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Reduction of Hexavalent Chromium by H₂O₂ in Acidic Solutions

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The rates of the reduction of Cr(VI) with H₂O₂ were measured in NaCl solutions as a function of pH (1.5–4.8), temperature (5–40 °C), and ionic strength (*I* = 0.01–2 M) in the presence of an excess of reductant. The rate of Cr(VI) reduction is described by the general expression $-d[\text{Cr(VI)}]/dt = k_2[\text{Cr(VI)}]^m[\text{H}_2\text{O}_2]^n[\text{H}^+]^z$, where *m* = 1 and *n* and *z* are two interdependent variables. The value of *n* is a function of pH between 2 and 4 ($n = (3 \times 10^a)/(1 + 10^a)$), where $a = -0.25 - 0.58\text{pH} + 0.26\text{pH}^2$ leveling off at pH < 2 (where *n* ≈ 1) and pH > 4 (where *n* ≈ 3). The rates of Cr(VI) reduction are acid-catalyzed, and the kinetic order *z* varies from about 1.8–0.5 with increasing H₂O₂ concentration, according to the equation $z = 1.85 - 350.1\text{H}_2\text{O}_2$ (M) which is valid for [H₂O₂] < 0.004 M. The values of *k*₂ (M^{-(*n*+*z*)} min⁻¹) are given by $k_2 = k/[\text{H}^+]^z = k_1/[\text{H}_2\text{O}_2]^n[\text{H}^+]^z$, where *k* is the overall rate constant (M^{-*n*} min⁻¹) and *k*₁ is the pseudo-first-order rate constant (min⁻¹). The values of *k* in the pH range 2–4 have been fitted to the equation $\log k = 2.14\text{pH} - 2.81$ with $\sigma = \pm 0.18$. The values of *k*₂ are dependent on pH as well. Most of the results with H₂O₂ < 3 mM are described by $\log k_2 = 2.87\text{pH} - 0.55$ with $\sigma = \pm 0.54$. Experimental results suggest that the reduction of Cr(VI) to Cr(III) is controlled by the formation of Cr(V) intermediates. Values of *k*₂ and *k* calculated from the above equations can be used to evaluate the rates of the reaction in acidic solutions under a wide range of experimental conditions, because the rates are independent of ionic strength, temperature, major ions, and micromolar levels of trace metals (Cu²⁺, Ni²⁺, Pb²⁺). The application of this rate law to environmental conditions suggests that this reaction may have a role in acidic solutions (aerosols and fog droplets) in the presence of high micromolar concentrations of H₂O₂.

Introduction

The two oxidation states of chromium commonly found in the environment are trivalent [Cr(III)] and hexavalent [Cr(VI)] chromium. These two redox states are characterized by markedly different chemical behavior, bioavailability, and toxicity (1–7). The distribution of chromium between its two

main redox states has shown significant deviations with respect to thermodynamic predictions either in oxic (8) or anoxic waters (9). These widely quoted discrepancies, which highlight the limited knowledge of processes responsible for Cr(III)–Cr(VI) interconversions in environmental matrices, have stimulated our interest in studying the kinetics of the redox reactions of chromium.

We have studied the oxidation of Cr(III) with H₂O₂ in basic solutions (10–11) and found that this oxidant controls the rates of oxidation of Cr(III) in surface waters. We have also studied the rates of reduction of Cr(VI) with H₂S (12–13) and, more recently, with Fe(II) (14). Under neutral to alkaline conditions, Fe(II) controls the reduction of Cr(VI) in natural anoxic systems (14), while under acid conditions, other reductants may be more efficient than Fe(II).

A half-life for Cr(VI) reduction with humic acids of 3.6 h has been reported at pH 2 and 25 °C, while the reduction takes place on a timescale of days in the pH range 4–7 at 20–800 μM Cr(VI) (15). The reduction of Cr(VI) with Cu(I), produced by radiolysis experiments in dilute solutions in the presence of Cu(II), has recently been proposed to play an important role in atmospheric and surface waters with low ionic strength and pH (16). Hydrogen peroxide was also formed during radiolysis experiments; however, on the basis of the similarity of the rates measured at pH 7.1 in experiments in which 300 μM H₂O₂ were added before radiolysis, it was concluded that H₂O₂ did not play any effect on the rates of the reduction of Cr(VI) (16).

However, the pe–pH relationships of CrO₄²⁻/Cr(OH)₃ and O₂/H₂O₂ couples clearly show that H₂O₂ is an oxidant of Cr(III) at pH > 7.5, while it becomes a reductant at lower pH and its strength as a reductant strongly increases at low pH. By assuming 0.2 atm O₂, 10⁻⁷ M H₂O₂, and a concentration ratio of 1:1 for Cr(VI)/Cr(III), the values of pe for CrO₄²⁻/Cr(OH)₃ and O₂/H₂O₂ are 9.9 and 8.6 at pH 6.0; 6.4 and 6.5 at pH 8.1; and 4.9 and 5.6 at pH 9.0.

Cr(VI), indeed, reacts with H₂O₂ in aqueous solutions (17–20), producing various chromium peroxy derivatives under different experimental conditions (pH, reactant ratios, temperature, etc.). In acid wastes receiving freshwater and particularly in atmospheric aqueous media where pH values range from about 1 in aerosols to about 5 in clouds or fog droplets (21), the reduction of Cr(VI) with H₂O₂ is thermodynamically possible. This reaction is also used in treatment processes for removing Cr(VI) from aqueous wastes (22).

The atmospheric chemistry of chromium has been recently reviewed, and its most important redox reactions have been discussed (21). In this work, H₂O₂ was mentioned among the possible reductants of Cr(VI), but its real role in environmental matrices could not be investigated because no rate expression for this reaction was available at that time.

Accordingly, to evaluate the potentialities of H₂O₂ in reducing Cr(VI) in acid environmental aquatic matrices, we have investigated the reaction of H₂O₂ with Cr(VI) in deaerated NaCl solutions over a wide range of reactant concentrations, pH, ionic strength, and temperature. Results in deaerated media have also been compared with the rates in the presence of oxygen, and the effects of possible interfering ions have been investigated. These results yield a rate expression for the reduction of Cr(VI) with H₂O₂ and suggest that this reaction may play a role in strongly acid matrices (pH < 3) as in aerosols and fog droplets.

Experimental Section

Reaction Vessel. The reactions were studied in a 400 mL glass thermostatically controlled vessel. The temperature was

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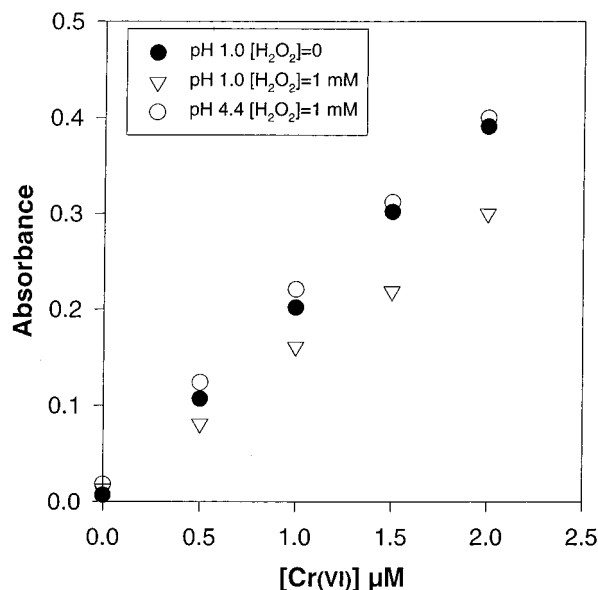


FIGURE 1. Effect of pH conditions and H₂O₂ concentrations on the calibration line of Cr(VI) with the diphenylcarbazide method.

controlled to ± 0.01 °C with a circulating bath. The vessel was closed with a glass cover in which an automatic Teflon dispenser was screwed. The cover had three more openings for an N₂ bubble, a Radiometer combination pH electrode, and a reagent port. The solutions were stirred with a Teflon-coated magnetic multiple stirrer.

Chemicals and Procedure. All of the solutions were prepared using 0.2 μ M filtered 18 M Ω Millipore water, and the reagents were analytical grade. Reduction rates were studied in previously deaerated NaCl (0.05–2 M) solutions over a wide range of pH and temperature. Some kinetic runs were also performed without any preliminary deaeration, and the results were compared with those in the absence of oxygen. After equilibration at the desired temperature, a small aliquot of a stock K₂Cr₂O₇ solution (2.42 mM) was added to a 250 mL sample. The pH of the samples was previously adjusted with a small amount of dilute HCl solutions in order to have the desired final pH after the addition of Cr(VI) and H₂O₂. Variations in the pH during the experiments were within ± 0.05 units of the initial value, and no pH buffer was needed. The initial Cr(VI) concentration was 1.9 μ M, in most of the kinetic runs, while that of H₂O₂ ranged from 100 to 4000 μ M. H₂O₂ was added from 1 M H₂O₂ stock solutions (Fluka) prepared immediately before use by diluting concentrated H₂O₂ with Milli Q water. The concentration of H₂O₂ in most of the runs was high enough as compared to that of Cr(VI) so the experiments were pseudo-first-order. In a limited number of kinetic runs, at very acid pH, the H₂O₂/Cr(VI) molar ratio was in the range 10–50 to make the kinetic experiments possible with the batch method used. At a low H₂O₂/Cr(VI) ratio, we limited our measurements to only a 30–40% decrease of the initial Cr(VI) to keep them pseudo-first-order. The reduction of Cr(VI) was followed by measuring its disappearance as a function of time after the addition of H₂O₂. The determination of Cr(VI) was performed using a modified diphenylcarbazide (DPC) method at pH 4.4. The standard method (23) suggests a pH of 1.0 ± 0.3 adjusted with 0.2 N H₂SO₄ (23); however, it explicitly quotes, “the matter of optimum pH range is currently being considered by Standard Methods”. We have shown that the reaction of Cr(VI) with DPC occurs at higher pH, although it takes a slightly longer time for full color development under these conditions. Figure 1 shows the absorbance of the Cr(VI)–DPC complex in the presence of 1 mM H₂O₂ at two different experimental conditions (pH 1 and 4.4) and at pH 1 in the

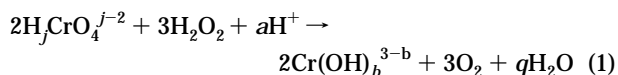
TABLE 1. Values of the Pseudo-First-Order Rate Constant (k_1 , min⁻¹) for the Reduction of Various Cr(VI) Concentrations in 0.01 M NaCl at 25 °C and Two Different pH Conditions and H₂O₂ Concentrations

[Cr(VI)] μ M	pH 1.9	pH 3.4
	[H ₂ O ₂] = 100 μ M	[H ₂ O ₂] = 1500 μ M
0.5	0.0079 \pm 0.0002	0.0021 \pm 0.0003
1.0	0.0109 \pm 0.0003	0.0021 \pm 0.0002
2.0	0.0104 \pm 0.0004	0.0024 \pm 0.0002
3.0	0.0101 \pm 0.0003	0.0023 \pm 0.0002
4.0	0.0106 \pm 0.0002	0.0024 \pm 0.0001

absence of H₂O₂. It clearly shows that the values of absorbance at pH 4.4 in the presence of 1 mM H₂O₂ are similar to those obtained at pH 1 without any addition of H₂O₂. On the basis of the findings by Zhang and Lay (24), Cr(V) species may be formed in the presence of H₂O₂ at pH 4.4 before the addition of diphenylcarbazide. However, the similarity of results obtained at pH 4.4 in the presence of 1 mM H₂O₂ with those at pH 1 in the absence of H₂O₂ indicates that if these Cr(V) species occur, they are determined by the DPC method used along with Cr(VI) species. The fact that V(v) also reacts with diphenylcarbazide under these conditions supports this point. Typically, an aliquot of 16.5 mL was withdrawn from the reaction vessel, added to a 20 mL flask containing 2 mL ammonium acetate at pH 4.5 and 1.5 mL of diphenylcarbazide in acetone (20 g/L), and mixed. The colored chromium–diphenylcarbazide product developed in about 10 min under our experimental conditions, and its absorbance was analyzed spectrophotometrically at 540 nm in 5-cm path length cells within 2–3 min of the color development. A few experiments were also carried out using the standard DPC method at pH about 1. These experiments indicated that H₂O₂ does not significantly affect the slope of a ln[Cr(VI)] versus time curve and, thus, the pseudo first-order rate constant, although it may influence the Cr(VI) determination. The detection limit of the DPC method under our experimental conditions is about 0.05 μ M with a 5% precision in the concentration range 0.5–2.0 μ M. Appropriate calibration runs were performed in the same experimental conditions (medium, ionic strength, temperature) as the kinetic experiments. Tris buffer was used to calibrate the pH electrode on a free molal scale (25).

Results

The reduction of Cr(VI) with H₂O₂ in the pH range <5 can be described by the general reaction



where the possible hydrolyzed species are defined by $j = 1-2$, $b = 0-2$, $a = 4 + 2(2 - j) - 2(2 - (3 - b))$, and $q = a - (2 - 2j)$. The rate equation for the reaction may be expressed by

$$-d[\text{Cr(VI)}]/dt = k_2[\text{Cr(VI)}]^m[\text{H}_2\text{O}_2]^n[\text{H}^+]^z \quad (2)$$

where m , n , and z are the order of the reaction with respect to the concentration of Cr(VI), H₂O₂, and H⁺.

The experimental data for the reduction of chromate in NaCl solutions as a function of reactant concentrations, pH, ionic strength, and temperature are summarized in Tables 1–5. The data are expressed in terms of the pseudo-first-order rate constant (k_1 , min⁻¹). The errors in the k_1 data in most of kinetic runs were largely within 10%. Preliminary kinetic runs in deaerated 0.01 M NaCl showed that ln[Cr(VI)] was a linear function of time, suggesting a first-order

TABLE 2. Effect of H₂O₂ Concentrations on the Reduction of Cr(VI) at Various pH^a

pH	H ₂ O ₂ (μM)	k ₁ (min ⁻¹)	pH	H ₂ O ₂ (μM)	k ₁ (min ⁻¹)
1.80	100	0.0217	3.40	500	0.0001
	150	0.0311		700	0.0003
	200	0.0453		900	0.0008
	300	0.0594		1000	0.0008
	400	0.0740		1100	0.0011
2.65	274	0.0013		1300	0.0016
	392	0.0025		1400	0.0019
	588	0.0046		1500	0.0024
	685	0.0061		1600	0.0027
	783	0.0071		1800	0.0039
2.70	980	0.0100		2000	0.0052
	588	0.0025		2000	0.0048
	783	0.0047	3.90	1500	0.0015
	980	0.0072		2000	0.0029
	1300	0.0105		2500	0.0064
2.90	274	0.0006		3000	0.0104
	392	0.0015		3500	0.0164
	588	0.0018		4000	0.0268
	685	0.0025	4.30	1500	0.0008
	783	0.0034		2000	0.0026
3.15	980	0.0051		2500	0.0037
	588	0.0004		3000	0.0081
	685	0.0005		3500	0.0118
	783	0.0012		4000	0.0178
	800	0.0011	4.75	1500	0.0004
	980	0.0017		2000	0.0009
	1100	0.0025		2300	0.0011
	1200	0.0026		2500	0.0018
	1500	0.0036		3000	0.0036
				3500	0.0037
				4000	0.0079

^a [Cr(VI)] = 1.9 μM; I = 0.01 M NaCl; 25 °C.

TABLE 3. Effect of pH on the Reduction of Cr(VI) with Various H₂O₂ Concentrations^a

H ₂ O ₂ (μM)	pH	k ₁ (min ⁻¹)	H ₂ O ₂ (μM)	pH	k ₁ (min ⁻¹)
100	1.5	0.0693	2000	2.5	0.0552
	1.8	0.0216		2.8	0.0189
	2.0	0.0118		3.0	0.0107
	2.2	0.0039		3.3	0.0061
	2.4	0.0018	3000	2.5	0.0679
250	1.7	0.0768		2.8	0.0292
	2.0	0.0267		3.0	0.0238
	2.3	0.0074		3.3	0.0133
	2.6	0.0020	4000	2.8	0.0531
500	2.0	0.0520		3.0	0.0466
	2.3	0.0169		3.5	0.0270
	2.5	0.0084		4.0	0.0210
	2.8	0.0023		4.4	0.0153
1000	2.0	0.0916	4.8	4.8	0.0083
	2.3	0.0315			
	2.5	0.0169			
	3.0	0.0031			

^a [Cr(VI)] = 1.9 μM; I = 0.01 M NaCl; 25 °C.

dependence of the rates of the reduction on [Cr(VI)]. The effect of Cr(VI) concentration on the kinetics of the reaction was further investigated in deaerated 0.01 M NaCl solutions at 25 °C at pH 1.9 and 3.4. Results shown in Table 1 indicate that similar slopes were obtained when different initial concentrations of Cr(VI) were used at constant pH, temperature, ionic strength, and H₂O₂. These measurements clearly demonstrate that the reaction is first-order with respect to [Cr(VI)]. Average half times of Cr(VI) in 0.01 M NaCl at 25 °C were 70 ± 8 min at pH 1.9 and [H₂O₂] = 100 μM and 308 ± 21 min at pH 3.4 and [H₂O₂] = 1500 μM.

TABLE 4. Values of the Pseudo-First-Order Rate Constant (k₁, min⁻¹) for the Reduction of 1.9 μM Cr(VI) with H₂O₂ as a Function of Ionic Strength at 25 °C and Two Different Values of pH^a

I (M)	pH 2.0	pH 2.4	pH 2.5
	500 μM H ₂ O ₂	500 μM H ₂ O ₂	800 μM H ₂ O ₂
0.01	0.0461		
0.01	0.0476		
0.01			0.0138
0.01 ^b			0.0130 ^b
0.20			0.0112
0.20 ^b			0.0120 ^b
0.50	0.0388	0.0084	
0.50	0.0364	0.0077	
1.00	0.0359	0.0082	
2.00	0.0370	0.0095	

^a Experiments were carried out in NaCl solutions unless otherwise specified. ^b NaNO₃ solutions.

TABLE 5. Values of the Pseudo-First-Order Rate Constant (k₁, min⁻¹) for the Reduction of 1.9 μM Cr(VI) with 500 μM H₂O₂ as a Function of Temperature in 0.01 M NaCl at Two Different Values of pH

T °C	pH 2.2	pH 2.7	T °C	pH 2.2	pH 2.7
5	0.0309	0.0044	40	0.0357	0.0048
15	0.0243	0.0042	40	0.0404	0.0048
25	0.0290	0.0042			

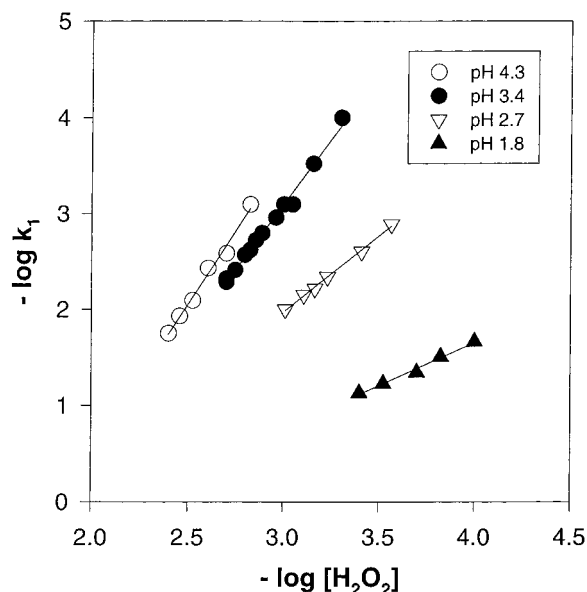


FIGURE 2. Effect of H₂O₂ concentrations on the pseudo-first-order rate constant for the reduction of 1.9 μM Cr(VI) in deaerated 0.01 M NaCl solutions at 25 °C and various pH.

Therefore, eq 2 can be expressed by

$$-d[\text{Cr(VI)}]/dt = k_1[\text{Cr(VI)}] \quad (3)$$

where $k_1 = k_2 [\text{H}_2\text{O}_2]^n [\text{H}^+]^z$ and [Cr(VI)] is the concentration of Cr(VI) at any time. k_1 may be also given by $k_1 = k[\text{H}_2\text{O}_2]^n$, where k is the overall constant (M⁻ⁿ min⁻¹).

The effect of the reductant on the kinetics of the reaction was examined next. Four series of runs in deaerated 0.01 M NaCl solutions at 25 °C and pH 1.8, 2.7, 3.4, and 4.3 were carried out (Figure 2). These results showed a marked change in the kinetic order of the reaction with respect to H₂O₂ from

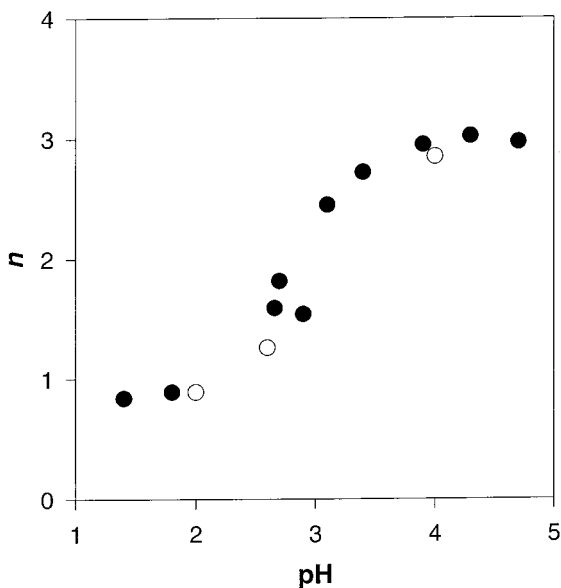


FIGURE 3. Effect of pH on the kinetic order (n) with respect to H_2O_2 for the reduction of $1.9 \mu\text{M}$ Cr(VI) in 0.01 M NaCl solutions at 25°C . Empty circles refers to experiments in which the standard DPC method at pH 1 was used for measuring Cr(VI).

about 1 at low pH to about 3 at high pH. To confirm these results and better characterize the transition from the low-to-high kinetic order, many runs as a function of H_2O_2 were carried out at different values of pH in the range 1.5–4.7 (Table 2 and Figure 3). From these results, it appears that the kinetic order with respect to H_2O_2 (n) changes as a function of pH from 2 to 4, according to the equation

$$\log(n/3 - n) = -0.25 - 0.58\text{pH} + 0.26\text{pH}^2 \quad \sigma = \pm 0.22 \quad (4)$$

At $\text{pH} > 4$, the order (n) is ≈ 3 , and eq 4 becomes increasingly inaccurate, while at $\text{pH} < 2$, n tends to 1.

In an attempt to elucidate the effect of pH on the order of the reaction, we have investigated the rates of the reaction as a function of pH at various levels of H_2O_2 (Table 3). The measurements indicate a decreasing kinetic order (z) as a function of the proton with increasing H_2O_2 levels (Figure 4). Values varied from about 1.8 at low H_2O_2 concentrations to < 0.5 at high H_2O_2 concentrations. Data have been fitted to the following equation

$$z = 1.85 - 350.1[\text{H}_2\text{O}_2] \quad \sigma = \pm 0.05 \quad (5)$$

which is valid for H_2O_2 in the range $0.0001\text{--}0.004 \text{ M}$.

The effect of ionic strength ($I = 0.01\text{--}2 \text{ M}$) was studied in deaerated NaCl solutions with $1.9 \mu\text{M}$ Cr(VI) and $500 \mu\text{M}$ H_2O_2 at 25°C and two values of pH (2.0 and 2.4). The results given in Table 4 do not show any significant concentration dependence, with the slopes of $\log k_1$ versus $I^{0.5}$ being equal to -0.009 ± 0.003 and 0.13 ± 0.41 at pH 2.0 and 2.4, respectively.

The effect of temperature ($5\text{--}40^\circ\text{C}$) was studied in 0.01 M NaCl solutions with $1.9 \mu\text{M}$ Cr(VI) and $500 \mu\text{M}$ H_2O_2 at two different pH values (2.2 and 2.7; Table 5). The results do not show any significant effect of temperature, as was observed in the case of the reduction of Cr(VI) with Fe(II) in acidic solutions (14).

The rates of the reduction were also investigated in oxygenated solutions at 25°C with $1.9 \mu\text{M}$ Cr(VI) and $500 \mu\text{M}$ H_2O_2 . The results obtained showed a tendency of k_1 values (in 0.01 M NaCl: 0.1626 at pH 1.7; 0.0381 and 0.0409

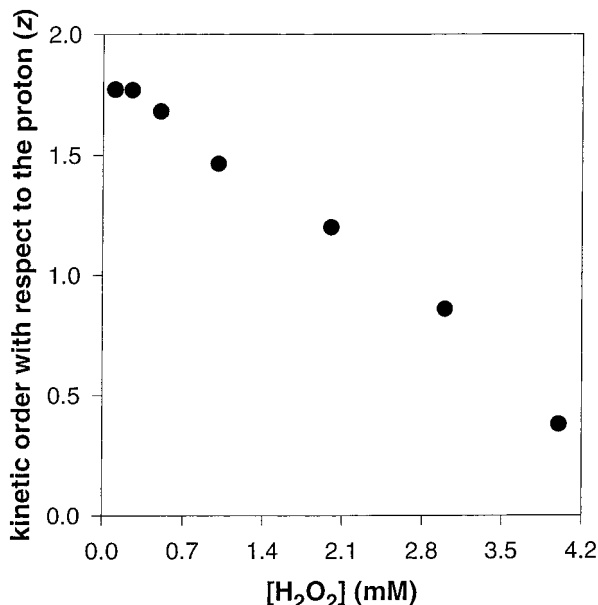


FIGURE 4. Changing of the kinetic order with respect to the proton for the reduction of Cr(VI) as a function of H_2O_2 concentrations in deaerated 0.01 M NaCl solutions at 25°C .

TABLE 6. Effect of Major and Minor Ions Added to 0.01 M NaCl Solutions on the Rates of Reduction of $1.9 \mu\text{M}$ Cr(VI) with H_2O_2^a

pH	T ($^\circ\text{C}$)	H_2O_2	ion	k_1 (min^{-1})
3.9	25	2000	0.010 M Ca^{2+}	0.0028 ± 0.0006
3.9	25	2000	0.058 M Mg^{2+}	0.0029 ± 0.0008
2.0	20	500	$0.028 \text{ M SO}_4^{2-}$	0.0612 ± 0.0092
2.5	20	500	$0.028 \text{ M SO}_4^{2-}$	0.0081 ± 0.0012
3.9	25	2000	0.002 M HCO_3^-	0.0030 ± 0.0007
2.6	20	500	$0.57 \text{ mM PO}_4^{3-}$	0.0058 ± 0.0015
2.9	20	500	$1 \mu\text{M Pb}^{2+}$	0.0016 ± 0.0003
3.9	25	2000	$2 \mu\text{M Pb}^{2+}$	0.0033 ± 0.0005
2.9	20	500	$1 \mu\text{M Cu}^{2+}$	0.0015 ± 0.0003
3.9	25	2000	$2 \mu\text{M Cu}^{2+}$	0.0035 ± 0.0008
3.9	25	2000	$2 \mu\text{M Ni}^{2+}$	0.0032 ± 0.0004

^a Errors were calculated on the basis of at least three replicates.

at pH 2.0; 0.0130 at pH 2.3) to be slightly lower as compared to those in deaerated solutions, although the significance of the difference was only moderate. Some kinetic runs were finally carried out in the presence of natural levels of major ions (Ca^{2+} , Mg^{2+} , SO_4^{2-} , HCO_3^- , PO_4^{3-}) and μM concentrations of Cu^{2+} , Ni^{2+} , and Pb^{2+} . The results did not show any significant change in the rates (Table 6).

Discussion

The results obtained clearly show that the order of the reaction with respect to the proton and H_2O_2 concentrations are interrelated. At low pH ($\text{pH} \approx 2$; Figure 3), the rate of the reduction is first-order with respect to H_2O_2 concentration, and at low concentrations of H_2O_2 , the kinetic order with respect to the proton is about 1.7–1.8 (see Figure 4). Therefore, the results in the low pH range and at low concentrations of H_2O_2 can be explained by considering that H_2CrO_4 and HCrO_4^- are the main species reacting with H_2O_2 . At higher pH (3–4), a second or third order dependence of the rates on $[\text{H}_2\text{O}_2]$ concentrations occurs (see Figure 3). The dependence of the rates on the proton changes from about 2 to less than 0.5 as a function of increasing H_2O_2 concentration (Figure 4).

Changes in the kinetic order with respect to the proton and the concentration of the reductant have already been reported for redox reactions of chromium. Cr(VI) oxidizes thiosulfate, for example, with different mechanisms at different pH values (26). At pH 4, the reaction is closely first-order in Cr(VI) and H⁺ and second-order in S₂O₃²⁻. In the pH range 5.3–6.4, the reaction is always first-order in Cr(VI), while the order with respect to hydrogen was near unity at higher pH and fell at pH < 6, and the order with respect to thiosulfate was near zero at low concentrations but rose toward unity above a concentration of S₂O₃²⁻ equal to 0.1 M.

The rates of the reaction of Cr(VI) with H₂O₂ were previously investigated by using a stopped-flow apparatus at Cr(VI) concentrations that were 2 orders of magnitude higher than those in this study (18–19). H₂O₂ concentrations in these previous studies varied from 2.1 to 49.5 mM and were more than 1 order of magnitude higher than those in our study at a similar pH. Experimental conditions were 0.1 M ionic strength, temperatures in the range 0.8–25 °C, and pH < 2.0. These previous workers were particularly interested in studying the kinetics of the formation and decomposition of Cr(VI) peroxy derivatives. To this end, they measured the absorbance of the blue peroxochromic acid CrO₅(H₂O) at 580 nm, where this species absorbs and all the other chromium species give negligible absorption. The rates of the formation of CrO₅(H₂O) were found to be first-order in H⁺, H₂O₂, and HCrO₄⁻ concentrations, according to the equation rate

$$d[\text{CrO}_5]/dt = k_f[\text{H}^+][\text{H}_2\text{O}_2][\text{HCrO}_4^-] \quad (6)$$

where CrO₅ is a simplified formula of peroxochromic acid and k_f is the third-order rate constant with the value $2.0 \times 10^4 \text{ M}^{-2} \text{ sec}^{-1}$ at 25 °C (18).

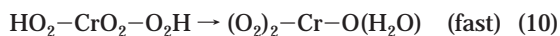
The mechanism proposed for the formation of CrO₅(H₂O) was



The monoperoxy species produced in the rate-determining step (eq 8) reacts with a second molecule of hydrogen peroxide exchanging OH for O₂H



Finally, the product of this step (eq 9) undergoes an internal rearrangement, leading to the formation of the diperoxy-chromium derivative, through two protons moving from the O₂H groups to one double-bonded oxygen and one water molecule are thought to remain in the intermediate (27)



The rates of the formation of CrO₅(H₂O) by the reaction of Cr(VI) with H₂O₂ were also studied in a tri-*n*-butyl phosphate–cyclohexane mixture (28).

The subsequent decomposition of peroxochromic acid is usually slow enough not to interfere with its formation, unless the acidity is very high ($\geq 2 \text{ M}$), according to the following rate law (19)

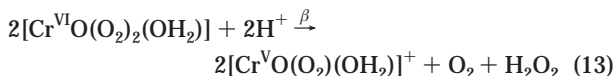
$$-d[\text{CrO}_5]/dt = k_d[\text{CrO}_5][\text{H}^+]^2 \quad (11)$$

where the suffix d refers to the rate constant for the decomposition of CrO₅, while k_f in eq 6 refers to the rate constant for the formation.

In a more recent study (29), the rates of decomposition of the chromium(VI)–peroxo complex were given by

$$\begin{aligned} -d[\text{CrO}_5]/dt &= k_2[\text{CrO}(\text{O}_2)_2][\text{H}^+] + k_3[\text{Cr}(\text{OH})(\text{O}_2)_2^+][\text{H}^+] \\ &= ((k_2 + k_3K^H[\text{H}^+])/(1 + K^H[\text{H}^+]))[\text{H}^+][\text{CrO}_5] \quad (12) \end{aligned}$$

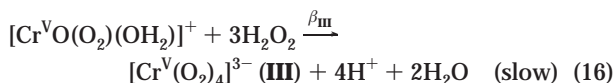
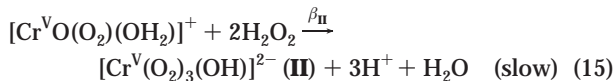
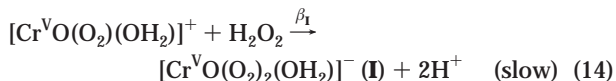
where k_2 and k_3 are the specific rate constants for the decomposition of the free and protonated peroxochromium(VI) complex, respectively, K^H is the equilibrium formation constant of H₂CrO₄, and [CrO₅] is the sum of the concentrations of free and protonated Cr(VI) diperoxy species. According to eq 12, the rates of decomposition are first-order in [H⁺] at an acidity lower than about 0.3 M, while they showed an increase in the kinetic order at an acidity higher than 1 M (29). The rates of decomposition of CrO₅ were found to be independent of [H₂O₂]. This contrasts with the rates observed in this study, which showed a kinetic order (n) with respect to H₂O₂ in the range 1–3 and suggests that the conversion of CrO₅ to Cr³⁺ involves some other intermediate. It is worth remarking that previous workers measured the rates for the loss of CrO₅(H₂O), not the rates of formation of Cr(III). The presence of an intermediate during the decomposition of CrO₅(H₂O) was indeed expected because chromium is undergoing a three-electron change and peroxide a two-electron change (30). Because the DPC method used in this study gives the sum of Cr(VI) and Cr(V) species, we postulate that the decomposition of CrO₅ and its conversion to Cr(III) is mediated by the formation of Cr(V) peroxy species. The reduction of CrO₅(H₂O) to Cr(V) follows one-electron transfer from a coordinated peroxo group to the central chromium. This one-electron reduction, which is probably facilitated by protonation, controls the decomposition of CrO₅, according to the eq 13



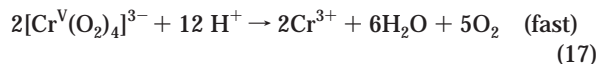
which is consistent with the independence of the loss of CrO₅(H₂O) on H₂O₂, previously reported (29).

Funahashi et al. (29), in their discussion on the mechanisms for the decomposition of CrO₅, did not rule out the possibility of a Cr(V) pathway, and recently, Zhang and Lay (24) have obtained, through EPR spectroscopy, experimental evidences for the presence of Cr(V) peroxy species in the pH range 4–9. At pH < 4, they were not able to obtain Cr(V) signal, probably owing to the increased reactivity of these species with decreasing pH. These Cr(V) species add to the blue peroxochromic acid and its violet deprotonated derivative, which are present at pH < 4 and in the pH range 4–7, respectively.

The Cr(V) monoperoxocomplex, obtained following reaction 13, gives rise to rate-determining reactions leading to the formation of chromium(V) di- (I), chromium(V) tri- (II), and chromium(V) tetraperoxide (III), according to



The Cr(V) species **I**, **II**, and **III** quickly undergo decomposition to Cr(III). In the case of tetraperoxychromate (**III**), the reaction is



The smooth transition of the kinetic order with respect to the proton and H_2O_2 concentrations which result from our data suggests that reactions (14–16) whose relative importance depends on the pH and $\text{H}_2\text{O}_2/\text{Cr(VI)}$ ratio (24) control the decomposition of $\text{CrO}_5(\text{H}_2\text{O})$ and its final conversion to $\text{Cr}(\text{H}_2\text{O})_6^{3+}$.

However, the rates observed in this study are similar to those specifically reported for the loss of $\text{CrO}_5(\text{H}_2\text{O})$. Orhanovic' and Wilkins (19) reported a pseudo-first-order rate constant of 0.0046 s^{-1} , which gives a half-life of 150.7 s for the decomposition of $\text{CrO}_5(\text{H}_2\text{O})$ at 0.097 M acid, 4 °C, and 6 M ionic strength with 2 mM H_2O_2 and 100 μM Cr(VI). Funahashi et al. (29) give, at 25 °C, 3.0 M ionic strength, and pH 1, a conditional first-order rate constant of 0.0274 s^{-1} for the reaction of $8 \times 10^{-5} \text{ M}$ Cr(VI) with 2.61–10.4 mM H_2O_2 , corresponding to a half-life of 25.3 s. Our results in much more diluted solutions (0.01 M NaCl), with significantly lower concentrations of reactants (1.9 μM Cr(VI) and 100 μM H_2O_2), give a value for the pseudo-first-order rate constant at pH 1.5 (our lowest pH) of 0.0693 min^{-1} (see Table 3). Because the rates at this low pH were first-order with respect to H_2O_2 concentrations (see Figure 3), we can calculate a value of 1.386 min^{-1} with 2 mM H_2O_2 and pH 1.5, which gives a half-life of 30 s. On the other hand, the regression equation of $\log k_1$ data as a function of pH at 100 μM H_2O_2 (see Table 3) gives a value of 0.57 min^{-1} at pH 1, which corresponds to $k_1 = 11.4 \text{ min}^{-1}$ with 2 mM H_2O_2 . A half-life of 3.6 s results from the latter k_1 value; temperature and ionic strength should not significantly affect this half-life because the rates of the reduction were independent of these variables. Therefore, it can be compared with $t_{1/2}$ of 150.7 and 25.3 s resulting from previous works (19, 29) and suggests that the rates of the reaction in this study are a factor of about 40 and 7 faster, respectively.

According to reactions 14–16, the rates of the reduction of Cr(VI) to Cr(III) may be expressed as

$$-d[\text{Cr(VI)}]/dt = [\text{Cr}^{\text{V}}\text{O}(\text{O}_2)(\text{OH}_2)]^+ (k_{\text{I}}[\text{H}_2\text{O}_2] + k_{\text{II}}[\text{H}_2\text{O}_2]^2 + k_{\text{III}}[\text{H}_2\text{O}_2]^3) \quad (18)$$

where k_{I} , k_{II} , and k_{III} are the specific rate constants for the reaction (14–16). The concentrations of the Cr^V monoperoxocomplex are given by

$$[\text{Cr}^{\text{V}}\text{O}(\text{O}_2)(\text{OH}_2)]^+ = \beta^{1/2} [\text{Cr}^{\text{VI}}\text{O}(\text{O}_2)_2(\text{OH}_2)] [\text{H}^+] / p\text{O}_2^{1/2} [\text{H}_2\text{O}_2]^{1/2} \quad (19)$$

where β is the equilibrium constant for eq 13.

According to this model, the independence of the rates on ionic strength reflects the presence of at least one neutral molecule in the rate-controlling step, while the near independence on temperature reflects a balance between two opposite effects of increasing temperature (the decrease in the concentration of the Cr^V monoperoxocomplex because of the decrease in the equilibrium constant for the formation of peroxychromic acid (29) and the probable increase in the rate constants k_{I} , k_{II} , and k_{III}).

Unfortunately, the lack of thermodynamic data for the Cr^V monoperoxocomplex (24) prevents any evaluation of the specific rate constants of the reacting species.

However, on the basis of the results of this study, we can express the overall constant k in terms of the pseudo-first-

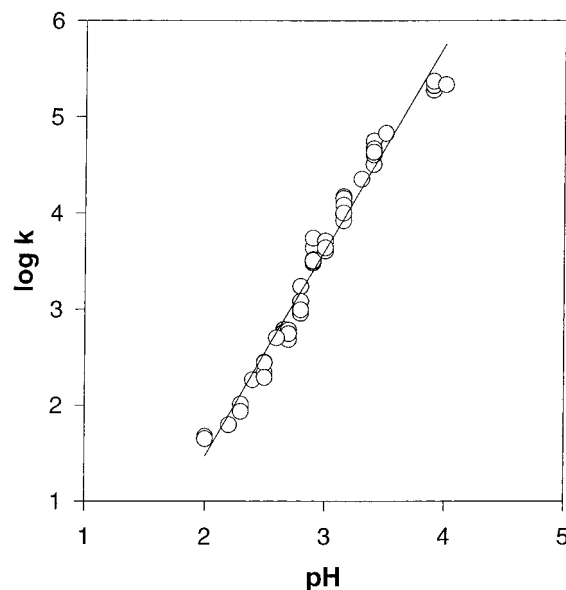


FIGURE 5. Estimated values of $\log k$ ($k, \text{M}^{-n} \text{min}^{-1}$) for the reduction of Cr(VI) with H_2O_2 as a function of pH.

Estimated values of k_2 as a function of pH

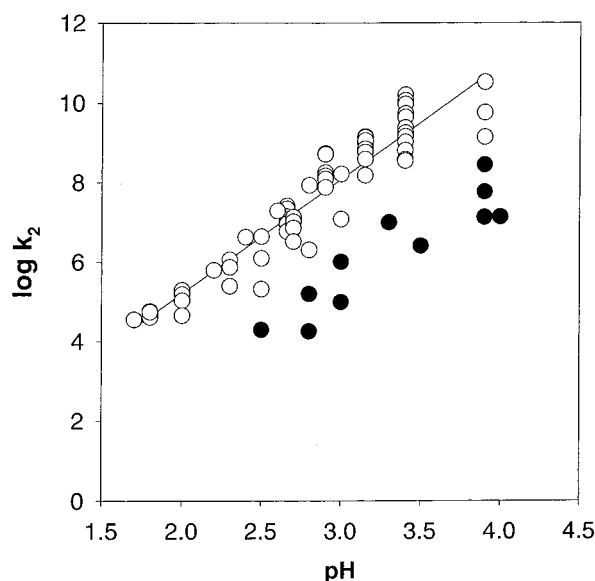


FIGURE 6. Estimated values of $\log k_2$ ($k_2, \text{M}^{-(n+2)} \text{min}^{-1}$) as a function of pH. The regression line fits all of the data (64 out of 75), with H_2O_2 concentrations of <3 mM (empty circles).

order constant (k_1) and the value (n), which is given by the relationship 4, according to

$$\log k = \log k_1 - ((3 \times 10^3)/(1 + 10^3)) \log [\text{H}_2\text{O}_2] \quad (20)$$

Equation 20 is valid in the pH range 2–4, where n tends to increase; given the nearly independence of rates on ionic strength and temperature, this equation may be applied from 0.01 to 2 M and 5 to 40 °C. The values of $\log k$ (Figure 5) calculated by the eq 20 are described in the pH range 2–4 by

$$\log k = 2.14\text{pH} - 2.81 \quad \sigma = \pm 0.18 \quad (21)$$

We have also calculated the values of k_2 according to the eqs 2 and 3 and found that they are dependent on pH as well (Figure 6). The k_2 data appear to be grouped in two different

groups, corresponding to the concentrations of H_2O_2 at either $< \text{ or } \geq 3 \text{ mM}$. The value of k_2 with $[\text{H}_2\text{O}_2] < 3 \text{ mM}$ using 85% of the data is described by

$$\log k_2 = 2.87\text{pH} - 0.55 \quad \sigma = \pm 0.54 \quad (22)$$

Therefore, the rates for the reduction of Cr(VI) with H_2O_2 may be calculated through the eq 6, where n , z , and k_2 are given by eqs 4, 5, and 22 and the kinetic order with respect to Cr(VI) (m) is equal to 1.

This reaction may have a role in acidic environmental solutions in the presence of high micromolar concentrations of H_2O_2 . Aerosols and fog droplets where pH is in the range of 1–3 and H_2O_2 concentrations may be $> 100 \mu\text{M}$ (16, 21) are possible solutions where this reaction can occur. By using the scenario considered in previous simulations (21) (liquid-coated particles with $\text{pH} = 1$, liquid water content $= 10^{-4} \text{ g/m}^3$, and $[\text{H}_2\text{O}_2] = 1.4 \cdot 10^{-6} \text{ g/m}^3$), we can calculate a half-life for the reaction of Cr(VI) with H_2O_2 of about 0.02 s. This is comparable with the fastest half-lives resulting from these simulations in the presence of 10^{-8} and 10^{-7} g/m^3 of V(II) and Fe(II), respectively (21). With H_2O_2 concentrations of 10^{-3} M , half-lives for Cr(VI) are about 4 h and 18 min at pH 3 and 2 and are comparable with those resulting for the copper-catalyzed photoreduction of Cr(VI), which range from 3 min to 2 h (16).

Therefore, this process may affect the atmospheric transport and deposition of reduced and oxidized species of chromium. The reduction of Cr(VI) with H_2O_2 may also be of interest for engineered systems concerned with the removal of Cr(VI) from wastewaters, which includes a preliminary conversion of Cr(VI) to Cr(III) and its subsequent precipitation.

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