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Development and Application of a Redox Indicator Method for the Kinetics of Oxidation of Vanadium(II) Ions by Hydrogen Peroxide and Alkyl Hydroperoxides

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The addition of the methyl viologen radical cation ($PQ^{\bullet+}$) to solutions of $V(H_2O)_6^{2+}$ and hydrogen peroxide or alkyl hydroperoxide provides a method for measuring the initial reaction rate. The kinetic data so obtained are consistent with the rate equation $-d[\text{peroxide}]/dt = k_1[V^{2+}][\text{peroxide}]$. Kinetic data are given for H_2O_2 ($k_1 = 15.4$ M^{-1} s^{-1} at 25.0 °C) and for $RC(CH_3)_2OOH$, with R = CH_3 (3.0 M^{-1} s^{-1}), C_2H_5 (5.2 M^{-1} s^{-1}), and $CH_2C_6H_5$ (4.8 M^{-1} s^{-1}).

Introduction

In general, the very low molar absorptivities of $V(H_2O)_6^{2+}$ and $V(H_2O)_6^{3+}$ often make it difficult to obtain kinetic data spectrophotometrically with low concentrations of the vanadium species. One might of course make measurements at the stronger absorption bands in the UV, but this can be risky, since no well-defined spectral maxima are observed, and minor species (that may or may not accurately reflect the reaction of interest) can distort the absorbance–time profile. Also, the dinuclear V(III) species VOV^{4+} (or $V(OH)_2V^{4+}$), which is formed from $V(H_2O)_6^{3+}$ but is not in rapid equilibrium with it,[1] has a strong UV absorption. And there is a further problem that, if V^{2+} and V^{3+} are oxidized at comparable rates, then the production of VO^{2+}, and its subsequent rapid (but not instantaneous[1]) reaction with V^{2+}, will complicate the interpretation and analysis of the kinetic data.

To circumvent these problems we have developed a new method for measuring the *initial* reaction rate of V^{2+} oxidation under circumstances where V^{3+} is rapidly reduced back to V^{2+}. For this we have employed the oxidation of the intensely absorbing methyl viologen radical cation ($PQ^{\bullet+}$) by V^{3+}, a reaction that occurs rapidly and completely.[2] This method and its application to the oxidation of vanadium(II) ions by hydrogen peroxide is the subject of this report, along with an extension to presumably analogous reactions of alkyl hydroperoxides.

There were a number of unresolved questions that encouraged this reinvestigation of the hydrogen peroxide reaction. Among these is the serious disagreement between the early results of Swinehart[3] and a recent investigation by Rush and Bielski.[4] Swinehart reports a rate constant $>10^2$ M^{-1} s^{-1} (assuming a second-order rate law), whereas Rush and Bielski establish a second-order reaction with $k = 17.2 \pm 2.0$ M^{-1} s^{-1} (at 21 °C and $[H^+] = \mu = 0.12$ M). According to Swinehart,[3] a substantial proportion of the reaction proceeds directly to VO^{2+} via a two-electron pathway; in contrast, Rush and Bielski[4] specifically preclude appreciable formation of VO^{2+}. In addition, we wanted to provide more detail concerning whether the reactions between V^{2+} and H_2O_2 and ROOH involve a Fenton-type mechanism, in which case hydroxyl and alkoxyl free radicals ($HO^\bullet$, $RO^\bullet$) occur as intermediates. If so, the occurrence of the β-scission reactions of the alkoxyl radicals derived from suitably constituted hydroperoxides will provide further insight into the reactions of alkyl radicals with V^{2+}.[5-8]

Experimental Section

Reagents. Solutions of VO^{2+} ions were used as the sulfate or perchlorate, the latter obtained by eluting vanadyl ions from a column of Dowex 50W-X4 cation-exchange resin with 1.6 M perchloric acid. Solutions of V^{2+} were prepared by zinc amalgam reduction in dilute hydrochloric (usually) or perchloric acid (occasionally). Concentrations of VO^{2+} were determined spectrophotometrically ($\epsilon_{760} = 17.5$ M^{-1} cm^{-1}) and of V^{2+} by the Co^{2+} produced from its reaction with $(NH_3)_5CoBr^{2+}$.[9]

Samples of *tert*-amyl hydroperoxide[10] and α,α-dimethyl-β-phenethyl hydroperoxide,[11] the respective precursors of ethyl and benzyl radicals, were prepared by the methods cited, whereas others were the commercial products: *tert*-butyl hydroperoxide (Aldrich) and hydrogen peroxide (Mallinckrodt). The samples of peroxides were analyzed by iodometric titration.[12]

Methyl viologen ion, or paraquat (1,1′-dimethyl-4,4′-bipyridinium ion, which we abbreviate PQ^{2+}), was purchased as $(PQ)Cl_2$ (Aldrich). For some purposes it was converted to the perchlorate. Solutions of the radical cation $PQ^{\bullet+}$ were prepared by reduction with zinc amalgam (carried only to 30% completion to avoid formation of the diradical) or by cathodic reduction at a mercury-pool electrode at −0.8 V relative to SSCE.

Measurements. Gaseous organic products (methane and ethane) and acetone were determined by gas chromatography on VZ10 and OV-101 columns, respectively, calibrated with the authentic materials. Spectrophotometric measurements were made on various instruments, with kinetic data collected by using a Cary 219 instrument. Most measurements were made at 600 nm, very close to the absorption maximum of $PQ^{\bullet+}$ at 609 nm ($\epsilon_{600} = 13{,}000$ M^{-1} cm^{-1}). All of the preparations and measurements were carried out under rigorously anaerobic conditions (syringe–septa techniques) since the reagents, particularly $PQ^{\bullet+}$, are sensitive to oxygen.

Kinetic data obtained under the conditions used in most experiments followed pseudo-zeroth-order kinetics. An example is shown in Figure 1. Pseudo-zeroth-order kinetics were particularly well followed for H_2O_2 and *t*-BuOOH, where the absorbance–time tracing from the spectrophotometer was linear usually for 60–80% reaction. Linearity extended less far in other cases, presumably because certain side reactions were of greater importance, as discussed subsequently. The slope of the absorbance–time line determined during the linear stage of the reaction directly from the chart paper is designated $-dD_{600}/dt$ (*D* = absorbance). This value was converted to the chemical reaction rate $R_{PQ} = -d[PQ^{\bullet+}]/dt$ by division by the molar absorptivity of the radical ($\epsilon_{600} = 13000$ M^{-1} cm^{-1} was used) and the optical path length, 1 or 2 cm.

Results

Reaction of V^{2+} and H_2O_2. The hydrogen peroxide reaction is the only one examined previously, and it is the one for which conflicting data[3,4] were cited earlier. This seemed like a good reaction to use to develop and test the initial-rate method based on $PQ^{\bullet+}$, since useful comparisons could thus be made. Relatively high concentrations of vanadium(II) ions (2.6–18 mM) were used previously,[4] with the reaction progress monitored in the UV region at 250 and 270 nm.

The simplest version of a possible reaction scheme, with several real or possible side reactions for the moment ignored, is shown

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Table I. Initial-Rate Kinetic Data for the Oxidation of Vanadium(II) Ions by Hydrogen Peroxide[a]

initial concn/mM			initial rate[b]	k_1/M^{-1} s^{-1}	
[V^{2+}]	[H$_2$O$_2$]	[PQ$^{\bullet+}$]	$10^6 R_{PQ}$/M s^{-1}	eq 4	cor[c]
0.0507	0.453	0.0165	0.703	15.5	15.9
0.103	0.214	0.0121	0.652	15.0	16.2
0.105	0.403	0.0128	1.24	14.8	16.9
0.109	0.522	0.0193	1.71	15.2	16.3
0.139	0.355	0.0362	1.44	15.0	15.3
0.209	0.299	0.0317	1.87	15.4	15.7
0.245	0.283	0.0365	1.83	13.7	14.0
0.281	0.295	0.0454	2.17	13.6	13.8
0.397	0.310	0.0208	2.82	(11.7)[d]	14.6
1.01	0.299	0.0165	4.26	(7.2)[d]	(~13)[d]
				av 14.8 ± 0.7	av 15.4 ± 0.9

[a] At 25.0 °C in chloride medium with [H$^+$] = 9–27 mM and variable ionic strength. [b] $R_{PQ} = -(dD_{600}/dt)b\epsilon_{600}$, with $\epsilon_{600} = 1.3 \times 10^4$ M^{-1} cm^{-1}. [c] Corrected by numerical solutions of the rate equations (see text). [d] Excluded from the average.

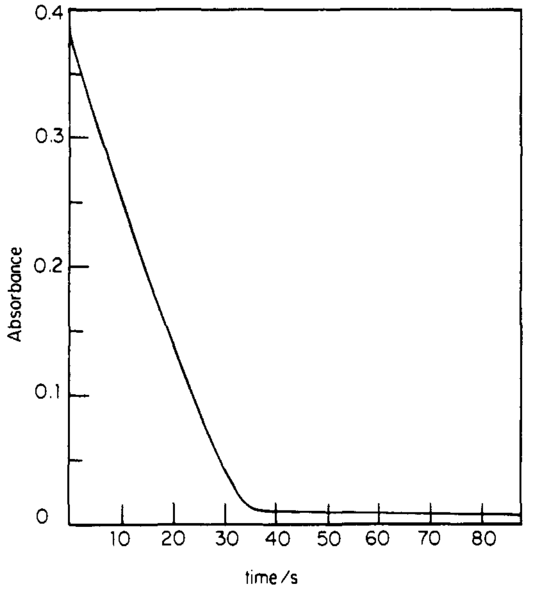

Figure 1. Absorbance of PQ$^+$ added to a reaction between V^{2+} and *tert*-butyl hydroperoxide, decreasing with time according to pseudo-zeroth-order kinetics for >60% completion. The reaction was monitored at 600 nm; this experiment had the reaction conditions [V^{2+}]$_0$ = 0.129 mM, [*t*-BuOOH]$_0$ = 1.19 mM, [PQ$^{\bullet+}$]$_0$ = 0.0288 mM, and [HClO$_4$] = 11.7 mM, at 25 °C.

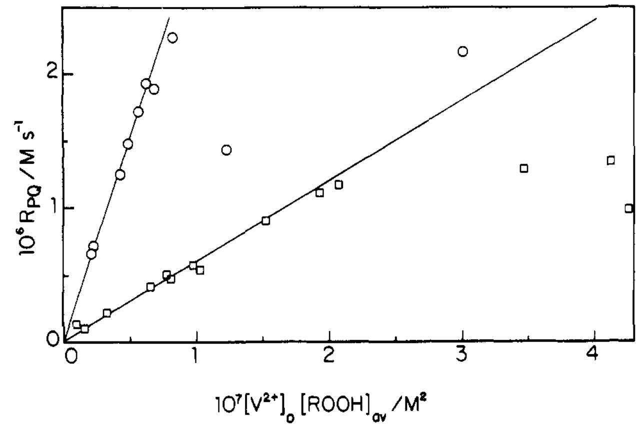

Figure 2. Initial rate of reaction, R_{PQ}, varying linearly with product of the concentrations of vanadium(II) ions and peroxide. The data for hydrogen peroxide (circles) and *tert*-butyl hydroperoxide (squares) are given in Tables I and II. Substantial deviations occur at high [V^{2+}], as discussed in the text.

in eq 1–3 (where, of course, the acidic and basic V(III) species are rapidly equilibrated; V^{3+} + H$_2$O = VOH^{2+} + H$^+$).

$$V^{2+} + H_2O_2 \rightarrow VOH^{2+} + HO^\bullet \qquad (1)$$

$$V^{2+} + HO^\bullet \rightarrow VOH^{2+} \qquad (2)$$

$$V^{3+} + PQ^{\bullet+} \rightarrow V^{2+} + PQ^{2+} \qquad (3)$$

Justification for these particular reactions will be given in due course, but the analysis of the kinetic data is clearer if this simplified scheme is given at the outset. According to it, the rate-limiting reaction is the first shown, and the others occur more rapidly. The second of these reactions has not been evaluated directly, but on the basis of analogous reactions,[13] we infer that it occurs very rapidly. The rate constants for reaction 3 are known:[2] $k_3 = 9 \times 10^4$ M^{-1} s^{-1} and $k_{-3} = 2.3$ M^{-1} s^{-1} at 25 °C. The standard potentials of V$^{3+/2+}$ and PQ$^{2+/+}$ (–0.255 and –0.43 V, respectively) indicate that equilibrium in eq 3 lies well to the right. This reaction is sufficiently rapid to keep [V^{3+}] at a very low value. In effect, V^{3+} can be treated as a steady-state intermediate during the stage of the reaction where PQ$^{\bullet+}$ is present, and because of that, [V^{2+}] remains essentially constant during this period. These assertions are examined in more detail later. Assuming for now that they are valid, we can express the reaction rate in terms of the measured species, PQ$^{\bullet+}$. The equation expected from this scheme is

$$R_{PQ} = -d[PQ^{\bullet+}]/dt = 2k_1[V^{2+}]_0[H_2O_2] \qquad (4)$$

According to eq 4, a plot of the initial rate of loss of PQ$^{\bullet+}$ will be a linear function of the concentration product and will be independent of [PQ$^{\bullet+}$]$_0$. The applicable concentration of vanadium(II) is its initial value, since [V^{2+}] remains constant at [V^{2+}]$_0$ during the PQ$^{\bullet+}$-consuming stage, for the reasons outlined above. The concentration of hydrogen peroxide used in the calculation was [H$_2$O$_2$]$_0$ – [PQ$^{\bullet+}$]$_0$/4, but the correction for peroxide consumption, as represented by the second term, was nearly negligible. Over much of the concentration range, the data follow eq 4, as indicated by the linearity of the plot in Figure 2 and by the constancy of the value of k_1 (Table I).

Deviations from this function are noted at high concentrations of vanadium(II). The extent of adherence to pseudo-zeroth-order kinetics throughout a given experiment was also less at higher [V^{2+}]. This effect appears to be due to the failure of the steady-state approximation for [V^{3+}] under certain concentration conditions. That is, the rate of the indicator reaction is not sufficient to "keep up with" that of the initial step in eq 1 when the rate is relatively high. The full set of rate equations could not be solved in closed form under those conditions, and so a numerical solution using the program KINSIM was carried out.[14] The last column of Table I shows a values of the rate constant k_1 so corrected; the average is 15.4 ± 0.9 M^{-1} s^{-1} at 25.0 °C.

Reaction of V^{2+} and Alkyl Hydroperoxides. An analogous treatment was used, although of course additional reactions of

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Table II. Initial-Rate Kinetic Data for the Oxidation of Vanadium(II) Ions by *tert*-Butyl Hydroperoxide[a]

initial concn/mM			initial rate[b]	k_1/M^{-1} s^{-1}	
[V^{2+}]	[*t*-BuOOH]	[$PQ^{\bullet+}$]	$10^6 R_{PQ}$/M s^{-1}	eq 4	cor[c]
0.0403	0.520	0.0063	0.139	3.33	3.40
0.0634	1.04	0.0085	0.407	3.09	3.29
0.0640	0.250	0.0136	0.101	3.21	3.21
0.0641	0.520	0.0161	0.206	3.12	3.12
0.0697	1.12	0.0125	0.496	3.19[d]	3.29
0.0700	1.16	0.0177	0.468	2.89	2.89
0.120	1.73	0.0230	1.16	2.80	2.83
0.127	0.780	0.0150	0.564	2.86	2.92
0.129	1.19	0.0288	0.899	2.95[d]	2.95
0.212	0.500	0.0392	0.544	2.58	2.58
0.301	0.655	0.0331	1.11	2.85	2.85
0.532	0.680	0.114	1.29	(1.86)[e]	(1.86)[e]
0.602	0.750	0.010	0.922	(1.03)[e]	(~1.6)[e]
1.07	0.420	0.135	1.34	(1.62)[e]	(1.62)[e]
				av 2.99 ± 0.22	av 3.03 ± 0.25

[a] At 25.0 °C with [H^+] = 9–28 mM and variable ionic strength, 0.01–0.03 M. [b] $R_{PQ} = -(dD_{600}/dt)/b\epsilon_{600}$ with $\epsilon_{600} = 1.3 \times 10^4$ M^{-1} cm^{-1}. [c] Corrected for the failure of the steady-state approximation for [V^{3+}] (see text). [d] In ClO_4^- solution; other data were obtained in Cl^- solution. [e] Excluded from the average.

the alkoxyl radical and species derived from it, presumably all rapid, must also be considered as given later. The initial step, by analogy with eq 1 and with other peroxide reactions,[15,16] is as given in eq 1a.

$$V^{2+} + (CH_3)_3COOH \rightarrow VOH^{2+} + (CH_3)_3CO^\bullet \quad (1a)$$

The data for *tert*-butyl hydroperoxide (Table II) were analyzed by the same method as used for hydrogen peroxide. As before, the plot of R_{PQ} versus the product [V^{2+}][ROOH] (Figure 2) is linear over a wide range of the concentration variables and gives $k_{1a} = 3.00 \pm 0.20$ M^{-1} s^{-1} at 25.0 °C.

Deviations well outside the experimental error were noted in the three experiments run at the higher vanadium(II) concentrations. Corrections using KINSIM were made, but as shown (Table II), they are much smaller throughout because the initial rate and k_1 are themselves much smaller for *t*-BuOOH than for H_2O_2. Indeed, this treatment is insufficient to resolve the problem found for the data taken at higher [V^{2+}], and we later suggest reasons for this.

A more limited set of experiments for two other alkyl hydroperoxides ($RC(CH_3)_2OOH$, R = C_2H_5 and CH_2Ph) gave respective values of k_1 of 5.2 and 4.8 M^{-1} s^{-1}. The data for the latter were obtained with acetonitrile cosolvent owing to the low solubility of this hydroperoxide in water.

Hydrocarbon Products. The formation of acetone and methane (primarily) and ethane (traces) from the reaction of V^{2+} and *t*-BuOOH in the absence of $PQ^{\bullet+}$ was confirmed. This is consistent with the initial step being formation of an alkoxyl radical by reaction 1a, followed by oxidation of vanadium(II) ions by the methyl radical that results from the β-scission of the *tert*-butoxyl radical:

$$(CH_3)_3CO^\bullet \rightarrow (CH_3)_2CO + {}^\bullet CH_3 \quad (5)$$

$$^\bullet CH_3 + V^{2+} + H^+ \rightarrow CH_4 + V^{3+} \quad (6)$$

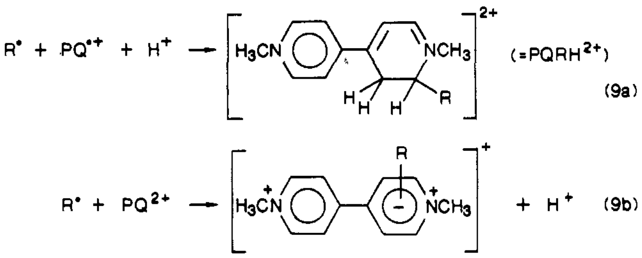
When the reaction was carried out in 1:1 methanol–water, formaldehyde was formed. This is consistent with the reaction between this alkoxyl radical and the alcohol, eq 7, known to occur in preference over β-scission. This may lead to a chain process, since more of the alkoxyl radical is produced, directly as in eq 8a and by the sequence of eq 8b and 1a.

$$(CH_3)_3CO^\bullet + CH_3OH \rightarrow (CH_3)_3COH + {}^\bullet CH_2OH \quad (7)$$

$$^\bullet CH_2OH + (CH_3)_3COOH \rightarrow HCHO + (CH_3)_3CO^\bullet + H_2O \quad (8a)$$

$$^\bullet CH_2OH + V^{3+} \rightarrow HCHO + V^{2+} + H^+ \quad (8b)$$

In contrast, no gaseous C_1–C_4 products were observed from the reaction of *tert*-butyl and *tert*-amyl hydroperoxides with $PQ^{\bullet+}$. This implicates certain other reactions of the alkyl radicals, perhaps addition to the methyl viologen radical, with accompanying protonation, eq 9a, or possibly (by analogy to the reaction of alkyl radicals with $M(phen)_3^{3+}$ complexes)[17] addition to the pyridine ring of the methyl viologen cation and reductive displacement of H^+, eq 9b.



Related Reactions. The reaction between hydrogen peroxide and $PQ^{\bullet+}$ has been reported to be relatively slow.[18] Although the kinetic data are not highly precise, an average second-order rate constant of ca. 2.6 M^{-1} s^{-1} was reported. Similarly, slow oxidation of $PQ^{\bullet+}$ by the alkyl hydroperoxides was observed.[19] It was also shown that VO^{2+} is reduced much more slowly than V^{3+} by $PQ^{\bullet+}$, with $k \sim 3$ M^{-1} s^{-1} at 0.03 M H^+. The slowness might arise because simple electron transfer does not give stable products directly, but the dependence of the rate on [H^+] was not evaluated.

The occurrence of a direct reaction between alkyl radicals and $PQ^{\bullet+}$ was confirmed. The test was run with $R^\bullet = PhCH_2$, not only because this should be the least reactive of the radicals but also because it is readily available from the homolysis of $CrCH_2Ph^{2+}$. The concentration of $PQ^{\bullet+}$ did indeed decline during the period of homolysis, and the limited data obtained appeared consistent with the reaction scheme

$$CrCH_2Ph^{2+} \rightleftarrows Cr^{2+} + {}^\bullet CH_2Ph \quad (10)$$

$$PQ^{\bullet+} + {}^\bullet CH_2Ph \xrightarrow{H^+} PQ(CH_2Ph)H^{2+} \quad (11)$$

According to this, the rate of reaction is given by eq 12. Analysis of the mixed zeroth- and first-order kinetic trace gave, with known values[20,21] of k_{10} and k_{-10}, the estimate $k_{11} \sim 1 \times 10^9$ M^{-1} s^{-1}.

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$$\frac{-d[PQ^{\bullet+}]}{dt} = \frac{k_{10}k_{11}[CrCH_2Ph^{2+}][PQ^{\bullet+}]}{k_{-10}[Cr^{2+}] + k_{11}[PQ^{\bullet+}]} \qquad (12)$$

Other checks were also performed to trace the possible source of the deviations at high [V^{2+}] either to a fault in a reagent or to side reactions. Using only glass and Teflon fittings throughout did not alter the situation nor did using V^{2+} prepared from ion-exchanged VO^{2+} or $PQ^{\bullet+}$ prepared electrochemically rather than by zinc reduction. Identical rate constants were obtained in chloride and perchlorate media, and the values were independent of [H^+] and ionic strength. The same increase in the apparent rate constant at high [V^{2+}] was observed when barium perchlorate was used to maintain constant ionic strength and reaction medium by maintaining [V^{2+}] + [Ba^{2+}] = 2.60 mM. Because of that, we continued to use the literature values of k_3 and k_{-3}, determined at μ = [H_3O^+] = 1.0 M, even though the present experiments were run at 9 $\leq$ [H_3O^+] $\leq$ 27 mM. At most, these reactions cause but a minor correction to the form for R_{PQ} given in eq 4; as such, any revisions in the values are of secondary importance.

Direct spectrophotometric measurements showed that negligible association between V^{2+} and $PQ^{\bullet+}$ occurs. Although association of $PQ^{\bullet+}$ pairs has been reported,[22] that equilibrium is not the problem here.[23] The product of eq 9a is a modified methyl viologen, which can be independently prepared by oxidation of $PQ^{\bullet+}$ with alkyl hydroperoxides:

$$2PQ^{\bullet+} + RC(CH_3)_2OOH + 2H^+ = PQ^{2+} + PQRH^{2+} + (CH_3)_2CO + H_2O \qquad (13)$$

The reduction of $PQRH^{2+}$ (prepared in situ according to eq 13) with V^{2+} produces an intensely blue monocation, which decomposes within a few minutes in weakly acidic solutions.[24] The formation and subsequent decomposition of small amounts of these reduced species in the alkyl hydroperoxide reactions with V^{2+} may be responsible for the deviations from pseudo-zeroth-order kinetics and the erroneous rate constants at high [V^{2+}]. The chemistry of $PQ^{\bullet+}$ and related species has recently been reviewed.[25]

In the final analysis, we failed to eliminate completely the kinetic deviations at high [V^{2+}] for the ROOH reaction. The data are otherwise in such good conformity to the rate law of eq 4 that, despite this difficulty, we feel this method gives a correct evaluation of k_1, the second-order rate constant for the rate-limiting step of the sequence.

Discussion

Kinetic Data. The rate constant for the hydrogen peroxide reaction, 15.4 M^{-1} s^{-1} at 25.0 °C, is in good agreement with the value given by Rush and Bielski,[4] 17.2 M^{-1} s^{-1} at 21 °C. The small difference might be ascribed to systematic errors inherent in the use of the very different experimental methods or to the difference in reaction medium (low and variable ionic strength here, versus 0.12 M perchloric acid in the reported data[4]).

Another area of agreement in the two studies concerns the lack of VO^{2+} formation. VO^{2+} would have been very evident in the UV method used earlier, yet it was not seen. There was also no evidence for VO^{2+} formation in the present series of experiments. This also contradicts an earlier report.[3]

Inner-Sphere Mechanism. The rate constants for all of the peroxides lie within the range generally attributed to ligand substitution in the primary coordination sphere of the hexaaquavanadium(II) ion.[26] Since outer-sphere reductions of peroxides are rare and are perhaps without precedent,[27] it seems likely that rate-limiting inner-sphere substitution precedes the electron-transfer step.

The options for the immediate products of the inner-sphere reaction are several. The precursor complex might yield {VO^{2+} + ROH} or {VOH^{2+} + $RO^{\bullet}$}. The first set is inconsistent with both inorganic and organic products obtained, whereas the latter is in good agreement. This has been detailed in eq 5 and 6 and is supported by the methanol trapping experiment represented by eq 7 and 8.

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Registry No. V^{2+}, 15121-26-3; H_2O_2, 7722-84-1; $PQ^{\bullet+}$, 25239-55-8; *tert*-butyl hydroperoxide, 75-91-2; *tert*-amyl hydroperoxide, 3425-61-4; α,α-dimethyl-β-phenethyl hydroperoxide, 1944-83-8.

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[22] Kosower, E. M. In *Free Radicals in Biology*; Pryor, W. A., Ed.; Academic: New York, 1978; Vol. II. This author gives $K = 4 \times 10^3$ M^{-1} for $2PQ^{\bullet+} = (PQ_2)^{2+}$.

[23] Association of $PQ^{\bullet+}$ pairs is not of a magnitude to cause the effect noted at the concentrations of $PQ^{\bullet+}$ used. This association reaction is very rapid (we could not observe it by stopped-flow dilution with solvent), and the small difference in molar absorptivity between PQ^+ and its dimer cannot cause the problem in calculation of R_{PQ}.

[24] These features suggest a bipyridyl radical cation $(PQRH)^{\bullet+}$, a species we would expect to be very similar to $PQ^{\bullet+}$. It could participate in eq 3 and other reactions, and give rise to the effects noted.

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Kinetics and Mechanism of the Reactions of Alkylchromium Complexes with Aqueous Sulfur Dioxide

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The organopentaaquochromium(III) complexes, $(H_2O)_5CrR^{2+}$ (R = alkyl, substituted alkyl, benzyl, and substituted benzyl), react with SO_2 in aqueous perchloric acid solutions to yield $(H_2O)_6Cr^{3+}$ (~80%), $(H_2O)_5Cr(SO_2)R^{2+}$ (~20%), and alkanesulfinic acids. The reactivity pattern within the series (CH_3 > 1° ~ benzyl ≫ 2°) closely matches that observed earlier in electrophilic substitution reactions of these and other organometallic complexes. The competition between the solvent water and the oxygen or sulfur of the leaving RSO_2^- group is responsible for the formation of the two chromium products.

Introduction

Several mechanistic pathways have been identified in the reactions of SO_2 with organometallic species.[1-3] Coordinatively saturated complexes usually react by electrophilic substitution or a radical mechanism to yield sulfur- or oxygen-bonded insertion products. Electrophilic substitution is typified by the lack of the

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