**54.** *Structure and Reactivity of the Oxyanions of Transition Metals. Part VII.* Kinetics and Mechanism of the Alkaline Decomposition of Per-ruthenate.*

By A. CARRINGTON and M. C. R. SYMONS.

The rate of decomposition of per-ruthenate in aqueous sodium hydroxide solution to give ruthenate and oxygen has been measured spectrophotometrically. A second-order dependence on the concentration of per-ruthenate was found, after deviations during the initial stages of the reaction.

A mechanism in which hydrogen peroxide is formed as an intermediate gives a rate equation consistent with most of the experimental features.

THERE is a close resemblance between the behaviour of the manganese and ruthenium oxyanions in alkaline solution. Corresponding to the ions MnO_4^-, MnO_4^{2-}, and MnO_4^{3-} are the molecule RuO_4 and the ions RuO_4^- and RuO_4^{2-}. Both ruthenium tetroxide and potassium per-ruthenate decompose in alkaline solution to give oxygen:

$$4RuO_4 + 4OH^- \longrightarrow 4RuO_4^- + 2H_2O + O_2$$
$$4RuO_4^- + 4OH^- \longrightarrow 4RuO_4^{2-} + 2H_2O + O_2$$
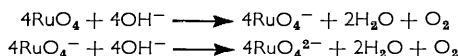
These reactions appear very similar to the corresponding reactions involving the permanganate and the manganate ion.[1,2]   In this case we have chosen to study the decomposition

* Part VI, *J.*, 1959, 3269.

[1] Symons, *J.*, 1953, 3956.
[2] Symons, *J.*, 1954, 3676.

of per-ruthenate, rather than of ruthenium tetroxide, since the latter is a toxic, volatile gas which decomposes extremely readily. On the other hand, potassium per-ruthenate can be obtained in a pure crystalline form, and potassium ruthenate, the product of the alkaline decomposition, appears to be stable in alkaline solution. Neither of these reactions has previously been studied kinetically and there is little information on the oxidising ability of these ions in alkaline solution.

EXPERIMENTAL

The usual precautions were taken to ensure that apparatus and water were free from impurities.[1] Potassium per-ruthenate was prepared from ruthenium tetroxide. Metallic ruthenium was oxidised with sodium peroxide in molten potassium hydroxide, and the melt then treated with acidified potassium permanganate to generate ruthenium tetroxide. This was distilled into a receiver flask containing aqueous M-potassium hydroxide. The solution was cooled in ice, potassium per-ruthenate crystallising as small dark needles as the ruthenium tetroxide was reduced by the alkali. The crystals were filtered off, washed with aqueous 0·2M-potassium hydroxide, and stored *in vacuo*, the salt being then stable. The spectrum was measured in 0·2M-sodium hydroxide, and the salt was also allowed to decompose in 8M-alkali, undergoing quantitative conversion into ruthenate, the spectrum of which was also measured. Our results are in good agreement with those by Larsen and Ross.[3] Particular attention was paid to the relative molar extinction coefficients at 465 mμ: the values we have used are $\varepsilon = 1730$ for RuO_4^{2-} and 330 for RuO_4^{-}. The spectrophotometric measurements were made by using a Unicam SP. 600 spectrophotometer.

For kinetic measurements, a fresh stock solution of potassium per-ruthenate in aqueous 0·2M-sodium hydroxide was prepared for each run. Two samples of this solution were allowed to decompose in 8M-alkali to ruthenate, the concentration of which was estimated spectrophotometrically, thus giving the concentration of the stock per-ruthenate solution. A third sample was run into the desired quantities of sodium hydroxide and water at zero time. Reactions were studied in both " Polythene " and glass vessels without noticeable difference. Samples of the reacting solution were removed for direct measurement at 465 mμ. We consider this method of following the reaction to be superior to any involving attempts to quench the reaction. The reaction can indeed be quenched by dilution with water, but then great care must be taken to avoid disproportionation. Because of the sensitivity of the reaction rate to traces of impurities, it is desirable to limit manipulation as much as possible.

Sodium hydroxide solutions were prepared by making up a saturated solution in a " Polythene " vessel and storing the cold solution over alumina for several days. The clear solution was then decanted and diluted with water to a concentration of 4—5M, giving the stock solution. The results obtained with several stock solutions were identical.

All runs were carried out at 25° ± 0·05°. Variation of oxygen pressure had no measurable effect on the rate of the reaction. Many of the results reported have been obtained in duplicate and reproducibility was confirmed.

Attention was focused on the initial stages of the reaction, and initial rates were determined by assuming that the decomposition could be represented by a cubic equation in time t:[4] $x = At + Ct^2 + Dt^3$. The initial rate is then given by:

$$(\mathrm{d}x/\mathrm{d}t)_0 = 1/t[3x_1 - (3/2)x_2 + (1/3)x_3]$$

where x_1, x_2, and x_3 are the concentrations of ruthenate after times t, $2t$, and $3t$. $(\mathrm{d}x/\mathrm{d}t)_0$ was calculated for decreasing time intervals, and the results were found to converge at intervals of 2 and 3 min. This method gave consistent results and was preferred to the graphical method of drawing tangents to the curve of time and decomposition at zero time, although the results obtained from the two methods were usually in good agreement.

RESULTS

Plots of x and log $(a - x)$ against time gave curves, but plots of $1/(a - x)$ against time were linear after initial deviations which were more pronounced the lower the concentration

[3] Larsen and Ross, *Analyt. Chem.*, 1959, **31**, 176.
[4] Livingstone, " Rates and Mechanisms of Reactions," ed. Weissberger, Interscience Inc., New York, 1953, p. 183.

of hydroxide. a is the initial concentration of per-ruthenate and $(a - x)$ is the concentration after time t.   Fig. 1 shows some of these plots with varying per-ruthenate and alkali concentrations.   For reasons which will be apparent later, we have plotted $[a/(a - x)] - 1$ against time rather than $1/(a - x)$.   The slopes of these lines are roughly proportional to the third power of the base concentration.   This dependence is shown in Fig. 2 which includes all the results summarised in the Table.   This suggests a rate law of the form:

$$\mathrm{d}x/\mathrm{d}t = k_{app}\,(\mathrm{RuO_4}^-)^2(\mathrm{OH^-})^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which, when integrated, becomes:

$$t = \frac{1}{k_{app}} \cdot \frac{1}{b^3 a} \cdot \left[\frac{a}{(a - x)} - 1 \right] \quad . \quad . \quad . \quad . \quad . \quad (2)$$

since the base concentration is effectively constant for a given run.   A value for k_{app} of 0·427 has been estimated from the slope of the line depicted in Fig. 2.
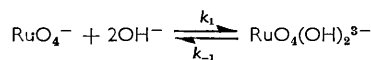
Summary of experimental results.

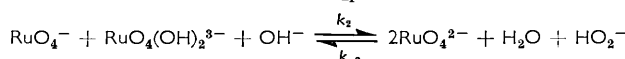| Run	[OH$^-$] (moles/l.)	10^3[RuO$_4^-$] (moles/l.)	10^3(dx/dt)$_0$ (moles/min.)	S_2 (min.)	Run	[OH$^-$] (moles/l.)	10^3[RuO$_4^-$] (moles/l.)	10^3(dx/dt)$_0$ (moles/min.)	S_2 (min.)
A I	1·57	1·142	—	572	C I	2·62	1·309	0·015	97
II		1·582	—	422	II		1·520	0·021	89
III		3·360	—	224	III		3·800	0·124	43
					IV		6·560	0·335	27
B I	1·86	1·475	0·009	254					
II		2·950	0·026	152	D I	3·29	1·427	0·039	58
III		3·280	0·034	133	II		2·755	0·125	25
					III		5·710	0·470	15

This simple treatment cannot accommodate the initial deviations unless these are ascribed to experimental errors.   To check this possibility, the initial rates were estimated and also found to be proportional to the second power of the per-ruthenate concentration and the third power of the base concentration.   This dependence is illustrated in Fig. 3, from which plot a value of 0·437 has been estimated for the rate constant.   That these two rate constants are nearly equal means that the initial deviations cannot be ascribed to experimental error and hence that the simple rate expression given in equation (1) is inadequate.

Mechanism.—It is convenient to discuss these results in terms of the following mechanism, which we will examine from a chemical viewpoint below:
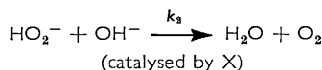
Stage (1):

$$\mathrm{RuO_4}^- + 2\mathrm{OH}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{RuO_4(OH)_2}^{3-}$$

Stage (2):

$$\mathrm{RuO_4}^- + \mathrm{RuO_4(OH)_2}^{3-} + \mathrm{OH}^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2\mathrm{RuO_4}^{2-} + \mathrm{H_2O} + \mathrm{HO_2}^-$$

Stage (3):

$$\mathrm{HO_2}^- + \mathrm{OH}^- \overset{k_3}{\longrightarrow} \mathrm{H_2O} + \mathrm{O_2}$$
(catalysed by X)

If we assume that $\mathrm{RuO_4(OH)_2}^{3-}$ and $\mathrm{HO_2}^-$ can be treated as stationary-state intermediates, application of Christiansen's formulation [5] leads to the rate equation:

$$\frac{\mathrm{d}t}{\mathrm{d}x} = \frac{K_1}{(a - x)b^2} + \frac{K_2}{(a - x)^2 b^3} + \frac{K_3 x^2}{(a - x)^2 b^4 [\mathrm{X}]} \quad . \quad . \quad . \quad . \quad (3)$$

where $K_1 = 1/k_1$, $K_2 = k_{-1}/k_1 k_2$, $K_3 = k_{-1}k_{-2}/k_1 k_2 k_3$, [X] is the concentration of an unknown catalyst (see below), and b is the concentration of hydroxide ion.
    On integration, this expression becomes:

$$t = \frac{xK_3'}{b^4} + \ln \frac{a}{(a - x)} \left(\frac{K_1}{b^2} - \frac{2aK_3'}{b^4} \right) + \left(\frac{a}{(a - x)} - 1 \right)\left(\frac{K_2}{b^3 a} + \frac{aK_3'}{b^4} \right) \quad . \quad (4)$$

where $K_3' = K_3/[\mathrm{X}]$.

[5] Christiansen, *Z. phys. Chem.*, 1936, B, **33**, 145; 1937, B, **37**, 374.

The relevant experimental results are that a plot of t against $[a/(a - x) - 1]$ is linear but when extrapolated does not pass through the origin. These results are compatible with equation (4) provided that the magnitude and rate of change of the third term are great compared with those for the first and the second term in the range of concentrations studied. The slopes (S_2) of the lines shown in Fig. 1 will then be given by

$$S_2 = K_2/b^3 a + aK_3'/b^4 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (5)$$

Since a is very small in our experiments, the term involving K_2 will be large compared with that involving K_3' even if $K_3' \gg K_2$. Hence to a first approximation we can neglect the term involving K_3' and the equation then predicts that a plot of $S_2 b^3$ against $1/a$ should be linear with a slope giving K_2. Such a plot is shown in Fig. 2, discussed earlier, and it is evident that we can now identify K_2 with $1/k_{\mathrm{app}}$.

FIG. 1. *Decomposition of per-ruthenate in alkaline solution.*

(a) is the initial $[\mathrm{RuO_4^-}]$ and $(a - x)$ the value after time t. See Table for details.
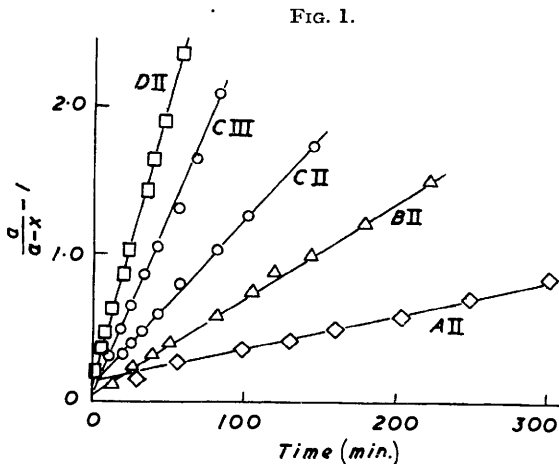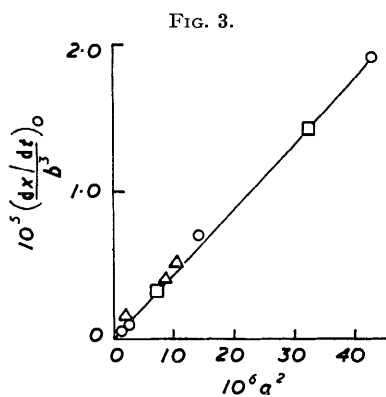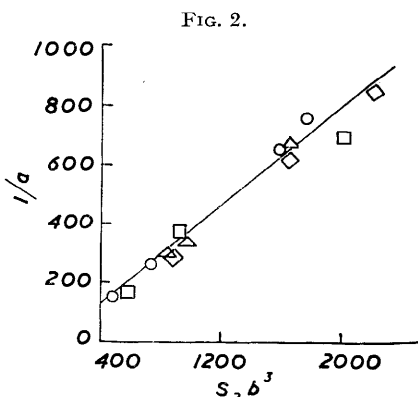
FIG. 2. *Decomposition of per-ruthenate in alkaline solution: test of equation (5).*
Symbols refer to FIG. 1.

FIG. 3. *Initial rates: test of equation (6).*

FIG. 1.

FIG. 2.

FIG. 3.

From equation (3) the rate at zero time is given by:

$$(\mathrm{d}x/\mathrm{d}t)_0 = a^2 b^3/(K_1 ab + K_2) \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (6)$$

Again, since a is small, the term involving K_1 may well be small compared with that involving K_2. In this case the initial rates will be proportional to the second power of the per-ruthenate concentration and the third power of the base concentration, as is demonstrated in Fig. 3. Again we can estimate a value for K_2 from the slope of the line depicted and, as was shown earlier, this value is in good agreement with that obtained from Fig. 2.

The results do not enable us to estimate K_1 and K_3' precisely, but upper limits may be given. If $K_1 \leqslant 1$ and $K_3' \leqslant 5 \times 10^3$, the terms involving these constants in equations (6) and (5) respectively are insignificant.

Using these upper limits for K_1 and K_3', we have estimated values for t in equation (4) for representative values of b and a. A plot of these values for t against $[a/(a-x)-1]$ was found to be linear and to have the slope predicted by equation (5). However, in contrast to some of the experimental lines, these constructed lines pass through the origin.

The above kinetic treatment was used because of its generalised nature, and because it does not involve arbitrary assumptions regarding rate-determining steps. However, the results do suggest that stage (1) can be pictured as a rapid equilibrium with stage (2) as a rate-determining step.

The mechanism proposed does not accommodate the initial deviations which are particularly significant when the concentration of alkali is low. However, the mechanism also fails to take account of the fact that hydrogen peroxide reacts readily with per-ruthenate in aqueous alkali.[6] The inclusion of a reaction of the form

$$RuO_4^- + HO_2^- \xrightarrow{k_3} \text{Products}$$
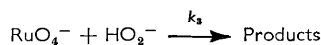
as an alternative to stage (3) leads to the rate expression:

$$\frac{dt}{dx} = \frac{K_1}{(a-x)b^2} + \frac{K_2}{(a-x)^2 b^3} + \frac{K_3 x^2}{(a-x)^3 b^3} \quad . \quad . \quad . \quad . \quad (7)$$

which, on integration, becomes:

$$t = \ln \frac{a}{(a-x)} \left(\frac{K_1}{b^2} + \frac{K_3}{b^3} \right) + \left(\frac{a}{(a-x)} - 1 \right) \left(\frac{K_2}{b^3 a} - \frac{K_3}{2b^3} \right) + \left(\frac{a^2}{(a-x)^2} - 1 \right) \frac{K_3}{2b^3} \quad (8)$$
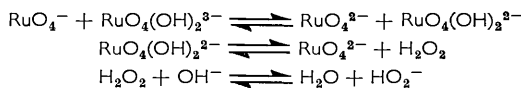
Provided K_3 is not much greater than K_2, this equation fits the experimental data equally satisfactorily, when values for K_1 and K_2 deduced above are used. As x approaches a, however, the last term in equation (8) should become increasingly important and this might well lead to deviations not found experimentally.

It is probable that a combination of these alternative mechanisms would correctly reproduce all the results. It is significant that a plot of log (dx/dt) against log $(a-x)$, the slope of which normally gives the order of the reaction, can be divided into two sections for all the kinetic runs. From these plots, the first 10—20% of the reaction appears to be of the third order in per-ruthenate, the remainder of the reaction being of the second order. This result is consistent with the idea that reaction of hydrogen peroxide with per-ruthenate will be particularly important at the beginning of a run. A similar scheme was invoked to account for the kinetics of the alkaline decomposition of permanganate.[1]

DISCUSSION

The initial rate studies, besides indicating that the deviations from linearity shown in Fig. 1 are real, also eliminate two alternative possibilities for the first stage of the reaction. These are an electron-transfer reaction to give hydroxyl radicals, as postulated for permanganate,[1] or disproportionation to give ruthenium tetroxide and ruthenate followed by decomposition of the tetroxide.

We have formulated the proposed mechanism in terms of three stages in order to keep the overall rate equation simple. In fact, stage (1) could be written as two successive equilibria and stage (2) could be written:

$$RuO_4^- + RuO_4(OH)_2^{3-} \rightleftharpoons RuO_4^{2-} + RuO_4(OH)_2^{2-}$$
$$RuO_4(OH)_2^{2-} \rightleftharpoons RuO_4^{2-} + H_2O_2$$
$$H_2O_2 + OH^- \rightleftharpoons H_2O + HO_2^-$$

[6] Connick and Hurley, *J. Amer. Chem. Soc.*, 1952, **74**, 5012.

The rate equation would then be similar to equation (4) but would contain more constants.

The most unsatisfactory part of the proposed mechanism is that represented by stage (3). It was previously found necessary to invoke catalytic decomposition of HO_2^- in order to explain certain kinetic features of the alkaline decomposition of permanganate,[1] but the precise nature of the catalyst and the mode of decomposition are obscure. It is known that hydrogen peroxide decomposes rapidly in concentrated alkaline solution although the rate is reduced if the alkali has been specially purified.[7] Unfortunately quantitative information on the rates is not available. There is good evidence, both for the reversibility of stage (2), and for the catalytic decomposition of hydrogen peroxide in this system. Connick and Hurley[6] found that addition of hydrogen peroxide to per-ruthenate in M-sodium hydroxide gave ruthenate, but that even with excess of hydrogen peroxide conversion into ruthenate was incomplete and catalytic decomposition of the peroxide occurred. It is not clear if the catalysis is due to a ruthenium species or to other metal-ion impurities present in the alkali.

Larsen and Ross[3] have shown that hydrogen peroxide is, in fact, a product of the alkaline decomposition of per-ruthenate. They allowed potassium per-ruthenate to decompose completely in 9M-alkali to ruthenate, diluted the solution with water to an alkali concentration of 1M, and detected per-ruthenate spectrophotometrically. However, if the ruthenate solution was boiled, dilution with water did not re-form per-ruthenate and addition of hydrogen peroxide was necessary to effect oxidation. This is consistent with both the forward and the reverse reaction comprising stage (2) in our mechanism.

The postulate that co-ordination of hydroxide ion to per-ruthenate is important, is a feature which should be discussed further. It is relevant to indicate certain trends in the behaviour of transition-metal oxions insofar as expansion of their co-ordination shell is concerned. First, there is no evidence that the $3d$-transition-metal oxions do co-ordinate with hydroxide in this way. For alkaline decomposition of permanganate, use was made of sodium hydroxide enriched in ^{18}O and it was found[2] that all the oxygen evolved in the reaction came from the solvent, showing that exchange of oxygen between permanganate and solvent does not occur. If co-ordination of hydroxide to manganese did occur, one would expect to find oxygen exchange.

On the other hand $5d$-transition-metal oxions are able to expand their co-ordination shells. The per-rhenate ion, ReO_4^-, is not affected by dilute aqueous alkali but in very concentrated potassium hydroxide is converted into the yellow mesoper-rhenate ion, formulated in the literature[8] as ReO_5^{3-}. This process can be formulated as:

$$ReO_4^- + 2OH^- \rightleftharpoons ReO_4(OH)_2^{3-} \rightleftharpoons ReO_5^{3-} + H_2O$$
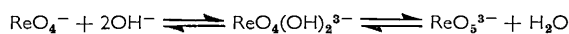
The reaction is fully reversible, for we have found that addition of water regenerates per-rhenate quantitatively. Similarly OsO_4 dissolves in alkali to give a yellow solution from which $K_2OsO_4(OH)_2$ has been isolated.[9] Thus one might well expect to find that ruthenium represents an intermediate case, in that co-ordination of hydroxide occurs to a very small extent, but that the co-ordinated species are unstable.

We conclude, first, that, in contrast to the decomposition of permanganate, co-ordination of hydroxide to the per-ruthenate is important and hydroxyl radicals are not formed; and, secondly, that hydrogen peroxide is an important intermediate in the production of oxygen.

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[7] Shanley and Greenspan, *Ind. Eng. Chem.*, 1947, **39**, 1536.
[8] Noddack and Noddack, " Das Rhenium," Voss, Leipzig, 1933.
[9] Tschugaev, *Compt. rend.*, 1918, **167**, 162; Krauss and Wilken, *Z. anorg. Chem.*, 1925, **145**, 151.

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