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Articles

Novel Pathways in the Reactions of Superoxometal Complexes

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The reaction of a 1:1 mixture of $(H_2O)_5Cr(^{16}O_2)^{2+}$ and $(H_2O)_5Cr(^{18}O_2)^{2+}$ at pH 1 did not yield measurable amounts of $^{16}O^{18}O$. This result rules out a Russell-type mechanism ($2(H_2O)_5CrO_2^{2+} \rightarrow 2(H_2O)_5CrO^{2+} + O_2$) for the bimolecular decomposition reaction. Evidence is presented in support of unimolecular (S_H1) and bimolecular (S_H2) homolyses as initial steps in the decomposition of $(H_2O)_5CrO_2^{2+}$ in strongly acidic solutions (pH ≤ 1). In the pH range 4−5, $(H_2O)_5CrO_2^{2+}$ undergoes hydrolysis-induced disproportionation to $(H_2O)_5CrO_2H^{2+}$, $Cr(H_2O)_6^{3+}$ and O_2. The first step produces $HO_2^{\bullet}/O_2^{\bullet -}$, which in further reaction with $(H_2O)_5CrO_2^{2+}$ yields the observed products.

Introduction

Superoxometal complexes, MO_2, are frequent intermediates in reactions involving dioxygen and transition metals in environments ranging from biological systems to industrial catalytic oxidations.[1−7] These complexes undergo a variety of reactions depending on the ligand environment and the presence of suitable substrates. Examples include hydrogen atom abstraction reactions,[8−10] chemical or electrochemical reduction to the corresponding metal hydroperoxides[11−15] or dimetallic peroxides,[16,17] oxidative homolysis,[18] and hydrolysis to $O_2^{\bullet -}$ and M^+.[19]

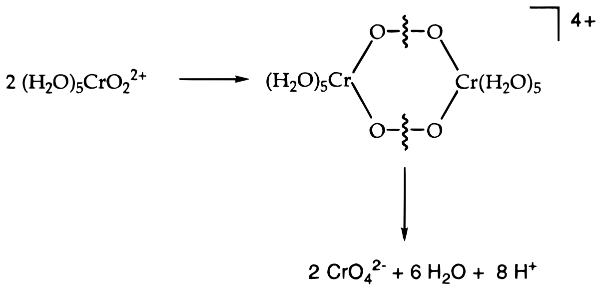
In the absence of reactive substrates, the complexes MO_2 usually decompose by homolysis (S_H1) of the metal−dioxygen bond, followed by the reaction between M and MO_2, eqs 1 and 2, to yield the dimetallic peroxide MO_2M,[16,17] which can be a long-lived, isolable species,[20] or a short-lived transient.[21]

$$M + O_2 \rightleftarrows MO_2 \qquad (1)$$

$$M + MO_2 \rightleftarrows MO_2M \rightarrow \text{products} \qquad (2)$$

In contrast to their nonmetallic analogs, alkylperoxyl ($RO_2^{\bullet}$)[22,23] and hydroperoxyl ($HO_2^{\bullet}$)[24] radicals, the superoxometal complexes usually do not react in bimolecular self-reactions. In some cases this may be partly due to the low concentrations of MO_2 generated, so that reactions with substrates prevail. However, the reactivity of MO_2 in bimolecular self-reactions seems to be inherently low, and our earlier report on the second-order transformation of $(H_2O)_5CrO_2^{2+}$ (hereafter CrO_2^{2+}) into (mostly) chromate[25] in acidic aqueous solutions still appears to be the only example of such reactivity.

In an earlier work,[25] we proposed that the reaction proceeds through a cyclic transition state or intermediate, as shown in eq 3.



(3)

In a parallel reaction, CrO_2^{2+} undergoes unimolecular homolysis, followed by the reaction between Cr^{2+} and CrO_2^{2+}, eqs 4 and 5. This path has been analyzed in detail previously.[25,26]

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$$CrO_2^{2+} \rightleftarrows Cr^{2+} + O_2 \qquad (4)$$

$$Cr^{2+} + CrO_2^{2+} \rightarrow [CrOOCr^{4+}] \rightarrow nCrO^{2+} \xrightarrow{Cr^{2+}} \text{Cr(III) products} \qquad (5)$$

Recently we have shown that the lifetime of CrO_2^{2+} increases substantially in the presence of alcohols.[2] This effect was traced to the involvement of CrO^{2+} as an intermediate in reaction 5. The reduction of CrO^{2+} to Cr^{2+} by the alcohol and the capture of Cr^{2+} by O_2 then regenerate CrO_2^{2+}, reactions 6 and 4.[26]

$$CrO^{2+} + CH_3OH \rightarrow Cr^{2+} + CH_2O \qquad (6)$$

We found that alcohols also slow down the bimolecular path, indicating that CrO^{2+} is involved in this process too. Our original reaction scheme, eq 3, does not account for this observation. In this paper we reexamine the mechanism of the bimolecular self-reaction of CrO_2^{2+} in acidic aqueous solution. In addition, we present evidence that the decomposition of CrO_2^{2+} in the pH range 4−5 proceeds by a novel mechanistic pathway.

Experimental Section

Solutions of CrO_2^{2+} were prepared by injecting small amounts of Cr^{2+} into an ice-cold, O_2-saturated, acidic aqueous solution containing 0.3 M MeOH (experiments at pH 1) or 0.6 M 2-PrOH (pH 4−5). The same procedure was used in the preparation of $Cr(^{18}O_2)^{2+}$ from Cr^{2+} and $^{18}O_2$ (97%, Matheson).

For the determination of $O^{16}O^{18}$ as a possible product of the bimolecular decomposition of superoxochromium ion, 10 mL of 0.28 mM $Cr(^{16}O_2)^{2+}$ and 10 mL of 0.29 mM $Cr(^{18}O_2)^{2+}$ (each saturated with the appropriate isotope of O_2 and containing 0.1 M $HClO_4$, 0.9 M $LiClO_4$, and 0.3 M 2-PrOH) were injected into an argon-filled, septum-sealed 20 mL Erlenmeyer flask. The flask was filled almost to capacity (head space <2 mL) and most of the argon was vented through an outlet needle. The reaction temperature was kept at 0 °C (ice−water bath) until ∼75% of superoxochromium had decomposed (9 h). The solution was then stirred on a magnetic stirrer for 30 min to ensure the equilibration of dioxygen between the gas phase and the solution phase. The analysis of the gas was carried out by GC-MS (Finnigan 4500 equipped with a 1 μ DB-1 column, operated at 100 °C).

The decomposition of CrO_2^{2+} in the pH range 4−5 was initiated by mixing a solution of CrO_2^{2+} (pH 3) with an O_2- or air-saturated buffer (formate or acetate) solution. The ionic strength was adjusted at 9.0 mM with sodium acetate or formate, and the desired pH was achieved by the addition of the required amounts of formic or acetic acid. All the experiments had 0.6 M 2-PrOH and 0.42−1.26 mM O_2. The reaction was conducted at 25 °C and monitored at a maximum in the spectrum of CrO_2^{2+} (290 nm, $\epsilon = 3000$ M^{-1} cm^{-1}). Occasionally, the kinetics were monitored at the 350 nm maximum of chromate. Within standard error, identical rate constants were obtained at the two wavelengths. At a given pH, the kinetics were independent of the nature of the buffer (formate or acetate). Depending on the reaction rate, either a Shimadzu 3101 PC or an Applied Photophysics DX-17MV stopped flow spectrophotometer was employed in the kinetic measurements.

In the decomposition of CrO_2^{2+} at pH 4.5, hydrogen peroxide was detected and quantified iodometrically. Measured amounts of $HClO_4$ and NaI were added to the reaction solution, and the absorbance increase at 350 nm ($\epsilon(I_3^-) = 26\,000$ M^{-1} cm^{-1}) was recorded as a function of time. The kinetics unequivocally identified H_2O_2 as the oxidant in this reaction. The yield of H_2O_2 was calculated from the absorbance change during the kinetic process.

Molecular O_2 was determined by use of an O_2-sensitive electrode (YSI Model 5300 biological oxygen monitor equipped with a Model 5331 oxygen probe).

Results and Discussion

Second-Order Decomposition of CrO_2^{2+} at pH 1. Having ruled out the mechanism of eq 3, we considered[2] several other mechanistic options. Any plausible mechanism has to involve CrO^{2+} as an intermediate to explain the inhibiting effect of alcohols on the decomposition rate and the formation of chromate.

The disproportionation of the coordinated superoxide, eq 7, may be feasible, $10^1 > K_7 > 10^{-6}$,[2] especially because the rapid dissociation of O_2 from CrO_2^{3+}, eq 8, would make the reaction irreversible. The decomposition of the other product, CrO_2H^{2+}, would account for the observed formation of chromate.[27] This scheme has to be ruled out, however, because it does not involve CrO^{2+} and cannot explain the alcohol effect.

$$2CrO_2^{2+} \overset{H^+}{\rightleftarrows} CrO_2^{3+} + CrO_2H^{2+} \qquad (7)$$

$$CrO_2^{3+} \rightarrow Cr^{3+} + O_2 \qquad (8)^{18}$$

The next possibility[2] is shown in eq 9, which was written in analogy with the well-established Russell mechanism for the self-reaction of alkylperoxyl radicals, eq 10.[22,23,28]

$$2CrO_2^{2+} \rightarrow [CrOOOOCr]^{4+} \rightarrow 2CrO^{2+} + O_2 \qquad (9)$$

$$2RO_2^{\bullet} \rightarrow [ROOOOR] \rightarrow 2RO^{\bullet} + O_2 \qquad (10)$$

This mechanism is fully consistent with all the experimental data available so far. However, it did not pass the isotopic labeling test, as described below.

According to the mechanism of eq 9, a mixture of $Cr(^{16}O_2)^{2+}$ and $Cr(^{18}O_2)^{2+}$ should yield a statistical mixture of $^{16}O_2$, $^{18}O_2$, and $^{16}O^{18}O$. The reaction was carried out as described in the Experimental Section. The conditions (low temperature, high ionic strength, and the presence of 2-PrOH and O_2) were adjusted to maximize the second-order path and to slow down the S_H1 reaction of eq 4−5.[25]

At ∼75% completion, the signal at $m/e = 34$ ($^{16}O^{18}O$) was 0.8% of the sum of the signals corresponding to $^{16}O_2$ and $^{18}O_2$. This amount, corresponding to 10 μM $^{16}O^{18}O$ in solution, is identical to that obtained on a 1:1 mixture of $^{16}O_2$ and $^{18}O_2$ that had never been in contact with chromium. A 20% increase in $m/e = 34$ over the background would have been detected. Thus the concentration of $^{16}O^{18}O$ produced in the reaction is ≤ 2 μM.

On the basis of the activation parameters for the two decomposition pathways, we calculate that >90% of the reaction at 0 °C takes place by the bimolecular route. If the mechanism of eq 9 applies, ∼50 μM $^{16}O^{18}O$ should have been produced. This value reflects the fact that the reaction was only 75% complete, and that only 50% of the O_2 produced would appear in the mixed isomer form (*m/e* 34). Moreover, significant amounts of CrO^{2+}, produced in reaction 9, should be recycled to CrO_2^{2+}, eqs 6 and 4, and yield more $^{16}O^{18}O$. Judging by the effect of alcohols on the lifetime of CrO_2^{2+}, the recycling of different chromium species may increase the total yield of $^{16}O^{18}O$ severalfold. Even if this effect is ignored, the amount found experimentally is less than 4% of that calculated and clearly rules out reaction 9 as a significant reaction path.

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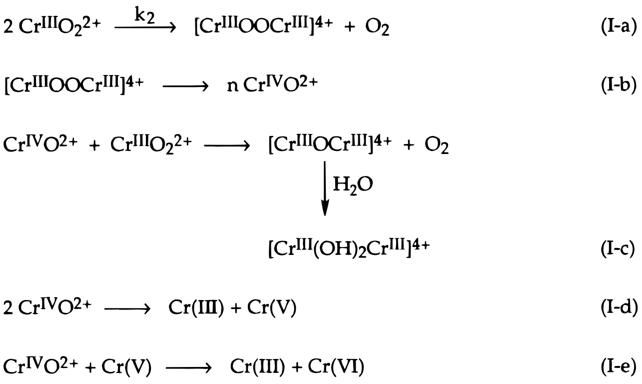
Scheme 1



The mechanism proposed in Scheme 1 accommodates all the observations, including second-order kinetics, involvement of CrO^{2+}, formation of chromate and O_2, reduced yields of chromate in the presence of alcohols, and the failure to detect $O^{16}O^{18}$ in labeling experiments.

The CrO^{2+} ion is converted back to CrO_2^{2+} when alcohols and O_2 are present, eqs 6 and 4, as already mentioned. Also, the yield of chromate is lower in alcohol-containing solutions, because reaction 6 reduces the steady-state concentration of CrO^{2+}, making the bimolecular reaction I-d less favorable than the Cr(III)-producing reaction I-c.

The bimolecular homolytic displacement reaction (S_H2), eq I-a, eventually produces CrO^{2+} and O_2. Such a reaction of a superoxometal complex has not been reported before, but all the available data[20] indicate that the positions trans to the superoxo and peroxo ligands are labile, making reaction I-a feasible. As commented earlier,[2] the superoxo- and alkylchromium complexes have many features in common. S_H2 reactions of CrR^{2+} (R = alkyl) have been well documented,[29,30] and similar reactivity of CrO_2^{2+} in reaction I-a is reasonable.[31] The same is true for the other S_H2 reaction in Scheme 1, eq I-c, which appears to be important only at very low steady-state concentrations of CrO^{2+}, i.e. when reaction I-d is slow. In effect, reactions I-a and I-c are inner-sphere oxidations of CrO_2^{2+} to Cr(III) and O_2. Such oxidations by an outer sphere mechanism have been reported recently.[18]

The peroxodichromium intermediate, $CrOOCr^{4+}$, produced in reaction I-a is identical to that formed in the S_H1 route of eqs 4 and 5.[25] This species has not been observed in the course of the decomposition of CrO_2^{2+}, but such intermediates are common in transition metal−dioxygen chemistry.[20] The $CrOOCr^{4+}$ ion is converted to CrO^{2+}, either spontaneously or in a redox reaction with Cr^{2+}. This chemistry is similar to the autoxidation of chromium porphyrins to Cr(IV) products.[32−34]

A species identified as $CrOOCr^{4+}$ has been prepared independently.[35] It survives in solution for several minutes and by itself does not yield CrO^{2+}. However, Cr^{2+} successfully reduces $CrOOCr^{4+}$ to CrO^{2+}, probably as shown in eq 11.[26]

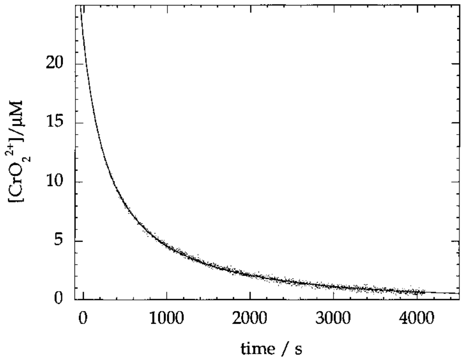


Figure 1. Kinetic trace at 290 nm and the fitted curve (eq 13) for the decay of CrO_2^{2+} (20 μM) at pH 4 (acetate buffer) and 9 mM ionic strength (sodium acetate) in the presence of 0.6 M 2-PrOH, $T = 25.0 \pm 0.2$ °C.

$$CrOOCr^{4+} + Cr^{2+} \rightarrow CrOCr^{4+} + CrO^{2+} + H_2O \quad (11)$$

The fact that the bimolecular path produces CrO^{2+} even when steady-state concentrations of Cr^{2+} are too small for reaction 11 to operate leads us to conclude that either reaction I-a yields CrO^{2+} directly, or there are other, as yet unidentified reactions that convert $CrOOCr^{4+}$ to CrO^{2+}. For this reason the stoichiometric factor n in eq 5 and I-b remains undefined.

The rest of the chemistry in Scheme 1 has been discussed already in the context of the S_H1 path.[2,25,26] It is worth noting that the two pathways for the decomposition of CrO_2^{2+} involve all the same intermediates, except for Cr^{2+}, which is produced only in the S_H1 path.[25] The greater the contribution of this path to the overall reaction, the greater the steady-state concentrations of Cr^{2+} and therefore the larger the amount of the reduced product, Cr(III), relative to Cr(VI).

Decomposition of CrO_2^{2+} at pH 4−5. The lowering of [H$^+$] to <0.05 M accelerates the decay of CrO_2^{2+} to Cr(III) and Cr(VI). At pH > 4 and 1 M ionic strength, the decomposition is completed in several minutes, even in the presence of alcohols.

The kinetic data in the presence of 0.6 M 2-PrOH obeyed the mixed first- and second-order rate law of eq 12, and were fitted to eq 13. Figure 1 shows an experimental trace and the fitted curve at pH 4.

$$-d[CrO_2^{2+}]/dt = 2k_{hydr}[CrO_2^{2+}] + 2k_2[CrO_2^{2+}]^2 \quad (12)$$

$$[CrO_2^{2+}]_t = \frac{k_{hydr}[A]_o}{e^{2k_{hydr}t}(k_{hydr} + k_2[A]_o) - k_2[A]_o} \quad (13)$$

The rate constants k_{hydr} and k_2 are both proportional to 1/[H$^+$], Figure 2, and are independent of the concentration of O_2. The linear least-squares fits to the data in Figure 2 yielded $k_{hydr}/s^{-1} = (4.6 \pm 0.2) \times 10^{-8}/[H^+]$, and $k_2/M^{-1}\ s^{-1} = (50 \pm 20) + (2.5 \pm 0.3) \times 10^{-3}/[H^+]$. The positive intercept in the k_2 plot probably results from the uncertainties in the concentration of CrO_2^{2+}. One of the reaction products, CrO_4^{2-}, absorbs at 290 nm, $\epsilon = 2000\ M^{-1}\ cm^{-1}$ at pH 4−5. The yields of CrO_4^{2-} were typically ∼20%, but varied somewhat with $[CrO_2^{2+}]_0$ and pH. An average $\Delta\epsilon_{290}$ of 2500 $M^{-1}\ cm^{-1}$ was used in all the calculations, where $\Delta\epsilon_{290}$ is the difference in molar absorptivities between the reactants and products at 290 nm. The intercept in Figure 2b is several times larger than the value of k_2 (6 ± 3 $M^{-1}\ s^{-1}$) derived from the measurements at pH 1.[25]

The inverse [H$^+$]-dependence of k_2 can be accounted for by reactions 14 and 15, so that $k_2 = K_{14}k_{15}/[H^+]$. The acidity constant of $(H_2O)_5CrO_2^{2+}$, K_{14}, has not been determined, but for the labile *trans*-H_2O it is reasonable to expect a value

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[31] The formation of $CrOOCr^{4+}$ by disproportionation of CrO_2^{2+} has been considered, and rejected, previously.[25] The ion $CrOOCr^{4+}$ was at that time believed to be an exclusive intermediate on the way to Cr(III). It is now clear that the two pathways have common intermediates.

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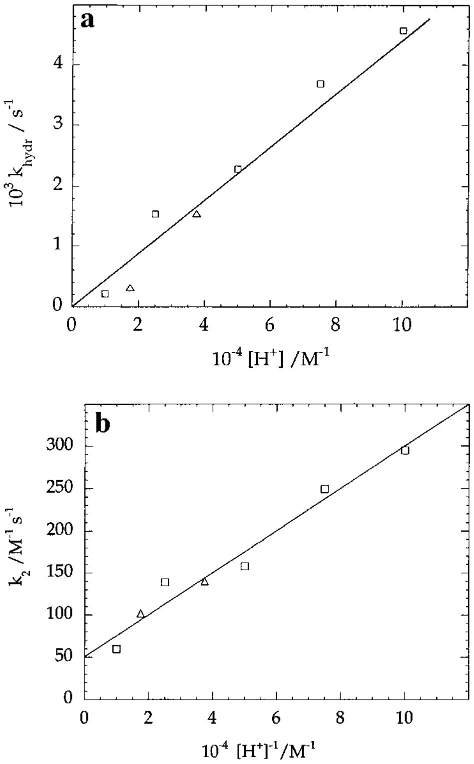

Figure 2. Plot of the rate constants k_1 (a) and k_2 (b) against the reciprocal of $[H^+]$ in solutions buffered with acetate (squares) or formate (triangles) at 25 °C and 9 mM ionic strength adjusted with sodium acetate or formate. Conditions: $[CrO_2^{2+}]_0 = 10-22\ \mu M$; [2-PrOH] = 0.6 M.

smaller than 10^{-5} M. The chemistry of $(H_2O)_4(OH)CrOOCr(H_2O)_5^{3+}$, formed in reaction 15, is expected to parallel that of the protonated form, $CrOOCr^{4+}$, shown in Scheme 1. The acid dependence arises from the stabilizing effect of coordinated hydroxide on the Cr(III) state in the dimeric peroxo species, and on the intermediate 4+ and 5+ oxidation states in Scheme 1.

$$(H_2O)_5CrO_2^{2+} \rightleftarrows (H_2O)_4(OH)CrO_2^{+} + H^+ \qquad (14)$$

$$(H_2O)_4(OH)CrO_2^{+} + (H_2O)_5CrO_2^{2+} \rightarrow (H_2O)_4(OH)CrOOCr(H_2O)_5^{3+} + O_2 \qquad (15)$$

Hydrolysis-Induced Disproportionation of CrO_2^{2+}. The first-order path at pH 1 has been established to take place by an S_H1 mechanism.[25] It appears unreasonable that this path would be accelerated by an increase in pH. Previous examples have shown that the deprotonation of superoxometal complexes stabilizes the higher oxidation state of the metal and **inhibits** homolysis.[36,37] In support of this argument, the first-order path at pH 4−5 is independent of $[O_2]$ and therefore clearly not the homolysis.

We consider a heterolytic dissociation of CrO_2^{2+} to Cr(III) and $HO_2^{\bullet}/O_2^{\bullet -}$, eqs 16 and 17, as a more probable reaction.

$$(HO)CrO_2^{+} \rightarrow (HO)Cr^{2+} + O_2^{\bullet -} \qquad (16)$$

$$HO_2^{\bullet} \rightleftarrows H^+ + O_2^{\bullet -} \qquad pK_a = 4.69^{38} \qquad (17)$$

The experimental detection of superoxide would provide a strong support for reaction 16. Experiments conducted in the presence of tetranitromethane as a scavenger for $O_2^{\bullet -}$, eq 18, were inconclusive, because the strongly absorbing $C(NO_2)_3^-$ ($\epsilon_{350} = 1.4 \times 10^4\ M^{-1}\ cm^{-1}$) was produced over a period of several minutes at pH 5 even in the absence of chromium.

$$C(NO_2)_4 + O_2^{\bullet -} \rightarrow C(NO_2)_3^- + NO_2 + O_2 \qquad (18)$$

The superoxide ion, produced in eq 16, will either disproportionate, eq 19, or react with CrO_2^{2+}, possibly yielding CrO_2H^{2+} and O_2, eq 20. The CrO_2H^{2+} ion eventually dissociates to H_2O_2 and Cr^{3+}, eq 21.[27]

$$2\ O_2^{\bullet -} \xrightarrow{2H^+} H_2O_2 + O_2 \qquad (19)$$

$$HO_2^{\bullet} + CrO_2^{2+} \rightarrow CrO_2H^{2+} + O_2 \qquad (20)$$

$$CrO_2H^{2+} + H^+ \rightarrow H_2O_2 + Cr^{3+} \qquad (21)$$

The formation of CrO_2H^{2+} in the course of the reaction at pH 4.5 was confirmed. The decomposition of CrO_2^{2+} (22 μM) was allowed to proceed to 90% completion (15 min). At this point a small amount of Ce(IV) was injected giving [Ce(IV)] = 50 μM. The UV spectrum showed an immediate recovery of ~30% of CrO_2^{2+} by the known chemistry in eq 22. This test is believed to be specific for CrO_2H^{2+}, because no other chromium species has been found to be oxidized by Ce(IV) to CrO_2^{2+}. The less than quantitative recovery is consistent with the fact that only a fraction of the reaction proceeds as in eq 16, and that some hydrolysis of CrO_2H^{2+}, eq 21, takes place during the course of the reaction.

$$CrO_2H^{2+} + Ce(IV) \rightarrow CrO_2^{2+} + Ce(III) + H^+ \qquad (22)$$

The total yield of H_2O_2 was determined in an independent experiment after all of the CrO_2^{2+} (initial concentration 22 μM) and CrO_2H^{2+} had decomposed. The concentration of H_2O_2 was found to be 6 μM, i.e. 27% of $[CrO_2^{2+}]_0$, in good agreement with the 6.6 μM expected on the basis of eqs 16 and 19−21, and Scheme 1. The experimentally found $[CrO_4^{2-}]$, 4 μM, is somewhat greater than the calculated amount, 3 μM, but acceptable in view of the complicated reaction scheme.

Reactions 16 and 20 provide a mechanism for disproportionation of CrO_2^{2+}. The kinetics are first-order because the process is initiated by hydrolysis, followed by a rapid loss of the second mole of CrO_2^{2+}, according to the rate law of eq 23.

$$-d[CrO_2^{2+}]/dt = 2k_{hydr}\,[CrO_2^{2+}]/[H^+] = 2K_{14}k_{16}[CrO_2^{2+}]_T/[H^+] \qquad (23)$$

The stoichiometric factor of 2 and the involvement of $HO_2^{\bullet}/O_2^{\bullet -}$ in the disappearance of the second mole of CrO_2^{2+} are strongly supported by the effect of Cu^{2+}, a good scavenger for $HO_2^{\bullet}/O_2^{\bullet -}$.[24] In the presence of 0.1−1 mM Cu^{2+}, the rate constant k_{hydr} for the disappearance of CrO_2^{2+} at pH 4.0 decreased by a factor of 1.7, from $3.9 \times 10^{-4}\ s^{-1}$ to $2.2 \times 10^{-4}\ s^{-1}$. This decrease is close to the expected factor of 2, and strongly supports the mechanism of eqs 16 and 19−21. By use of $k = 1 \times 10^9\ M^{-1}\ s^{-1}$ for the reaction of Cu^{2+} with $HO_2^{\bullet}/O_2^{\bullet -}$ at pH 4.0,[39] we estimate that $HO_2^{\bullet}/O_2^{\bullet -}$ reacts with CrO_2^{2+} with $k_{20} \le 5 \times 10^8\ M^{-1}\ s^{-1}$ at pH 4.0.

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Reaction 20 also requires that O_2 be produced. This was confirmed experimentally, but this test is not mechanism-specific, because the parallel S_H2 reaction also produces O_2. The S_H1 reaction is too slow at pH 4−5 to produce measurable amounts of O_2.

Conclusions

A detailed picture for the decomposition of CrO_2^{2+} has evolved. In strongly acidic solutions the reaction proceeds in two parallel pathways, acid-independent unimolecular homolysis, and $1/[H^+]$-catalyzed bimolecular homolysis of the Cr−O_2 bond. The two pathways involve identical intermediates, with the exception of Cr^{2+}, which is produced only in the S_H1 reaction. In the pH range 4−5, the hydrolysis of CrO_2^{2+} produces $HO_2^•/O_2^{•-}$ and Cr(III). In a rapid follow-up step, $HO_2^•$ reacts with another equivalent of CrO_2^{2+} to yield CrO_2H^{2+} and O_2, in effect resulting in disproportionation of CrO_2^{2+}. The yields of the two final products, Cr(III) and Cr(VI), depend onthe reaction conditions, which affect directly the importance of each of the three paths.

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