Mechanistic Study of the Co-ordination of Hydrogen Peroxide to Methylrhenium Trioxide

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The activation parameters ($\Delta H^\ddagger$, $\Delta S^\ddagger$, $\Delta V^\ddagger$) for the co-ordination of hydrogen peroxide to methylrhenium trioxide have been determined. They indicate a mechanism involving nucleophilic attack. The protons lost in converting H_2O_2 to a co-ordinated η^2-O_2^{2-} group are transferred to one oxide oxygen, which remains on the metal as an aqua ligand. The rate of reaction is not pH dependent, consistent with the deuterium kinetic isotope effect (k_H/k_D = 2.8). The method used to study the reaction is based on the ability of $ReMeO_3$ to catalyse the reaction between Br^- and H_2O_2. The activation parameters for the uncatalysed reaction of Br^- and H_2O_2 were also determined. The value found for $\Delta V^\ddagger$ is consistent with the accepted mechanism, proton-assisted nucleophilic displacement.

The non-radical chemistry of hydrogen peroxide remains a subject of intrinsic and contemporary interest. Also, the use of hydrogen peroxide is of some practical importance, and now holds an even greater potential for synthetic applications in processes that are environmentally acceptable.[1,2] In most cases, however, it reacts too slowly to be useful, and catalytic activation is needed. Early transition metals in high oxidation states are useful in this context and electrophilic activation can be attained with titanates, vanadates, molybdates, *etc.*

It has recently been recognized that the organometallic oxide $ReMeO_3$ activates hydrogen peroxide toward a number of transformations of this general type, *e.g.* alkenes to epoxides.[3] It also catalyses the conversion of the cobalt thiolate complex $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$ [here $Co(SR)^{2+}$] (en = ethane-1,2-diamine) into the sulfenato complex, then much more slowly to the sulfinato complex, as in equation (1).[4] The first step in the catalytic oxidation is the binding of peroxide to the rhenium.

$$Co(SR)^{2+} \xrightarrow{H_2O_2,\ ReMeO_3} Co[S(O)R]^{2+} \xrightarrow{H_2O_2,\ ReMeO_3} Co[S(O)_2R]^{2+} \quad (1)$$

The structural evidence unequivocally demonstrates that the catalytically active species in solution contains one or two chelated peroxide dianions.[5] Even more striking, an additional water molecule is strongly bound to the rhenium in the 1:2 complex, which has been characterized crystallographically.[5] Solution studies of the $ReMeO_3$–H_2O_2 equilibria show that two consecutive reaction steps are involved, the first of which is shown in equation (2).[6] We sought to learn more about the mechanism of this step, since a thorough kinetic characterization is lacking.

$$H_2O_2 + ReMeO_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{A}}{ReMeO_2(\eta^2\text{-}O_2)(H_2O)} \quad (2)$$

Thus we undertook a detailed study of the first step of peroxide binding. An earlier study of the kinetics was complicated not only by the occurrence of the reverse reaction, but even more by the binding of a second peroxide which is favoured more thermodynamically but less kinetically.[6] Given these complications, we elected not to refine that approach but to develop a better method to study the peroxide binding. This method uses the advantage of catalysed reactions, such as that involving the cobalt thiolate complex[4] mentioned above, and similarly, but perhaps more advantageously, bromide ions.[7] The objective was then to evaluate k_1 accurately under a range of conditions, including the variation of temperature and pressure. This allowed the determination of the activation parameters. The deuterium kinetic isotope effect was also determined, to learn about the role of the protons of hydrogen peroxide and water in this transformation. The use of the bromide ion reaction in addition allowed the activation parameters to be evaluated for this nucleophilic displacement, which is the uncatalysed component of this system [equation (3)].[8]

$$H_2O_2 + Br^- + H^+ \xrightarrow{k_u} H_2O + HOBr \quad (3)$$

Experimental

Materials.—Methylrhenium trioxide was prepared from the reaction of dirhenium heptaoxide with tetramethyltin[9] in the presence of perfluoroglutaric anhydride.[10] The product was purified first by sublimation, then by recrystallization from dichloromethane–hexane, and finally by another sublimation. Its purity was checked by IR, ^1H NMR, and UV/VIS spectroscopy; the values found matched exactly those reported previously.[4,10–12] The other compounds were reagent-grade materials, used without purification: sodium bromide, hydrogen peroxide (30%), sodium perchlorate and perchloric acid. The solutions were made up in high-purity water, obtained by passing laboratory distilled water through a Millipore-Q water-purification system. The reactions were carried out in quartz cuvettes of 1, 2 or 5 cm optical path. The reaction solutions were thermostatted at the desired temperature. Air was not excluded, since it had no effect.

Measurements.—Kinetic experiments were conducted at a constant temperature in the range 1–45 °C. Measurements at high pressures (to P = 150 MPa) were carried out to evaluate the volume of activation. These experiments employed the special high-pressure cell previously described.[13,14] The high-pressure measurements were carried out at 25.0 °C only. Although the catalytic kinetics are, in general, quite complex, the studies here were conducted with $[Br^-]$ so high that first-order kinetics always applied. We shall examine the explicit requirement, which arises from kinetic constants not simply from the use of bromide ions in stoichiometric excess. The increase in the absorbance of Br_2/Br_3^- was recorded at 452 nm, an isosbestic wavelength (ε 108 $dm^3\ mol^{-1}\ cm^{-1}$). The rate constant for bromine build-up in each experiment, k_ψ, was

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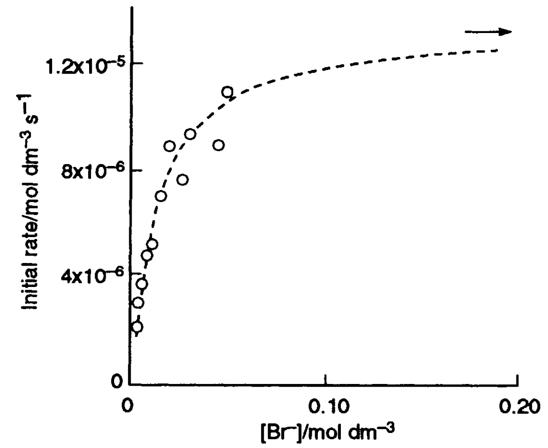


Fig. 1 The rate of bromine formation from solutions of H_2O_2, H^+ (1.00 mol dm^{-3}) and Br^- (1.00 mol dm^{-3}). A plateau is attained at high $[Br^-]$, at which limit the only kinetic processes are the k_1 step and a small background contribution from the uncatalysed reaction between these components

evaluated by fitting the absorbance *vs.* time readings to the equation $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_\psi t)$. The method of initial rates was sometimes used, but those values were not employed in the quantitative calculations.

Results

The spontaneous reaction of bromide ions with H_2O_2 [equations (3) and (4) at 25 °C, $I = 0.40$ mol dm^{-3}] is quite

$$H_2O_2 + 2Br^- + 2H^+ \longrightarrow Br_2 + 2H_2O \qquad (4)$$

$$v_u = (3.8 \times 10^{-7} + 2.3 \times 10^{-4}[H^+])[H_2O_2] \times [Br^-] \text{ mol dm}^{-3} \text{ s}^{-1} \qquad (5)$$

slow. The rate constants are such that only the acid-dependent term was significant at the $[H^+]$ used in this study. This reaction is strongly catalysed by $ReMeO_3$, and at high concentrations of bromide ion the rate was independent of $[Br^-]$, being limited by the rate at which the catalytically active molecule **A** is formed in reaction (2). This is shown in Fig. 1, which depicts the fact that the reaction rate attains a plateau in the limit of high bromide concentration. The rate of the catalysed reaction is then given by the forward rate of reaction (2), since the catalysed bromine-forming steps are much more rapid in this limit. An analysis of the data in Fig. 1, together with the more exhaustive data on Br_2 formation,[7] shows that bromide-ion concentrations approaching 1 mol dm^{-3} are needed to attain this limit fully.

This method of isolating k_1 from the group of catalytic steps also required high $[H^+]$, so that bromine and not oxygen would be formed. There are other conditions where the net consequence of the action of $ReMeO_3$–H_2O_2 on bromide ions is the disproportionation of hydrogen peroxide, not bromine formation,[7] because the HOBr intermediate can react competitively with Br^-/H^+ or with H_2O_2. The present set of experiments was therefore carried out at 1.00 mol dm^{-3} Br^- and 1.00 mol dm^{-3} H^+, with the ionic strength maintained at 2.00 mol dm^{-3}, to accommodate these concentrations. This is a major change in medium from $I = 0.1$ mol dm^{-3} used previously,[6] which changes the rate constant. It is at high $[Br^-]$, however, that the uncatalysed rate of bromine formation is the most important. Since it cannot be neglected entirely, the expected rate law is (6).

$$v_{Br_2} = v_c + v_u = k_1[Re]_T[H_2O_2] + k_u[Br^-][H_2O_2][H^+] \qquad (6)$$

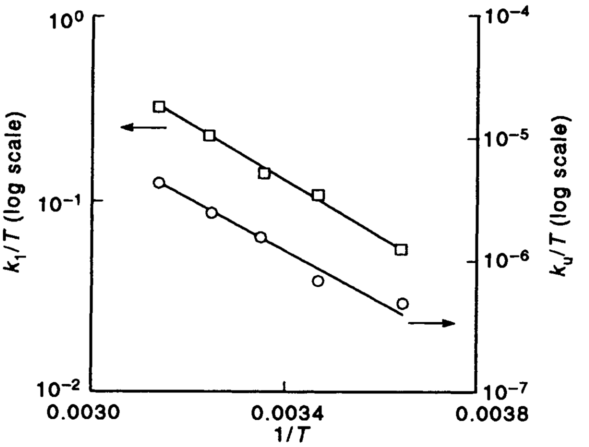


Fig. 2 Plots showing the analysis of the temperature dependence of the rate constants k_1 and k_u according to transition-state theory

Table 1 Experimental first-order rate constants at various $[ReMeO_3]$ and pressures; 20.0 °C, $I = 2.00$ mol dm^{-3}, $[Br^-] = 1.00$ mol dm^{-3}, $[H_3O^+] = 1.00$ mol dm^{-3}

$10^6[ReMeO_3]$/ mol dm^{-3}	$10^4k_\psi/s^{-1}$			
	$P = 5$	50	100	150 MPa
5.0	4.64	6.16	7.25	8.38
10.0	7.15	9.22	11.3	13.0
15.0	9.65	12.4	14.7	17.1
20.0	11.8	15.2	17.8	21.3

At ambient pressure, $10^4k_\psi = 11.6$, 26.0 and 33.5 s^{-1} at 20×10^{-6}, 50×10^{-6} and 70×10^{-6} mol dm^{-3} $ReMeO_3$.

Temperature Variations.—In one series of experiments the temperature was varied from 1 to 45 °C, in roughly 10° increments. At each temperature, $[ReMeO_3]$ was varied, to resolve the observed rate constant into its two terms, and a plot of k_ψ *versus* $[Re]_T$ was linear, with slope k_1. The treatment of the data according to transition-state theory is shown in Fig. 2. From transition-state theory the activation parameters for k_1 are $\Delta H^\ddagger = 29.0 \pm 1.5$ kJ mol^{-1} and $\Delta S^\ddagger = -116 \pm 5$ J K^{-1} mol^{-1}. Values of k_u at each temperature were obtained by dividing the intercept of such plots by $[Br^-][H^+]$ (unity in these experiments), which affords $\Delta H^\ddagger = 39.2 \pm 4.9$ kJ mol^{-1} and $\Delta S^\ddagger = -177 \pm 16$ J K^{-1} mol^{-1}. This is also shown in Fig. 2.

Pressure Variations.—Under the same conditions, several sets of experiments were carried out at pressures between 0.1 and 150 MPa at 25.0 °C and $I = 2.00$ mol dm^{-3}. The values are given in Table 1. Plots of k_ψ *versus* $[Re]_T$ were linear at each pressure, as shown in Fig. 3. Their intercepts and slopes were used to define the values of k_u and k_1 at each pressure, according to equation (6). The values of k_1/dm^3 mol^{-1} s^{-1} are 44.3 (P = 0.1), 60.7 (50), 70.0 (100) and 85.5 (150 MPa); the corresponding values of $k_u/10^{-4}$ dm^6 mol^{-2} s^{-1} are 2.81, 3.16, 4.00 and 4.25. The pressure dependence of each of these rate constants was used to calculate its volume of activation according to equation (7). The

$$\partial \ln k/\partial P = -\Delta V^\ddagger/RT \qquad (7)$$

values of $\Delta V^\ddagger$ are -10.6 ± 1.4 cm^3 mol^{-1} for k_1 and -7.5 ± 1.1 cm^3 mol^{-1} for k_u.

Solvent Kinetic Isotope Effect.—A series of experiments was conducted in D_2O with variable $[ReMeO_3]$, 50–300 μmol dm^{-3}, also at $[Br^-] = [D^+] = 1.00$ mol dm^{-3}. These gave $k_1^D = 15.0$ dm^3 mol^{-1} s^{-1}. From this, we calculate the deuterium kinetic isotope effect as $k_1^H/k_1^D = 2.8$.

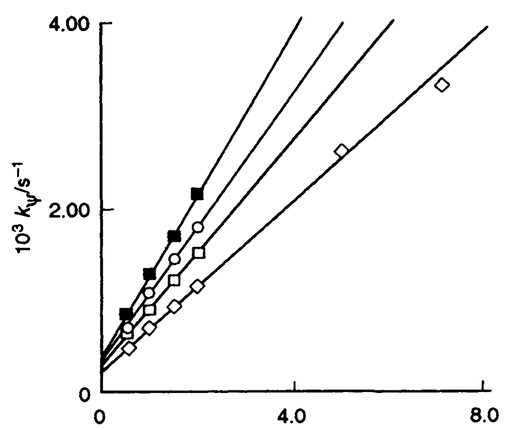
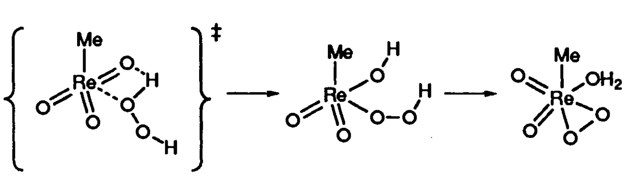


Fig. 3 Pseudo-first-order rate constant for bromine build-up as a function of the total concentration of $ReMeO_3$ at various pressures: 5 (◇), 50 (□), 100 (○) and 150 MPa (■). Data were obtained with $[Br^-] = [H^+] = 1.00$ mol dm^{-3} at 25.0 °C and 2.00 mol dm^{-3} ionic strength



Scheme 1

Discussion

The chemical reactivity suggests that the catalytic intermediate A has an η^2-peroxide structure.[4] Recent structural data confirms that the diglyme (2,5,8-trioxanonane) adduct of the 2:1 peroxide–rhenium complex is seven-co-ordinate, with two η^2-O_2^{2-} groups.[5] It also contains an 'extra', tightly held water molecule. It is plausible to infer that A is also a hydrated species, as shown in equation (2). Proton transfer from the entering hydrogen peroxide to one oxide ligand may produce the co-ordinated water molecule, although other mechanisms can be envisaged.

Numerous complexes are now known in which an η^2-peroxo structure is found. They are mostly of transition metals with low d-electron counts. A few examples are: $[MoO(O_2)_2(hmpa)(H_2O)]$,[15] $[Ti(O_2)(pyca)_2(hmpa)]$,[16] $[Th(O_2)(pyca)_2]$,[17] $K_3[Cr(O_2)_4]$[18] and $[Nb(O_2)_2(C_2O_4)_2]$,[19] where pyca = pyridine-2-carboxylate and hmpa = $(Me_2N)_3PO$. The ^{17}O NMR spectra of peroxo complexes of V^V, Mo^{VI} and W^{VI} in solution show that the peroxide oxygens are equivalent, retaining their η^2 structures in solution.[20,21]

Quite clearly, in the formation of species A from $ReMeO_3$ and H_2O_2, at least two protons must move, yet the rate is independent of pH in the range 0–4, and probably 0–7, as shown in previous work.[6] The question of how this might take place is an aspect that we shall address along with the issue of a possible hydroperoxo intermediate.

Consider that A may be formed *via* an intermediate σ-hydroperoxo complex. A reasonable transition state, featuring such a hydroperoxo intermediate, is shown in Scheme 1. The chemical reactivity of A does not suggest that it is a σ-hydroperoxo complex, and alkyl hydroperoxides were found not to co-ordinate to $ReMeO_3$, or to be activated by it. That is, the σ-hydroperoxo structure cannot account directly for the reactivity observed for A without it undergoing further activation. Thus the intermediate σ-hydroperoxo complex, if present at all, never attains a high concentration, and evidently undergoes no reaction other than conversion into the η^2-O_2^{2-} structure. It is probable, however, that the first step of Scheme 1 is rate-controlling, for reasons given below.

Let us now examine the arguments that can be advanced in support of this model. Isolable hydroperoxides are not numerous, although certain compounds have been characterized: $[MoO(O_2)_2(O_2H)]\cdot2C_5H_5N$,[22] $[Pd(O_2CR)(O_2H)]_2$ (R = Me or CF_3),[23] and $[Pt(L\text{-}L)(CF_3)(O_2H)]$ [L-L = $Ph_2P(CH_2)_nPPh_2$].[24–26] Two species known to date only in solution have also been characterized as hydroperoxo complexes by their chemical reactivity: $[Cr(H_2O)_5(O_2H)]^{2+}$[27] and $[Co(cyclam)(H_2O)(O_2H)]^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane).[28,29]

The rate constant k_1 is characterized by a low activation enthalpy (29 kJ mol^{-1}), a substantial and negative activation entropy (-116 J K^{-1} mol^{-1}), and a negative activation volume (-10.6 cm^3 mol^{-1}). The three activation parameters consistently point to a rate-controlling step that features bond making more than bond breaking. Thus only a small enthalpy barrier presents itself. The structure of the transition state appears to be a highly ordered one, not far advanced toward the product. These values of the activation parameters suggest that the first step of Scheme 1 is rate controlling. Also, the model must allow for incomplete O–H bond making/breaking in light of the kinetic isotope effect. By way of comparison, the reaction of aquated Cr^{II} with H_2O_2 is also characterized by a low activation enthalpy (26 kJ mol^{-1}) and a negative activation entropy (-131 J K^{-1} mol^{-1}), but by an almost zero activation volume (-1.1 ± 1.3 cm^3 mol^{-1}).[30] In this case H_2O_2 is bound *via* a rapid ligand-exchange process, followed by a rate-determining homolysis of co-ordinated H_2O_2 to produce $[Cr(H_2O)_5(OH)]^{2+}$ and $^{\bullet}OH$. In general, homolysis is accompanied by a significant increase in volume,[31] which in this case will be offset by a volume collapse due to the oxidation of Cr^{II} to Cr^{III}. It follows that the significantly negative activation volume found for k_1 in the present study must be related to a rate-determing bond-formation process.

Further to explore the meaning of $\Delta V^\ddagger$, we must turn to systems other than hydroperoxo complexes or reactions that bind hydrogen peroxide, none of which seems to have been the subject of a high-pressure study. Other data provide useful comparisons. Values of $\Delta V^\ddagger$ ranging from -7 to -17 cm^3 mol^{-1} were found for the binding of O_2 to polyaminocarboxylato complexes of iron(II).[32] These reactions also proceed in two steps [equation (8)]. In this case the observed value of $\Delta V^\ddagger$

$$Fe^{II}L + O_2 \overset{K}{\rightleftharpoons} Fe^{II}LO_2 \xrightarrow{k} [Fe^{III}L]^+ + O_2^{\bullet -} \quad (8)$$

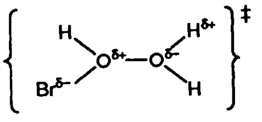
is a composite quantity of $\Delta V^\circ(K)$ and $\Delta V^\ddagger(k)$, since it can be shown that electron transfer is rate-controlling. The rate-controlling step will involve bond breaking and charge creation, to some extent cancelling one another in terms of the associated volume changes, so this step is not expected to involve a major volume change. The prior equilibrium may by accompanied by the release of co-ordinated water molecules for some of the complexes, but the major contribution to the substantially negative values of $\Delta V^\ddagger$ appears to come from the co-ordination of oxygen.

It is also useful to compare the value of $\Delta V^\ddagger(k_1)$, -10.6 cm^3 mol^{-1}, with that for the co-ordination of a water molecule, for which a maximum volume collapse of -13 cm^3 mol^{-1} has been predicted.[33] If we consider the transition state in Scheme 1 the entrance of hydrogen peroxide into the co-ordination sphere may have a very similar value. Furthermore, some lengthening of bonds to rhenium due to the depicted hydrogen bonding and the change in the bond order of one rhenium–oxygen bond will occur. The kinetic isotope effect is really quite substantial, but it must be regarded with caution since water (solvent and possibly co-ordinated) as well as hydrogen peroxide are deuteriated. Nonetheless, it appears to signal an involvement in the transition state of proton transfer, despite there being no kinetic dependence on $[H_3O^+]$. From the latter, we conclude that the proton-transfer process is intramolecular. One proton from hydrogen peroxide transfers to the oxo group, which is in the process of becoming the co-ordinated water. This process is not

Table 2 Volumes of activation for nucleophilic displacement reactions[a]

Reaction	Range of $-\Delta V^{\ddagger}$/cm^3 mol^{-1}	Citation[b]
$PhCH_2Cl + H_2O \longrightarrow PhCH_2OH + H^+ + Cl^-$	9–10	182–184
$Pr^iBr + H_2O \longrightarrow Pr^iOH + H^+ + Br^-$	9–15	242–246
$Bu^nBr + H_2O \longrightarrow Bu^nOH + H^+ + Br^-$	10.5	269–270
$RX + H_2O \longrightarrow ROH + H^+ + X^-$	11–14	275–277
$MeCO_2Et + OH^- \longrightarrow MeCO_2^- + EtOH$	5.6–7.6	601–603
$MeCO_2R + OH^- \longrightarrow MeCO_2^- + ROH$	5.6–6.6	607–610

[a] Values in water near ambient temperature, taken from the compilation in ref. 34. [b] As it appears in ref. 34.



B

expected to involve any major volume changes and should not influence the value of $\Delta V^{\ddagger}$. The magnitude of the isotope effect signals a compensation between the bond-breaking and -making processes. In light of this, of the analogies cited in the preceding paragraph, of the finding of an 'extra' water molecule bound to rhenium,[5] and of the proton shifts necessary to convert the reactants into **A**, we present Scheme 1 as the most plausible representation of the mechanism.

The study also gave the value of the activation volume for the uncatalysed reaction between bromide ions and hydrogen peroxide. This is a proton-assisted nucleophilic displacement, occurring in two steps (9) and (10). This model defines the

$$H_2O_2 + H^+ \underset{}{\overset{K}{\rightleftharpoons}} H_3O_2^+ \qquad (9)$$

$$H_3O_2^+ + Br^- \xrightarrow{k} HOBr + H_2O \qquad (10)$$

experimental $\Delta V^{\ddagger}(k_u) = \Delta V^{\circ}(K) + \Delta V^{\ddagger}(k)$. The first component is likely to be rather small, since the equilibrium does not involve charge neutralization or charge concentration, and H^+ is a very small ion. The transition state, which involves nucleophilic attack of Br^- on the electrophilic oxygen of $H_3O_2^+$, can be depicted as in **B**.

The experimental value of $\Delta V^{\ddagger}$ of -7.5 cm^3 mol^{-1} can be compared to the volumes of activation for typical S_N2 reactions in organic chemistry. A value between -5 and -10 cm^3 mol^{-1} is usually taken to indicate bond formation.[34] These examples, unlike the present reaction, do not involve charge neutralization; on the other hand, the site of protonation is remote from the point of nucleophilic attack, minimizing in this zwitterionic transition state a contribution to $\Delta V^{\ddagger}$ from this source. We cite in Table 2 the values of $\Delta V^{\ddagger}$ for six families of nucleophilic displacement reactions. All refer to determinations in water at temperatures near ambient. Inspection of these values suggests that the one we have found, $\Delta V^{\ddagger} = -7.5$ cm^3 mol^{-1}, is very reasonably assigned to an associative bond-formation process that does not involve major charge neutralization in the transition state. The very negative value of $\Delta S^{\ddagger}$ also points to a highly ordered transition state. These data bear on the process which is one of the rate-controlling steps for catalytic bromine formation,[7] as well as other catalytic processes[4,6] in which $ReMeO_3$ electrophilically activates hydrogen peroxide.

Finally, comments must be offered on the nearly two-fold changes in k_1 with ionic strength: 77 dm^3 mol^{-1} s^{-1} from studies of the $ReMeO_3$-catalysed oxidation of $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$ and Br^-,[4,7] and from the direct $ReMeO_3$–H_2O_2 interaction,[6] all referring to 25.0 °C and $I = 0.10$ mol dm^{-3}; 44.3 dm^3 mol^{-1} s^{-1} in the present study at 25.0 °C and $I = 2.00$ mol dm^{-3}. Control experiments were done to show that both measurements remain valid and reproducible. This deserves comment, since one normally associates sizable ionic strength effects with the reactions of charged species. Here, however, both reagents are uncharged and other reagents such as H_3O^+ do not enter the transition state. Very likely, therefore, this effect signals a change in the activity of water with salt concentration. One cannot be entirely specific as to how it perturbs the system, but it should be noted that Lewis bases co-ordinate to $ReMeO_3$.[35,36] Thus it is plausible that the starting species is really $ReMeO_3(H_2O)_n$ (n = 1 or 2), which will mean that the binding of H_2O_2 will involve the displacement of a co-ordinated solvent molecule. However, species **A** may interact with the solvent, and H_2O_2 is certainly strongly hydrogen bonded to the solvent. It is therefore not unreasonable to attribute the change in k_1 to the decrease in the activity of water.

Acknowledgements

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