, there can be no doubt that the reaction velocity, as represented by (4), passes through a minimum value, the incidence of this corresponds with a value of $x$ which is far too small for quantitative measurement. The *M.V.* point would appear to be reached in about 2 minutes, and because of the large catalytic effect of the water molecules ($v_w = 0{\cdot}69 \times 10^{-6}$) as compared with that due to the hydrogen and hydroxyl ions ($v_h + v_{OH} = 0{\cdot}06 \times 10^{-6}$), the incidence of minimum velocity has very little influence on the course of the autocatalysed reaction.

In the derivation of (4*b*) it was assumed that the concentration of the mesityl oxide remains constant throughout the autocatalysed reaction. When this is not the case, the equation for the velocity becomes

$$dx/dt = k_h x(1 - x/m) + v_w(1 - x/m) \quad . \quad . \quad (5a)$$

which on integration becomes

$$k_h t = 2{\cdot}30/(1 + v_w/k_h m) . \log_{10}(x + v_w/k_h)/(1 - x/m) + \text{constant} \quad (5b)$$

where $m$ is the molar concentration of the mesityl oxide.

In the experiment shown in Fig. 2, the total fall in the concentration of the mesityl oxide amounts to 2%, and when equation (4*b*) is applied to the interval between $t = 163$ and $t = 193$ minutes, at which stage of the reaction the effect of the water molecules is small compared with that due to the hydrogen ion, we obtain $k_h = 0{\cdot}01435$, and this, when corrected for the fall in the mesityl oxide concentration below the standard value of 0·035 mol. per litre, gives $k_h = 0{\cdot}0146$, in close agreement with the figure previously given.

*Comparison of the Coefficients for the Acetone and Mesityl Oxide Reactions.*—As a matter of practical convenience, the velocity coefficients which have been derived from the experiments with acetone and mesityl oxide are in both cases expressed in terms of the respective concentrations of these substances which were actually used in the observations. The concentration of the acetone was 0·272 molar (20·0 c.c. per litre), and that of the mesityl oxide 0·035 molar (4·00 c.c. per litre). In the comparison instituted in Table V, the two series of coefficients are referred to molar concentration of the ketone. The last column shows the ratios of the corresponding coefficients.

TABLE V.

| Catalytic coefficient. | Acetone reaction. | Mesityl oxide reaction. | Ratio. |
|---|---|---|---|
| $k_h$ | $1{\cdot}72 \times 10^{-3}$ | $420 \times 10^{-3}$ | 233 |
| $k_{OH}$ | 25 | 185 | 7·5 |
| $k_w = v_w/55$ | $5 \times 10^{-10}$ | $3700 \times 10^{-10}$ | 750 |
| $k_m$ ($CH_3{\cdot}CO_2H$) | $5{\cdot}5 \times 10^{-6}$ | $100 \times 10^{-6}$ | 18 |
| $k_a$ ($CH_3{\cdot}CO_2^-$) | $15 \times 10^{-6}$ | $200 \times 10^{-6}$ | 13 |

In considering these ratios, it should be noted that the value for $k_h$ can be determined much more precisely than the values for the other catalytic entities. Indirect methods have to be used in the derivation of the value for $k_{OH}$, and in the case of $k_w$ the activity of the water molecule in the acetone reaction is so very small that the degree of precision is limited. It is, however, quite clear that the ratio varies widely with the nature of the catalysing entity. In the case of the hydroxyl ion, the acetic ion, and the acetic acid molecule, the change in the magnitude of the catalytic coefficient on passing from the acetone to the mesityl oxide reaction is of the same order; for the hydrogen ion and for the water molecule the change is much greater. It does not seem possible to explain these differences.

## *Summary.*

The reaction between mesityl oxide and iodine in dilute aqueous solution is similar to, but more rapid than, the reaction between acetone and iodine.

The iodine takes no part in the primary change, but the rate at which it disappears affords a measure of the transformation of the mesityl oxide, which is probably of the keto–enol type. The reaction is catalysed by hydrogen ions, hydroxyl ions, and water molecules, and also by other acid molecules and the corresponding anions.

The catalytic coefficients for $H^+$, $OH^-$, $H_2O$, $CH_3{\cdot}CO_2H$, $CH_3{\cdot}CO_2^-$, $H_2PO_4^-$, and $HPO_4^=$ have been determined. The relative values of these coefficients for the mesityl oxide reaction differ very considerably from their relative values for the acetone reaction.

The course of the autocatalysed reaction can be explained in terms of the joint catalytic action of the hydrogen ion and the water molecule.

Mesityl oxide has been prepared in pure condition, and anomalies recorded in the literature of this substance are ascribed to the presence of impurities.

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