1306 *Inorg. Chem.* **1989**, *28*, 1306-1310

tations concerning the length of Cu(1)–Cu(3) and associated Cu–O distances. A hydrogen atom also appears to be lacking on the face trans to Cu(1,2,3), namely Cu(4,5,6), although there is no corresponding effect on the associated Cu–Cu, P geometries. (Among the equatorial distances in the study of the dmf solvate, Cu(2)–Cu(1,3) distances were noted as unusually long; it seems unlikely that this was the result of any partial decomposition in that core since there was no corresponding lengthening of Cu(1)–Cu(3).)

Pentameric thf Solvate. 1:1 copper(I) hydride:monodentate ligand adducts have thus far only been structurally characterized as hexamers;[2-4] with oligodentate ligands, dimeric[5] and octameric species[4] have been structurally authenticated, μ_3-bridging hydrogen atoms being located in the former. In this context, the isolation of the present pentamer was unexpected. The five copper atoms are disposed in a trigonal-bipyramidal array (Figure 2). This array is distorted from ideal trigonal-bipyramidal symmetry in two ways: first, one pyramid shows $Cu_{ax}\cdots Cu_{eq}$ bond lengths ca. 0.1 Å longer than the other, and second, the equatorial copper atoms form an isosceles rather than an equilateral triangle ($Cu_{eq}\cdots Cu_{eq}$ = 2.608 (7), 2.592 (8), and 2.492 (8) Å). The $Cu_{ax}\cdots Cu_{ax}$ distance is 4.034 (8) Å. Comparison of this cluster with pentameric clusters in the anions $[Cu_5(\mu_2\text{-S}^tBu)_6]^-$[11] and $[Cu_5Ph_6]^-$[12] shows important differences in the geometries. In these latter compounds, the pentanuclear skeleton has been described as a "squashed" trigonal bipyramid. For example, in $[Li(thf)_4][Cu_5Ph_6]$,[12] the $Cu_{ax}\cdots Cu_{ax}$ distance is 3.269 (4) Å while the $Cu_{eq}\cdots Cu_{eq}$ distances are 3.165 (4) Å. The $\langle Cu_{ax}\cdots Cu_{eq}\rangle$ distance of 2.452 (4) Å, the atoms here being bridged by Ph^- ligands, is similar to the value found for **2**.

The five triphenylphosphine ligands form single Cu–P bonds to each of the copper atoms with distances ranging between 2.16 (1) and 2.21 (1) Å. These distances are shorter than those found in the regular hexamer, and in the general context of (PPh_3)–Cu compounds, shorter distances have been found only for $(PPh_3)Cu(\eta\text{-}C_5H_5)$.[13]

The question of location of the hydride anions in this complex is of considerable interest; the answer to which is not, as yet, available from the structural data. The evidence from the hexamer structure suggests that facial center locations are likely to be preferred. In the present array, differentiation of one of the six faces might be expected to result in the face devoid of hydrogen atoms having significantly longer edges; no face in the present structure presents itself as an obvious candidate in this respect. A further possibility is that the cluster may be the $[(PPh_3)_5Cu_5H_6]^-$ anion. While this is consistent with the relatively symmetrical disposition of the copper atoms in the cluster, we have not, as yet, been able to provide supporting evidence, such as the presence of a counterion.

Acknowledgment. We gratefully acknowledge support of this work by the Australian Research Grant Scheme.

Registry No. **1**·0.5thf, 119390-52-2; **1a**·thf, 119390-56-6; **2**·thf, 119390-54-4; $[(PPh_3)_3CuCl]$, 15709-76-9.

Supplementary Material Available: Thermal parameters (Tables SUP 1–SUP 3), ligand hydrogen parameters (Table SUP 4), ligand non-hydrogen geometries (Tables SUP 5–SUP 7), and crystal data (Table SUP 8) (18 pages); tables of structure factor amplitudes (63 pages). Ordering information is given on any current masthead page.

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Contribution from the Central Leather Research Institute,
Adyar, Madras 600 020, India

Kinetics and Mechanism of Hydrogen Peroxide Reactions of Diperoxo(amine)chromium(IV) Complexes: Evidence for Formation of an Oxodiperoxochromium(VI) Intermediate

C. K. Ranganathan, T. Ramasami,* D. Ramaswamy, and M. Santappa

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The kinetics of the reactions of hydrogen peroxide with two chromium(IV)–diperoxo complexes $Cr(O_2)_2(en)(H_2O)$ and $Cr(O_2)_2(dien)$ have been investigated in aqueous acidic media at 30 °C, I = 1.00 ($NaClO_4$). Two kinetic stages were observed. The first stage corresponded to the formation of a blue diperoxo intermediate of the form $Cr(O)(O_2)_2L$ where L = en or dien and water ligands (if any) are omitted. A mechanism involving the entry of free peroxide ligand into the coordination sphere of the metal ion prior to a redox process involving the conversion of Cr(IV) to Cr(VI) has been favored on the basis of kinetic results.

Introduction

Peroxo complexes of transition-metal ions have attracted much attention,[1,2] and comparisons of the reactivity of peroxo derivatives of d^0 transition-metal ions with that of free hydrogen peroxide have been made.[3-6] However, little is known of the reactivity of diperoxo derivatives of d^2 ions like chromium(IV). Among the few well-characterized complexes of chromium(IV), the derivatives diperoxoaqua(ethylenediamine)chromium(IV), $Cr(O_2)_2(en)(H_2O)$ (**1**), and diperoxo(diethylenetriamine)chromium(IV), $Cr(O_2)_2(dien)$ (**2**), have many unusual and interesting features.[7-10] These complexes have formed useful intermediates in the synthesis of chromium(III) amine complexes.[7-9] the mechanistic studies, on these complexes, however, have been limited.[10,11]

Since complexes **1** and **2** contain both Cr(IV) and O_2^{2-} ligands, which are capable of reduction as well as oxidation, the redox

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reactions of the diperoxo derivatives are of interest.[11b] The kinetics of the reaction of H_2O_2 with complexes **1** and **2** have been investigated, and the evidence for the formation of a blue oxodiperoxochromium(VI) intermediate as a primary product is presented here.

Experimental Section

Materials. The diperoxochromium(IV) derivatives were prepared by using literature methods.[7-9] Diperoxoaqua(ethylenediamine)chromium(IV) was prepared by the simultaneous (and dropwise) addition of a solution (50 mL) containing chromium trioxide (BDA, AnalaR, 30 g) and copper sulfate (BDH, AnalaR, 0.5 g) and 30% hydrogen peroxide (100 mL) to a precooled and freshly distilled solution of ethylenediamine (25 mL) diluted with 500 mL of distilled water. The reaction was carried out at 10 °C, and when the mixture was kept at ca. 2 °C overnight, fine olive green crystals separated out. The crystals were washed with ice-cold water and dried in vacuo.

Diperoxo(diethylenetriamine)chromium(IV) was prepared by adding potassium dichromate (BDH, AnalaR, 5 g) dissolved in 10 mL water and 30% hydrogen peroxide (Sarabhai Merck, Reagent Grade, 15 mL) dropwise with stirring over a period of 3 h to a precooled solution of diethylenetriamine (6 mL) diluted with 20 mL of water. The temperature of the mixture was maintained throughout at ca. 5 °C. Pale green crystals of the desired product were obtained when the reaction mixture was kept at ca. 2 °C for 10 h. The product was filtered onto a sintered funnel, sucked dry, washed with ethyl alcohol, and dried in vacuo.

Authentic samples of oxodiperoxo(1,10-phenanthroline)chromium(VI), $OCr(O_2)_2(phen)$, were prepared by using literature methods.[12] Similarly, oxodiperoxochromium(VI) was also generated in solution as reported previously.[13] These complexes were used for spectral comparisons in the analysis of products of the reaction of H_2O_2 with **1** and **2**. Freshly prepared and standardized solutions of H_2O_2 were used and concentrations determined periodically.

Product Analysis and Determination of Stoichiometry. Solutions of diperoxoaqua(ethylenediamine)chromium(IV), at $[Cr(IV)] = (2-3) \times 10^{-4}$ M, were mixed with hydrogen peroxide (0.1 M) and perchloric acid (0.05–0.10 M H^+). An unstable (intense) blue species was formed initially, which could be extracted in chloroform. In order to minimize the time needed for extraction, the Cr(IV) complex was reacted with hydrogen peroxide in a separating funnel, with chloroform being added within 2 min after mixing. The extraction was completed within 3 min.

The blue intermediate was relatively stable (ca. 30 min) in chloroform, and reproducible electronic spectra could be obtained. In the case of $Cr(O_2)_2(dien)$, however, the yield of the blue intermediate was relatively low (<15%) under most $[H^+]$ (0.05–0.3 M) and $[H_2O_2]$ ($(1-5) \times 10^{-2}$ M) conditions employed. A blank experiment was conducted in which Cr(VI) taken as chromate was mixed with H_2O_2 in comparable $[H^+]$ conditions, viz. 0.05 M, and the resulting blue oxo peroxo species was extracted in chloroform. The electronic spectra of the blue species from Cr(IV) and Cr(VI) as starting materials were recorded in the region 700–400 nm.

The stoichiometry for the reaction of H_2O_2 with Cr(IV) complexes leading to the formation of blue intermediates was determined by means of spectrophotometric titrations in a stopped-flow mixing chamber at 370 nm and $[Cr(IV)] = 1.1 \times 10^{-3}$ M and with $[H_2O_2]$ varying in the range $(0-5) \times 10^{-3}$ M, by mixing Cr(IV) solutions at $[H^+] = 10^{-5}$ M and H_2O_2 solutions at $[H^+] = 10^{-3}$ M.

The blue intermediate was also analyzed for chromium:nitrogen ratios by using chromate and micro Kjeldhal methods[14,15] and decomposed in aqueous acidic media ($[H^+] = 0.3$ M). The resulting mixture was analyzed for the nature of products formed, and typically in the case of $Cr(O_2)_2(en)(H_2O)$, $Cr(en)(H_2O)_4^{3+}$ was obtained as the only identifiable chromium product.

The overall stoichiometry for the reaction including the second stage was examined in the case of reactions involving $Cr(O_2)_2(en)(H_2O)$. To do this, Cr(IV) (2.5×10^{-4} M) and H_2O_2 (2.5×10^{-3} M) solutions at $[H^+] = 0.01$ M were mixed and at the end of the reaction the mixture was loaded on a Dowex 50W-X2 column to remove the cationic products. Since the washings did not contain any Cr(VI) products as examined by UV spectral measurements, unreacted H_2O_2 was analyzed by iodometric methods.

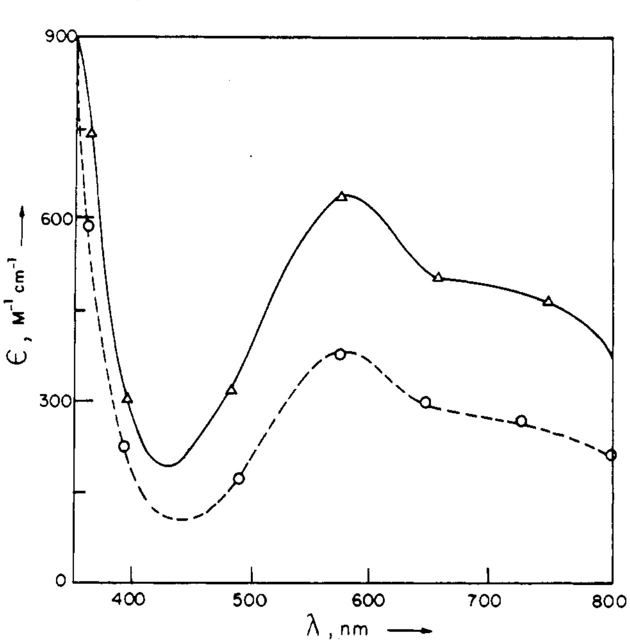

Figure 1. UV–visible spectra of the blue oxo peroxo intermediates generated by the reaction of hydrogen peroxide with Cr(VI) (○) and $Cr^{IV}(O_2)_2(en)(H_2O)$ (△).

Kinetic Studies. There were two kinetic stages in the H_2O_2-associated decomposition of Cr(IV) diperoxo derivatives. Typically in the case of $Cr(O_2)_2(en)(H_2O)$, two kinetic steps having half-lives of the order of 10–300 ms and 5–40 s, respectively, were observed. In the case of $Cr(O_2)_2(en)(H_2O)$, the $t_{1/2}$ values of the first and second stages differed by more than 1 order of magnitude and pseudo-first-order plots for both kinetic stages corresponding to the formation and decay of a blue intermediate were linear to at least 4 half-lives. The formation of the blue intermediate could be monitored conveniently at both 680 and 370 nm, and rate constants obtained were wavelength-independent. The decay of the blue intermediate from **1** could be monitored at 680 nm. In the case of $Cr(O_2)_2(dien)$, however, the acid decomposition of the Cr(IV) adduct competed with H_2O_2-assisted decomposition and the yield of blue intermediate was low. Therefore, the formation of the blue intermediate was followed at 400 nm, where the secondary reactions had negligible optical changes and the decay of the blue derivative was not monitored.

The kinetics of the reactions of Cr(IV) complexes with H_2O_2 were measured at $[Cr(IV)] = (1-3) \times 10^{-4}$ M, $[H_2O_2] = (1-5) \times 10^{-2}$ M, $[H^+] = 0.01-0.70$ M, $I = 1.0$ M ($NaClO_4$), and $T = 30$ °C. The reactions of $Cr(O_2)_2(en)(H_2O)$ were investigated, and the pseudo-first-order rate constants for the first step, k_f, and the second step, k_s, were obtained by standard methods.[16] The observed rate constants for the reaction of $Cr(O_2)_2(dien)$ with hydrogen peroxide under acidic conditions, k_f', were also obtained similarly. The values of k_f, k_f', and k_s were determined as functions of $[H^+]$ and $[H_2O_2]$ and analyzed by using suitable rate laws and the Los Almos program implemented on an IBM 370 computer.[17]

Results and Discussion

The absorption maxima of the blue intermediates formed from the reactions of H_2O_2 with H_2CrO_4 as well as **1** with chloroform as the solvent are similar, as shown in Figure 1. The spectral data for the blue intermediate from **1**, viz. 578 nm (640 M^{-1} cm^{-1}) and 705 nm (480 M^{-1} cm^{-1}), compare favorably with those of an authentic sample of $Cr(O_2)_2(O)(phen)$ with respect to peak positions (within ±4 nm). Although reliable electronic spectral measurements on the blue species from **2** were difficult, qualitative similarities with respect to absorption maxima, viz. 580 and 705 nm, were observed when they were compared to the data for the

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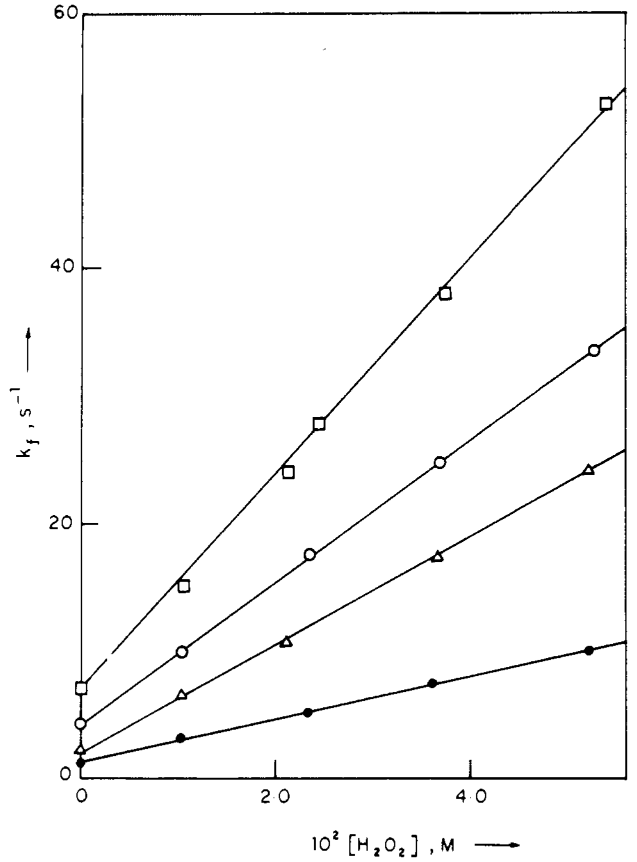

Figure 2. Dependence of the pseudo-first-order rate constant, k_f, on [H_2O_2] for the reaction of $Cr(O_2)_2(en)(H_2O)$ at [H^+] = 0.10 (●), 0.25 (△), 0.40 (○), and 0.60 M(□).

intermediates from the reaction of H_2O_2 with **1**. The analysis of chromium to nitrogen ratios in the peroxo species revealed 1:(2.0 ± 0.05) and 1:(2.8 ± 0.2) for ethylenediamine and diethylenetriamine species, respectively. The X-ray structure of $OCr(O_2)_2(phen)$ has been reported,[12a] which reveals the binding of peroxo groups in an η^2 fashion in the equatorial plane and the oxo group in the apical position to afford pentagonal-bipyramidal geometry. Similar formulations may be assigned to the blue peroxo species obtained from Cr(IV) diperoxo complexes reacting with H_2O_2.

The stopped-flow spectrophotometric titration carried out for the reaction of $Cr(O_2)_2(en)(H_2O)$ revealed a Cr(IV):H_2O_2 stoichiometry of 1:(1.13 ± 0.05) for the first stage. When a chloroform extract of the blue species obtained from Cr(IV) peroxo derivatives was treated with an aqueous acidic solution at [H^+] = 0.02 M, aqua amine complexes, $Cr(H_2O)_4(en)^{3+}$ and $Cr(H_2O)_4(dienH)^{4+}$, as well as minor quantities of $Cr(H_2O)_6^{3+}$ (typically ~7%), could be obtained, which were identified by their characteristic electronic spectra after ion-exchange separations on a Dowex 50W-X2 bed.[18] The decomposition pattern of the blue intermediates seemed to indicate a weak dependence on [H^+].

It has been shown previously that in the acid decomposition of $Cr(O_2)_2(en)(H_2O)$ and $Cr(O_2)_2(dien)$, both aqua amine complexes and $Cr(H_2O)_6^{3+}$ in addition to $Cr_2O_7^{2-}$ are formed.[10] Under the [H^+] and [H_2O_2] conditions employed, the absence of any $Cr_2O_7^{2-}$ type products is as expected.

The competitive decay of Cr(IV) diperoxo complexes through both acid- and H_2O_2-assisted decomposition needs to be taken into account. The pseudo-first-order rate constants observed for the first stage, k_f, and k_f' have been listed in Supplementary Table I. The plots of k_f as a function of [H_2O_2] at various [H^+] conditions, are as shown in Figure 2. The intercepts of the linear lines in Figure 2 were in satisfactory agreement (±7%) with the acid decomposition rate constants reported earlier.[10] Similar results were obtained when k_f' was plotted against [H_2O_2] at various [H^+] conditions. Therefore, typically the first-stage decomposition rate, k_f, for the reaction of $Cr(O_2)_2(en)(H_2O)$, for example, can be treated as a sum of k_a and k_p, which represent the first-order rate constants for the acid- and peroxide-assisted decomposition processes, shown in eq 1 and 2, respectively.

Table I. Second-Order Rate Constants k_b for the Formation of Cr(VI) Diperoxo Complexes from $Cr(O_2)_2L$ and H_2O_2 at various [H^+] Conditions (T = 30 °C; I = 1.00 M ($NaClO_4$))

L	[H^+], M	k_b, M^{-1} s^{-1}	L	[H^+], M	k_b, M^{-1} s^{-1}
en	0.10	200 ± 15	dien	0.01	0.92 ± 0.02
	0.18	300 ± 15		0.02	0.96 ± 0.02
	0.25	420 ± 20		0.05	1.6 ± 0.10
	0.40	610 ± 25		0.10	3.1 ± 0.15
	0.60	910 ± 15		0.20	5.6 ± 0.25
				0.30	8.2 ± 0.4

$$Cr(O_2)_2(en)(H_2O) + H^+ \xrightarrow{k_a} \text{products} \quad (1)$$

$$Cr(O_2)_2(en)(H_2O) + H_2O_2 \xrightarrow{k_p} \text{products} \quad (2)$$

The products formed through eq 1 have been identified earlier to be $Cr(en)(H_2O)^{3+}$, Cr(VI), and $Cr(H_2O)_6^{3+}$,[10] whereas the final major product identified after the secondary reaction following eq 2 is $Cr(en)(H_2O)_4^{3+}$ with some minor quantities of $Cr(H_2O)_6^{3+}$. Since the values of k_a at any given [H^+] have been determined independently (in the absence of any added H_2O_2), the values of k_p can be determined as ($k_f - k_a$) and the bimolecular rate constants, k_b, for the H_2O_2-assisted reactions can be determined from the slopes of the linear lines shown in Figure 2. The second-order rate constants, k_b, for the H_2O_2-assisted pathways in the decompositions of $Cr(O_2)_2(en)(H_2O)$ of $Cr(O_2)_2(dien)$ are given in Table I. The reaction sequence given in eq 1 and 2 is further supported by the optical changes measured at 705 nm, where the products of the acid decomposition do not absorb. Typically at [H^+] = 0.40 M and [Cr(IV)] = 1 × 10^{-3} M, the optical charges observed at 705 nm are 0.43 ± 0.01 (average of three determinations). This amounts to ~90% of Cr(IV) reacting by the H_2O_2-assisted decomposition, and the kinetic data, viz. k_p/k_f ratios, are consistent with such an optical change.

The values of k_p for the reactions of both $Cr(O_2)_2(en)(H_2O)$ and $Cr(O_2)_2(dien)$ could be fitted to the general rate expression given in eq 3.

$$k_p = \frac{(k_1 + k_2K_H[H^+])[H_2O_2]}{1 + K_H[H^+]} \quad (3)$$

The rate law given in eq 3 implies that the second-order rate constants k_b (obtained as $k_p/[H_2O_2]$) exhibit a linear dependence on [H^+] with an intercept corresponding to k_1 and slope corresponding to k_2K_H, when $1 + K_H[H^+] \sim 1$. Typical plots of k_b against [H^+] for the reactions of Cr(IV) diperoxo derivatives are as shown in Figure 3.

The rate law given in eq 3 and the data given in Table I as well as Figure 3 may be treated in terms of the following reaction scheme (with water ligands being omitted for convenience) using $Cr(O_2)_2(en)(H_2O)$ as an example:

$$Cr(O_2)_2en + H^+ \overset{K_H}{\rightleftharpoons} Cr(O_2)(O_2H)en^+ \quad (4)$$

$$Cr(O_2)_2en + H_2O_2 \xrightarrow{k_1} Cr(O)(O_2)_2(en) + H_2O \quad (5)$$

$$Cr(O_2)(O_2H)en^+ + H_2O_2 \xrightarrow{k_2} Cr(O)(O_2)(O_2H)(en)^+ + H_2O \quad (6)$$

where k_1 and k_2 are the bimolecular rate constants for the reactions of un- and monoprotonated diperoxochromium(IV) derivatives with hydrogen peroxide and water in eq 5 and 6, the latter compounds being the reduction products of H_2O_2. The protonation behavior of Cr(IV) diperoxo derivatives under acidic conditions in the [H^+] range of 0.10–1.0 M has been shown, and the O_2^{2-}

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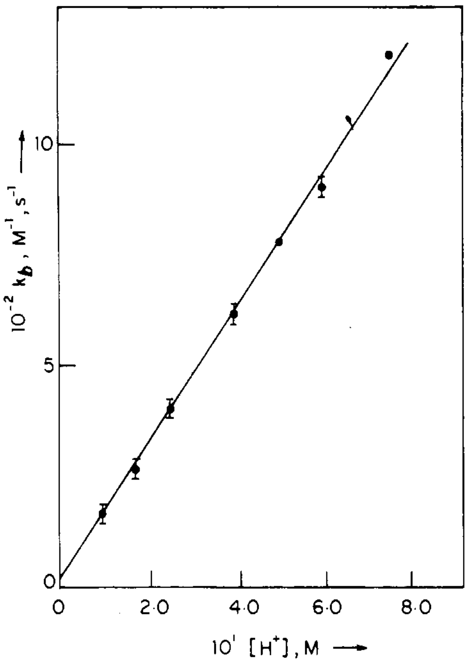

Figure 3. Dependence of the bimolecular rate constant, k_b, on [H^+] for the reaction of $Cr(O_2)_2(en)(H_2O)$ with H_2O_2.

Table II. Kinetic Parameters for the Formation of Chromium(VI) Diperoxo Complexes from $Cr(O_2)_2L$ and H_2O_2 (T = 30 °C; I = 1.00 M ($NaClO_4$))

	pathways		
L	k_1, M^{-1} s^{-1}	k_2K_H, M^{-2} s^{-1}	K_H,[a] M^{-1}
en	48 ± 6	1440 ± 50	(0.01)
dien	0.8 ± 0.1	25 ± 4	0.3 ± 0.1

[a] Estimated from the previous study[10] on the acid decomposition of $Cr^{IV}(O_2)_2L$ complexes.

ligands have been proposed as the sites of protonation. Proposals that peroxo groups are more probable sites of protonation than the oxo group in Cr(VI) products have also been made earlier.[6,19] The values of k_p at various [H^+] and [H_2O_2] conditions were fitted to eq 3 by using a IBM 370 computer.

The values of k_1 and k_2K_H as well as the estimates of K_H (obtained from an earlier study[10]) have been listed in Table II. It is evident that the protonated derivative of Cr(IV) reacted with H_2O_2 faster than the corresponding unprotonated analogue. It is of interest that the formation of the blue oxo diperoxo intermediate starting from Cr(VI) is reported to exhibit a first-order dependence on [H^+] and [H_2O_2]. The formation of an adduct between H_2CrO_4 and H_2O_2 and a two-step mechanism involving the rate-limiting formation of a monoperoxochromium(IV) intermediate were suggested.[3] A rate coefficient of 10^4 M^{-2} s^{-1} was reported for the H_2O_2–H_2CrO_4 system.[3] Although there is no change in the coordination number in the conversion of the Cr(IV) diperoxo system to the Cr(VI) oxo peroxo species, the reaction of Cr(IV) with H_2O_2 under comparable conditions was slower than the H_2O_2 reaction.

The second-order rate coefficient, k_1, for the reaction of H_2O_2 with $Cr(O_2)_2(en)(H_2O)$ leading to the formation of $OCr(O_2)_2(en)$ is 48 M^{-1} s^{-1}. This rate can be discussed in terms of both a 2e outer-sphere and an inner-sphere pathway in which the formation of an adduct between the Cr(IV) diperoxo system and H_2O_2 precedes the redox process.

It is known from the structural studies that $Cr^{IV}(O_2)_2(en)(H_2O)$ as well as $OCr^{VI}(O_2)(bpy)$ exhibits a pentagonal-bipyramidal arrangement of the ligand donor atoms. However, Cr^{IV}–OH_2 and $Cr^{VI}{=}O$ bond lengths reported are 2.04 ± 0.02 and 1.57 ± 0.02 Å, respectively. Similarly large nuclear changes are expected for the $H_2O_2 \rightarrow H_2O + O$ couple also. In other words, a 2e outer-sphere pathway for the H_2O_2 oxidation of the Cr(IV) derivatives may be associated with large reorganization barriers and slow rates. Hence, it is tempting to consider the alternative involving an inner-sphere mechanism and the formation of an adduct **3** as in eq 7–9.

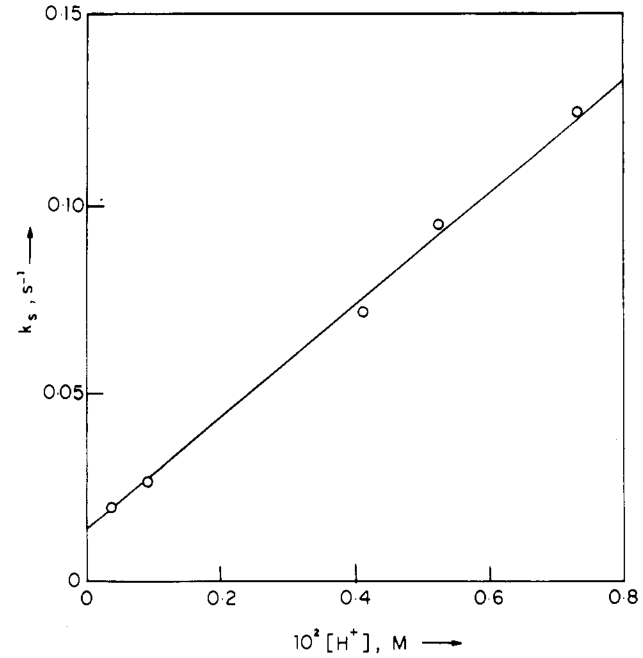

Figure 4. Dependence on [H^+] of the rate constant, k_s, observed for the second stage in the reaction of $Cr(O_2)_2(en)(H_2O)$ with H_2O_2.

$$Cr^{IV}(O_2)_2(en)(H_2O) \rightleftarrows Cr(O_2)_2(en) + H_2O \qquad (7)$$

$$Cr^{IV}(O_2)_2en + H_2O_2 \rightleftarrows \underset{\mathbf{3}}{Cr^{IV}(O_2)_2(en)\cdot H_2O_2} \qquad (8)$$

$$\mathbf{3} \rightarrow OCr^{VI}(O_2)_2(en) + H_2O \qquad (9)$$

The second-order rate coefficient, k_1, for the reaction of $Cr(O_2)_2(en)(H_2O)$, viz. 48 M^{-1} s^{-1}, is of the same order of magnitude as the rate of aqua ligand substitution in $Cr(O_2)_2(en)(H_2O)$ by I^-.[11a] A dissociative reaction model was suggested for the reaction of I^- with **1**.[11a]

If the reaction scheme in eq 7–9 were correct, the slower reactivity of the dien derivative when compared to that of the ethylenediamine analogue is more easily rationalized on the basis of the arguments that **3** would be less readily formed when a tridentate ligand such as diethylenetriamine is coordinated.[20] The protonation of complexes **1** and **2** leads to marked differences in the reactivities of Cr(IV) diperoxo complexes. Factors such as differences in mechanisms, as well as changes in reorganizational barriers and the driving force involved in the reaction, may account for the differernces in k_1 and k_2 paths. The protonation of a coordinated peroxide ligand in Cr(IV) complexes may well render the ligand unidentate and thereby enable easier formation of Cr(IV)–H_2O_2 adducts. However, it is difficult to discuss and analyze quantitatively the reasons for the nearly 3 orders of magnitude differences in the values of k_1 and k_2 for both Cr(IV) diperoxo systems on the basis of available kinetic data. Similarly,

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(19) Tanaka and co-workers[3] have formulated $HCr(O)(O_2)_2$ as $Cr(OH)(O_2)_2^+$. On the other hand, Quilitzsch and Wieghardt[6] proposed the $V(O)(O_2)(OOH)L$ formulation at [H^+] = 0.01 M. In the case of $Cr^{IV}(O_2)_2L$ type complexes, however, there is little doubt[10] that O_2^{2-} is the protonating site.

(20) An associative mode of substitution of the aquo ligand by H_2O_2 may well be visualized in place of eq 7 and 8. Since in the final product chromium is assigned a formal oxidation state of VI, it is necessary to discuss the overall redox process in terms of an inner-sphere pathway involving intermediates such as **3** or an outer-sphere mechanism. In view of the large reorganizational components associated with the Cr^{IV}—OH_2 and $Cr^{VI}{=}O$ bonds, the inner-sphere pathway has been favored in our treatment. However, the need to invoke the intermediacy of **3** may be overcome by considering a transition state of closely related structure.

a fundamental point of interest in this study is the identification of the origin of the oxo ligand in the Cr(VI) oxo diperoxo products. Direct experimental evidence for a possible oxygen atom transfer from H_2O_2 could have been obtained by reacting Cr(IV) with labeled H_2O_2. Experimental difficulties arising from the secondary reaction of $OCr(O_2)_2L$ type complexes precluded such labeling studies.

The decomposition of oxodiperoxochromium(VI) generated by the reaction of H_2CrO_4 and H_2O_2 has already been investigated.[3] The decomposition of $OCr(O_2)_2(en)$ has been studied, and the kinetic data are presented in Supplementary Table II, which in turn shows that whereas the pseudo-first-order rate constants, k_s, are independent of $[H_2O_2]$, they exhibit a zero- as well as a first-order dependence on $[H^+]$ as seen in Figure 4. These data are consistent with the second stage in the Cr(IV)–H_2O_2 reaction corresponding to an acid-assisted self-decomposition of the blue oxodiperoxochromium(VI) complexes rather than any bimolecular process involving H_2O_2. A wide variety of mechanistic pathways involving the formation of $OCr^V(O_2)_2L^+$, $OCr^{IV}(O_2)L$, $OCr^{III}L^+$, O_2^-, and O_2H intermediates can be visualized. Due to the complicated nature of the system, unambiguous identification of the nature of intermediates formed, if any, during the decomposition of $OCr^{VI}(O_2)L$ type complexes to Cr(III) products appears difficult. Previous studies on analogous Cr(VI) diperoxo systems seem to suggest that Cr(V) intermediates with sufficient lifetime for detection of ESR may not be formed.[3] Our data on the second-stage kinetics are not inconsistent with the either of the two mechanistic pathways discussed by earlier workers in cases of related complexes.[3]

In summary, the results of this study show that the H_2O_2 reaction with $Cr^{IV}(O_2)_2L$ affords blue $Cr(O)(O_2)_2L$ intermediates through possibly an inner-sphere pathway involving $Cr^{IV}(O_2)_2\text{-}L\cdot H_2O_2$ type adducts, which later decompose to Cr(III) products.

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Supplementary Material Available: Listings of kinetic data (4 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Stanford University, Stanford, California 94305

Coordination Chemistry and Redox Properties of Polypyridyl Complexes of Vanadium(II)

John C. Dobson and Henry Taube*

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Polypyridyl vanadium(II) complexes of the type $[V^{II}(trpy)(bpy)(L)]^{n+}$ (trpy = 2,2′:6′,2″-terpyridine; bpy = 2,2′-bipyridine; L = Cl, H_2O, CH_3CN) have been synthesized and characterized by a combination of elemental analyses, FAB mass spectroscopy, cyclic voltammetry, and UV-vis spectroscopy. The substitution chemistry and redox properties of the ions were investigated by cyclic voltammetry. The $E_{1/2}$ values of the V(III/II) couples have been compared to those of the structurally equivalent ions of Ru(II) and Os(II) to assess the extent of π-back-bonding in d^3 V(II) systems. The reactivity of the V(II) ions toward dioxygen and CO_2 is discussed in terms of the development of redox catalysts for the activation of small molecules.

Introduction

The development of the coordination chemistry of vanadium(II) has been hindered by the susceptibility of the V(II) species to oxidation. As the techniques for manipulating air-sensitive complexes have become more commonplace, the number of synthetic routes to complexes other than the aqua ions and tris chelate complexes of vanadium(II) has gradually increased.[1] Di- and trivalent complexes of vanadium are of increasing interest because of their potential applications in the reversible binding of dioxygen,[2] multielectron redox catalysis,[3] and modeling of intermediates formed in the hydrodesulfurization of crude oils.[4]

Our interest in low-valent vanadium chemistry dates back two decades when it was discovered in our laboratories[5] that V(II) complexes, when acting as 1e reductants, differ from other structurally analogous first-row M(II) polypyridyl complexes. For $[V^{II}(bpy)_3]^{2+}$ and $[V^{II}(trpy)_2]^{2+}$ (bpy = 2,2′-bipyridine; trpy = 2,2′:6′,2″-terpyridine) it was shown that upon oxidation to V(III) in aqueous solution the coordination sphere is in every instance disrupted and that the V(III) species formed is unstable with respect to oxidation to V(IV). An estimate of $E°$ for the $[V(bpy)_3]^{3+/2+}$ couple was made on the basis of the Marcus cross-relation theory. Since that time, Saji and Aoyagui have reported[6] polarographic data for $[V^{II}(bpy)_3]^{2+}$ and, more recently, Shah and Maverick have reported the results of cyclic voltammetric studies.[3a,c] However, redox potential data for complexes of V(II) remain extremely limited.[7] Herein we report the results we have obtained in a study of coordination and redox chemistry of polypyridyl complexes of V(II) containing a single labile coordination site, i.e. $[V^{II}(trpy)(bpy)(L)]^{n+}$. Of special interest to us are substitution processes that leave much of the coordination sphere intact and any evidence to be obtained on the extent of π-back-bonding in d^3 V(II) systems. We hope to compare the results with the wealth of information known for d^6 systems. In addition, it was hoped that the reactivity of the complexes with dioxygen would be amenable to detailed kinetic and mechanistic investigation. The reactivity to dioxygen of divalent complexes of the first-row metals (Cr^{II}, Fe^{II}, Co^{II}) has been studied extensively,[8] but considerably less is known about kinetics and mechanism of dioxygen reactivity with V(II).[2d] In an equally important but opposite sense is the potential reactivity of the low-valent V(I) and V(0) species, which, in principle, can be generated by chemical or electrochemical

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