The Involvement of Perruthenate in the $RuCl_3$-catalysed Oxidation of Alcohols in Base in the Presence of Peroxodisulphate

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It has been observed that the perruthenate formed on addition of ruthenium trichloride to peroxodisulphate solution in base decomposes, with loss of oxygen, to form ruthenate. Contrary to thermodynamic prediction, the latter species appears to be highly stable in the presence of excess of peroxodisulphate providing reactive organic species such as alcohols are not present. Addition of alcohols to the ruthenate–peroxodisulphate mixture at high pH affords a perruthenate–alcohol complex, the latter acting as an effective catalyst for the homogeneous oxidation of primary or secondary alcohols by the peroxodisulphate. A mechanism based on α-hydride abstraction has been proposed for the latter reaction, and the simultaneous formation of the insoluble dioxide $RuO_2{\cdot}xH_2O$ attributed to further reaction of the two products, ruthenate and aldehyde. Although there have been several claims to the contrary, ruthenate (RuO_4^{2-}) species do not directly oxidize alcohols (other than methanol); they are, however, capable of readily oxidizing aldehydes.

RECENT work by us[1] indicated that with regard to electro-organic oxidation reactions in aqueous media at high pH, the high electrocatalytic activity of commercially important, dimensionally stable anodes, based on RuO_2-coated titanium, is due to the presence of surface-bonded, quasi-solution, ruthenate or perruthenate groups. Such groups are assumed to occur mainly at defect sites (*e.g.* kink sites) on the high surface area RuO_2 film where significant hydration of surface-bonded oxy-cations can occur. The mechanism of electrocatalysis involved is essentially the same as in bridge-assisted redox reactions,[2] the oxidation occurring *via* a higher oxidation state of the central metal ion in the catalyst molecule, the latter in the case of the RuO_2 electrode remaining permanently linked to the oxide surface.

The higher oxides of ruthenium are known to be unusually reactive oxidizing agents in homogeneous solution [3-6] where they are frequently used as catalysts or co-oxidizing agents in the presence of a strong oxidant, *e.g.* peroxodisulphate, $S_2O_8^{2-}$, whose rate of reaction with the organic material is extremely slow. It has been postulated that ruthenate (RuO_4^{2-}) species in base, either alone [5] or in the presence of peroxodisulphate,[6] will oxidize benzyl alcohol to benzoate under quite mild conditions. However, the electrochemical work[1] suggested that whereas benzaldehyde can be readily oxidized by ruthenate, benzyl alcohol only reacts with perruthenate (RuO_4^-). Since ruthenate and perruthenate species in solution can be distinguished readily by spectroscopic techniques,[7,8] we have re-investigated the solution reaction in some detail. Our approach was similar to that of Schröder and Griffith[6] in that dissolved ruthenium was present only in catalytic quantities, the main oxidant being peroxodisulphate. The results show that alcohol oxidation at high pH involves reaction with a perruthenate–alcohol complex, and a possible explanation of the apparent reaction of alcohols with ruthenate under certain conditions is outlined.

EXPERIMENTAL

Materials.—All chemicals were at least G.P.R. grade and most were AnalaR grade. De-ionized water was triply distilled, once from alkaline permanganate, prior to use. The $RuCl_3$ stock solution was prepared by dissolving $RuCl_3{\cdot}xH_2O$ (1 g) (38.98% metal, Engelhard Industries Ltd.) per 500 cm³ of aqueous HCl (0.1 mol dm⁻³), the acid being present to suppress hydrolysis. In kinetic experiments involving benzyl alcohol oxidation, the solvent consisted of 10% (by volume) of acetone in water, the ketone being necessary to ensure complete solubility of the aromatic alcohol; similar work with more water-soluble compounds, *e.g.* ethanol and isopropyl alcohol, indicated that the presence of acetone had little influence on the oxidation kinetics.

Reaction Procedure.—To aqueous acetone (100 cm³) containing both KOH and $K_2S_2O_8$ (typically 0.5 and 0.125 mol dm⁻³ respectively) was added the volume of $RuCl_3$ stock solution to give the required concentration of Ru catalyst (usually 1.5×10^{-4} mol dm⁻³). After equilibration in a water-bath at 30 °C (a temperature high enough to ensure solubility of the peroxodisulphate but low enough to avoid significant oxidation in the absence of the Ru catalyst) the organic reactant (typically 0.0025 mol) was added by microsyringe and the mixture was shaken vigorously for *ca.* 30 s.

Reaction Monitoring.—Samples of the reaction mixture were withdrawn at regular intervals and analysed for peroxodisulphate by reaction with excess of ammonium iron(II) sulphate, the extent of the excess being estimated by back titration with potassium dichromate.[9] While such a simple procedure was a useful guide to the course of reaction, especially in cases (such as aldehyde or secondary alcohol oxidation) where only one product was obtained, it was of limited use with primary alcohols where two products, aldehyde and acid, were obtained. In the case of such consecutive reactions the respective disappearance and formation of organic reactants and products was followed using gas chromatography (Perkin-Elmer Sigma 4B or Phase Separations LC2 gas chromatograph, fitted with Carbowax columns). Sample treatment involved diethyl ether extraction plus addition of phenyl acetate as an internal standard. Carboxylic acids were converted into the corresponding methyl esters by reaction with methyl iodide prior to analysis. The oxidation products of each organic starting material were isolated and characterized (m.p., C and H analysis, u.v. and i.r. spectra) in a separate series of experiments.

Variations in the RuO_4^- and RuO_4^{2-} concentrations were monitored by following changes in absorbance at 385 nm (or 390 nm when an alcohol was present) and 465 nm respectively, using a Perkin-Elmer 402 recording spectrophotometer. The solutions in the reference and sample containers were identical except that the former had no Ru species present. Preliminary experiments (as described later) showed that on addition of $RuCl_3$ to the alkaline peroxodisulphate solution the initial perruthenate product decomposed with loss of oxygen gas to form ruthenate. This reaction, which was unaffected by the presence of acetone and partially reversed in the presence of alcohol, is an important feature of oxyruthenium-catalysed oxidation reactions. The absorbance at 465 nm was used directly to measure the RuO_4^{2-} concentration from a Beer's law calibration plot; standards for the latter were prepared by adding $RuCl_3$ stock solution (standardized by evaporation to dryness, reduction in hydrogen, and weighed as the metal[8]) to $K_2S_2O_8$ (0.125 mol dm^{-3}) in KOH (0.5 mol dm^{-3}) and waiting *ca.* 30 s for total conversion into RuO_4^{2-}. Analysis of RuO_4^- in the presence of RuO_4^{2-} was complicated by the fact that the latter also absorbed at both 385 and 390 nm. To correct for such interference, it was necessary to draw up calibration plots for RuO_4^{2-} at these wavelengths. The difference between the total absorbance and the ruthenate contribution was then used to estimate the RuO_4^- concentration; the absorption coefficient, ε_{385}, determined by Woodhead and Fletcher[10] for the latter compound was employed in this case and the same value was assumed to hold for the slightly displaced peak ($\lambda_{max.}$ = 390 nm) observed in the presence of alcohols. The validity of the latter assumption was borne out by the fact that towards the end of the alcohol-oxidation experiments (Figure 3), when RuO_2 was no longer present, the sum of the RuO_4^{2-} and RuO_4^- concentrations (determined independently, the latter as the RuO_4^-–alcohol complex, by spectrophotometric means) was equal to the final concentration of RuO_4^{2-} (all ruthenium species were eventually converted into the latter form in the presence of $S_2O_8^{2-}$ in base).

In experiments carried out to determine the concentration of Ru species present during the $RuCl_3$ to RuO_4^{2-} reaction in the absence of alcohol (see Figure 1), the shortness of the reaction time, especially at high base concentration, usually precluded the use of a sampling technique. The reaction was, therefore, carried out in a quartz cell in the spectrophotometer. To correct for the light blocked off by the opaque solid RuO_2 formed during the course of reaction, the variation in solution transmittance at 600 nm (a region where neither RuO_4^- nor RuO_4^{2-} absorbs) was noted. By comparing the variation in transmitted light intensity in this region during the course of reaction with the value recorded at the end of the experiment (when no RuO_2 was present) it was possible to correct the absorbances at 385 and 465 nm for variations in transmitted light intensity. As a check on the accuracy of this procedure the solid present in some runs at low base concentration (1.50 × 10^{-4} mol dm^{-3} $RuCl_3$, 0.125 mol dm^{-3} $K_2S_2O_8$, 0.05 mol dm^{-3} KOH, no alcohol), and, hence, relatively slow reaction rate, the suspended solid RuO_2 (at values close to the maximum concentration of the latter, see Figure 1) was quickly filtered off. On subsequent dissolution and spectrophotometric analysis (as RuO_4^{2-}) the amount of ruthenium in the solid was found to be virtually identical (within the error limits shown in Figure 1) to that estimated using the corrected spectrophotometric technique. Furthermore, analysis of the filtrate after all ruthenium species were converted into RuO_4^{2-} gave the same ruthenium concentration value as that estimated for the dissolved state by the modified spectrophotometric procedure at the time of filtering. A similar check on the validity of the ruthenium analysis procedure in the presence of RuO_2 was carried out in the case of the benzyl alcohol oxidation reaction; satisfactory results were obtained also in this case (at least within the range of steady-state RuO_2 concentrations, see Figure 3).

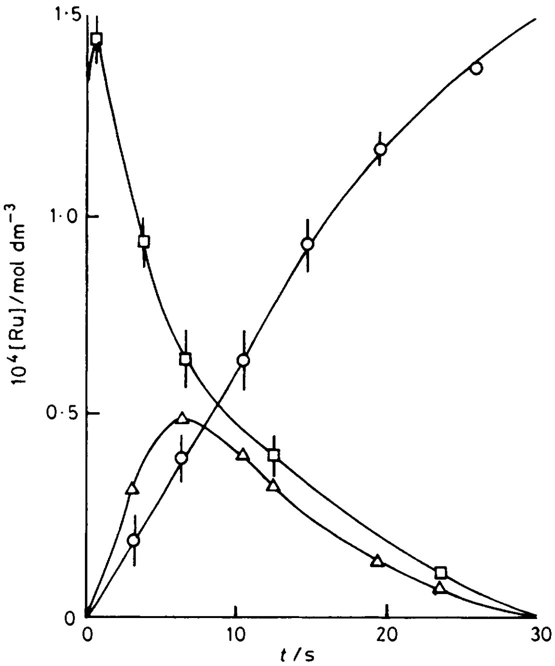


FIGURE 1 Variation of the concentration of RuO_4^- (□), RuO_4^{2-} (○), and RuO_2 (△) with time following addition, at *t* = 0, of $RuCl_3$ (1.5 × 10^{-4} mol dm^{-3}) to an aqueous solution of $K_2S_2O_8$ (0.125 mol dm^{-3}) in base (0.5 mol dm^{-3} KOH) at 30 °C

The spread of results, indicated by the error bars in Figure 1, was obtained from a sequence of 16 separate kinetic experiments. Reproducibility was much higher in the case of the organic oxidation experiments whose results are summarized in Figure 3; slower reaction rates, less critical mixing conditions in the initial stages, and a smaller proportion of solid RuO_2 in the system are probably important in this respect. Usually the concentration of RuO_2 present was estimated from the difference between the net amount of ruthenium present (as determined by RuO_4^{2-} analysis at the end of a run) and the sum of RuO_4^{2-} and RuO_4^- determined photometrically during the course of reaction.

RESULTS

The changes that occurred following addition of 1.5 × 10^{-5} mol of $RuCl_3$ to a 100-cm^3 solution of 0.125 mol dm^{-3} $K_2S_2O_8$ in base (0.5 mol dm^{-3} KOH) are summarized in Figure 1. Evidently the Ru^{III} was oxidized almost immediately to Ru^{VII} but the perruthenate formed was unstable and decomposed with some evolution of oxygen gas to form a mixture of ruthenate and insoluble ruthenium dioxide. The latter was re-oxidized by peroxodisulphate and the cycle continued until all the ruthenium was converted to ruthenate. The kinetics of perruthenate decomposition, or ruthenate formation, did not follow a simple kinetic pattern, as might perhaps be expected in view of the involvement of the insoluble dioxide. However, it is clear from the results shown in Figure 2 that the rate of reaction increased rapidly with increasing base concentration.

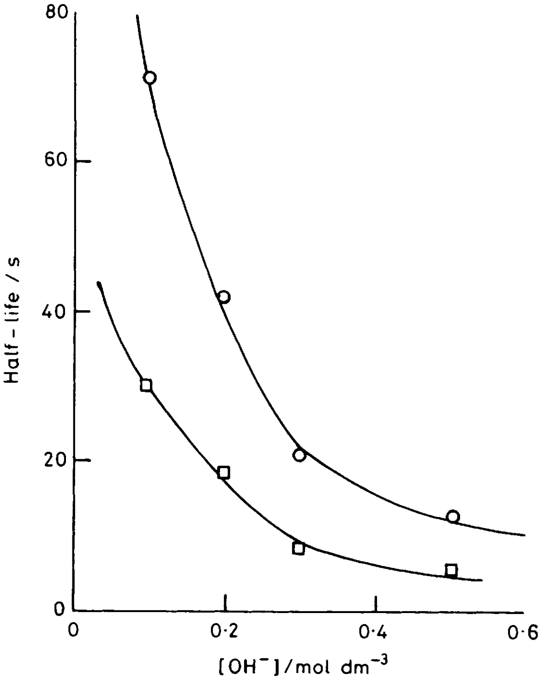


FIGURE 2 Effect of base concentration on the half-life for the decay of RuO_4^- (□) and the formation of RuO_4^{2-} (○) following addition of $RuCl_3$ to $K_2S_2O_8$ in aqueous KOH solution. Conditions, apart from base concentration, were the same as in Figure 1

The rate of decomposition of perruthenate in basic peroxodisulphate solution was influenced by the presence of alcohols. For instance, on addition of Bu^{t}OH, which showed no tendency to oxidize, the time for the perruthenate decay reaction, under conditions similar to those outlined in Figure 1, was extended to *ca.* 230 min when an equimolar ruthenium–alcohol ratio was present. A slight shift in the perruthenate absorption peak (from $\lambda_{max.} = 385$ nm to $\lambda_{max.} = 390$ nm) was also generally observed in the presence of alcohols.

The addition of a reactive alcohol (*i.e.* one capable of being oxidized at a reasonably fast rate, *e.g.* benzyl alcohol) to an equilibrated brown solution of ruthenate in the presence of peroxodisulphate (*i.e.* the final mixture obtained at the conclusion of the experiment outlined in Figure 1) resulted in the reappearance of the characteristic green colour of the perruthenate, together with a slight trace of suspension of the black dioxide. As illustrated in Figure 3 the Ru^{VII} oxidation state predominated over most of the reaction period, *i.e.* the first two hours. After that the Ru^{VII} species gradually disappeared, all the ruthenium eventually being re-converted to the Ru^{VI} state, the brown colour being restored. The variation of alcohol, aldehyde, and acid concentrations during the course of reaction is illustrated in Figure 4. Evidently a consecutive reaction was involved (alcohol→aldehyde→acid), the rate of alcohol loss being first order with respect to its concentration. While it is clear from Figures 3 and 4 that the bulk of the oxidation is completed after *ca.* 2 h, it took about a further 4 h (Figure 3) for all the ruthenium to return to the Ru^{VI} state. Apparently towards the end of the reaction a very slow rate of oxidation (possibly of co-ordinated alcohol molecules) was involved. During the course of these reactions no oxygen evolution was observed at any stage (despite the presence of significant quantities of Ru^{VII} which is normally unstable in aqueous media).

Further experiments showed that replacing the benzyl alcohol by cinnamyl alcohol ($C_6H_5CH{=}CHCH_2OH$) increased the rate of oxidation, whereas a significant drop in rate was observed with crotyl alcohol ($CH_3CH{=}CHCH_2OH$), *i.e.* electron-releasing groups favoured the reaction. The rate of oxidation of methanol was found to be very rapid; with higher non-branching primary aliphatic alcohols (C_2—C_{10}) the rate decreased gradually with increasing chain length; the rates for the latter group were about an order of magnitude slower than those for the unsaturated alcohols.

The influence of base concentration on the rate of benzyl alcohol oxidation by peroxodisulphate in the presence of the oxyruthenium catalyst is illustrated in Figure 5. Also shown in this diagram is the effect of base concentration on the fraction of the ruthenium catalyst present in the Ru^{VII} state at a time 5 min after the start of the reaction. As can be seen from Figure 3 this fraction altered little until

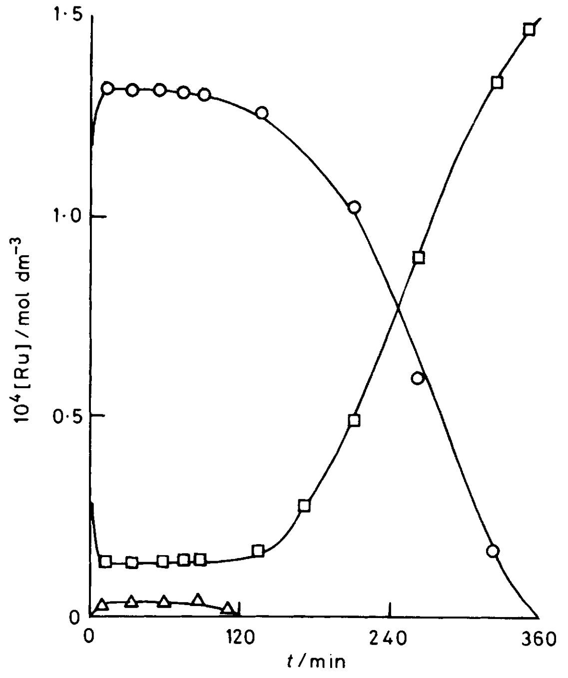


FIGURE 3 Variation with time of the concentration of Ru present as RuO_2 (△), RuO_4^{2-} (□), and RuO_4^- (○) after addition, at $t = 0$, of benzyl alcohol (0.025 mol dm^{-3}) to RuO_4^{2-} (1.5×10^{-4} mol dm^{-3}) in a 10% acetone–water mixture containing $K_2S_2O_8$ (0.125 mol dm^{-3}) and KOH (0.5 mol dm^{-3}) at 30 °C

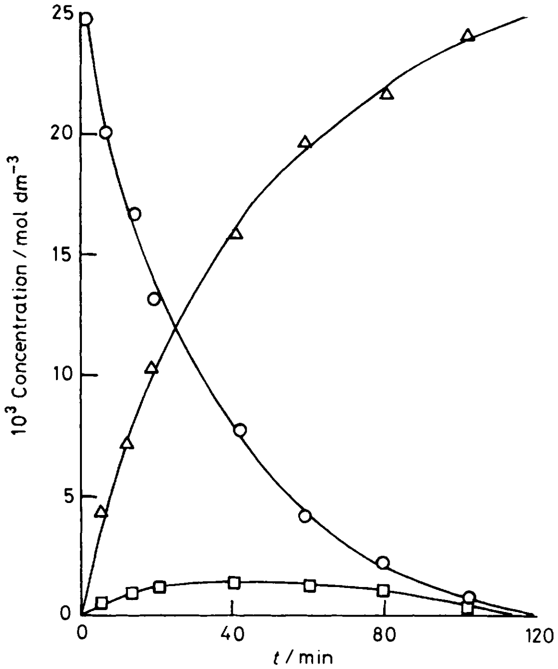


Figure 4 Variation with time of the concentration of benzyl alcohol (○), benzaldehyde (□), and benzoic acid (△) in the same experiment as outlined in Figure 3

the alcohol had been almost totally oxidized. Although the rate of reaction is a non-linear function of base concentration, linear correlation was observed between the reaction rate and the Ru^{VII} concentration of these solutions (Figure 6).

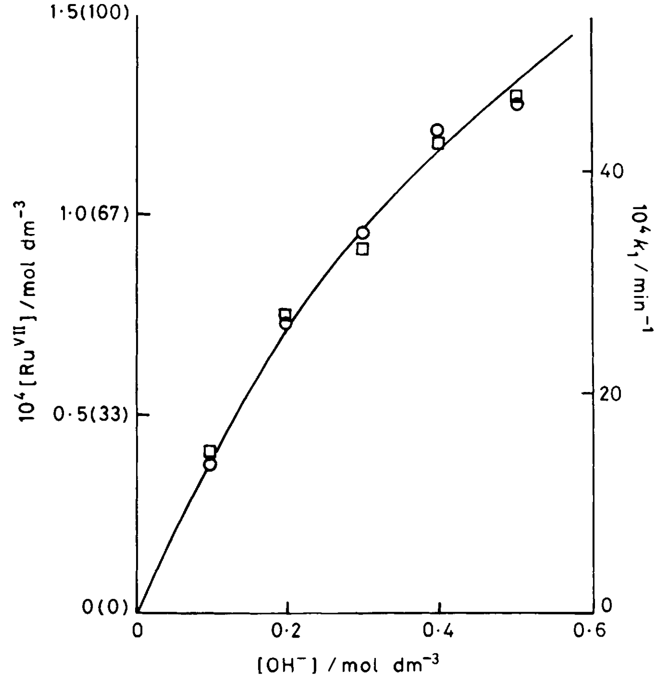


Figure 5 Effect of base concentration on both the concentration of RuO_4^- (□) present over most of the reaction period (see Figure 3) and the pseudo-first-order rate constant for benzyl alcohol oxidation (○). Conditions, apart from the base concentration, were the same as those in Figure 3. The figures in parentheses refer to the percentage of RuO_4^- present as a function of the total Ru concentration

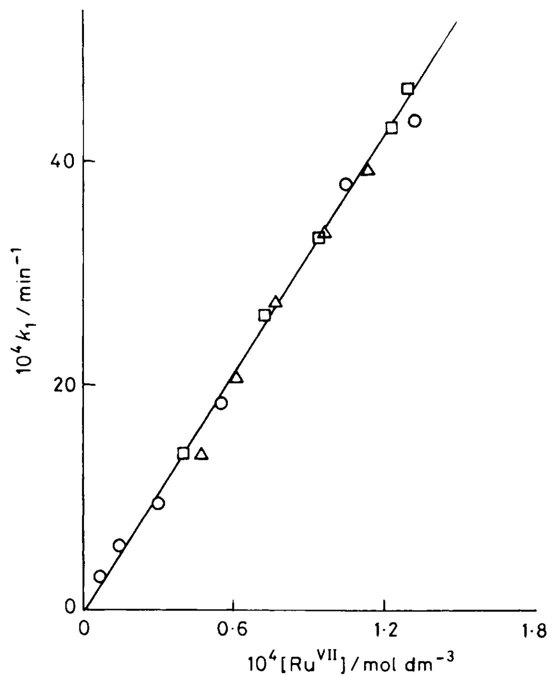


Figure 6 Influence of perruthenate concentration on the pseudo-first-order rate constant for benzyl alcohol oxidation. The data for this diagram were obtained using solutions of different base concentration (Figure 5) (□), different $RuCl_3$ concentration (Figure 7) (○), and different peroxodisulphate concentration (Figure 8) (△). The experimental conditions involved are specified in the captions of these other diagrams

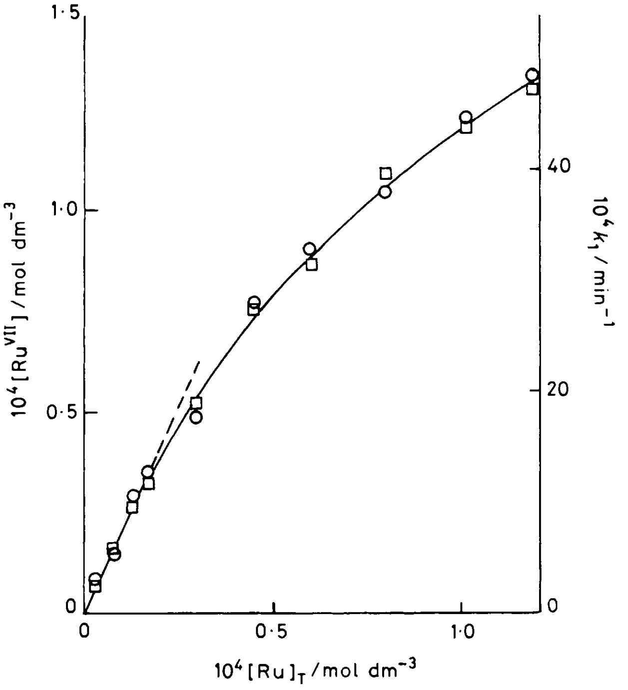


Figure 7 Variation with total catalyst, *i.e.* $RuCl_3$, concentration of both the level of RuO_4^- present over most of the reaction period (□) and the pseudo-first-order rate constant for benzyalcohol oxidation (○). Conditions, apart from the catalyst concentration, were the same as those in Figure 3

The variation of both the rate constant for oxidation and the percentage of the total ruthenium present in the Ru^{VII} form are shown as a function of the catalyst concentration in Figure 7. At low catalyst concentration all the ruthenium was present in the Ru^{VII} form and it was only in this region that the rate increased linearly with increasing net concentration of dissolved ruthenium. However, a linear correlation was again observed (Figure 6) over the entire range of catalyst concentrations between the rate of oxidation and concentration of Ru^{VII} present during the main reaction period. Similar results are shown in Figure 8 for the effect of peroxodisulphate concentration. Once again the important factor appeared to be the concentration of Ru^{VII} as the rate of oxidation varied linearly with the latter (Figure 6) over the entire range of peroxodisulphate concentration investigated in this series of experiments.

$$+S_2O_8^{2-}$$

$$RuO_4^- + 2OH^- \longrightarrow RuO_4(OH)_2^{3-} \text{ (fast)} \quad (1)$$

$$RuO_4(OH)_2^{3-} + RuO_4^- + OH^- \longrightarrow 2RuO_4^{2-} + O_2H^- + H_2O \text{ (fast)} \quad (2)$$

$$RuO_4^{2-} + O_2H^- + H_2O \longrightarrow RuO_2 + 3OH^- + O_2 \text{ (slow)} \quad (3)$$

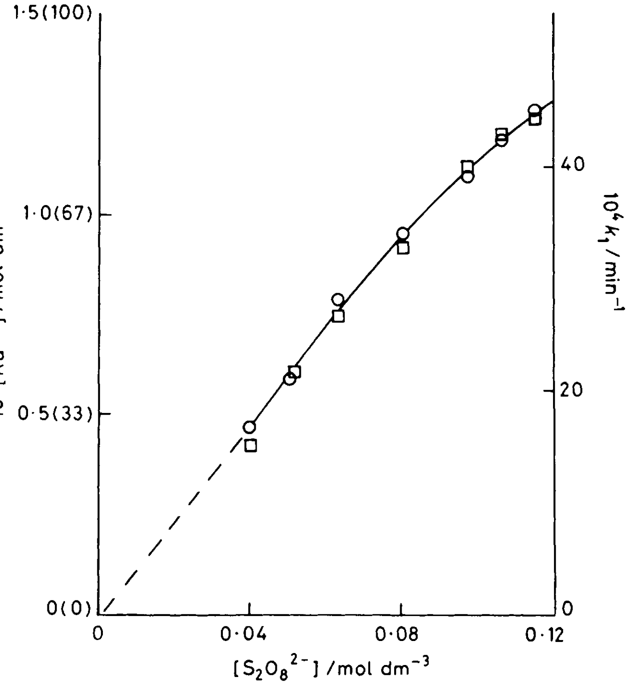


FIGURE 8 Variation with peroxodisulphate concentration of both the level of RuO_4^- present over most of the reaction period (□) and the pseudo-first-order rate constant for benzyl alcohol oxidation (○). Conditions, apart from the $K_2S_2O_8$ concentration, were the same as listed in Figure 3. The figures in parentheses refer to the percentage of RuO_4^- present as a function of the total Ru concentration

Further work on the mechanism of oxidation involved a comparison of the rate of reaction of $C_6H_5CH_2OH$ and $C_6D_5CD_2OH$ (same conditions as Figure 3). The observed isotope effect ($k_H/k_D = 4.9$) showed that the rate-determining step involved rupture of a C–H bond. Oxidation of cyclobutanol may be used to determine whether a reagent acts as a one- or two-electron oxidant [11,12] (in the latter case two one-electron steps may be involved, the transfer of the second electron being quite rapid). Since cyclobutanone was the only detectable product, the oxidant is assumed to operate *via* a two-electron mode.

DISCUSSION

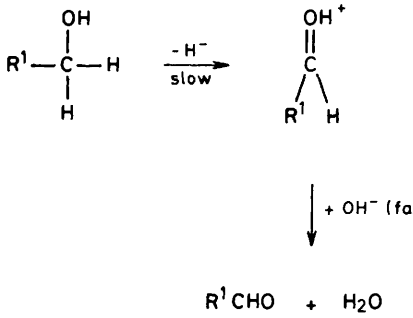
The decomposition of perruthenate in aqueous alkaline solution, in the absence of peroxodisulphate, has been investigated by Carrington and Symons [13] who postulated an intermediate formed by co-ordination of hydroxide by perruthenate ions. A similar scheme, modified in this case to take into account the effect of peroxodisulphate, is outlined in equations (1)—(3). The basic reaction in this case may be written as equation (4). However, since the dioxide is re-oxidized in the present

$$2RuO_4^- \longrightarrow RuO_4^{2-} + RuO_2 + O_2 \quad (4)$$

case by the peroxodisulphate, virtually all the ruthenium is eventually converted into ruthenate. The latter is not the most stable form of ruthenium in the presence of such a powerful oxidizing agent as peroxodisulphate; however, in the absence of reducible species such as benzyl alcohol no trace of perruthenate was observed in the final mixture. Evidently, for reasons as yet unclear, the continuous conversion of ruthenate into perruthenate is inhibited in peroxodisulphate-containing media at high pH. The increased rate of perruthenate decomposition on raising the base concentration (Figure 2) may be explained in terms of the increased concentration of peroxy-species in the rate-determining step [equation (3)]. The above reaction scheme, involving partial regeneration of a reactant *via* a heterogeneous reaction step, is scarcely amenable to precise kinetic formulation. However, this does not detract from the basic aim of the study which was to investigate the involvement (or otherwise) of perruthenate in the catalytic oxidation of alcohols.

As far as oxidation of the alcohol was concerned, one of the most interesting features of the present results is the excellent correlation observed (Figure 6) between the pseudo-first-order rate constant and the concentration of Ru^{VII}. This strongly suggests that the latter is the effective oxidizing agent. The inhibition of the perruthenate ⟶ ruthenate reaction [equations (1)—(3)] in the presence of a low level of the rather unreactive tertiary alcohol, the stabilization of the perruthenate during the course of the oxidation reaction (Figure 3), and indeed for a considerable period after completion of the main reaction, together with the small shift in the maximum of the perruthenate absorbance peak in the presence of alcohol, may be taken as evidence for the formation of a rather stable perruthenate–alcohol complex. However, in view of the relatively small change in the perruthenate absorption as a result of this complex formation it appears unlikely that a major perturbation of the perruthenate species is involved. Possibly some type of solvation interaction is involved here, the change in solvation sphere affecting the decomposition reaction [equations (1)—(3)] by inhibiting hydroxide ion co-ordination. The latter reaction frequently involves loss of protons from water molecules co-ordinated to the central metal ion (*i.e.* hydrolysis); such a reaction would obviously be less likely if some of the bound water was replaced by alcohol.

Oxygen derivatives of transition-metal ions, *e.g.* ferrate[14] and permanganate,[15] have frequently been quoted as good hydride-abstracting agents and this is proposed here as the rate-determining step in the alcohol-oxidation reaction. Support for this is provided by the isotope effect, $k_H/k_D = 4.9$, being quite close to the value of 4.6 quoted by Lee and van den Engh[16] for the oxidation of propan-2-ol by RuO_4^- a reaction for which the same type of slow step was proposed. The observations that electron-releasing groups facilitate the reaction, and (as shown by the cyclobutanol-oxidation reaction) that alcohol oxidation involves a two-electron reaction step, are also consistent with an α-hydride abstraction rate-determining step. The proposed route for reaction is, therefore, assumed to be that of equation (5). The hydride ion is abstracted by the perruthenate complex, possibly with formation of a ruthenium(V) species. The presence of ruthenium dioxide in the reaction system (Figure 3) could arise either as a result of disproportionation ($2Ru^V \longrightarrow Ru^{IV} + Ru^{VI}$) or as a result of further reaction of the product of equation (5) with ruthenate, the dioxide formed being gradually reconverted into perruthenate by reaction with peroxodisulphate.



(5)

$$RuO_4^{2-} + R^1CHO + H_2O \longrightarrow RuO_2 + R^1COOH + 2OH^- \quad (6)$$

According to the scheme outlined above in equation (5), the alcohol oxidation should occur according to the rate law $-d[ROH]/dt = k[Ru^{VII}][ROH]$. However, since the concentration of the ruthenium(VII) complex is virtually constant over the main reaction period (Figure 3), the oxidation reaction under the present conditions occurs in a pseudo-first-order manner. It is clear from Figures 5—8 that all other variables in this system, base, peroxodisulphate, and ruthenium concentration, influence the rate of oxidation only in so far as they alter the concentration of the perruthenate–alcohol complex.

As mentioned earlier, there have been a number of claims[5,6] that ruthenates, either alone or in the presence of peroxodisulphate in base, will oxidize alcohols without the intervention of perruthenate. Both the present work and electrochemical data[1] indicate that these conclusions are incorrect. In the case of Lee and co-workers[5,17] the ruthenate was synthesized by oxidizing RuO_2 in water using sodium periodate (or sodium hypochlorite). The tetraoxide formed was extracted into carbon tetrachloride from which, on treatment with aqueous base, a solution of the orange-brown ruthenate salt was obtained. The reagent thus prepared was capable of oxidizing various alcohols, including benzyl alcohol. We have confirmed these observations but observed a slight green colour in the alcohol solution just prior to the conversion of all ruthenium species into the insoluble dioxide (excess of alcohol was present in the reaction mixture). Spot tests[18] showed, however, that ruthenate solutions prepared by the above procedure contain traces of periodate (or hypochlorite when the latter is used as oxidant to generate RuO_4). This is perhaps not too surprising in view of the known ability of perruthenate to form complexes with periodate.[19] It is, therefore, suggested that quantities of perruthenate, stabilized in the complex form, were present in the solutions used by Lee and co-workers and that it was this higher oxidation state of the metal that was responsible for the alcohol oxidation. In support of this argument it was shown that ruthenate prepared by the same procedure but using various other oxidants, *e.g.* lead tetra-acetate, sodium bismuthate, or chromic acid, did not oxidize any alcohol apart from methanol (which behaves in an anomalous manner in any event in this type of reaction). In the earlier work the brown colour of the excess of ruthenate evidently masked the green colour of the complexed perruthenate. It is suggested that after reaction with an alcohol molecule [equation (7)] the ruthenium(VII) state was restored by reaction

$$Ru^{VII} + RCH_2OH \longrightarrow Ru^V + RCHO + 2H^+ \quad (7)$$

with ruthenate, the other product of this reaction ending up as the insoluble dioxide, equation (8). The observation of a green colouration towards the end of the reaction (when the ruthenate colour is no longer masking) strongly supports the above proposal. It was found during the present work that, in contrast to alcohols, all aldehydes reacted readily with ruthenates, irrespective of the method of preparation of the latter.

$$Ru^V + Ru^{VI} \longrightarrow Ru^{VII} + Ru^{IV} \quad (8)$$

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