3694 *Inorg. Chem.* **1986**, *25*, 3694-3697

Contribution from the Department of Chemistry,
University of Missouri, Columbia, Missouri 65211

Reduction of Peroxotitanium(IV) by Iodide, Thiodiethanol, Thioxane, and Thiourea in Acidic Solution

John D. Lydon and Richard C. Thompson*

Received April 10, 1986

The reduction of TiO_2^{2+} with excess iodide ion, thiodiethanol, thioxane, and thiourea was shown to proceed by both a direct reaction and reduction of H_2O_2 present in equilibrium with the peroxo complex. Values of the rate parameters ($M^{-1}\ s^{-1}$) determined for the direct reactions in 1.00 M $HClO_4$ at 25 °C are 3.0×10^{-3} (iodide), 3.1×10^{-2} (thiodiethanol), 4×10^{-5} (thioxane, in 0.16 M $HClO_4$ and $I = 1.0$ M), and 5.6×10^{-3} (thiourea). The rate constants for the competitive reduction of hydrogen peroxide by the substrate were also determined in the kinetic analysis and are in reasonable agreement with values measured in direct studies. In general, TiO_2^{2+} is much less reactive toward reducing agents than is H_2O_2. In contrast, large rate enhancements relative to rates for H_2O_2 are reported for the diperoxo complexes of the d^0 metal ions vanadium(V) and especially molybdenum(VI), at least for the iodide systems. It is concluded that the metal ion center and the degree of peroxide complexation, as well as the solvent, acidity, and nature of the other ligands, are in general important factors in determining the potential catalysis of peroxide reactions by d^0 transition-metal ions.

Introduction

We found in a previous study that the reductions of peroxotitanium(IV), TiO_2^{2+}, by sulfur(IV), titanium(III), and iron(II) in acidic solution were substantially slower than the corresponding reductions of hydrogen peroxide.[1] It was not established whether this rate retardation for peroxotitanium(IV) was general or due to the choice of reductants. While pertinent data are scarce, it has been shown that the reduction of hydrogen peroxide by iodide ion is catalyzed by the d^0 metal ions vanadium(V)[2] and especially molybdenum(VI)[3] due to the formation of peroxo complexes. It is also known that several d^0 metal ions are effective catalysts in promoting the epoxidation of olefins by peroxides, although under quite different experimental conditions than our acidic, aqueous solutions.[4]

We have extended our earlier study by investigating the rate of reduction of peroxotitanium(IV) by iodide ion, thiodiethanol, thioxane, and thiourea. These reductants are known to be reactive toward hydrogen peroxide through a nonradical mechanism involving nucleophilic displacement on peroxide.[5] A further rationale for these studies is that they provide important information for our current investigation of the reactivity of superoxotitanium(IV). In the latter systems peroxotitanium(IV) is an important reduction product and serves as well as the precursor to the superoxo complex.

Experimental Section

Reagents. Thiodiethanol and thioxane were purified by distillation at reduced pressures. Thiourea was recrystallized from water before use. Formamidine disulfide was obtained as the chloride salt by a published procedure.[6] The preparation and analysis of the other reagents have been described previously.[1,8a]

Kinetic Procedures. A large excess of the reductant was used in all the kinetic experiments, both to promote the otherwise very slow reaction rate and to help maximize the reaction with peroxotitanium(IV) rather than the traces of hydrogen peroxide present in equilibrium with TiO_2^{2+}. The reactions were monitored spectrophotometrically by use of a Zeiss PMQII spectrophotometer. The TiO_2^{2+}–I^- reaction was monitored at 469 nm, an isosbestic[7] for I_2 and I_3^- with $\epsilon = 730\ M^{-1}\ cm^{-1}$. The other systems were monitored at the 410 nm absorption maximum of TiO_2^{2+} ($\epsilon = 717\ M^{-1}\ cm^{-1}$ in 1 M $HClO_4$ at 25 °C).

The TiO_2^{2+}–I^- system was studied under a N_2 atmosphere to prevent oxidation of I^- by O_2. The reaction was initiated by addition of an aliquot of concentrated, aqueous NaI into a cell containing the other reagents. It was shown in separate experiments that no detectable reduction of TiO^{2+} by I^- occurred. The thiourea reactions were initiated by addition of a freshly prepared, concentrated aqueous solution of the reductant. The thiodiethanol and thioxane reactions were initiated by the addition of an equilibrated TiO_2^{2+} solution. In this way problems with the addition and slow dissolution of the viscous thiodiethanol and with the volatility and limited solubility of thioxane were minimized.

Results

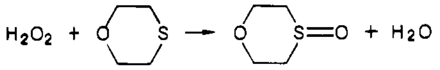
Reaction Stoichiometries. The stoichiometry of the reduction of TiO_2^{2+} by excess I^- was shown to be in accord with eq 1 and is analogous to the H_2O_2–I^- reaction given in eq 2.[9] The other

$$TiO_2^{2+} + 3I^- + 2H^+ \rightarrow TiO^{2+} + I_3^- + H_2O \qquad (1)$$

$$H_2O_2 + 3I^- + 2H^+ \rightarrow I_3^- + 2H_2O \qquad (2)$$

TiO_2^{2+} reactions were assumed to correspond to the stoichiometries established previously for the H_2O_2 systems (eq 3-5).[10] The

$$H_2O_2 + (C_2H_4OH)_2S \rightarrow (C_2H_4OH)_2SO + H_2O \qquad (3)$$



(4)

$$H_2O_2 + 2(NH_2)_2CS + 2H^+ \rightarrow (NH_2)_2CSSC(NH_2)_2^{2+} + 2H_2O \qquad (5)$$

sulfide reactions (thiodiethanol and thioxane) are not complicated by side reactions in the presence of excess reductant. Even with excess hydrogen peroxide the sulfoxide products are only very slowly oxidized further. The thiourea system can be considerably more complex. Reaction 5 is commonly used in the synthesis of salts of formamidine disulfide, $(NH_2)_2CSSC(NH_2)_2^{2+}$. The solids are reasonably stable when dry, but the disulfide is slowly hydrolyzed in acidic, aqueous solution. It has been shown that the stoichiometry given in eq 5 is approximately obeyed during the rapid reaction of 0.10 M thiourea and 0.50 M H_2O_2 in perchloric acid solution.[5] However, we find that the reaction is considerably

---

(1) Thompson, R. C. *Inorg. Chem.* **1986**, *25*, 184.
(2) Secco, F, *Inorg. Chem.* **1980**, *19*, 2722.
(3) Smith, R. H.; Kilford, J. *Int. J. Chem. Kinet.* **1976**, *8*, 1.
(4) (a) Chong, A. O.; Sharpless, K. B. *J. Org. Chem.* **1977**, *42*, 1587. (b) Mimoun, H.; Postel, M.; Casabianca, F.; Fischer, J.; Mitschler, A. *Inorg. Chem.* **1982**, *21*, 1303. (c) Mimoun, H.; Saussine, L.; Daire, E.; Postel, M.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1983**, *105*, 3101. (d) Chaumette, P.; Mimoun, H.; Saussine, L.; Fischer, J.; Mitschler, A. *J. Organomet. Chem.* **1983**, *250*, 291. (e) Mimoun, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 734. (f) Sheldon, R. A.; Kochi, J. K. In *Metal-Catalyzed Oxidations of Organic Compounds*; Academic: New York, 1981; pp 48-97. (g) Sharpless, K. B.; Woodard, S. S.; Finn, M. G. *Pure Appl. Chem.* **1983**, *55*, 1823. (h) Mimoun, H. *Isr. J. Chem.* **1983**, *23*, 451. (i) Bach, R. D.; Wolber, G. J.; Coddens, B. A. *J. Am. Chem. Soc.* **1984**, *106*, 6098.
(5) Hoffmann, M.; Edwards, J. O. *Inorg. Chem.* **1977**, *16*, 3333.
(6) Preisler, P. W.; Berger, L. *J. Am. Chem. Soc.* **1947**, *69*, 322.
(7) Kern, D. M.; Kim, C. H. *J. Am. Chem. Soc.* **1965**, *87*, 5309.
(8) (a) Thompson, R. C. *Inorg. Chem.* **1984**, *23*, 1794. (b) Orhanovic, M.; Wilkins, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 278.
(9) Leibhafsky, H. A.; Mohammed, A. *J. Am. Chem. Soc.* **1933**, *55*, 3977.
(10) (a) Thiodiethanol: Ross, S. D. *J. Am. Chem. Soc.* **1946**, *68*, 1484. (b) Thioxane: Dankleff, M. A. P.; Curci, R.; Edwards, J. O.; Pyun, H. Y. *J. Am. Chem. Soc.* **1968**, *90*, 3209. (c) Thiourea: reference 5.

0020-1669/86/1325-3694$01.50/0 © 1986 American Chemical Society

Table I. Kinetic Results for the Peroxotitanium(IV)–Iodide System[a]

T, °C	[HClO$_4$], M	10^3[TiO^{2+}]$_0$, M	$10^3k'$, M^{-1} s^{-1} [b]	10^3k_1, M^{-1} s^{-1} [c]
25.0	0.065	3.42	3.79	3.0_8
25.0	0.112	6.84	3.63	3.1_3
25.0[d]	0.149	9.15	3.47	3.0_1
25.0	0.225	8.88	3.52	3.0_6
25.0	0.337	9.28	3.71	2.8_7
25.0	0.527	9.28	4.20	2.9_7
25.0	0.815	9.28	4.63	2.8_2
25.0	0.830	3.42	7.73	3.0_7
				3.0 ± 0.1 (av)
17.0	0.527	9.28	1.41	0.98_3
10.0	0.527	9.28	0.551	0.38_6

[a] Unless otherwise indicated, $[\mathrm{NaI}]_0 = 0.219–0.225$ M, $[\mathrm{TiO_2}^{2+}]_0 = 5.19 \times 10^{-4}$ M, and the ionic strength is 1.0 M (LiClO$_4$). [b] Determined from the slope of plots of $-\ln [A_\infty - A]$ vs. t, where $k' = \mathrm{slope}/[\mathrm{I^-}]_{\mathrm{av}}$. [c] Calculated by means of eq 7, with use of literature values for k_2, k_3, and k_4. [d] $[\mathrm{NaI}]_0 = 0.115$ M.

more complicated under our conditions of excess thiourea. For example, if 0.19 M thiourea in 1 M HClO$_4$ is rapidly mixed with an aliquot of H$_2$O$_2$ to give an initial $[\mathrm{H_2O_2}] = 2.65 \times 10^{-3}$ M, the reaction profile monitored at 310 nm (where $\epsilon = 13._6$ M^{-1} cm^{-1} for formamidine disulfide) is one of continually increasing absorbance with the ultimate formation of colloidal sulfur. An identical profile is observed if 2.65×10^{-3} M formamidine disulfide is used instead of hydrogen peroxide. While we have been unable to characterize the reactions responsible for this behavior, we suggest that a product of the slow decomposition of formamidine disulfide, probably HSOH, reacts with the excess thiourea to produce highly absorbing polysulfides, which eventually yield colloidal sulfur. Fortunately, this complex chemistry does not appear to *significantly* affect our kinetic determination of the reduction of dilute peroxotitanium(IV) by excess thiourea (vide infra).

Kinetic Studies. A large excess of the reductant was used in the kinetic experiments. Plots of $-\ln [A - A_\infty]$ (or $-\ln [A_\infty - A]$ for the iodide system) vs. time were linear to 90–95% of complete reaction, in agreement with eq 6, where values of k_{obsd} are obtained

$$-\mathrm{d}[\mathrm{TiO_2}^{2+}]/\mathrm{d}t = k_{\mathrm{obsd}}[\mathrm{TiO_2}^{2+}] \qquad (6)$$

from the slopes. The values of $k' = k_{\mathrm{obsd}}/[\mathrm{reductant}]_{\mathrm{av}}$ decreased with an increase in the excess [TiO^{2+}]. This variation is satisfactorily correlated by eq 7, where $[\mathrm{TiO}^{2+}]_{\mathrm{av}}$ and $[\mathrm{R}]_{\mathrm{av}}$ are the

$$k' = k_{\mathrm{obsd}}/[\mathrm{R}]_{\mathrm{av}} = k_{1,\mathrm{R}} + k_2k_{4,\mathrm{R}}/\{k_3[\mathrm{TiO}^{2+}]_{\mathrm{av}} + k_{4,\mathrm{R}}[\mathrm{R}]_{\mathrm{av}}\} \qquad (7)$$

values of the concentrations of the excess titanium(IV) and reductant at 50% of total reaction, respectively. This expression is derived from the reaction scheme shown in eq 8–10 if the

$$\mathrm{TiO_2}^{2+} + \mathrm{R} \rightarrow \mathrm{TiO}^{2+} + \mathrm{Ox} \quad k_{1,\mathrm{R}} \qquad (8)$$

$$\mathrm{TiO_2}^{2+} + \mathrm{H_2O} \rightleftarrows \mathrm{TiO}^{2+} + \mathrm{H_2O_2} \quad k_2, k_3 \qquad (9)$$

$$\mathrm{H_2O_2} + \mathrm{R} \rightarrow \mathrm{Ox} + \mathrm{H_2O} \quad k_{4,\mathrm{R}} \qquad (10)$$

steady-state approximation is made for the free, uncomplexed [H$_2$O$_2$]. In this scheme Ox is the oxidation product. The $k_{1,\mathrm{R}}$ term in eq 7 corresponds to the direct reaction of TiO$_2^{2+}$ and R, while the second term refers to the indirect reduction of the traces of H$_2$O$_2$ in equilibrium with TiO$_2^{2+}$. The initial values of the ratio $[\mathrm{TiO_2}^{2+}]/[\mathrm{H_2O_2}]$ typically ranged from 30 to 313 under our experimental conditions. Values of k_2 and k_3 were taken or interpolated from data reported previously.[8a]

The kinetic results and experimental conditions for the TiO$_2^{2+}$–I$^-$ system are summarized in Table I. Since the H$_2$O$_2$–I$^-$ reaction has been investigated extensively, values of k_4 in eq 7 at each acidity and temperature were taken from the literature.[9] The calculated values of k_1 are listed in the last column of Table I. Within experimental error, this rate parameter is independent of the excess [TiO^{2+}], the excess [I$^-$], and [H$^+$] over the range investigated. Values of the activation parameters $\Delta H^{\ddagger} = 22._4 \pm 0._6$ kcal/mol and $\Delta S^{\ddagger} = 5 \pm 2$ cal/(deg mol) were calculated from the temperature dependence of k_1.

The kinetic results for the TiO$_2^{2+}$–(C$_2$H$_4$OH)$_2$S system are summarized in Table II. The reduction of hydrogen peroxide by thiodiethanol has been investigated only to a limited extent and under rather different experimental conditions than we employed.[10a] Therefore, both k_1 and k_4 were allowed to be adjustable parameters in eq 7 in a nonlinear least-squares analysis. The calculated values of the two rate parameters at each acidity and temperature are listed in the last two columns of Table II. The k_1 parameter for the direct reaction between TiO$_2^{2+}$ and (C$_2$H$_4$OH)$_2$S increased by 25% over a fourfold decrease in [H$^+$] at 25 °C. The H$_2$O$_2$–(C$_2$H$_4$OH)$_2$S reaction exhibited a [H$^+$] dependence at 25 °C in agreement with eq 11. Ross reported a

$$k_4 = (3.0 \pm 0.1) \times 10^{-3}\ \mathrm{M^{-1}\ s^{-1}} + \{(2.8 \pm 0.1) \times 10^{-2}\ \mathrm{M^{-2}\ s^{-1}}\}[\mathrm{H^+}] \qquad (11)$$

Table II. Kinetic Results for the Peroxotitanium(IV)–Thiodiethanol System[a]

T, °C	[HClO$_4$], M	10^2[TiO^{2+}], M	$10^4k'$, M^{-1} s^{-1} [b]	10^4k_1, M^{-1} s^{-1} [c]	10^2k_4, M^{-1} s^{-1} [c]
25.0	1.00	2.01	3.21 (3.24)	1.5 ± 0.2	3.1 ± 0.1
25.0	1.00	1.03	5.10 (4.91)		
25.0[d]	1.00	0.948	5.07 (5.25)		
25.0	1.00	0.543	8.08 (8.00)		
25.0[d]	1.00	0.474	9.05 (9.11)		
25.0	0.50	2.01	2.68 (2.72)	1.8 ± 0.1	1.7 ± 0.1
25.0	0.50	1.03	3.71 (3.65)		
25.0	0.50	0.690	4.58 (4.59)		
25.0	0.50	0.445	6.18 (6.19)		
25.0	0.25	1.52	2.76 (2.72)	2.0 ± 0.1	0.98 ± 0.03
25.0	0.25	1.03	3.07 (3.08)		
25.0	0.25	0.788	3.43 (3.43)		
25.0	0.25	0.543	4.13 (4.13)		
17.0	1.00	1.52	1.50 (1.49)	0.71 ± 0.02	1.8 ± 0.1
17.0	1.00	0.788	2.22 (2.23)		
17.0	1.00	0.543	2.93 (2.92)		
10.0	1.00	1.52	0.572 (0.565)	0.23 ± 0.03	1.3 ± 0.1
10.0	1.00	0.788	0.863 (0.878)		
10.0	1.00	0.543	1.18 (1.17)		

[a] Unless otherwise indicated, $[\mathrm{TiO_2}^{2+}]_0 = 4.01 \times 10^{-4}$ M, $[\mathrm{thiodiethanol}]_0 = 0.947$ M, and the ionic strength is 1.0 M (LiClO$_4$). [b] Determined from the slope of plots of $-\ln [A - A_\infty]$ vs. t, where $k' = \mathrm{slope}/[\mathrm{thiodiethanol}]_{\mathrm{av}}$. Values in parentheses were calculated by use of eq 7. [c] Determined by a nonlinear least-squares adjustment of the indicated data to eq 7, with use of literature values for k_2 and k_3. Uncertainties are standard deviations. [d] $[\mathrm{thiodiethanol}]_0 = 0.408$ M.

Table III. Kinetic Results for the Peroxotitanium(IV)–Thioxane System[a]

$[HClO_4]$, M	$10^2[TiO^{2+}]_0$, M	$10^4k'$, $M^{-1}\ s^{-1}$ [b]	10^5k_1, $M^{-1}\ s^{-1}$ [c]	10^2k_4, $M^{-1}\ s^{-1}$ [c]
1.00	1.48	3.31 (3.42)	2.0 ± 2.4	4.2 ± 0.1
1.00	0.991	5.09 (4.97)		
1.00	0.747	6.49 (6.44)		
1.00	0.503	9.08 (9.29)		
1.00[d]	0.503	9.53 (9.38)		
0.161	1.48	1.17 (1.15)	3.7 ± 1.2	1.0 ± 0.1
0.161	0.991	1.48 (1.52)		
0.161	0.747	1.91 (1.89)		

[a] Unless otherwise indicated, $T = 25.0$ °C, $[TiO_2^{2+}]_0 = 4.13 \times 10^{-4}$ M, $[\text{thioxane}]_0 = 0.410$ M, and the ionic strength is 1.0 M ($LiClO_4$). [b] Determined from the slope of plots of $-\ln [A - A_\infty]$ vs. t, where $k' = \text{slope}/[\text{thioxane}]_{av}$. Values in parentheses were calculated by means of eq 7. [c] Determined by a nonlinear least-squares adjustment of the indicated data to eq 7, with use of literature values for k_2 and k_3. Uncertainties are standard deviations. [d] $[\text{thioxane}]_0 = 0.205$ M.

value for k_4 of 0.016 $M^{-1}\ s^{-1}$ in 0.5 M HCl at 25 °C.[10a] Our value of 0.017 $M^{-1}\ s^{-1}$ in 0.50 M $HClO_4$ at an ionic strength of 1.0 M is in excellent agreement. Activation parameters determined in 1.0 M $HClO_4$ from our data are as follows: for k_1, $\Delta H^\ddagger = 20 \pm 3$ kcal/mol and $\Delta S^\ddagger = -8 \pm 10$ cal/(deg mol); for k_4, $\Delta H^\ddagger = 9 \pm 1$ kcal/mol and $\Delta S^\ddagger = -34 \pm 4$ cal/(deg mol).

The kinetic results for the peroxotitanium(IV)–thioxane system are summarized in Table III. Both k_1 and k_4 in eq 7 were again treated as adjustable parameters. It proved difficult to establish conditions where the direct reaction competed favorably with the H_2O_2 pathway. The kinetic data for 1.0 M $HClO_4$ at 25 °C do not provide convincing evidence for the direct reaction, as indicated by the uncertainty associated with k_1. Since the direct reactions we have measured show little if any $[H^+]$ dependence whereas the H_2O_2–thioxane system exhibits a major $[H^+]$-dependent pathway, several experiments were performed in 0.16 M $HClO_4$. Under this condition a statistically meaningful value of k_1 was determined. The accompanying value of $(1.0 \pm 0.1) \times 10^{-2}\ M^{-1}\ s^{-1}$ for k_4 compares favorably with the directly determined value of $8.2 \times 10^{-3}\ M^{-1}\ s^{-1}$ reported by Edwards.[10b]

The kinetic results for the TiO_2^{2+}–thiourea system are summarized in Table IV. The pseudo-first-order kinetic plots and the fit of the individual sets of experiments at a common temperature and $[H^+]$ to eq 7 were of exceptionally high quality. However, the resulting values of k_4 are less than half the values reported by Hoffmann and Edwards[5] in a direct study of the H_2O_2–thiourea reaction.[11] We performed a few experiments with much lower concentrations of TiO^{2+} to maximize the contribution from the k_4 pathway. The kinetics were monitored at the 410 nm absorption maximum of TiO_2^{2+}, again with a large excess of thiourea. Best-fit values for k_4 were determined by numerical integration of eq 8–10, under the assumption that reactions 8 and 10 produce an intermediate that is rapidly converted to the final product (presumably formamidine disulfide) by the excess thiourea. Values of k_1, taken from Table IV, and previously reported values of k_2 and k_3 were fixed in the analysis. The resulting fits of $[TiO_2^{2+}]$ vs. time were satisfactory with the optimal values of k_4 summarized in Table IV. There is fair agreement between the values determined in the two different ways.

We also performed a few experiments without TiO^{2+} under conditions similar to those used by Hoffmann and Edwards,[5] in which the formation of formamidine disulfide was followed at 310 nm. The results are summarized in Table V. The values of k_4 appropriate to rate expression 12 are in reasonable agreement with

$$-d[H_2O_2]/dt = k_4[H_2O_2][(NH_2)_2CS] \qquad (12)$$

our values summarized in Table IV but are significantly smaller than the value of 0.75 $M^{-1}\ s^{-1}$ reported by Hoffmann and Edwards.[11] The stoichiometric determinations summarized in the last column of Table V are in reasonable agreement with that predicted in eq 5.

The values of k_1 for the direct reaction of TiO_2^{2+} and thiourea increase slightly with decreasing $[H^+]$. Activation parameters determined in 1.0 M $HClO_4$ are $\Delta H^\ddagger = 18._5 \pm 0._3$ kcal/mol and $\Delta S^\ddagger = -7 \pm 1$ cal/(deg mol).

Discussion

The principal motivation for this study was to test the generality of the premise that peroxotitanium(IV) is less reactive than hydrogen peroxide toward a variety of reducing agents in acidic, aqueous solution. A quantitative comparison is awkward due to the different hydrogen ion dependencies of the two reactions with a given substrate. We have assembled in Table VI values of k_4/k_1 at two different acidities. The data clearly illustrate the rate retardation that occurs when peroxide is coordinated to titanium(IV). A comparison of the available activation parameters shows in general a substantially larger activation enthalpy and a less negative activation entropy for the reduction of TiO_2^{2+} relative to H_2O_2 by a given substrate.

While our results do not reveal the mechanistic features of the peroxotitanium(IV) reactions, there is no compelling reason to assume that they are substantially different from those for the corresponding hydrogen peroxide reactions—Fenton type chemistry with iron(II) and titanium(III) and nucleophilic displacement on peroxide with the sulfides, iodide, and thiourea. There is little doubt that peroxotitanium(IV) has the η^2 (triangular) geometry, as do most other d^0 transition-metal peroxo complexes. It is conceivable that traces of peroxotitanium(IV) are present as a more reactive, singly bonded complex. If so, our kinetic results require a rapid equilibrium between the two geometries, since the rate expressions are first order with respect to both peroxotitanium(IV) and the reductant.

An important issue to address is how our results can be reconciled with the established ability of d^0 transition-metal ions to promote and even catalyze peroxide reactions under certain conditions. Other investigators have found a striking rate enhancement for the iodide reduction of the diperoxo complexes of vanadium(V) and molybdenum(VI), as may be seen from the entries in Table VI. However, it is interesting to note that the monoperoxo complexes of vanadium(V) and molybdenum(VI) show little if any enhanced reactivity relative to that of hydrogen peroxide, at least toward iodide ion. It appears that the identity of the d^0 metal ion center and the number of coordinated peroxide ions are crucial factors in determining the reactivity of these peroxo complexes. The solvent acidity, and nature of the other ligands may also be important. A rate comparison between the peroxo complexes and hydrogen peroxide appears to be the best strategy for assessing these factors.

We have been reasonably successful in determining reliable values for both the TiO_2^{2+} (k_1) and H_2O_2 (k_4) reactions in our studies, even though conditions were sought where the direct reaction was predominant. Agreement between the k_4 values determined in this way with those determined in direct studies of the H_2O_2 systems provides a crucial test of our experimental approach. The uncertainties listed for our determined k_4 values are standard deviations and are meant only to indicate the quality of the fit of the kinetic data to eq 7. These uncertainties are unrealistically small as true indicators for how well k_4 has been determined, since no error in the independently measured equilibrium rate constants (k_2 and k_3) was included. Clearly, the best way to measure the kinetics of reduction of hydrogen peroxide is a direct study. However, using peroxotitanium(IV) as a marker may be useful for certain peroxide reactions that are very difficult to monitor otherwise. In these cases it may prove useful to add sufficient titanium(IV) to complex approximately half of the total hydrogen peroxide and monitor the disappearance of peroxotitanium(IV) spectrophotometrically. Our results strongly suggest that under these conditions it is safe to assume that the peroxotitanium(IV) will be unreactive relative to the hydrogen peroxide in equilibrium with it.

---

(11) The rate constants reported in ref 5 refer to $-d[\text{thiourea}]/dt = k[H_2O_2][\text{thiourea}] = -2d[H_2O_2]/dt$. Therefore, their values must be halved for comparison with ours.

Table IV. Kinetic Results for the Reduction of Peroxotitanium(IV) and Hydrogen Peroxide by Thiourea[a]

$[HClO_4]$, M	10^3(init concn), M				$10^3k'$, M^{-1} s^{-1} [b]	10^3k_1, M^{-1} s^{-1} [c]	k_4, M^{-1} s^{-1} [c]
	TiO_2^{2+}	H_2O_2	TiO^{2+}	$(NH_2)_2CS$			
1.00	0.449	0.0027	18.9	53.9	7.44 (7.48)	5.56 ± 0.04	0.320 ± 0.003
1.00	0.447	0.0041	12.5	53.9	8.46 (8.44)		
1.00	0.459	0.0041	12.9	27.7	8.38 (8.36)		
1.00	0.444	0.0070	7.32	53.9	10.4 (10.4)		
1.00	0.441	0.011	4.73	53.9	12.8 (12.8)		
0.99	0.245	0.183	0.147	40.8			0.35[d]
0.75	0.245	0.183	0.147	40.8			0.33[d]
0.50	0.449	0.0027	18.9	51.9	7.24 (7.29)	6.18 ± 0.07	0.186 ± 0.005
0.50	0.447	0.0041	12.5	51.9	7.90 (7.85)		
0.50	0.444	0.0070	7.32	51.9	9.02 (8.98)		
0.50	0.441	0.011	4.73	51.9	10.4 (10.4)		
0.50	0.250	0.187	0.150	20.8			0.24[d]
0.50	0.245	0.188	0.147	40.8			0.25[d]
0.25	0.245	0.183	0.147	40.8			0.17[d]
0.20	0.449	0.0027	18.9	56.0	7.08 (7.06)	6.46 ± 0.05	0.100 ± 0.003
0.20	0.447	0.0041	12.5	56.0	7.37 (7.37)		
0.20	0.444	0.0070	7.32	56.0	7.93 (7.98)		
0.20	0.441	0.011	4.73	56.0	8.79 (8.76)		
1.00[e]	0.450	0.0015	18.9	72.7	2.81 (2.82)	2.23 ± 0.03	0.170 ± 0.003
1.00[e]	0.450	0.0023	11.8	72.7	3.13 (3.11)		
1.00[e]	0.448	0.0040	7.31	72.7	3.68 (3.70)		
1.00[e]	0.445	0.0061	4.72	72.7	4.46 (4.45)		
1.00[f]	0.450	0.0014	12.5	69.6	1.43 (1.44)	1.01 ± 0.05	0.138 ± 0.008
1.00[f]	0.450	0.0025	7.31	69.6	1.75 (1.73)		
1.00[f]	0.449	0.0038	4.72	69.6	2.08 (2.09)		

[a] Unless otherwise indicated, $T = 25.0$ °C and the ionic strength is 1.0 M ($LiClO_4$). [b] Determined from the slope of plots of $-\ln [A - A_\infty]$ vs. t, where $k' = \text{slope}/[\text{thiourea}]_{av}$. Values in parentheses were calculated by use of eq 7. [c] Determined by a nonlinear least-squares adjustment of the indicated data to eq 7, with use of literature values for k_2 and k_3. Uncertainties are standard deviations. [d] Determined by numerical integration of the reaction scheme shown in eq 8–10. In this analysis, k_4 was the only adjustable parameter. [e] $T = 17.0$ °C. [f] $T = 10.0$ °C.

Table V. Kinetic Results for the Reaction of Excess Hydrogen Peroxide and Thiourea[a]

$[H_2O_2]_0$, M	$[(NH_2)_2CS]_0$, M	k_4, M^{-1} s^{-1} [b]	R[c]
0.459	0.0500	0.43	2.23
0.230	0.0500	0.41	2.17
0.207	0.0397	0.38	2.06
0.106	0.0203	0.35	2.09
0.0414	0.0397	0.41[d]	1.99

[a] Kinetics monitored at 310 nm in 1.00 M $HClO_4$ at 25.0 °C. [b] Determined from plots of $-\ln [A_\infty - A]$ vs. t, where $k_4 = \text{slope}/(2[H_2O_2]_{av})$, except for the last experiment. [c] $R = [(NH_2)_2CS]_0/[(NH_2)_2CSSC(NH_2)_2^{2+}]_\infty$. Values of ϵ for H_2O_2, $(NH_2)_2CS$, and $(NH_2)_2CSSC(NH_2)_2^{2+}$ were determined for the two spectrophotometers used in these experiments (Durrum D-110 stopped flow and Zeiss PMQII). [d] Determined from plot of $\ln \{[H_2O_2]/[(NH_2)_2CS]\}$ vs. t, where $k_4 = \text{slope}/\{2[H_2O_2]_0 - [(NH_2)_2CS]_0\}$.

Table VI. Relative Rates of Reduction of Hydrogen Peroxide (k_4) and d^0 Transition-Metal Peroxo Complexes (k_1) at 25 °C

oxidant	reductant	k_4/k_1		ref	
		0.20 M $[H^+]$	1.0 M $[H^+]$	k_4	k_1
TiO_2^{2+}	sulfur(IV)	*a*	*a*	13	1
TiO_2^{2+}	thioxane	270	(2100)	10b	*b*
TiO_2^{2+}	thiodiethanol	43	207	10a	*b*
TiO_2^{2+}	iodide	15	62	9	*b*
TiO_2^{2+}	thiourea	15	58	5	*b*
TiO_2^{2+}	titanium(III)	13	49	14	1
TiO_2^{2+}	iron(II)	18	22	15	1
VO_3^+	iodide	0.85	0.96	9	2
VO_5^-	iodide	1.5×10^{-3}	1.2×10^{-3}	9	2
$H_2MoO_4(H_2O_2)_2$[c]	iodide	1.4×10^{-4}	5.7×10^{-4}	9	3

[a] No direct reaction was detected. [b] This study. [c] Other formulations are possible for this diperoxo complex.

A case in point is the H_2O_2–thiourea reaction under conditions of excess thiourea. We have been unsuccessful in developing a spectrophotometric or titrimetric procedure for monitoring this reaction directly. Although the rate of formation of formamidine disulfide cannot be measured usefully at 310 nm owing to the competitive formation of a highly absorbing side product, this problem is minimized by the experimental conditions used by Hoffmann and Edwards[5] for at least two reasons. First, the high reactant concentrations drive the H_2O_2–thiourea reaction to completion rapidly, and reasonably stable A_∞ values are observed at 310 nm. Second, the excess peroxide effectively eliminates the thiourea-promoted formation of the highly absorbing species from the formamidine disulfide or one of its decomposition products. We find that the growth of absorbance at 310 nm from solutions of formamidine disulfide is significantly inhibited by the presence of hydrogen peroxide.

Spectral interferences are absent at 410 nm, and our titanium(IV) method for the determination of the rate constant for the reaction of excess thiourea and hydrogen peroxide appears to be successful. The values of k_4 determined in this manner (Table IV) are in reasonable agreement with those determined directly with excess hydrogen peroxide (Table V). We cannot account for the discrepancy between our results and those reported by Hoffmann and Edwards.[5]

Finally, the very limited data available indicate that peroxotitanium(IV) is also more resistant to oxidation than is hydrogen peroxide.[8a] We have found that chlorine is quite unreactive toward TiO_2^{2+} and instead reacts exclusively by oxidation of traces of H_2O_2 present under the experimental conditions. While cerium(IV) rapidly oxidizes the peroxotitanium(IV) to the superoxo complex, it reacts with hydrogen peroxide much more rapidly.[12]

Acknowledgment. This research was supported by the U.S. Army Research Office.

Registry No. TiO_2^{2+}, 12179-34-9; H_2O_2, 7722-84-1; I^-, 20461-54-5; thiodiethanol, 111-48-8; thioxane, 57917-36-9; thiourea, 62-56-6.

---

(12) Samuni, A.; Czapski, G. *J. Chem. Soc., Dalton Trans.* **1973**, 487.
(13) (a) Hoffmann, M. R.; Edwards, J. O. *J. Phys. Chem.* **1975**, *79*, 2096. (b) McArdle, J. V.; Hoffmann, M. R. *J. Phys. Chem.* **1983**, *87*, 5425.
(14) Samuni, A.; Meisel, D.; Czapski, G. *J. Chem. Soc., Dalton Trans.* **1972**, 1273.
(15) Po, H. N.; Sutin, N. *Inorg. Chem.* **1968**, *7*, 621.