oxidized to the one-electron reduced and to the two-electron reduced states. An approximately linear relationship between electrode potential and the CO stretching frequency is found for both ^{12}CO and ^{13}CO, but the variation in the position with potential is somewhat smaller than in the aqueous electrolyte. The shift in the nonaqueous electrolyte is about 20 cm^{-1} V^{-1}. The shift of the stretching frequency upon replacement of ^{12}C by ^{13}C is about the same as in the aqueous solution, 35 cm^{-1}.

The results illustrated in Figures 2–4 are in accord with the conclusion that increased electron density at the Pt surface will result in a lower frequency for CO bound to the surface of the Pt. The magnitude of the shift in frequency is quite similar to that found by other workers[13,14] for CO on smooth Pt in acidic aqueous solution, even though the earlier work was carried out in a different potential regime, generally no more negative than the H_2 evolution potential. The results presented here elaborate the earlier findings in showing that the electrode potential can be used to effect variations in the properties of coordinated CO in a wide range of media and for situations where the Pt surface area is high. Since the shift in the CO stretching frequency varies with a change in the n-Si electrode potential, it can be concluded that the dispersed Pt is in charge-transfer equilibrium with the Si via the redox polymer. This conclusion has been drawn independently from studies of H_2 evolution from electrodes like that represented in Scheme I.[2–4]

We have developed the results as if the changes in the CO stretching frequency occur because the Pt is moved more negative in potential and its surface is therefore more electron-rich. It must be noted that the mechanism for achieving the lower stretching frequencies involves reduction of the redox polymer, which changes the environment about the Pt. Not only does the redox polymer change, but the number of anions is also diminished. In one view, the redox polymer can be regarded as a coligand with adjustable electron donor ability to the Pt. This is analogous to being able to adjust the electron donor ability of the arene group in (arene)$M(CO)_3$, for example, without changing the steric properties. Another mechanism for affecting the CO stretching frequency of electrode-bound CO is the electric field changes associated with the near-electrode region. The bound CO is certainly in the double-layer region, and it is not clear whether the field can alter the spectral properties to the extent and in the direction found. It is known that there can be consequences on electrode reaction rates associated with species in the double-layer region.[17] But whatever the mechanism, the point is that a large amount of CO that can be bound to dispersed Pt can be manipulated with respect to important physical and chemical properties to a significant extent when the redox polymer can equilibrate with the Pt and with the conducting substrate onto which the polymer is immobilized.

It is interesting to compare the absolute magnitude of the shifts in the CO stretching frequencies with discrete metal complexes like those mentioned in the introduction. The magnitude of the shift that can be observed for the CO bound to the dispersed Pt is of the same order as can be obtained for variation in substituents in ligands like C_6H_6 or $C_5H_5^-$,[5–7] and interestingly, the variation found here is also of the same order as typically found upon one-electron oxidation or reduction of metal carbonyl species.[8,22] Since there are many situations where large changes in reactivity of coordinated ligands can be effected by changes in the electron density on the metal, the results found here suggest that high-surface-area electrodes based on dispersed metals may prove useful in modulating the reactivity of substrates that coordinate to the metal. A reaction that may illustrate such effects is represented by the exchange of oxygen of H_2O with the oxygen of CO bonded to metals.[23] Work on such exchange chemistry is under way in this laboratory to attempt to demonstrate that electrode potential can be used to modulate the reactivity of coordinated molecules in a manner consistent with changes in the spectroscopy of coordinated ligands. Correlating the potential dependence of spectral changes and reaction rates may allow conclusions regarding the mechanism of effecting the changes in the infrared spectrum of electrode-bound CO.

Acknowledgment. We thank the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, for support of this research. J.-F.A. also acknowledges support as a Postdoctoral Fellow from the Swiss National Science Foundation, 1983–1985. We wish to acknowledge the contributions of Drs. Raymond N. Dominey and Alan B. Fischer in the early work on the carbonylation of Pt-impregnated redox polymer, including the spectral results presented in Figure 1.

Registry No. I, 74173-49-2; $LiClO_4$, 7791-03-9; LiCl, 7447-41-8; ^{13}CO, 1641-69-6; Si, 7440-21-3; Pt, 7440-06-4.

---

(22) Summers, D. P. Ph.D. Thesis, Massachusetts Institute of Technology, 1984.

(23) (a) Muetterties, E. L. *Inorg. Chem.* **1965**, *4*, 1841. (b) Darensbourg, D. J.; Froelich, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 4726.

Contribution from the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Kinetics and Mechanism of the Reaction of CrO_2^{2+} with Hydrazinium Ions in Aqueous Acidic Solutions

Suzanne L. Bruhn, Andreja Bakac, and James H. Espenson*

Received August 19, 1985

Hydrazinium ion is oxidized by CrO_2^{2+} in aqueous perchloric acid at a rate given by $-d[CrO_2^{2+}]/dt = (k_0 + k[N_2H_5^+][H^+])[CrO_2^{2+}]$, with $k_0 = 7 \times 10^{-4}$ s^{-1} and $k = 58.1$ ($\mu = 0.10$) and 50.4 ($\mu = 1.0$) M^{-2} s^{-1} at 25.0 °C. The rate-limiting step is believed to be formation of the protonated hydrazyl radical cation, which reacts further when $HCrO_4^-$ is added but otherwise disproportionates.

Introduction

In dilute aqueous solutions neither N_2H_4 nor $N_2H_5^+$ reacts with O_2, although neat hydrazine does react with molecular oxygen. Since O_2 can be activated by coordination,[1–4] we have investigated CrO_2^{2+} (eq 1). It is a species[5,6] that is sufficiently long-lived and well characterized[7] to be studied *in the absence of* Cr^{2+} *and* O_2.

$$Cr^{2+} + O_2 \xrightarrow{k = 1.6 \times 10^8\ M^{-1}\ s^{-1}} CrO_2^{2+} \qquad (1)$$

---

(1) Endicott, J. F.; Kumar, K. *ACS Symp. Ser.* **1982**, *No. 198*, 425.

(2) Spiro, T. G., Ed. "Metal Ion Activation of Dioxygen"; Wiley: New York, 1980.

(3) Hayaishi, O., Ed. "Molecular Mechanisms of Oxygen Activation"; Academic Press: New York, 1976.

(4) Schultz, J., Cameron, B. F., Eds. "The Molecular Basis for Electron Transport"; Academic Press: New York, 1972.

0020-1669/86/1325-0535$01.50/0

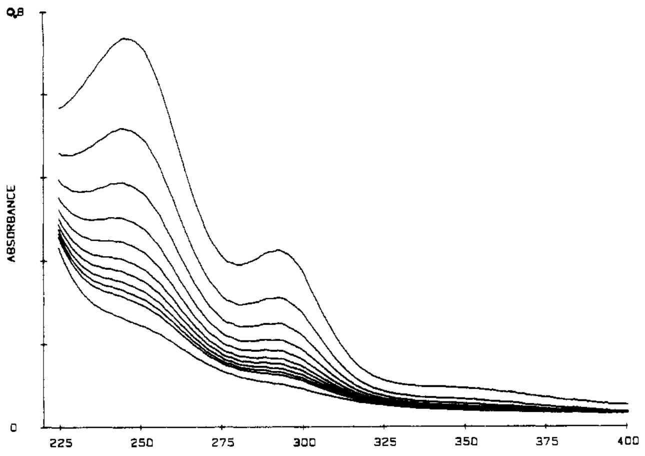


Figure 1. UV spectrum of CrO_2^{2+}. The spectrum fades as CrO_2^{2+} reacts with $N_2H_5^+$; the run shown has respective initial concentrations of 62 μM and 3.01 mM at 0.200 M H^+ and ionic strength 1.0 M. Spectra were recorded intermittently with a diode-array spectrophotometer, the first 10 at intervals of 40.0 s and the lowest, corresponding to complete reaction, after a total elapsed time of 560 s.

The reaction between Cr^{2+} and $N_2H_5^+$ in aqueous perchloric acid solutions has been attempted. One report[8] (which we have independently verified) found no reaction between Cr^{2+} and $N_2H_5^+$ in 24 h at 25.0 °C; another,[9] under quite comparable conditions, noted a reaction (*reduction* of hydrazine by chromium(II) ions), which follows the rate law $-d[Cr^{2+}]/dt = 2k[Cr^{2+}][N_2H_5^+]$, with $k = 1.32\ M^{-1}\ s^{-1}$ at 25.0 °C, independent of $[H^+]$, 10^{-6}–1.0 M.

The conflicting reports might be better understood, if not resolved, should it have happened that the experimental procedure used by the latter workers allowed the entry of oxygen from the atmosphere. If so, then reactions of $N_2H_5^+$ with CrO_2^{2+} might have been responsible. This possibility provided an additional impetus for this work.

A reaction does indeed occur between CrO_2^{2+} and $N_2H_5^+$. To a first approximation, at least, the stoichiometry is represented by eq 2. The reaction kinetics are reported here, along with

$$CrO_2^{2+} + N_2H_5^+ = Cr^{3+} + H_2O_2 + {}^1/_2(N_2 + NH_3) \quad (2)$$

additional experiments relating to the detection and trapping of reaction intermediates.

Results

Products and Stoichiometry. The absorbance changes accompanying the reaction are illustrated for a typical run in Figure 1. The UV peaks of CrO_2^{2+} at 245 and 290 nm fade completely over the course of the reaction, to be replaced at the end by the weak spectrum of a Cr(III) complex. Cation-exchange chromatography on Sephadex C25 allowed us to identify it as $Cr(H_2O)_6^{3+}$. The monoammine complex $(H_2O)_5CrNH_3^{3+}$ was absent; a blank using the authentic complex[10,11] showed that it would not have escaped detection.

Attempts were made to detect the hydrogen peroxide shown in eq 2. That failed, however, but blanks showed that even a comparable concentration of deliberately added H_2O_2 was largely destroyed during the reaction. Since CrO_2^{2+} can be prepared only at very low concentrations, a full stoichiometric and product analysis could not be done; the nitrogen products were inferred to be N_2 and NH_3 on the basis of the reaction chemistry. In one run having $[N_2H_5^+]_0 >> [CrO_2^{2+}]_0$, the $[N_2H_5^+]$ remaining at the end of the run was determined. The value found was in essential agreement with the initial concentration, which confirmed that $N_2H_5^+$ was not being catalytically decomposed during the reaction.

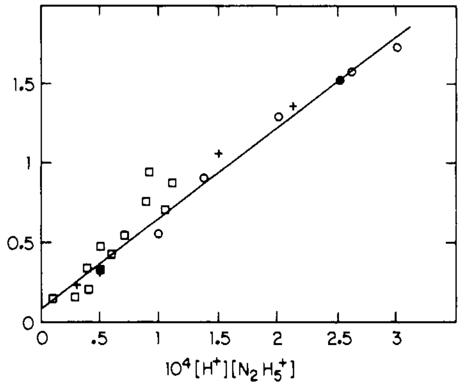


Figure 2. Kinetic data for the reaction between CrO_2^{2+} and $N_2H_5^+$ at 0.1 M ionic strength, shown as a plot of k_ψ vs. $[N_2H_5^+][H^+]$ in solutions containing 20–40 μM $HCrO_4^-$. The symbols refer to different $[H^+]$: 0.010 (squares), 0.030 (pluses), and 0.050 M (circles). The lack of effect of additional added $HCrO_4^-$ is shown by the two filled symbols for runs in which $[HCrO_4^-]_0$ = 90 μM.

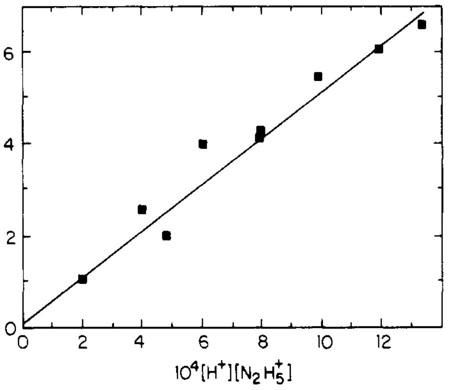


Figure 3. Kinetic data as in Figure 2 at 1.0 M ionic strength. The value of $[N_2H_5^+]$ was calculated from the species concentrations with K_a = 11.2 M. Data refer to 0.05 < $[H^+]$ < 0.50 M.

In 24 h, long after the complete disappearance of CrO_2^{2+}, a new, sharp UV peak at 320 nm grew in the spectrum. The species responsible was not identified, but we presume it is not a feature of this reaction because a similar peak begins to form when $Cr(H_2O)_6^{3+}$ and H_2O_2 are allowed to stand. Given the complexity of species formed in chromium–peroxide reactions,[12] this is not surprising.

Kinetics. The kinetic runs had $[CrO_2^{2+}]_0$ much lower than both $[N_2H_5^+]$ and $[H^+]$. *Provided $HCrO_4^-$ was present* (in the CrO_2^{2+} solution or added to the reaction at low concentration, typically 20–40 μM), the reaction followed pseudo-first-order kinetics. Pseudo-first-order rate constants measured at $0.010 \leq [H^+] \leq 0.05$ M vary linearly with the product $[N_2H_5^+][H^+]$ (eq 3), as

$$-d[CrO_2^{2+}]/dt = (k_0 + k[N_2H_5^+][H^+])[CrO_2^{2+}] \quad (3)$$

shown in Figure 2. A least-squares analysis gives $k_0 \sim 7 \times 10^{-4}\ s^{-1}$, in agreement with the known value,[7] and $k = 58.1 \pm 1.2\ M^{-2}\ s^{-1}$ at 25.0 °C and μ = 0.1 M.

Other determinations were carried out at ionic strength 1.0 M, with $0.050 \leq [H^+] \leq 0.50$ M. To allow for $N_2H_6^{2+}$ (which has $K_a = 11.2$ M[13]), the total concentration of hydrazine was multiplied by the factor $K_a/(K_a + [H^+])$, converting it to $[N_2H_5^+]$. The latter was used to calculate the abscissa of Figure 3. This treatment, which then represents the same kinetic analysis as in eq 3, yields $k = 50.4 \pm 2.4\ M^{-2}\ s^{-1}$ at μ = 1.0 M.

---

(5) Ilan, Y. A.; Czapski, G.; Ardon, M. *Isr. J. Chem.* **1975**, *13*, 15.

(6) Sellers, R. M.; Simic, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 6145.

(7) Further characterization of CrO_2^{2+} has been completed, and the pathways for its slow decomposition have been resolved. (Brynildson, M. E.; Bakac, A.; Espenson, J. H., submitted for publication.)

(8) Schmidt, W.; Swinehart, J. H.; Taube, H. *Inorg. Chem.* **1968**, 1984.

(9) Wells, C. F.; Salam, M. A. *J. Chem. Soc. A* **1968**, 1568.

(10) Espenson, J. H.; Carlyle, D. W.; *Inorg. Chem.* **1966**, *5*, 586.

(11) Ardon, M.; Mayer, B. E. *J. Chem. Soc.* **1962**, 2816.

(12) Adams, A. C.; Crook, J. R.; Bockhoff, F.; King, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 5761.

(13) Schwarzenbach, G. *Helv. Chim. Acta* **1936**, *19*, 178.

Kinetic Isotope Effect. The reaction between $(D_2O)_nCrO_2^{2+}$ and $N_2D_5^+$ in D_3O^+/D_2O solutions was also studied at ionic strength 0.10 M and 25.0 °C. The plot of k_{ψ} vs. $[N_2D_5^+][D^+]$ gives $k = 18.1 \pm 0.6$ M^{-2} s^{-1}. The kinetic isotope effect, $k_H/k_D = 3.2$, although substantial, represents the cumulative effect of a large number of hydrogens in the activated complex.

Experiments without $HCrO_4^-$. Pseudo-first-order kinetic plots tailed at long times, as if a second component of a biphasic system were present. The apparent rate constants from the first reaction stage were also linear functions of the product $[N_2H_5^+][H^+]$, with $k = 15 \pm 3$ M^{-2} s^{-1} at 1.0 M ionic strength and 25.0 °C, roughly a third of that obtained in the absence of $HCrO_4^-$. The intercept is $(5.5 \pm 0.7) \times 10^{-3}$ s^{-1}, about 8 times larger than the known value of k_0 (the latter is independent of whether or not $HCrO_4^-$ is present[7]).

The Hydrazyl Radical Intermediate. Efforts were made to establish whether the protonated hydrazyl radical cation $\cdot N_2H_4^+$ is an intermediate in this reaction. It has been shown that both Fe^{3+} and Cu^{2+} are reduced by hydrazyl radicals.[14-16] The former could not be employed at a sufficient concentration to learn whether it had an effect on the reaction, owing to its intense UV spectrum, which obscured that of CrO_2^{2+} and thus prevented kinetic measurements.

Even the highest concentration of Cu^{2+} used, 0.15 M, did not alter the rate. This may indicate (a) that $\cdot N_2H_4^+$ is not, in fact, an intermediate, (b) that a $\cdot N_2H_4^+$ intermediate enters the mechanism in such a way that "kinetic trapping", even if successful, will not be manifest in $-d[CrO_2^{2+}]/dt$ (e.g., if Cu^+ reacts with H_2O_2 rather than with CrO_2^{2+}), or (c) that a $\cdot N_2H_4^+$ intermediate may not be sufficiently reactive toward Cu^{2+}, as compared to its other reactivity, that it can be diverted in the circumstances of these experiments. The latter appears to be the case here.

The oxidation of $N_2H_5^+$ by Ce^{4+} produces $\cdot N_2H_4^+$, eq 4.[17] This reaction serves as a model for the reaction of CrO_2^{2+} with $N_2H_5^+$.[18]

$$N_2H_5^+ + Ce^{4+} \rightarrow \cdot N_2H_4^+ + Ce^{3+} + H^+ \qquad (4)$$

Discussion

Reaction Mechanism. The first-order dependence on $[H^+]$ suggests that the reactant pair is either $N_2H_6^{2+}$ and CrO_2^{2+} or $N_2H_5^+$ and CrO_2H^{3+}. We suggest the second of the following possible reactions since (a) addition of H^+ would make the hydrazinium ion an even poorer electron donor and (b) protonation of CrO_2^{2+} stabilizes the incipient Cr(III)-peroxide product, a species believed (e.g., compare H_2O_2, $pK_a = 11.9$) to have a very basic site.

$$N_2H_6^{2+} + CrO_2^{2+} \rightarrow \cdot N_2H_5^{2+} + CrO_2H^{2+} \qquad (5a)$$

$$N_2H_5^+ + CrO_2H^{3+} \rightarrow \cdot N_2H_5^{2+} + CrO_2H^{2+} \qquad (5b)$$

Both would give rise to the same products. The product, CrO_2H^{2+}, is thought to react further:

$$CrO_2H^{2+} + H_3O^+ \rightarrow Cr(H_2O)_6^{3+} + H_2O_2 \qquad (6)$$

The proposed steps in this mechanism are summarized in Scheme I, which also shows a plausible sequence of reactions that might follow the rate-limiting step.[19] We suggest that $\cdot N_2H_4^+$ is lost by disproportionation, a known reaction,[20,21] rather than by further oxidation by CrO_2^{2+}. Were the latter to occur, $HCrO_4^-$ would not have had the observed effect on the kinetics. We also suggest that the second and rate-limiting step is reversible. Such is proposed to be the case in the oxidation of $N_2H_5^+$ by $IrCl_6^{2-}$,[22b] for much the same reason; first-order kinetic plots were badly curved under conditions where the reverse reaction became important. The explanation we offer for the simplifying effect of $HCrO_4^-$ is that it reacts rapidly enough with the protonated radical cation to prevent the reverse step.

Scheme I

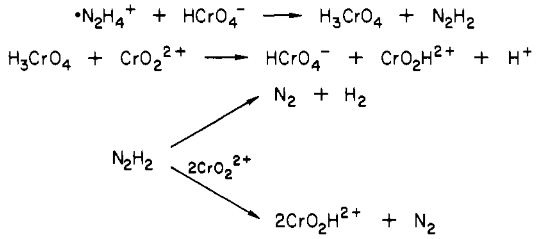
$$CrO_2^{2+} + H^+ \rightleftharpoons CrO_2H^{3+}$$

$$CrO_2H^{3+} + N_2H_5^+ \rightleftarrows CrO_2H^{2+} + \cdot N_2H_5^{2+}$$

$$\cdot N_2H_5^{2+} \rightarrow \cdot N_2H_4^+ + H^+$$

$$2(\cdot N_2H_4^+) \rightarrow N_2 + 2NH_4^+$$

Scheme II



Possible reactions detailing the effects of $HCrO_4^-$ are shown in Scheme II. That $\cdot N_2H_4^+$ might reduce $HCrO_4^-$ in a one-electron step is reasonable, as this radical is known to reduce Fe^{3+} and Cu^{2+}.[14-16] Likewise, it is reasonable that a chromium(V) product H_3CrO_4 would be readily reoxidized as in the reaction written for CrO_2^{2+}; indeed, the preferred reaction of chromium(V) is a one-electron transformation back to chromium(VI).[23] The next putative intermediate, diazene, might decompose on its own[22] or by reaction with CrO_2^{2+}. This scheme also rationalizes the way in which the rate of consumption of CrO_2^{2+} is enhanced when $HCrO_4^-$ is added, despite the fact that $HCrO_4^-$ and CrO_2^{2+} do not react directly with one another.

The rate of decomposition of CrO_2^{2+} in the absence of $HCrO_4^-$, extrapolated to $[N_2H_5^+] = 0$, is some 6–8 times higher than the directly observed value in the absence of hydrazine. ($k_0 = 7 \times 10^{-4}$ s^{-1}, independent of $HCrO_4^-$.[7]) The increase suggests that some marginaly efficient chain process may also enter; steps such as those in Scheme II could well contribute.

Experimental Section

Reagents. The solution containing CrO_2^{2+} at high dilution (20–80 μM) was prepared immediately prior to each experiment, since the complex is not stable for a long time.[7] It was prepared by rapidly mixing a freshly diluted solution of Cr^{2+} in perchloric acid with O_2-saturated water or perchloric acid.[24] As reported earlier,[5,6] solutions of CrO_2^{2+} are characterized by intense UV absorptions; maxima occur at 290 and 245 nm, with molar absorptivities of 3×10^3 and 6×10^3 M^{-1} cm^{-1}, respectively. The residual oxygen in each solution of CrO_2^{2+} was immediately removed by purging it with a vigorous stream of nitrogen introduced through a gas-dispersion tube for ca. 5 min.

---

(14) Cahn, J. W.; Powell, R. E. *J. Am. Chem. Soc.* **1954**, *76*, 2568.

(15) Higginson, W. C. E.; Wright, P. *J. Chem. Soc.* **1955**, 1551.

(16) Rosseinsky, P. R. *J. Chem. Soc.* **1957**, 4685.

(17) (a) Adams, J. Q.; Thomas, J. R. *J. Chem. Phys.* **1963**, *39*, 1904. (b) Falle, H. R. *Can. J. Chem.* **1968**, *46*, 1703.

(18) The ESR detection of $\cdot N_2H_4^+$ from eq 4 by use of a syringe-flow device was reproduced in our work to Ce(IV) concentrations as low as 10^{-3} M. Attempts to apply this method to CrO_2^{2+} gave no detectable signal, however, perhaps because of its low concentration or the enhanced reaction rate at the high $[N_2H_5^+]$ and $[H^+]$ (0.7 and 3 M, respectively) that were used in an attempt to increase $[\cdot N_2H_4^+]_{ss}$.

(19) It is important to recognize that considerable speculation enters; not only are all of the usual limitations of inferring the nature of rapid follow-up reactions from steady-state kinetics present but this particular system is an especially difficult one because CrO_2^{2+} is available only at unusually low concentrations, precluding a quantitative analysis of all of the products formed and the confident detection of reaction intermediates.

(20) Hayon, E.; Simic, M. *J. Am. Chem. Soc.* **1972**, *94*, 42.

(21) Inbar, S.; Cohen, S. G. *J. Am. Chem. Soc.* **1978**, *100*, 4490.

(22) (a) Stedman, G. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 113. (b) Morris, D. F. C.; Ritter, T. J. *J. Chem. Soc., Dalton Trans.* **1980**, 216.

(23) Espenson, J. H. *Acc. Chem. Res.* **1970**, *3*, 347 and references therein.

(24) In the initial stages of the work, the CrO_2^{2+} solutions were prepared by using 10 mL of 6×10^{-4} M Cr^{2+} and 40 mL of the O_2 solution; later, 10 mL of 2×10^{-4} M Cr^{2+} and 30 mL of O_2 solution were used. Both typically yielded ca. 50–60 μM CrO_2^{2+}, but the former contained a comparable concentration of chromium(VI), $HCrO_4^-$, whereas little if any $HCrO_4^-$ was detected spectrophotometrically in the latter solution. The distinction between the two is important because of the effect $HCrO_4^-$ has on the reaction of CrO_2^{2+} with $N_2H_5^+$, not because of its direct oxidation[25] of $N_2H_5^+$.

(25) Haight, G. P.; Huang, T. J.; Platt, H. *J. Am. Chem. Soc.* **1974**, *96*, 3137.

Stock solutions of hydrazinium ion were prepared by adding hydrazine hydrate to a boiled[26] solution of aqueous perchloric acid at equimolar concentration, effectively yielding $N_2H_5^+ClO_4^-$. The solution was standardized with potassium iodate.[27]

Other materials were reagent grade chemicals, or were prepared as described earlier.[28] For reactions in deuterated solvent, D_2O was used in the preparations described above, such that the reaction solutions contained a mole fraction of D $\geq$0.95.

Methods. The kinetic data were obtained spectrophotometrically, by continuously monitoring the UV absorbance in a cell of 5-cm optical path with a Varian Cary Model 219 spectrophotometer with a thermostated cell holder. Data were mostly obtained at 290 nm, although some data were collected at 245 nm, with identical results. A Perkin-Elmer diode-array spectrophotometer was also used in some experiments.

The experiments were conducted anaerobically with $[N_2H_5^+]$ and $[H^+]$ in great excess over $[CrO_2^{2+}]$. Reactions conducted with oxygen present gave absorbance-time traces that did not reach a stable end point reading or fit first-order kinetics; such experiments are not considered further here. The data we report followed pseudo-first-order kinetics and were evaluated by the standard methods. In experiments where $HCrO_4^-$ was not present, however, the reactions also did not follow pseudo-first-order kinetics; the rate constant for the initial stage was obtained by a biphasic kinetic analysis.

Acknowledgment. The principal support was provided by the National Science Foundation, Grant CHE-8418084.

Registry No. $N_2H_5^+$, 18500-32-8; CrO_2^{2+}, 34021-34-6; $\cdot N_2H_4^+$, 20771-51-1; D_2, 7782-39-0.

---

[26] Smith, P. A. S. "Derivatives of Hydrazine and Other Hydronitrogens Having N-N Bonds"; Benjamin/Cummings: Reading, MA, 1983; p 5.

[27] Vogel, A. I. "Textbook of Quantitative Inorganic Analysis"; Longman Group Ltd.: London, 1978; p 390.

[28] Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 2721.

Contribution from the Department of Chemistry,
Brandeis University, Waltham, Massachusetts 02254

Reaction between Permanganate Ion and Hydrogen Peroxide: Kinetics and Mechanism of the Initial Phase of the Reaction[1]

Reuben H. Simoyi,[2a] Patrick De Kepper,[2b] Irving R. Epstein,* and Kenneth Kustin*

Received September 20, 1985

The reaction between permanganate ion and hydrogen peroxide, studied by stopped-flow experiments, occurs in three stages: a fast initial phase, an induction period, and an autocatalytic step. The reaction is autocatalytic because manganous ion, a product of the reaction, catalyzes the reaction by combining with permanganate ion to form a complex whose breakdown products react faster with peroxide than does the complex. Retardation of the first phase to give the induction period is also due to manganous ion, which preferentially binds to permanganate, forming a relatively nonreactive intermediate, thus shutting down the first phase. At 25.0 ± 0.5 °C and ionic strength 1.0 M ($NaClO_4$), the spectrophotometrically determined stoichiometry of the fast initial phase reaction is $2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$. The rate law for the initial phase is $-{}^1/_2 d[MnO_4^-]/dt = (k_3 + k'[H^+])[MnO_4^-][H_2O_2]$ where k' is a composite rate constant that includes the protonation equilibrium constant of MnO_4^-, $k' = (3.1 \pm 0.5) \times 10^2\ M^{-2}\ s^{-1}$, and $k_3 = 23.2 \pm 3.0\ M^{-1}\ s^{-1}$. This reaction is explained by nucleophilic attack of H_2O_2 on manganese(VII) in an inner-sphere mechanism.

Introduction

Permanganate ion has several advantages as an analytical reagent.[3] Above all, it is a strong, vividly colored oxidant, serving as its own indicator. However, these advantages are only realized with rapidly reacting reductants, a requirement frequently fulfilled by adding manganous ion at the start of a titration. This expedient makes permanganate ion reactions generally useful, despite their often balky, irreproducible kinetics.[4]

For example, in closed (batch) reactions, under conditions of nearly equivalent permanganate ion and substrate concentrations or of excess substrate concentration, permanganate ion reactions exhibit complex dynamical behavior. With hydrogen peroxide as substrate, individual phases of the reaction show substrate inhibition and autocatalysis, while the initial rate exhibits maxima and minima in its dependence on substrate and product concentrations.[5,6] Similar behavior has been observed in the permanganate oxidation of the more slowly reacting oxalic acid.[7,8] In an open (flow) reactor, acidified permanganate ion-hydrogen peroxide exhibits bistability,[9] as does permanganate ion-oxalic acid.[10]

The Mn(II)/Mn(III) couple has been successfully introduced into oscillating reaction systems where a high oxidation potential is required, e.g., as a replacement for Ce(III)/Ce(IV).[11] However, its participation in oscillatory processes should be more widespread, owing to the several and relatively stable oxidation states between permanganate (+7) and manganous (+2) ions. Reactions of manganese with dioxygen species, especially, should be attractive candidates for the design of new chemical oscillators, if more were known about their kinetics.

To provide a better understanding of the kinetics of analytical procedures utilizing permanganate ion and to determine the origins of complex dynamical behavior in the permanganate-hydrogen peroxide reaction, we are investigating the different phases of this system. We report here a study of the kinetics of the initial phase of the permanganate ion-hydrogen peroxide reaction by stopped-flow spectrophotometry.

Experimental Section

Materials. The following reagents were used without further purification: manganous perchlorate (G. Frederick Smith Chemical Co.), hydrogen peroxide (30%), potassium permanganate, perchloric acid (70-72%), and sodium perchlorate (Fisher Scientific Co.). Stock solutions of sodium perchlorate (4.0 M) were first filtered before being used as the inert electrolyte to maintain ionic strength at unity.

Potassium permanganate solutions were prepared and standardized against sodium oxalate.[12] The procedure was performed only once to

---

(1) Systematic Design of Chemical Oscillators. 29. Part 28: Epstein, I. R. *Springer Ser. Synergetics* **1984**, *27*, 24.

(2) Permanent addresses: (a) Department of Chemistry, University of Zimbabwe, Mount Pleasant, Harare, Zimbabwe. (b) Centre de Recherche Paul Pascal, Domaine Universitaire, 33405 Talence Cedex, France.

(3) Skoog, D. A.; West, D. M. "Fundamentals of Analytical Chemistry", 1st ed.; Holt, Rinehart and Winston: New York, 1963; p 431.

(4) Stewart, R. "Oxidation in Organic Chemistry"; Wiberg, K. B., Ed.; Academic Press: New York, 1965; Part A., p 1.

(5) Casado, J.; Lizaso-Lamsfus, J. *An. R. Soc. Esp. Fis. Quim.* **1967**, *63*, 739.

(6) Senent, S.; Casado, J.; Lizaso-Lamsfus, J. *An. R. Soc. Esp. Fis. Quim.* **1971**, *67*, 1133.

(7) Malcolm, J. M.; Noyes, R. M. *J. Am. Chem. Soc.* **1952**, *74*, 2769.

(8) Adler, S. J.; Noyes, R. M. *J. Am. Chem. Soc.* **1955**, *77*, 2036.

(9) De Kepper, P.; Ouyang, Q.; Dulos, E. *Springer Ser. Synergetics* **1984**, *27*, 44.

(10) Reckley, J. S.; Showalter, K. *J. Am. Chem. Soc.* **1981**, *103*, 7012.

(11) Alamigir, M.; Epstein, I. R. *J. Phys. Chem.* **1984**, *88*, 2848.

(12) Kolthoff, I. M.; Sandell, E. G. "Textbook of Quantitative Inorganic Analysis", 3rd ed.; Macmillan: New York, 1952; p 564.

0020-1669/86/1325-0538$01.50/0