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# Kinetics of the Oxidation of Chromium(II) by Hydrogen Peroxide. Effect of Different Anions, Temperature, and Pressure

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The oxidation kinetics of aquated Cr(II) by $H_2O_2$ is accelerated by a factor of 2–5 in the presence of organic and inorganic anions. The reaction was studied in detail as a function of anion concentration, temperature, and pressure for nine different anions. The kinetic data exhibit saturation behavior at high anion concentration, which can be assigned to the formation of a 1:1 complex of the type $Cr^{II}(H_2O)_5(An)^+$. The rate and activation parameters are in line with an inner-sphere electron-transfer mechanism, in which both the inner-sphere complex formation and the electron-transfer rate constants are affected by the presence of the anion in the coordination sphere of Cr(II). Trans-labilization effects and the increased electron density on the metal center are suggested to account for the accelerating effect of the investigated anions.

## Introduction

In a number of recent studies performed in our laboratories, a systematic study of the effect of different organic and inorganic oxy anions on the kinetics of the formation and heterolysis reactions of organochromium(III) species was undertaken.[1–4] In these studies the formation of the chromium–carbon $\sigma$ bond was studied using pulse-radiolysis techniques,[5] whereas the heterolysis of this bond was studied using stopped-flow techniques. Both processes were found to exhibit a characteristic dependence on the presence of oxy anions. Activation parameters, determined from the temperature and pressure dependence of these reactions as a function of the anion concentration, were used to resolve the intimate nature of the mechanisms that would account for the observed anion dependencies. The accelerating effect of anions on the heterolysis reactions (see refs 1 and 2 and literature cited therein) was accounted for in terms of a trans-labilization effect of the coordinated anions on the Cr(III) center. The decelerating effect of acetate ions on the formation of the chromium–carbon bond[4] was accounted for in terms of the formation of a dimeric Cr(II) species in the presence of acetate, viz. $[Cr(H_2O)(Ac)_2]_2$.[6–8]

The oxidation of Cr(II) by $H_2O_2$ has not been studied in the presence of oxy anions before.[9] In the light of the work referred to above, and the general interest in the production of •OH radicals according to the modified Fenton reaction, we have undertaken a systematic kinetic study of the oxidation reaction in the presence of a series of anions. In addition we have also studied the temperature and pressure dependence of the oxidation process and report here the associated activation parameters. The oxidation of Cr(II) by $H_2O_2$ is the rate-determining step in the reaction sequence shown in (1), where $k_1 = 7.1 \times 10^4$,[9] $k_2 > 8 \times 10^8$,[10] and $k_3 \approx (5\text{–}10) \times 10^7\ M^{-1}\ s^{-1}$ at 25 °C. It follows that the reaction of Cr(II) with $H_2O_2$ is ca. $10^4$ times slower than the reaction with the alkyl radical •R to produce $Cr\text{–}R^{2+}$. The organochromium(III) species are characterized by absorption bands around 300 and 400 nm, which enable a kinetic analysis of the rate-determining oxidation process.

$$\begin{gathered}
\mathrm{Cr(H_2O)_6^{2+} + H_2O_2 \xrightarrow{k_1} Cr(H_2O)_5OH^{2+} + {}^{\bullet}OH + H_2O} \\
\mathrm{RH + {}^{\bullet}OH \xrightarrow{k_2} {}^{\bullet}R + H_2O} \qquad (1) \\
\mathrm{Cr(H_2O)_6^{2+} + {}^{\bullet}R \xrightarrow{k_3} Cr(H_2O)_5R^{2+} + H_2O}
\end{gathered}$$

## Experimental Section

Cr(II) solutions were prepared as described before.[1,2] The Cr(II) concentration was determined spectrophotometrically via the reaction with $Co(NH_3)_5Cl^{2+}$, which exhibits absorbance maxima at 326 ($\epsilon$ = 48.1) and 532 nm ($\epsilon$ = 49.6 $M^{-1}\ cm^{-1}$).[11] All other chemicals were of analytical reagent grade, and deionized Millipore water was used to prepare all solutions. UV–vis spectra were recorded on Varian Cary 1 and Shimadzu UV-250 spectrophotometers. The pH of the test solutions was measured under Ar atmosphere using a Metrohm 632 instrument. Ambient-pressure kinetic measurements were performed on a Durrum D110 stopped-flow instrument, whereas experiments at elevated pressure were performed on a homemade high-pressure stopped-flow unit capable of going to 200 MPa.[12] Both instruments were thermostated to ±0.1 °C. Data acquisition and handling were performed with on-line computer systems using the OLIS KINFIT set of programs.[13]

## Results and Discussion

All the investigated reactions exhibited a characteristic increase in absorbance between 320 and 330 nm due to the formation of the organochromium(III) species, and 321 nm was selected to follow the kinetics of the oxidation reaction. The test solutions contained $2 \times 10^{-4}$ M $H_2O_2$, (0.5–6.0) $\times 10^{-3}$ M Cr(II), and 0.25–1.0 M isopropyl alcohol or methanol. Due to the 2:1 stoichiometry of the overall reaction in (1), some reactions were performed with only a 5-fold excess of Cr(II) in order to obtain measurable spectral changes. Nevertheless, even under such extreme conditions the oxidation reaction exhibited excellent

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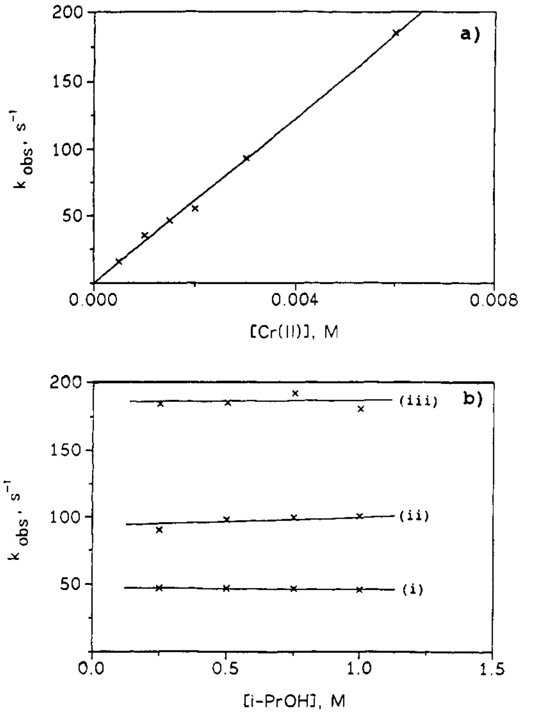


**Figure 1.** Dependences of $k_{obs}$ for the reaction of $Cr^{2+}$ with $H_2O_2$ on [Cr(II)] and [*i*-PrOH]. Experimental conditions: $[H_2O_2] = 2 \times 10^{-4}$ M; pH = 3.0; *T* = 25.0 °C; ionic strength = 0.5 M. Key: (a) [*i*-PrOH] = 0.5 M; (b) [Cr(II)] = $1.5 \times 10^{-3}$ (i), $3 \times 10^{-3}$ (ii), $6 \times 10^{-3}$ M (iii).

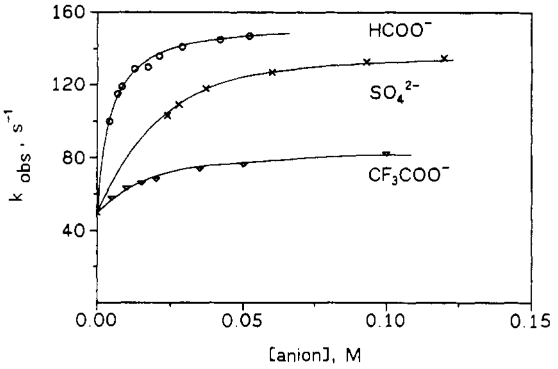


**Figure 2.** Dependence of $k_{obs}$ on the anion concentration. Experimental conditions: $[Cr(II)] = 2 \times 10^{-3}$ M; $[H_2O_2] = 2 \times 10^{-4}$ M; [*i*-PrOH] = 0.5 M; *T* = 25.0 °C; ionic strength = 0.5 M; pH = 4.5 ($HCOO^-$), 3.0 ($SO_4^{2-}$), 3.0 ($CF_3COO^-$).

pseudo-first-order behavior over the first two half-lives of the reaction. A systematic variation of the [Cr(II)] and [*i*-PrOH] resulted in the data reported in Figure 1, from which it follows that $k_{obs}$ depends linearly on [Cr(II)] and is independent of the [*i*-PrOH]. These observations are in line with the overall reaction sequence outlined in (1), according to which $k_{obs} = k_1[Cr(II)]$. The data in Figure 1a result in $k_1 = (3.1 \pm 0.5) \times 10^4$ $M^{-1}$ $s^{-1}$, which is smaller than the quoted literature value of $7.1 \times 10^4$ $M^{-1}$ $s^{-1}$.[9] This apparent discrepancy is probably due to the significantly different acidity and ionic strength selected in the two studies.

The effect of nine different organic and inorganic anions on the oxidation reaction is summarized in Figures 2–5. In most cases the reaction is significantly accelerated in the presence of these anions, whereas in some cases the acceleration reaches a maximum and then decreases at higher anion concentrations (see Figures 4 and 5). During the formation of $Cr-R^{2+}$ according to (1), the reaction of $Cr(H_2O)_6^{2+}$ with $H_2O_2$ is the rate-determining step.[9] The observed acceleration in the presence of various anions must be related to their influence on the latter reaction. The data in Figures 2–5 demonstrate that the different anions can accelerate the reaction by a factor of between 2 and 5 in the

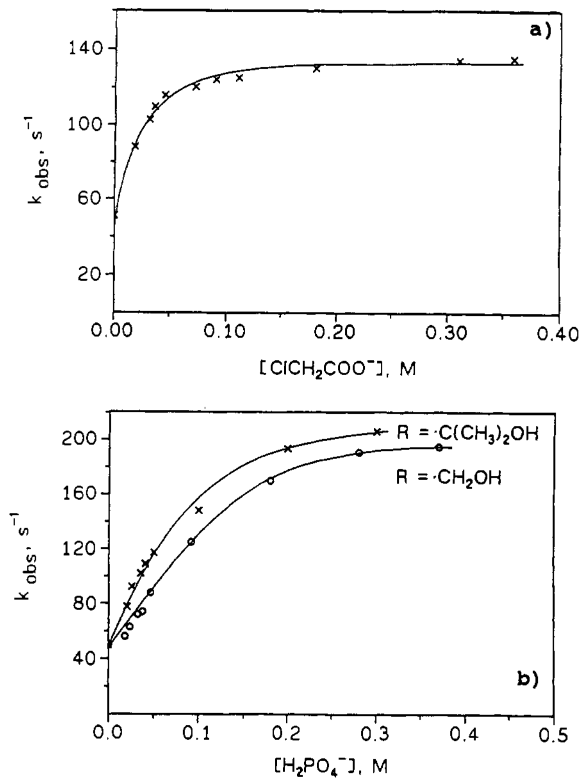


**Figure 3.** Dependence of $k_{obs}$ on the anion concentration. Experimental conditions: $[Cr(II)] = 2 \times 10^{-3}$ M; $[H_2O_2] = 2 \times 10^{-4}$ M; [*i*-PrOH] = 0.5 M; *T* = 25.0 °C; ionic strength = 0.5 M; pH = 3.8 ($ClCH_2COO^-$), 3.2 ($H_2PO_4^-$).

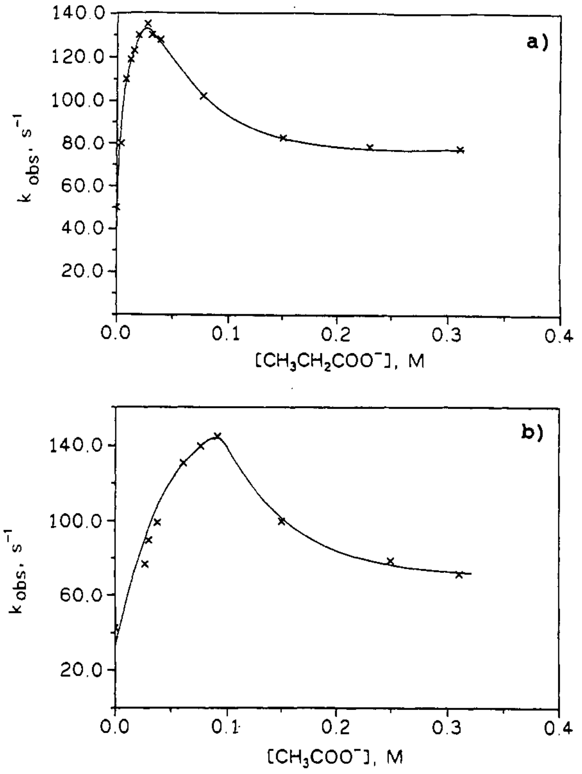


**Figure 4.** Dependence of $k_{obs}$ on the anion concentration. Experimental conditions: $[Cr(II)] = 2 \times 10^{-3}$ M; $[H_2O_2] = 2 \times 10^{-4}$ M; [*i*-PrOH] = 0.5 M; *T* = 25.0 °C; ionic strength = 0.5 M; pH = 5.4 ($CH_3CH_2COO^-$), 5.3 ($CH_3COO^-$).

sequence $CF_3COO^- < ClCH_2COO^- \sim SO_4^{2-} \sim HCOO^- \sim CH_3COO^- \sim CH_3CH_2COO^- \sim CH_3CH(OH)COO^- < HOCH_2COO^- < H_2PO_4^-$. This order roughly correlates with the basicity of the anion, with the exception of $H_2PO_4^-$, where the selection of an appropriate p$K_a$value is complicated by the

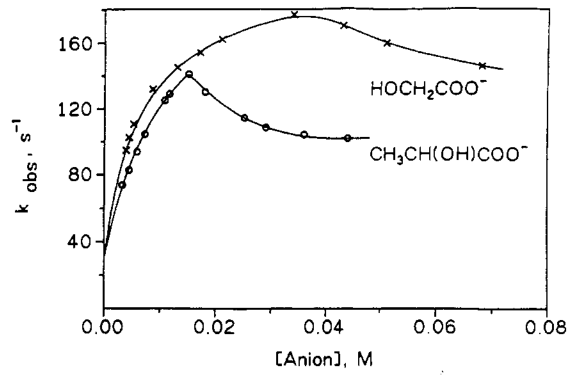
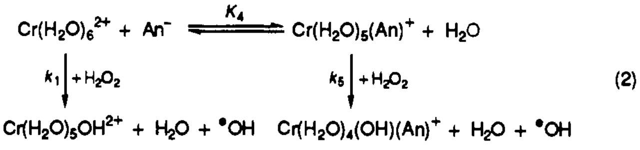


**Figure 5.** Dependence of $k_{obs}$ on the anion concentration. Experimental conditions: [Cr(II)] = $2 \times 10^{-3}$ M; [$H_2O_2$] = $2 \times 10^{-4}$ M; [*i*-PrOH] = 0.5 M; $T$ = 25.0 °C; ionic strength = 0.5 M; pH = 3.8 ($HOCH_2COO^-$), 3.5 ($CH_3CH(OH)COO^-$).

fact that the p$K_a$ of $H_2PO_4^-$ will decrease significantly during its interaction with $Cr^{2+}$.[2] A similar order in accelerating the heterolysis of Cr–$R^{2+}$ species was found for these ions and interpreted in terms of a labilization effect as a result of the coordination of these ions to Cr–$R^{2+}$ (refs 1 and 2 and literature cited therein). We therefore suggest the scheme shown in (2) to



$$\begin{tikzcd}
Cr(H_2O)_6^{2+} + An^- \arrow[r, shift left, "K_4"] \arrow[d, "k_1"', "+H_2O_2"] & Cr(H_2O)_5(An)^+ + H_2O \arrow[l, shift left] \arrow[d, "k_5"', "+H_2O_2"] \\
Cr(H_2O)_5OH^{2+} + H_2O + {}^\bullet OH & Cr(H_2O)_4(OH)(An)^+ + H_2O + {}^\bullet OH
\end{tikzcd} \qquad (2)$$

account for the general acceleration observed by an anion $An^-$ during the rate-determining step in reaction 1. An increase in [$An^-$] will shift the pre-equilibrium to the right and increase the concentration of $Cr(H_2O)_5(An)^+$, which reacts more rapidly with $H_2O_2$ than $Cr(H_2O)_6^{2+}$. This pre-equilibration will be extremely fast due to the rapid solvent exchange on $Cr^{2+}$.[5,14,15] The •OH radicals produced in the spontaneous ($k_1$) and anion-induced ($k_5$) reaction steps will rapidly react with the alcohol employed to produce •R and subsequently Cr–$R^{2+}$ species as shown in (1).[1,10] The corresponding expression for $k_{obs}$ is given in (3), from which

$$k_{obs} = \left\{ \frac{k_1 + k_5K_4[An^-]}{1 + K_4[An^-]} \right\} [Cr(II)] \qquad (3)$$

it follows that $k_{obs} = k_1[Cr(II)]$ at zero anion concentration and $k_{obs} = k_5[Cr(II)]$ at high [$An^-$]. A nonlinear least-squares fit of the data in Figures 2–5 for the increase in $k_{obs}$ with increasing [$An^-$] was used to estimate $k_5$ and $K_4$ reported in Table 1. The values of $K_4$ vary between 5 and 230 M$^{-1}$ and indicate the extent to which the $Cr(H_2O)_5(An)^+$ species is formed. The values of $k_5[Cr(II)]$ vary between 92 and 380 s$^{-1}$ and correspond to the maximum rate constants measured or expected to be reached in Figures 2–5.

In the above-outlined interpretation $Cr(H_2O)_6^{2+}$ and $Cr(H_2O)_5(An)^+$ are considered to be the only reactive species in solution. However, in two cases (see Table 1) the selected pH was around 5.3, which is the lower limit of the p$K_a$ value for $Cr(H_2O)_6^{2+}$ reported in the literature.[16] Although the latter value is rather uncertain,[16] it is such that a partial deprotonation to form $Cr(H_2O)_5OH^+$ may occur under the selected conditions. This is not expected to significantly affect the rapid ligand substitution reaction of aquated Cr(II) since that is controlled by Jahn–Teller distortion and follows an $I_d$ type of mechanism (see further discussion).[5]

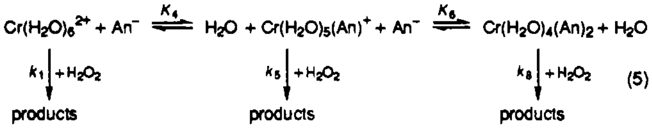
The [$An^-$] dependence of $k_{obs}$ reported for acetate and propionate in Figure 4 demonstrates that at high [$An^-$] the observed rate constant decreases again to reach a final limiting value. These anions are known to form stable complexes with $Cr^{2+}$, an aspect that has been studied in detail for acetate ($Ac^-$) and for which the equilibria are summarized in (4).[6-8]

$$Cr(H_2O)_6^{2+} + Ac^- \rightleftharpoons Cr(H_2O)_5Ac^+ + H_2O \qquad K_4 = 15\ M^{-1}$$

$$Cr(H_2O)_5Ac^+ + Ac^- \rightleftharpoons Cr(H_2O)_4(Ac)_2 + H_2O \qquad K_6 = 5\ M^{-1} \quad (4)$$

$$2Cr(H_2O)_4(Ac)_2 \rightleftharpoons [Cr(H_2O)(Ac)_2]_2 + 6H_2O \qquad K_7 = 2.2 \times 10^4\ M^{-1}$$

With the aid of this data we have calculated the speciation curves for the various species shown in Figure 6 and compared these with the rate data observed in the presence of acetate. It follows that the values of $k_{obs}$ as a function of [$CH_3COO^-$] almost exactly follow the curve for the concentration of the 1:1 monomeric complex, viz. $Cr(H_2O)_5Ac^+$. This indicates that the 1:2 and dimeric species do not contribute significantly toward the catalytic effect of acetate ion on the reaction of $Cr^{2+}$ with $H_2O_2$. A similar situation must account for the results observed for propionate. It follows that the decrease in $k_{obs}$ at higher [$An^-$] must be related to the formation of less reactive 1:2 and dimeric species. Thus the scheme presented in (2) can be modified to (5) for inclusion



$$\begin{tikzcd}
Cr(H_2O)_6^{2+} + An^- \arrow[r, shift left, "K_4"] \arrow[d, "k_1"', "+H_2O_2"] & H_2O + Cr(H_2O)_5(An)^+ + An^- \arrow[l, shift left] \arrow[r, shift left, "K_6"] \arrow[d, "k_5"', "+H_2O_2"] & Cr(H_2O)_4(An)_2 + H_2O \arrow[l, shift left] \arrow[d, "k_8"', "+H_2O_2"] \\
\text{products} & \text{products} & \text{products}
\end{tikzcd} \qquad (5)$$

$$k_{obs} = \left\{ \frac{k_1 + k_5K_4[An^-] + k_8K_4K_6[An^-]^2}{1 + K_4[An^-] + K_4K_6[An^-]^2} \right\} [Cr(II)] \qquad (6)$$

of the 1:2 complex, and the rate constants are such that $k_5 >> k_1, k_8$. The modified rate law will be of the form shown in (6). The initial increase in $k_{obs}$ with increasing [$CH_3COO^-$] (Figure 4b) can be used to fit the data to the simplified rate law (2), and the value found for $K_4$ (see Table 1) is close to that reported in the literature.[6-8]

A similar maximum in the plots of $k_{obs}$ versus [$An^-$] was found for glycolate and lactate (Figure 5) at relatively low anion concentrations. A similar result was observed for the catalytic effect of these ions on the heterolysis of Cr–$R^{2+}$ species[1] and was ascribed to the chelation of the anion, which is stronger for glycolate than for lactate. Such a chelate formation will result in a higher reactivity especially at low anion concentrations but will compete with the coordination of a second anion at higher concentrations. The latter will cause a decrease in reactivity as observed in the case of acetate and propionate.

The largest catalytic effect was observed for $H_2PO_4^-$, and the results in Figure 3b and Table 1 clearly indicate that the effect is almost independent of the selected alcohol, as would be expected on the basis of the reactions outlined in (1). The small differences noted are probably due to secondary medium effects related to the solvation and stabilization of the various complexes in solution as expressed in the value of $K_4$ in Table 1. With the data now available the crucial question to be answered is how do the investigated anions catalyze the reaction of $Cr(H_2O)_5(An)^+$ with

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**Table 1.** Rate and Equilibrium Data Calculated from the Anion Concentration Dependence of $k_{obs}$[a]

| anion | p$K_a$ | pH | [*i*-PrOH], M | [MeOH], M | $k_5$[Cr(II)],[b] s$^{-1}$ | $K_4$,[b] M$^{-1}$ |
|---|---|---|---|---|---|---|
| $CF_3COO^-$ | <0 | 3.0 | 1.0 | | 91.6 | 34.1 |
| $SO_4^{2-}$ | 1.9 | 3.0 | 0.5 | | 152 | 46.1 |
| $ClCH_2COO^-$ | 2.85 | 3.8 | 0.5 | | 143 | 46.6 |
| $CH_3CH(OH)COO^-$ | 3.1 | 3.5 | 1.0 | | 384 | 25.9 |
| $HCOO^-$ | 3.7 | 4.5 | 1.0 | | 154 | 227 |
| $HOCH_2COO^-$ | 3.8 | 4.5 | 1.0 | | 208 | 116 |
| $CH_3COO^-$ | 4.75 | 5.3 | 0.5 | | 250 | 10.5 |
| $CH_3CH_2COO^-$ | 4.9 | 5.4 | 0.5 | | 164 | 119 |
| $H_2PO_4^-/HPO_4^{2-}$ | 2.1/7.2[c] | 3.2 | 0.5 | | 258 | 10.3 |
| | | | | 0.5 | 281 | 4.9 |

[a] [Cr(II)] = 2 × $10^{-3}$ M; [$H_2O_2$] = 2 × $10^{-4}$ M; ionic strength = 0.5 M; *T* = 25.0 °C. [b] Calculated using a nonlinear least-squares fit of the data in Figures 2–5—see Results and Discussion. [c] Expected p$K_a$ value of coordinated $H_2PO_4^-$ will cause deprotonation to $HPO_4^{2-}$—see Results and Discussion.

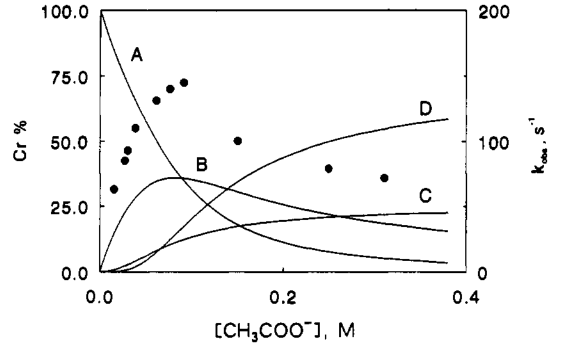

**Figure 6.** Comparison of the Cr(II)–acetate speciation and the effect of the acetate concentration on $k_{obs}$ for the reaction of $Cr^{2+}$ with $H_2O_2$. Kinetic data were taken from Figure 4b. Key: (A) [$Cr(H_2O)_6^{2+}$]; (B) [$Cr(H_2O)_5Ac^+$]; (C) [$Cr(H_2O)_4(Ac)_2$]; (D) 2 [$\{Cr(H_2O)(Ac)_2\}_2$].

$H_2O_2$. From the observed kinetic behavior and the lability of the Cr(II) center[5] it is safe to conclude that we are dealing with a reactive complex of the type $Cr(H_2O)_5(An)^+$ in the presence of the anions. This is also in agreement with the relatively large values of $K_4$ that cannot be assigned to ion-pair formation. In addition, it is also reasonable to expect that the $Cr(H_2O)_5(An)^+$ species will be at least as labile as $Cr(H_2O)_6^{2+}$ since the presence of the anion is expected, on the basis of our earlier studies,[1-3] to promote the trans-labilization of the coordinated solvent molecule. A similar argument will apply to the lability of the $Cr(H_2O)_5OH^+$ species as mentioned before. There are reports in the literature that have reported evidence for cis-labilization effects of coordinated anions on chromium complexes, but these are usually smaller than trans-labilization effects.[17,18] Thus $Cr(H_2O)_5(An)^+$ will rapidly bind $H_2O_2$ and the electron-transfer reaction will follow an inner-sphere mechanism, in agreement with that generally known about the tendency of $H_2O_2$ to react by an inner-sphere mechanism.[9,19]

The above arguments suggest that both $Cr(H_2O)_6^{2+}$ and $Cr(H_2O)_5(An)^+$ will rapidly coordinate $H_2O_2$, which is then followed by a rate-determining electron-transfer reaction in terms of an inner-sphere mechanism as shown in (7). A similar reaction

$$\begin{array}{c} Cr(H_2O)_5(An)^+ + H_2O_2 \xrightleftharpoons{K_{IS}} (H_2O)_4(An)Cr^{II}\text{–}O(H)OH^+ + H_2O \\ \Big\downarrow k_{ET} \\ (H_2O)_4(An)Cr^{III}\text{–}OH^+ + {}^\bullet OH \end{array} \qquad (7)$$

sequence can be written for the reaction with $Cr(H_2O)_6^{2+}$ (and $Cr(H_2O)_5OH^{2+}$), which means that both $k_1$ and $k_5$ are composite rate constants, viz. $K_{IS}k_{ET}$, the product of the inner-sphere complex formation constant, $K_{IS}$, and the electron-transfer rate constant, $k_{ET}$. Thus the presence of an anion in the coordination sphere of Cr(II) can promote either the formation of the inner-sphere complex or the electron-tranfer step, or both. The increased lability expected for $Cr(H_2O)_5(An)^+$ could lead to an increase in $K_{IS}$, i.e., $k_5$ will be larger than $k_1$. The presence of a stronger and significantly more basic nucleophile than water in the coordination sphere of Cr(II) will increase the electron density on the metal center, influence its redox potential, and so promote the electron-transfer reaction from the metal to the coordinated $H_2O_2$. The formed $H_2O_2^-$ then undergoes homolysis to produce coordinated $OH^-$ and a free $^\bullet OH$ radical.

**Table 2.** Values of $\Delta H^*$ and $\Delta S^*$ for the Reaction of Cr(II) Species with $H_2O_2$ in the Presence of Different Anions[a]

| anion | [anion], M | $k_{obs}$(25 °C), s$^{-1}$ | $\Delta H^*$, kJ·mol$^{-1}$ | $\Delta S^*$, J·(K·mol)$^{-1}$ |
|---|---|---|---|---|
| $CF_3COO^-$ | 0.01 | 68.2 | 6.5 ± 0.3 | −188 ± 1 |
| | 0.1 | 84.2 | 8.9 ± 0.3 | −178 ± 1 |
| $SO_4^{2-}$ | 0.02 | 87.0 | 5.5 ± 0.3 | −189 ± 1 |
| | 0.06 | 106 | 5.6 ± 0.4 | −187 ± 1 |
| $ClCH_2COO^-$ | 0.018 | 95.1 | 5.4 ± 0.1 | −189 ±0.4 |
| | 0.36 | 136 | 15.8 ± 0.5 | −151 ± 2 |
| $CH_3CH(OH)COO^-$ | 0.0044 | 71.4 | 12.0 ± 0.5 | −169 ± 1 |
| | 0.011 | 81.0 | 13.2 ± 0.4 | −164 ± 1 |
| $HCOO^-$ | 0.0042 | 118 | 8.0 ± 0.3 | −178 ± 1 |
| | 0.033 | 153 | 17.2 ± 1.2 | −145 ± 4 |
| $HOCH_2COO^-$ | 0.0043 | 115 | 4.5 ± 0.1 | −190 ± 1 |
| | 0.03 | 162 | 14.6 ± 0.9 | −154 ± 3 |
| $CH_3COO^-$ | 0.015 | 70 | 21.2 ± 1.9 | −139 ± 6 |
| | 0.31 | 75 | 26.3 ± 2.7 | −120 ± 9 |
| $CH_3CH_2COO^-$ | 0.0077 | 110 | 17.6 ± 1.4 | −146 ± 5 |
| | 0.31 | 130 | 16.3 ± 1.8 | −153 ± 6 |
| $HPO_4^{2-}$ | 0.018 | 101 | 21.2 ± 0.8 | −135 ± 3 |
| | 0.3 | 220 | 24.0 ± 1.9 | −119 ± 7 |
| $H_2O$[b] | | 24.2 | 25.9 ± 1.8 | −131 ± 6 |

[a] For experimental conditions not quoted, see Table 1. The reported activation parameters were calculated from the temperature dependence of $k_{obs}$. [b] Experimental conditions: [Cr(II)] = 1 × $10^{-3}$ M; [$H_2O_2$] = 1 × $10^{-4}$ M; pH = 3.0; [*i*-PrOH] = 0.5 M; ionic strength = 0.5 M; *T* = 25.0 °C.

**Table 3.** Values of $\Delta V^*$ for the Reaction of Cr(II) Species with $H_2O_2$ in the Presence of Different Anions[a]

| anion | [anion], M | pH | $\Delta V^*$, cm$^3$·mol$^{-1}$ |
|---|---|---|---|
| $CF_3COO^-$ | 0.01 | 3.0 | +3.5 ± 0.2 |
| | 0.1 | 3.0 | +5.4 ± 0.5 |
| $CH_3COO^-$ | 0.01 | 5.3 | +2.3 ± 0.6 |
| | 0.32 | 5.3 | −6.0 ± 0.2 |
| $H_2O$ | | 2.5 | −1.1 ± 1.3 |

[a] For experimental conditions, see Table 2.

In an effort to gain further insight into the reaction steps outlined in (7), we studied the temperature and pressure dependence of reaction 1 in the absence and presence of various anions for which the results are summarized in Tables 2 and 3. At low [An$^-$], eq 3 reduces to $k_{obs} = \{k_1 + k_5K_4[An^-]\}[Cr(II)]$, such that the activation parameters reported in Table 2 will be those for $k_1$ and $k_5K_4$. At high [An$^-$], eq 3 reduces to $k_{obsd} = k_5[Cr(II)]$ and the activation parameters are those for $k_5$. In general $\Delta H^*$ and $\Delta S^*$ are significantly smaller in the presence of anions than for the

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spontaneous reaction path $k_1$ measured in the absence of added anions. Thus the activation barrier for the rate-determining electron-transfer reaction is significantly lower in the presence of anions. Furthermore, the transition state is highly structured presumably due to stronger precursor formation in the presence of anions as discussed above. In a few cases, increasing the anion concentration causes an increase in $\Delta H^*$, which may be due to a contribution of $K_4$ at low [$An^-$] that disappears at high [$An^-$]. Some anions exhibit extremely low $\Delta H^*$ values, accompanied by very negative $\Delta S^*$ values, which indicate that the activation barrier for the anion catalyzed electron-transfer is indeed very low, almost as for diffusion-controlled processes.

The activation volumes reported in Table 3 are once again composite values for the contributions resulting from inner-sphere complex formation and the electron-transfer step. Such data have been discussed in detail for many electron-transfer reactions.[20-23] For the suggested inner-sphere mechanism the observed $\Delta V^* = \Delta\bar{V}(K_{IS}) + \Delta V^*(k_{ET})$. No major change in volume is expected during the formation of the inner-sphere species since the partial molar volumes of $H_2O$ and $H_2O_2$ are not expected to be very different, thus $\Delta\bar{V}(K_{IS}) \sim 0$. During the electron-transfer reaction in Cr–O(H)OH, Cr(II) is reduced to Cr(III), which is expected to be accompanied by a significant volume decrease as large as $-15$ cm$^3$ mol$^{-1}$.[5] This will be offset by a significant volume increase due to homolysis of the O–O bond in coordinated $H_2O_2$,[20] such that the overall $\Delta V^*(k_{ET})$ can be close to zero. The small positive $\Delta V^*$ reported in Table 3 may indicate that the anion-induced electron-transfer process may involve more bond cleavage in terms of lengthening of the O–O bond due to the increased electron density on the metal center. The negative $\Delta V^*$ value found at high [$CH_3COO^-$] results from the dissociation of the dimeric species at elevated pressure[4], thereby increasing the fraction of the monomeric species accompanied by an increase in $k_{obs}$. It follows that the $\Delta V^*$ data reported in Table 3 are in agreement with the mechanism suggested for the anion-catalyzed reaction mechanism.

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