14. *Binary and Ternary Mechanisms in the Iodination of Acetone.*

By R. P. Bell and P. Jones.

Measurements are reported on the rate of iodination of acetone at 25° in trimethylacetate, acetate, and glycollate buffers at a constant ionic strength of 0·2. The results confirm Dawson and Spivey's finding (*J.*, 1930, 2180) that the expression for the reaction velocity contains a small term involving the product of the concentrations of acid and anion. It is concluded that this term probably results from the production of enol by a ternary mechanism, but that its occurrence does not make it possible to decide whether or not the main reaction takes place by such a mechanism. Some general consequences of the ternary scheme are examined in the light of available experimental evidence, and it is concluded that the ternary mechanism is not of major importance in reactions catalysed by acids and bases in aqueous solution.

Swain (*J. Amer. Chem. Soc.*, 1950, **72**, 4578) has recently revived the suggestion originally put forward by Lowry and Faulkner (*J.*, 1925, 2883) that reactions catalysed by acids and bases normally occur by a ternary mechanism, involving simultaneous attack on the substrate by an acid and a base. One of the chief pieces of evidence produced in support of this view is Dawson and Spivey's finding (*J.*, 1930, 2180) that the expression for the rate of iodination of acetone in acetate buffers contains a small product term of the form $k_P[HOAc][OAc^-]$. Their data certainly require such a term, but it might be objected that they refer to solutions containing high and variable concentrations of electrolyte (>0·75N). It seemed desirable to repeat these measurements at constant and lower ionic strength, especially as recent work on the rate of hydration of acetaldehyde (Bell and Clunie, *Proc. Roy Soc.*, 1952, *A*, **212**, 33) has failed to detect a product term under conditions where it should be prominent according to Swain's treatment. Such measurements are now reported, together with some general considerations about the occurrence and detection of ternary mechanisms.

Experimental

Acetone was purified *via* the sodium iodide compound. Its concentration in the reaction mixtures was always 0·272M, the same as that used by Dawson and his collaborators. All solutions were made up with conductivity water. Acetate buffer solutions were made up from "AnalaR" acetic acid (99·8% pure by titration) and sodium hydroxide solution standardized against constant-boiling hydrochloric acid. Iodine was kept as a M/50-solution in M/4-potassium iodide, and its initial concentration in the reaction mixtures was 0·002M. The total ionic strength of the reaction mixture was made up to $I = 0{\cdot}2$ by adding sodium chloride.

The reactions were carried out at 25° ± 0·02° and were followed by extracting 10-ml. samples at intervals, and titrating them with 0·01N-thiosulphate (standardized with potassium iodate), starch being used as indicator. Plots of titre against time were strictly linear throughout, and the reaction velocities were calculated from the slopes of these plots.

Results.—The results obtained are given in Tables 1 and 2. The anion concentrations represent mean values, corrected for the small quantity of acid produced during the reaction; *r* is the stoicheiometric buffer ratio [HA]/[A⁻]. The reaction velocities v are all expressed in moles of iodine per l. per min., referred to unit concentration of acetone. The velocity v' represents the contribution due to catalysis by H_2O, H_3O^+, and OH^-. It is calculated from the expression

TABLE 1. *Iodination of acetone in acetate buffers.*

r = 1·00, $10^8v'$ = 9·7.

$100[OAc^-]$	2·45	2·59	4·89	5·74	7·54	8·69	10·19	13·10	17·50
10^8v, obs.	60·9	63·0	114	132	169	204	234	306	423
,, calc.	60·2	63·0	113	132	173	200	236	308	424

r = 2·00, $10^8v'$ = 16·5.

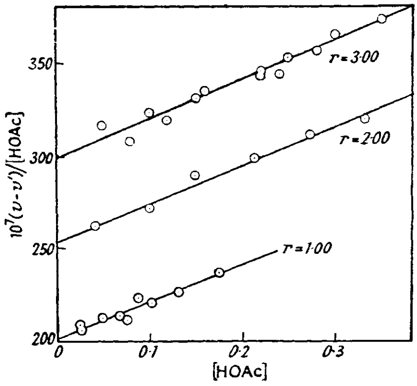
$100[OAc^-]$	2·06	4·98	7·41	10·65	13·68	16·60
10^8v, obs.	70·5	152	231	337	442	547
,, calc.	70·0	152	225	332	437	546

r = 3·00, $10^8v'$ = 23·4.

$100[OAc^-]$ ...	1·59	2·60	3·29	3·95	4·99	5·31	6·66	6·67	8·01	8·37	9·36	10·03	11·74
10^8v, obs. ...	73·7	103	130	150	189	201	252	254	299	319	358	393	462
,, calc. ...	72·9	106	129	152	189	201	251	252	304	318	359	389	462

$$v' = v_0 + k_{H_3O^+}[H_3O^+] + k_{OH^-}[OH^-] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Bell and Lidwell's values of the catalytic constants (*Proc. Roy. Soc.*, 1940, *A*, **176**, 88) being used, and the activity coefficients of all univalent ions being taken as $f_1 = 0{\cdot}70$ in calculating the values of $[H_3O^+]$ and $[OH^-]$. Since v' is in most solutions only a small fraction of the total velocity, it is not necessary to know it accurately : in particular the uncertain contribution of OH^- is very small throughout.



The general expression for the reaction velocity can be written in the form

$$v - v' = k_A[HOAc] + k_B[OAc^-] + k_P[HOAc][OAc^-] = [OAc^-]\{k_Ar + k_B + k_P[HOAc]\} \quad (2)$$

It is immediately obvious from the data in Table 1 that the term involving k_P is appreciable, since, if $v - v'$ is plotted against $[OAc^-]$, the data for any one buffer ratio give a line which is markedly convex to the concentration axis : moreover, the velocities observed at higher concentrations are considerably higher than those calculated from the catalytic constants derived by Bell and Lidwell (*loc. cit.*) from measurements at lower concentrations. The validity of equation (2) can be tested by plotting $(v - v')/[OAc^-]$ against [HOAc], which should give parallel straight lines for each buffer ratio of common slope k_P. The figure shows that this expectation is fulfilled within experimental error.

The best values of k_A, k_B, and k_P were obtained, together with their probable errors, by treating the experimental data statistically, assuming that all the experimental errors are in $v - v'$. The results are given in Table 2 (together with earlier values for comparison), and the values of v, calc., in Table 1 are calculated from equations (1) and (2) by use of our values of the constants. The agreement with experiment is excellent, but no such agreement would be obtained if the product term were omitted : the same point is established by the relatively small probable error in the value of $k_{\rm P}$. Our values of $k_{\rm A}$ and $k_{\rm B}$ agree reasonably with those of earlier workers, but our value of $k_{\rm P}$ is considerably greater than that obtained by Dawson and Spivey. This is presumably because they used high and variable salt concentrations (>0·75N), while our experiments refer to a constant ionic strength of $I = 0{\cdot}2$. The contribution of the product term would have been barely detectable in the work of Bell and Lidwell, since the catalyst concentrations were much lower than in the present work.

TABLE 2. *Iodination of acetone in acetate buffers.*

	Present work	Bell and Lidwell	Dawson and Spivey
$10^6k_{\rm A}$	5·02 ± 0·09	6·1	4·8
$10^6k_{\rm B}$	15·1 ± 0·2	14·7	12·1
$10^6k_{\rm P}$	20·4 ± 0·9	—	12·9

It might be suggested that the existence of an appreciable product term depended upon some particular property of acetate buffers, and a few experiments were therefore carried out with buffer solutions prepared from trimethylacetic acid or glycollic acid, the results being given in Table 3. For the former the values of v, calc., are obtained by putting $10k^6{}_{\rm A} = 4{\cdot}4$, $10^6k_{\rm B} = 25$, $10^6k_{\rm P} = 46$. Although there are not sufficient data to warrant the calculation of probable errors, the agreement with experiment shows that a product term of similar magnitude is also present in this catalyst system. The values of $k_{\rm A}$ and $k_{\rm B}$ are in reasonable agreement with those obtained by Bell and Lidwell in more dilute solutions. There are only two measured velocities for glycollate buffers, but these are 2% and 7% higher than those calculated from Bell and Lidwell's catalytic constants. This corresponds to a value of $k_{\rm P}$ of 7—14 × 10^{-6}, and we can therefore conclude that the occurrence of a product term is a general phenomenon in this reaction.

TABLE 3. *Iodination of acetone in trimethylacetate and glycollate buffers.*

Trimethylacetate : $r = 0{\cdot}644$, $10^8v' = 6{\cdot}2$.

$100[{\rm CMe_3{\cdot}CO{\cdot}O^-}]$ ...	1·66	3·43	5·19	6·96	8·13
10^8v, obs.	52·0	103	156	211	250
,, calc.	52·4	104	156	211	248

Glycollate : $r = 0{\cdot}201$, $10^8v' = 14{\cdot}9$.

$100[{\rm CH_2(OH){\cdot}CO{\cdot}O^-}]$ ...	12·1	17·2
10^8v, obs.	91	130

DISCUSSION

The above data confirm the presence of an appreciable cross term of the form $k_{\rm P}[{\rm HA}][{\rm A^-}]$ in the acetone–iodine reaction, and we must now consider whether this means that the whole of the observed reaction takes place by a ternary mechanism, as was concluded by Swain (*loc. cit.*) from Dawson and Spivey's results. Swain makes the reasonable assumption that, if the mechanism is a ternary one, the reaction velocity in a buffer solution can be expressed approximately in the form

$$v = C\{[{\rm H_2O}] + a_1[{\rm HA}] + a_2[{\rm H^+}]\}\{[{\rm H_2O}] + b_1[{\rm A^-}] + b_2[{\rm OH^-}]\} \quad . \quad . \quad (3)$$

Comparing this with equation (1) and (2), we find

$$\left.\begin{array}{ll} v_0/C = [{\rm H_2O}]^2 + a_2b_2K_w & k_{\rm A}/C = a_1[{\rm H_2O}] + a_2b_1K_{\rm A} \\ k_{\rm H^+}/C = a_2[{\rm H_2O}] & k_{\rm B}/C = b_1[{\rm H_2O}] + a_1b_2K_w/K_{\rm A} \\ k_{\rm OH^-}/C = b_2[{\rm H_2O}] & k_{\rm P}/C = a_1b_1 \end{array}\right\} \quad . \quad (4)$$

where K_w and $K_{\rm A}$ are the values of the ionic product of water and of the dissociation constant of HA in the solution in question. The expressions for v_0, $k_{\rm A}$, and $k_{\rm B}$ each contain two terms, corresponding to different acid–base pairs. For convenience we shall describe the terms corresponding to $\rm H_2O$–$\rm H_2O$, HA–$\rm H_2O$, and $\rm H_2O$–$\rm A^-$ as *direct terms*, and those corresponding to $\rm H_3O^+$–$\rm OH^-$, $\rm H_3O^+$–$\rm A^-$, and HA–$\rm OH^-$ as *indirect terms.*

Swain showed that it is possible to choose values of C, a_1, b_1, a_2, and b_2 which when inserted in equation (4) will reproduce Dawson and Spivey's observed catalytic constants to within a factor of 2. The same is true for the catalytic constants observed in the present work. We shall take throughout $[{\rm H_2O}] = 55$, $C = 10^{-11}$, $a_2 = 1{\cdot}2 \times 10^6$, $b_2 = 3{\cdot}0 \times 10^{10}$, $K_w = 1{\cdot}7 \times 10^{-14}$ (the appropriate value for $I = 0{\cdot}2$). For acetic acid, $K_{\rm A} = 3{\cdot}1 \times 10^{-5}$

at $I = 0 \cdot 2$, and if we then put $a_1 = 1 \times 10^2$, $a_1 = 10^4$, equations (4) yield the following results :

$$v_0 = 2 \cdot 5 \times 10^{-8} \qquad k_{\mathrm{H}^+} = 8 \cdot 3 \times 10^{-4} \qquad k_{\mathrm{OH}^-} = 17$$

$$k_\mathrm{A} = 7 \cdot 4 \times 10^{-6} \qquad k_\mathrm{B} = 1 \cdot 1 \times 10^{-5} \qquad k_\mathrm{P} = 2 \cdot 0 \times 10^{-5}$$

These values all agree to within a factor of 2 with experiment (cf. Table 2, and Bell and Lidwell, *loc. cit.*), and a similar agreement can be obtained by treating our data for trimethylacetate and glycollate buffers in the same way. It is tempting to follow Swain in regarding this agreement as compelling evidence that the reaction occurs throughout mainly by a ternary mechanism, but closer examination shows that this argument is illusory. The above numerical values being used, the coefficient a_1 makes only a small contribution to both k_A and k_B, so its value can be adjusted within wide limits to fit the observed value of k_P : in other words, any value of k_P between zero and $\sim 10^{-3}$ could be accommodated in the ternary scheme. We must conclude, therefore, that the magnitude of the observed product term does not provide any quantitative evidence for or against the ternary picture.

The ambiguity just mentioned depends upon the fact that in the present instance the dominant term in k_A is the indirect one $a_2b_1K_\mathrm{A}$, while the direct term $b_1[\mathrm{H_2O}]$ is dominant in k_B. We shall now examine the general consequences of the dominance of different terms in v_0, k_A, and k_B for any reaction showing general acid–base catalysis in aqueous solution. The various possibilities are as follows :

Dominant term in :

	v_0	k_A	k_B
(i)	Direct $[\mathrm{H_2O}]^2$	Direct $a_1[\mathrm{H_2O}]$	Direct $b_1[\mathrm{H_2O}]$
(ii)	Indirect $a_2b_2K_w$	Indirect $a_2b_1K_\mathrm{A}$	Indirect $a_1b_2K_w/K_\mathrm{A}$
(iii)	Direct $[\mathrm{H_2O}]^2$	Indirect $a_2b_1K_\mathrm{A}$	Indirect $a_1b_2K_w/K_\mathrm{A}$
(iv)	Indirect $a_2b_2K_w$	Direct $a_1[\mathrm{H_2O}]$	Direct $b_1[\mathrm{H_2O}]$
(v)	Direct $[\mathrm{H_2O}]^2$	Indirect $a_2b_1K_\mathrm{A}$	Direct $b_1[\mathrm{H_2O}]$
(vi)	Indirect $a_2b_2K_w$	Indirect $a_2b_1K_\mathrm{A}$	Direct $\mathrm{b}_1[\mathrm{H_2O}]$
(vii)	Direct $[\mathrm{H_2O}]^2$	Direct $a_1[\mathrm{H_2O}]$	Indirect $a_1b_2K_w/K_\mathrm{A}$
(viii)	Indirect $a_2b_2K_w$	Direct $a_1[\mathrm{H_2O}]$	Indirect $a_1b_2K_w/K_\mathrm{A}$

These will now be discussed separately.

(i). This gives $k_\mathrm{P}/k_\mathrm{A} = b_1/[\mathrm{H_2O}] = k_\mathrm{B}/v_0$, and $k_\mathrm{P}/k_\mathrm{B} = a_1/[\mathrm{H_2O}] = k_\mathrm{A}/v_0$. If general acid–base catalysis is to be readily detectable, both k_A and k_B must be much larger than v_0, and in consequence k_P must be much larger than either k_A or k_B, *i.e.*, the product term should account for a large proportion of the observed velocity even at low catalyst concentrations, which does not correspond with experiment. This is essentially the same argument as was used by Pedersen (*J. Phys. Chem.*, 1934, **38**, 590) to exclude the ternary mechanism in the iodination of acetone. It is not applicable to this reaction (*loc. cit.*) where treatment on the basis of equation (4) shows the direct terms to be dominant throughout, but no product term is detectable experimentally.

(ii). Similarly we find $k_\mathrm{P}/k_\mathrm{A} = a_1/a_2K_\mathrm{A} = k_\mathrm{B}/v_0$, $k_\mathrm{P}/k_\mathrm{B} = b_1K_\mathrm{A}/b_2K_w = k_\mathrm{A}/v_0$. The argument is the same as for (i), and we should again predict a large contribution from the product term.

(iii) and (iv). Neither of these is possible. Thus for (iii), if $a_2b_1K_\mathrm{A} \gg a_1[\mathrm{H_2O}]$ and $a_1b_2k_w/K_\mathrm{A} \gg b_1[\mathrm{H_2O}]$, then $a_2b_2k_w \gg [\mathrm{H_2O}]^2$; *i.e.*, the indirect term must also be dominant in v_0. The same argument excludes (iv).

(v) and (vi). For either of these we have $k_\mathrm{A}/k_\mathrm{B} = a_2K_\mathrm{A}/[\mathrm{H_2O}]$. Since a_2 is independent of the nature of the buffer system HA–A⁻, this means that for different buffers $k_\mathrm{A}/k_\mathrm{B}$ is proportional to K_A. If the observed catalytic constants obey the well-known relations $k_\mathrm{A} = G_\mathrm{A}K_\mathrm{A}{}^\alpha$, $k_\mathrm{B} = G_\mathrm{B}(1/K_\mathrm{A})^\beta$, this implies that $\alpha + \beta = 1$. The iodination of acetone falls into category (v), and experiment gives $\alpha = 0 \cdot 62$, $\beta = 0 \cdot 88$ (Bell, " Acid–Base Catalysis," Oxford, 1941, p. 91 ; Bell and Lidwell, *loc. cit.*), so the predicted relation is not obeyed. Moreover, data for other reactions lend no support to this relation : thus for the mutarotation of glucose (Brönsted and Guggenheim, *J. Amer. Chem. Soc.*, 1927, **49**, 2554), $\alpha = 0 \cdot 3$, $\beta = 0 \cdot 34$, while for the depolymerization of dihydroxyacetone (Bell and Baughan, *J.*, 1937, 1947), $\alpha = 0 \cdot 38$, $\beta = 0 \cdot 76$.

(vii) and (viii). Both of these give $k_A/k_B = K_A[H_2O]/b_2K_w$, leading again to the prediction $\alpha + \beta = 1$.

To sum up, the above considerations show that if equation (3) is applied to a reaction exhibiting general acid–base catalysis in aqueous solution, it predicts *either* that the product term $k_P[HA][A^-]$ should contribute a large proportion of the observed velocity in dilute buffer solutions, *or* that the relation $\alpha + \beta = 1$ should hold for the exponents of the Brönsted relations. The available experimental evidence contradicts both these predictions, and therefore indicates that a ternary mechanism is not of major importance in aqueous solution. It seems likely, however, that the product term observed in the iodination of acetone does represent a small contribution from a ternary mechanism, since it is too large to be interpreted in terms of a medium effect.

In order to make quite clear the distinction between the ternary mechanism and the usually accepted one involving successive proton-transfer, we shall consider an isomerization $HR \longrightarrow RH$ catalysed by a single acid–base pair A–B. The ternary mechanism is

$$B + HR + A \longrightarrow A + RH + B \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and the rate law predicted in the presence of a number of acid–base pairs is $v = \sum_i \sum_j k_{ij}[A_i][B_j]$. It is not necessary to envisage a simultaneous ternary collision, since the same kinetics result from successive steps such as

$$\left.\begin{array}{ll} & B + HR \rightleftharpoons B,HR;\ \ B,HR + A \longrightarrow A + RH + B \\ \textit{or} & HR + A \rightleftharpoons HR,A;\ \ B + HR,A \longrightarrow A + RH + B \end{array}\right\} \quad . \quad . \quad . \quad . \quad (6)$$

with the second step rate-determining. On the other hand, the binary mechanism supposes two alternative mechanisms, as follows :

$$\left.\begin{array}{l} \text{(a) \textit{Acid catalysis :}}\ \ HR + A \rightleftharpoons B + HRH^+ \longrightarrow A + RH \\ \text{(b) \textit{Base catalysis :}}\ \ B + HR \rightleftharpoons R^- + A \longrightarrow RH + B \end{array}\right\} \quad . \quad . \quad . \quad (7)$$

This scheme leads to a rate law of the form $v = \sum_i k_i^A[A_i] + \sum k_j^B[B_j]$. The essential kinetic distinction between (5) or (6) on the one hand and (7) on the other does not lie in the number of steps, but in the fact that in (6) the preliminary equilibria involve association of catalyst and substrate, while in (7) there is a proton-transfer to produce two separate species. This is a clear-cut distinction in a dissociating solvent such as water, but it becomes less clear in a solvent of low dielectric constant where there is likely to be association between the ions produced from the substrate and the catalysts (cf. Bell, *Adv. Catalysis*, 1952, **4**, 182). It has recently been shown (Swain and Brown, *J. Amer. Chem. Soc.*, 1952, **74**, 2534) that the mutarotation of tetramethyl glucose in benzene solution shows third-order kinetics in mixtures of acids and bases, but it is not justifiable to deduce from this that similar reactions proceed by a ternary mechanism in aqueous solution, especially as other catalysed reactions show quite different kinetics in hydrocarbon solvents (Bell and Rybicka, *J.*, 1947, 24).

PHYSICAL CHEMISTRY LABORATORY, OXFORD.

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