stable ion-pair formation between NCS⁻ and the sub-
strate. We conclude that anations of $Cr(NH_3)_5$-
H_2O^{+3} are governed by release of the coordinated water
molecule, quickly followed by incorporation of an
adjacent particle into the resulting vacancy in the
Cr(III) coordination sphere. Anions in the vicinity of
the site vacated by the water molecule, for reasons con-
nected with the formation of ion pairs or otherwise, are
trapped into the product. This may be regarded as the
collapse of the solvation shell originally associated with
the aquo ion.[31]

(31) We suggest "the solvent shell collapse mechanism" as an ap-
propriate designation for this process.

Kinetic Studies of the Reactions of Peroxy Compounds of Chromium(VI), Vanadium(V), and Titanium(IV) in Acid Media[1]

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Abstract: The kinetics of formation and decomposition in perchloric and other acids of blue chromium(VI)
diperoxy and the formation of red vanadium(V) monoperoxy, yellow vanadium(V) diperoxy, and orange titanium-
(IV) monoperoxy species have been examined by flow methods. Rate laws have been established, and mechanisms
are suggested for these reactions.

There has been a good deal of interest in, and develop-
ment of flow equipment for, the study of the
mechanism of formation, decomposition, and substrate
reactions of peroxy species of biologically important
iron(III) compounds such as the enzymes catalase and
peroxidases.[2] The kinetic behavior of the "simpler"
peroxy species of other transition metals have, however,
been little investigated. We have reported previously
a short study of the formation of blue peroxychromic
acid in aqueous solution over a limited range of con-
centrations of reactants.[3] We have now extended this
work to a higher acid region than previously examined,
thus enabling us to make some reasonable conclusions
about the detailed mechanisms of the formation reaction.
We have also investigated the kinetics of formation of
the red monoperoxy- and yellow diperoxyvanadium(V)
species as well as the orange monoperoxytitanium(IV)
complexes. All studies have been confined to acid
concentrations above about 10^{-2} M, where, with the
notable exception of titanium(IV), both reactant and
peroxy species have been reasonably well characterized.[4]

The titanium peroxy species are stable in acid
medium, the vanadium complexes only decompose very
slowly at room temperatures,[5,6] while CrO_5 decomposes
rapidly, especially at high acid concentrations. These
peroxy species are sufficiently stable then to allow the
study of their formation rates although in all cases
flow methods have to be used, using spectrophotometry
to study the strong color changes which accompany
these reactions.

Experimental Section

Materials. Sources of transition metal ions were Analar potas-
sium dichromate, ammonium vanadate, and freshly precipitated
titanium(IV) oxide from addition of base to $K_2[TiO(C_2O_4)_2]$ in
solution. Both stabilized (with sodium stannate) and nonstabilized
hydrogen peroxide (Fisher Reagent) were used with similar results.
Solutions of the required ionic strength and acid concentration
were prepared by treatment of sodium hydroxide solutions with
the appropriate amount of perchloric, sulfuric, or nitric acids.
Stock solutions of hydrogen peroxide were titrated with standard
cerium(IV) sulfate immediately after the completion of runs.

Kinetic Runs. A glass–Lucite stopped-flow apparatus was used.
The formation and decomposition of CrO_5 were studied at 580 mμ.
The two processes are sufficiently separated on a time scale that
both are easily measured, except at the highest acidities investigated
where, because of the $[H^+]^2$ dependence of decomposition, the latter
interferes seriously with the formation. Solutions of chromium-
(VI) in high nitric acid concentrations were used shortly after prep-

(1) Presented in part at the 151st National Meeting of the American
Chemical Society, Pittsburgh, Pa., March 1966.
(2) B. Chance in "Investigation of Rates and Mechanisms of Reac-
tions," Part II, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Inter-
science Publishers, Inc., New York, N. Y., 1963, p 1314.
(3) P. Moore, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, 5,
466 (1966).
(4) J. A. Connor and E. A. V. Ebsworth, *Advan. Inorg. Chem. Radio-
chem.*, 6, 279 (1964), for a well-written, critical account of the transition
metal peroxy compounds.

(5) G. Kakabadse and H. J. Wilson, *J. Chem. Soc.*, 2475 (1960).
(6) G. A. Dean, *Can. J. Chem.*, 39, 1174 (1961).

aration, since Cr(VI) decomposes to Cr(III).[7] The decomposition of Cr(VI) in corresponding perchloric acid concentrations appears to be considerably slower. The formation of the red monoperoxy-vanadium species was studied at 455 mμ (ϵ_{max} 280). The production of the yellow diperoxy species from VO_2^+ and excess H_2O_2 was followed at 455 mμ (ϵ 25) and 350 mμ (ϵ 610) via the intermediate red species, which could also be examined at 404 mμ (isosbestic point for red and yellow species,[6] ϵ 198). The formation of the yellow species from red, generated by the appropriate reaction, was also followed. All results obtained were consistent. The titanium peroxy species was observed at 415 mμ. All runs were carried out with pseudo-first-order conditions, and concentrations of reactants were arranged for at least 95% completion of reaction. In the majority of experiments, initial V and Ti concentrations were 2×10^{-4} M and Cr was 10^{-4} M. Modifying these concentrations had little effect on the first-order rate constant ($k_{obsd} = 0.693/t_{1/2}$). Good first-order kinetic plots were obtained. The results are given in Table I, where values of $k' = k_{obsd}/[H_2O_2]$ are recorded, all reactions being first order in H_2O_2 concentration, it having been established for Cr(VI),[3] except for the decomposition of the yellow to red peroxyvanadium species.

Equilibrium Constants. These were measured for the vanadium systems spectrally, using a Cary 14. The spectra of the red and yellow peroxy species were in good agreement with the literature.[6] By using the spectral characteristics of the two species (see above) equilibria constants were determined. For the reaction
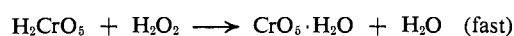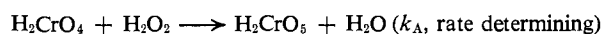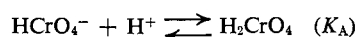
$$VO_3^+ + H_2O_2 \rightleftarrows VO_5^- + 2H^+$$
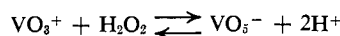
the equilibrium constant was determined in 0.1 M $HClO_4$ (1.4 $\pm$ 0.4 $\times$ 10^2 M^{-1}) and 1.0 M $HClO_4$ (1.2 $\pm$ 0.1 M^{-1}) at 23°, both with ionic strength (I) 1.0 M. Measurements of pH were made with a Beckman research pH meter.
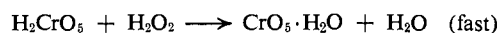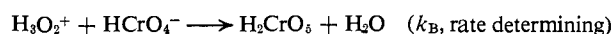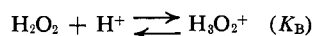
Results

Chromium(VI). For the third-order formation of $CrO(O_2)_2$, previously observed in the limited acid concentration range 0.01–0.05 M,[3] two mechanisms at least are obvious.

Mechanism A

$$HCrO_4^- + H^+ \rightleftarrows H_2CrO_4 \quad (K_A)$$

$$H_2CrO_4 + H_2O_2 \longrightarrow H_2CrO_5 + H_2O \ (k_A, \text{ rate determining})$$

$$H_2CrO_5 + H_2O_2 \longrightarrow CrO_5 \cdot H_2O + H_2O \quad (\text{fast})$$

Mechanism B

$$H_2O_2 + H^+ \rightleftarrows H_3O_2^+ \quad (K_B)$$

$$H_3O_2^+ + HCrO_4^- \longrightarrow H_2CrO_5 + H_2O \quad (k_B, \text{ rate determining})$$

$$H_2CrO_5 + H_2O_2 \longrightarrow CrO_5 \cdot H_2O + H_2O \quad (\text{fast})$$

Since H_2CrO_4 starts to appear in a moderate nitric or perchloric acid concentration,[7-10] it would be expected that with either mechanism the rate would reach a limiting value or at least deviate from a third-order rate law at high acidities. By lowering the concentrations of reactants previously employed, we have been able to study the formation of CrO_5 up to 6 M HNO_3, at which point formation and decomposition half-times become immeasurably short. Even with the runs at 25° in 0.1–0.8 M HNO_3 at unity ionic strength, a less than

(7) G. P. Haight Jr., D. C. Richardson, and N. H. Coburn, Inorg. Chem., 3, 1777 (1964).
(8) N. Bailey, A. Carrington, K. A. K. Lott, and M. C. R. Symons, J. Chem. Soc., 290 (1960).
(9) D. G. Lee and R. Stewart, J. Am. Chem. Soc., 86, 3051 (1964).
(10) J. Y. Tong, Inorg. Chem., 3, 1804 (1964).

Table I. Kinetic Data for Metal Peroxy Formation

Peroxy species formed	[Acid], M	[H₂O₂], mM	I, M	Temp, °C	10⁻³k',ᵃ M⁻¹ sec⁻¹
CrO_5	0.03	4.1	0.1	25.0	0.53[b]
$(NO_3^-)^c$	0.05	2.1	3.0	4.0	0.30
	0.2	2.1	3.0	4.0	1.2
	1.0	2.1	3.0	4.0	4.2
	1.0	2.1	6.0	4.0	4.4
	2.0	2.1	3.0	4.0	7.5
	3.0	2.1	3.0	4.0	11
	6.0	2.1	6.0	4.0	16
	0.1	2.1	1.0	25.0	1.1
	0.2	2.1	1.0	25.0	1.9
	0.4	2.1	1.0	25.0	3.4
	0.8	2.1	1.0	25.0	6.0
CrO_5	0.1	2.1	6.0	4.0	1.0
$(ClO_4^-)^d$	0.4	2.1	6.0	4.0	3.4
	0.7	2.1	6.0	4.0	5.0
	1.0	2.1	6.0	4.0	6.0
	2.0	2.1	6.0	4.0	13
VO_3^+	0.016	2.0	1.0	6.0	2.9
$(ClO_4^-)^d$	0.020	8.0	1.0	6.0	3.6(3.9)[f]
	0.024	8.1	1.0	6.0	3.3(3.2)
	0.030	4.6	3.0	6.0	2.5(2.7)
	0.045	4.6	1.0	6.0	2.2(2.1)
	0.053	2.0	1.0	6.0	1.9(1.8)
	0.10	4.6	1.0	6.0	1.5(1.3)
	0.10	4.6	3.0	6.0	1.3
	0.30	4.6	3.0	6.0	1.3
	0.60	4.6	3.0	6.0	1.7
	1.0	2.0	1.0	6.0	2.1
	1.0	8.0	1.0	6.0	1.9
	1.0	32.0	1.0	6.0	2.0
	2.0	4.2	3.0	6.0	3.5
	2.5	4.2	3.0	6.0	4.4
	3.0	3.7	3.0	6.0	5.4
	2.0	4.2	3.0	16.4	6.8
	2.0	4.2	3.0	25.9	11
VO_5^-	0.007	8.2	1.0	6.0	1.5
$(ClO_4^-)^d$	0.024	4.1	1.0	6.0	1.3
	0.024	8.1	1.0	6.0	1.3
	0.024	16.2	1.0	6.0	1.3
	0.056	56.4	1.0	6.0	1.2
	0.092	113	1.0	6.0	1.0
	0.016	11.3	1.0	0.5	0.96
	0.016	11.3	1.0	13.0	2.0
VO_3^+	0.3	1.0	1.2	6.0	~80[g]
from VO_5^-	0.3	4.0	1.2	6.0	~90[g]
$(ClO_4^-)^d$	0.6	4.0	1.2	6.0	>>80[g]
$Ti-H_2O_2$	0.1	23	1.0	25.0	0.11 (0.12)[f]
$(ClO_4^-)^d$	0.1	23	3.0	25.0	0.12 (0.12)
	0.3	23	3.0	25.0	0.14 (0.13)
	0.6	23	3.0	25.0	0.15 (0.15)
	1.2	6	3.0	25.0	0.17
	1.2	23	3.0	25.0	0.18 (0.19)
	1.2	117	3.0	25.0	0.18
	1.2	351	3.0	25.0	0.21
	2.0	23	3.0	25.0	0.25 (0.25)
	2.5	23	3.0	25.0	0.29 (0.29)
	3.0	23	3.0	25.0	0.34 (0.34)
	2.0	23	3.0	15.5	0.14
	2.0	23	3.0	35.0	0.46
$Ti-H_2O_2$	0.05	23	2.0	25.0	0.60
$(HSO_4^-)^e$	0.3	23	2.0	25.0	0.53
	1.2	23	2.0	25.0	0.52
	2.0	23	2.0	25.0	0.51
	3.0	23	3.0	25.0	0.59
	2.0	2.1	2.0	25.0	0.59
	2.0	10.3	2.0	25.0	0.57
	2.0	58.5	2.0	25.0	0.74
	2.0	10.3	2.0	6.5	0.15
	2.0	10.3	2.0	16.0	0.30

ᵃ $10^{-3}k' = 10^{-3}k_{obsd}/[H_2O_2]$. ᵇ Compares well with previous[3] value, 5.4 $\times$ 10². ᶜ Ionic strength made up from HNO_3 and $NaNO_3$. ᵈ $HClO_4$ and $NaClO_4$. ᵉ H_2SO_4 and $NaHSO_4$. ᶠ Calculated from expression in text. ᵍ k_{obsd}.

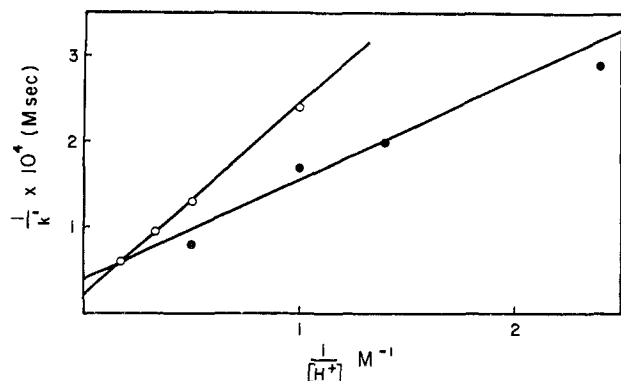Figure 1. Plot of $10^4/k'$ against $1/[H^+]$ for the formation of blue CrO$_5$. ○ represents results in $I = 6.0\ M$, HNO$_3$ + NaNO$_3$, 4°; ● represents results in $I = 6.0\ M$, HClO$_4$ + NaClO$_4$, 4°.

first-order dependence on [H$^+$] has become apparent, and by lowering the temperature the range of observation could be extended to 6 M HNO$_3$. A 30-fold change of acid concentration (0.2–6.0 M) produces only a 10-fold change in the observed rate constant. At 4°, k_{obsd} can be reasonably well represented as

$$k_{obsd} = 5.0 \times 10^3[H_2O_2][H^+]\{1 + 0.1[H^+]\}^{-1}$$

For mechanism A

$$\frac{d[CrO_5]}{dt} = k_A[H_2CrO_4][H_2O_2] = k_{obsd}[HCrO_4^- +$$

$$H_2CrO_4]k_{obsd}/[H_2O_2] = k' = \frac{k_A[H_2CrO_4]}{[HCrO_4^- + H_2CrO_4]}$$

or

$$\frac{1}{k'} = \frac{1}{k_A} + \frac{1}{k_A K_A[H^+]}$$

while for mechanism B

$$\frac{1}{k'} = \frac{K_A}{k_B K_B} + \frac{1}{k_B K_B[H^+]}$$

For both then, a plot of $1/k'$ against $1/[H^+]$ should be linear, and this relationship is shown to hold in Figure 1, both for nitric acid and (less accurately) perchloric acid solutions. For both mechanisms K_A = (intercept)/(slope). For HNO$_3$ medium, K_A = 0.1 at 4°, and, for perchloric acid, K_A = 0.35 at 4°, I = 6.0 M. This latter value is in satisfactory agreement with K_A obtained directly by spectrophotometry.[11] For mechanism A, k_A = 2.5 × 10^4 M^{-1} sec^{-1} at 4°, whereas, for mechanism B, k_B = K_A/(intercept)K_B; since K_B has been estimated[12,13] as ∼2 × 10^{-5}, k_B is ∼5 × 10^8 M^{-1} sec^{-1}, a highly improbable although not impossible value. For this reason we prefer mechanism A.

(11) Values of K_A = 0.20 at 25°, I = 1.0 or 3.0 M, with little dependence on temperature,[7] and 0.25[10] at 25°, I = 1.0 M, all perchlorate medium, have been reported. Data at varying acidities are also consistent with these values.[8,9]
(12) M. G. Evans and N. Uri, Trans. Faraday Soc., 45, 224 (1949).
(13) J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin Inc., New York, N. Y., 1964.

Extensive studies have been made of the complex decomposition of dilute hydrogen peroxide by chromium peroxy species and inter alia the decomposition of the peroxy species.[4,14] Most of the work has been confined to weakly acid media where more than one peroxy species is probably present. Both blue and violet species play an important but as yet incompletely understood role in the decomposition of H$_2$O$_2$ by Cr(VI). Incidental to our main interests we have studied the disappearance of CrO$_5$ in perchloric acid solution. The rate law

$$-d/dt(CrO_5) = k[CrO_5][H^+]^2$$

is obeyed over a wide range of Cr(VI), H$_2$O$_2$, and H$^+$ concentrations (Table II). In rate variation with temperature studies

$$k = 6.8 \times 10^9 \exp(-12,800/RT)\ M^{-2}\ sec^{-1}$$

with k = 2.7 at 25°. The immediate product of the decomposition slowly changes to the final Cr(H$_2$O)$_6{}^{3+}$ product. At the concentration used in the kinetic study the intermediate is not the green species detected and spectrally characterized as a product of Cr(VI) + H$_2$O$_2$ in perchloric acid.[15] We have evidence that at much higher (∼100 times) concentrations of reactants a green species does appear after the disappearance of CrO$_5$ and before the final bluish gray Cr(H$_2$O)$_6{}^{3+}$. Our intermediate is probably that described (and the slow decomposition of which was examined) recently.[16] A separate detailed study would be required to characterize the various species which arise between CrO$_5$ and Cr(H$_2$O)$_6{}^{3+}$. Oxygen is evolved during the decomposition of CrO$_5$ but does not interfere with the kinetic determination with the flow apparatus.

Table II. Kinetic Data for Decomposition of CrO$_5$ ([H$_2$O$_2$] = 2 × 10^{-3} M, [Cr(VI)] = 10^{-4} M, I = 6.0 M)

[Acid], M	Temp, °C	k_{obsd}, sec^{-1}	$k_{obsd}/[H^+]^2$, M^{-2} sec^{-1}
0.097	4.0	0.0046	0.49
0.4	4.0	0.11	0.65
0.7	4.0	0.26	0.51
1.0	4.0	0.44	0.43
1.0[a]	4.0	0.50	0.48
2.0	4.0	2.4	0.60
2.0[b]	4.0	1.9	0.48
2.0[c]	4.0	1.5	0.38
6.0	4.0	12.0	0.33
0.7	15.2	0.65	1.31
0.7	25.5	1.3	2.72

[a] [H$_2$O$_2$] = 0.3 M. [b] [H$_2$O$_2$] = 0.15 M. [c] [H$_2$O$_2$] = 0.15 M, Cr(VI) = 10^{-3} M.

Vanadium(V). At hydrogen ion concentrations above 0.01 M, vanadium(V) in low concentration exists only as the VO$_2{}^+$ cation.[17–19] With hydrogen peroxide

(14) J. Baxendale, Advan. Catalysis, 4, 75 (1952).
(15) M. Ardon and B. Bleicher, J. Am. Chem. Soc., 88, 858 (1966).
(16) J. I. Morrow, R. A. Pinkowitz, and J. Laufer, Inorg. Chem., 5, 934 (1966).
(17) F. J. C. Rossotti and H. Rossotti, Acta Chem. Scand., 10, 957 (1956).
(18) N. Ingro and F. Brito, ibid., 13, 1971 (1959).
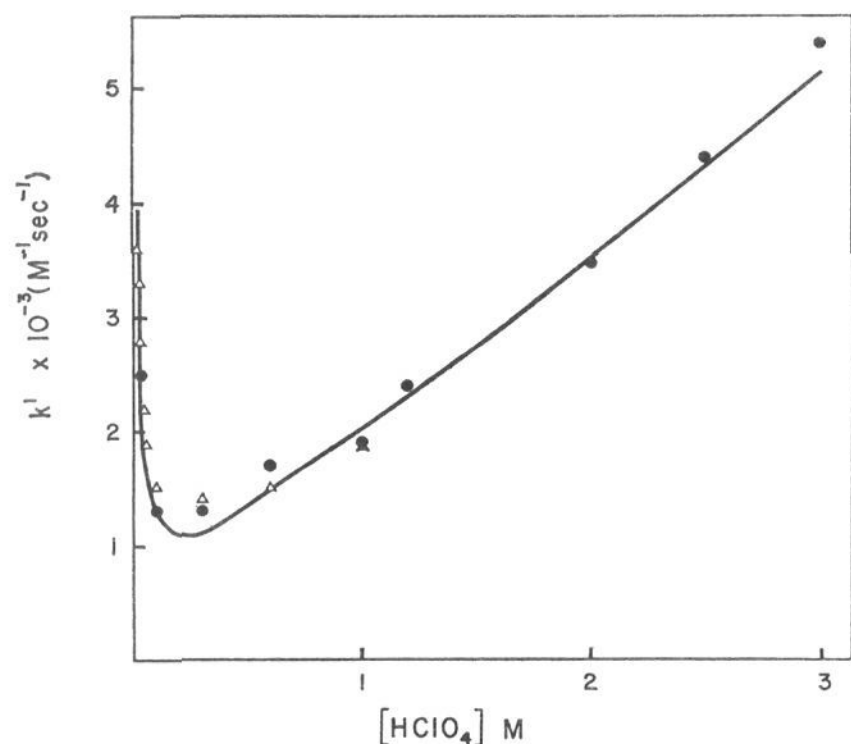(19) O. W. Howarth and R. E. Richards, J. Chem. Soc., 864 (1965).

Figure 2. Variation of $10^{-3}k'$ with [HClO$_4$] for the formation of red VO$_3^+$: $\triangle$, $I = 1.0\ M$; $\bullet$, $I = 3.0\ M$; HClO$_4$ + NaClO$_4$, 6°. Full line represents expected behavior on the basis of observed rate law.

Figure 3. Stopped-flow trace showing formation of yellow VO$_5^-$ from VO$_2^+$ and H$_2$O$_2$ *via* red VO$_3^+$. [Vanadium] = $2 \times 10^{-4}\ M$, [H$_2$O$_2$] = $5.1 \times 10^{-3}\ M$, [HClO$_4$] = $2 \times 10^{-2}\ M$, $I = 1.0\ M$, 6°. Each major division represents 0.10 sec. The rising portion represents an increase in optical density associated with formation of red species.

in acid solution, VO$_2^+$ forms well-characterized red 1:1 monoperoxy- and yellow 2:1 diperoxyvanadates, the latter favored in high hydrogen peroxide concentration and/or low hydrogen ion concentration. The formation of the red species VO(O$_2$)$^+$ is independent of the nature or concentration of acid and involves[6]

$$\text{VO}_2^+ + \text{H}_2\text{O}_2 \rightleftharpoons \text{VO(O}_2)^+ + \text{H}_2\text{O} \quad (K_1)$$

We have shown in the present study that the red and yellow forms, VO(O$_2$)$_2^-$, are related in perchloric acid as

$$\text{VO(O}_2)^+ + \text{H}_2\text{O}_2 \rightleftharpoons \text{VO(O}_2)_2^- + 2\text{H}^+ \quad (K_2)$$

incidently eliminating formulation of the yellow species as *e.g.*, VO$_2$(O$_2$)$_2^{3-}$.[4] We record that $K_1 = 3.5 \times 10^4$ and $K_2 = 1.3$, $I = 1.0\ M$ at 25°. The observations of an isosbestic point at 404 mμ,[6] confirmed in the present study, in addition to those on the rates of decomposition and formation of red and yellow species, show that these two species are the only ones of concern to us. These species are known to form rapidly,[5,6] but no previous determination of the rates has been reported.

The formation of VO$_3^+$ can be best expressed by the rate law

$$d(\text{VO}_3^+)/dt = k_1[\text{VO}_2^+][\text{H}_2\text{O}_2][\text{H}^+]^{-1} +$$
$$k_2[\text{VO}_2^+][\text{H}_2\text{O}_2] + k_3[\text{VO}_2^+][\text{H}_2\text{O}_2][\text{H}^+]$$

with the values for $k_1 = 0.07 \times 10^3$, $k_2 = 0.4 \times 10^3$, and $k_3 = 1.6 \times 10^3$ at 6.0° and $I = 3.0\ M$. Because of the complexity of the rate law, it was decided to determine the temperature variation of the rate only at the higher acid concentrations where the acid-catalyzed reaction is the predominant path. It was found that $k_3 = 1.9 \times 10^{11} \exp(-9900/RT)$. The agreement of the experimental data with the calculated value on the basis of the rate law is shown in Table I and Figure 2. The inverse [H$^+$] term could not be established over as wide

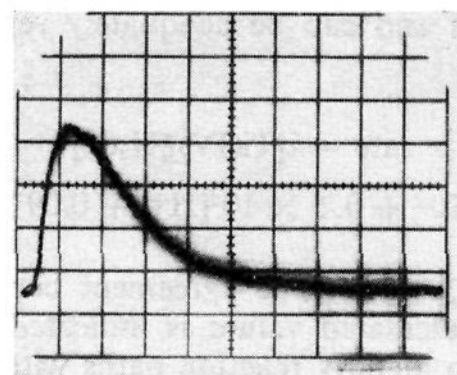a range of pH as desirable. It cannot arise solely from preferential participation of the excellent nucleophile HO$_2^-$ since such an assumption would lead to impossibly high rate constants for its reaction $(70/K_{\text{H}_2\text{O}_2} \sim 10^{13})$. However, reactions involving HO$_2^-$ and/or hydroxylated forms of vanadium might account for this dependence.[20]

The formation of VO$_5^-$ from VO$_3^+$, either as a starting material or as an intermediate formed from VO$_2^+$ (Figure 3), obeys a simple second-order rate law d/dt (VO$_5^-$) = k_1[VO$_3^+$][H$_2$O$_2$], $k_1 = 1.8 \times 10^{10} \exp(-9100/RT)$. This study was over an admittedly limited range of acid concentration, since high hydrogen peroxide concentrations (with attendant immeasurably fast rates) would be needed to effect formation of yellow species in too high acid concentrations. Some attempts were made to study the reverse reaction by generating VO$_5^-$ in low acid concentration and mixing rapidly with higher concentrations of acid, thereby producing red species. The rates were very rapid, almost too fast for the flow apparatus, and only approximate data were obtained. These did indicate, however, an acid-catalyzed transformation, independent of hydrogen peroxide concentration.

Titanium(IV). This was the most unsatisfactory portion of the study since there is still uncertainty as to the formulation of titanium(IV) in perchloric or sulfuric acids, or of the product of its reaction with H$_2$O$_2$. There is only general agreement that it is a monoperoxy species and that the establishment of equilibrium is probably unaccompanied by changes in [H$^+$].[21] The scheme, for example, in perchloric acid

$$\text{TiO}^{2+}(\text{aq}) + \text{H}_2\text{O}_2 \longrightarrow \text{TiO}_2^{2+} + \text{H}_2\text{O}$$
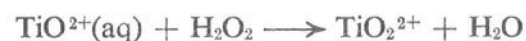
has been supported but cannot be regarded as established.[4] All studies were carried out above 0.1 M HClO$_4$, titanium(IV) precipitating below this acidity. The difference in behavior in perchloric and sulfuric acids is interesting. In sulfuric acid, the rate is k_1[Ti-(IV)][H$_2$O$_2$], $k_1 = 1.6 \times 10^{11} \exp(-11,500/RT)$ with $k_1 = 5.9 \times 10^2\ M^{-1}\ \text{sec}^{-1}$ at 25°, $\mu = 2.0\ M$, no sign of a proton-assisted reaction appearing even at $3M$ H$_2$SO$_4$. The rate behavior in perchloric acid, 0.1 to 3.0 M, is

(20) If the main vanadium species is a hydrated form of VO$_2^+$ such as VO(OH)$_2^+$, the rate law would result from H$_2$O$_2$ reaction with VO$_2$-(OH), VO(OH)$_2^+$, and V(OH)$_3^{2+}$, respectively.
(21) E. Gastinger, *Z. Anorg. Allgem. Chem.*, **275**, 331 (1954).

quite different and can be adequately represented by the expression

$$\text{rate} = k[\text{Ti(IV)}][\text{H}_2\text{O}_2]$$

$$k = 1.2 \times 10^2 + 0.5 \times 10^2[\text{H}^+] + 0.09 \times 10^2[\text{H}^+]^2$$

at 25°, $I = 3.0$ M. The agreement between experimental and calculated values is indicated in Table I. We hesitate to identify reaction paths with the various terms of the above expression because of the paucity of data on the reacting species. We are content to demonstrate acid catalysis and to determine that at $2.0\,M\,[\text{H}^+]$, $k = 1.6 \times 10^{10}\exp(-10,600/RT)$.

Discussion

The rapid formation of chromium, vanadium, and titanium peroxy species in acid solution has some similar characteristics. All reactions are first order in oxy ion and hydrogen peroxide. A rate term involving [H⁺] occurs in the three reactions involving the oxy ions in noncoordinating media. If this were associated with a very reactive H_3O_2^+, formed in a rapid preequilibrium, then the rather high over-all rate constants would lead to improbably high rate constants for the reaction between the transition metal ion and H_3O_2^+ ($\approx 10^8$ M^{-1} sec⁻¹). It is believed rather that the acid catalysis arises from a reactive protonated (or possibly with titanium(IV) dehydroxylated) form of the oxy ion. A first-order dependence on C_{H^+} has been established for the reactions of many oxy anions[13] and in the reactions of VO_2^+ with inorganic (*e.g.*, Fe(II))[22] and organic (*e.g.*, cyclohexanol)[23] reductants. Little data

(22) N. A. Daugherty and T. W. Newton, *J. Phys. Chem.*, **67**, 1090 (1963).

on kinetic reactions of titanium(IV) appear available. Further evidence that this is a reasonable interpretation is afforded by the fact that the rate of reaction of VO_3^+ or the titanium(IV) sulfate species (with both of which protonation is less likely to occur or produce a particularly reactive species) with hydrogen peroxide is acid independent. It is particularly difficult to see why H_3O_2^+, if this was the active species in these reactions, would not react as well with the anionic (?) titanium sulfate complex ion as the cationic titanium species in perchloric acid. Obviously, these ideas, if correct, do not imply that in the acid-catalyzed reactions of hydrogen peroxide with other nucleophiles such as halide ions, etc., H_3O_2^+ cannot be the reactive species either. Indeed, Edwards[13] has presented strong evidence that this is the cause of the rate dependence on [H⁺] with those oxidation–reduction reactions.

The third-order rate constants for the formation of all monoperoxy species are remarkably similar, although, since these are composite values, particular significance may not necessarily be attached to this. The formation of the diperoxychromate in low acidities and monoperoxy- and diperoxyvanadate and monoperoxytitanate species in perchloric and sulfuric acids is accompanied by enthalpies of activation of 3.9, 9.3, 8.5, 10.0, and 10.9 kcal mole⁻¹ and entropies of activation of -26, -9, -14, -14, and -9 eu, respectively. These low values are characteristic of many reactions of peroxides with nucleophiles. The negative values of $\Delta S^{\ddagger}$ have been ascribed to requirements of a precisely oriented transition state.[13]

(23) J. S. Littler and W. A. Waters, *J. Chem. Soc.*, 4046 (1959).

The Kinetics of the Iron(II)-Catalyzed Dissociation of the Monothiocyanate Complex of Iron(III)[1]

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Abstract: The kinetics of the iron(II)-catalyzed dissociation of FeNCS^{2+} have been studied by use of a flow technique. The approach to equilibrium is given by $k_{\text{obsd}} = [k_{\text{d}} + k_4(\text{Fe}^{2+})] + [k_{\text{d}} + k_4(\text{Fe}^{2+})]K_1(\text{Fe}^{3+})/[1 + K_2 \cdot (\text{Fe}^{2+})]$. The values of k_{d} and k_4 are 0.68 ± 0.04 sec⁻¹ and 10.5 ± 0.6 M^{-1} sec⁻¹, respectively, at 25.0° and ionic strength 3.0 M. The equilibrium constant for the reaction $\text{Fe}^{2+} + \text{SCN}^- \rightleftharpoons \text{FeNCS}^+$ is 7.0 ± 0.5 M^{-1}. The results are discussed in terms of remote and adjacent attack on the coordinated thiocyanate.

Both inner-sphere and outer-sphere mechanisms have been proposed for the electron-transfer reactions between iron(II) and anion complexes of iron(III).[2–4]

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.
(2) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

Recent studies of the iron(II)-catalyzed dissociation of the monochloro complex of iron(III) have shown that the FeCl^{2+}–Fe^{2+} exchange reaction proceeds mainly by an inner-sphere, chloride-bridged mech-

(3) J. Halpern, *Quart. Rev.* (London), **15**, 207 (1961).
(4) N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 285 (1962).