was formed in 46% yield; bp 109 ± 1 °C (50 mmHg).

The infrared spectrum of the liquid had the following bands (cm^{-1}): 3022 (m), 2997 (m), 1386 (vw), 1249 (wm), 1188 (w), 1148 (m), 1015 (mw), 850 (vs, b), 758 (ms), 730 (m), 664 (m), 610 (m), 585 (s, sh, at 574), 561 (ms), 504 (m). The ^{19}F NMR spectrum (AB$_4$) contained a complex doublet at ϕ 57.0 (SF$_4$) and a multiplet (nine-line pattern) at ϕ 74.6 (SF). The relative peak areas were 4.0 (SF$_4$) and 1.0 (SF). The ^{1}H NMR spectrum contained a doublet at δ 6.29 (band center) and a 20-line multiplet with a band center at δ 5.86 (peak areas 1.0 (SF$_5$C–H) and 1.0 (Br$_2$C–H); coupling constants J_{SF_4-F} = 147 Hz, J_{SF_4-CH} = 5.2 Hz, J_{SF-CH} = 0.45 Hz, and J_{CH-CH} = 1.4 Hz). The mass spectrum for SF$_5$CHBrCHBr$_2$ (70 eV) had the following m/e peaks: 396, 394, 392, 390, (SF$_5$C$_2$H$_2$^{79,81}Br$_3$)$^+$; 315, 313, 311, (SF$_5$C$_2$H$_2$^{79,81}Br$_2$)$^+$; 269, 267, 265, 263, (C$_2$H$_2$^{79,81}Br$_3$)$^+$; 203, 205, 207, (SF$_5$C$_2$H$_2$^{79,81}Br$_2$)$^+$; 188, 186, 184, (C$_2$H$_2$^{79,81}Br$_2$)$^+$; 127, (SF$_5$)$^+$; 107, 105, (C$_2$H$_2$^{79,81}Br)$^+$; 89, (SF$_3$)$^+$; 79, 81, (Br)$^+$; 70, (SF$_2$)$^+$; 45, (SCH)$^+$; 44, (SC)$^+$; 32, (S)$^+$. Anal. Calcd: C, 6.12; H, 0.51; F, 24.2. Found: C, 6.27; H, 0.59; F, 24.2.

Preparation of SF$_5$CBr=CHBr. To a 25-mL round-bottomed vessel equipped with a Teflon stirring bar were added 15.1 mmol of SF$_5$CHBrCHBr$_2$, 15.4 mmol of K$_2$CO$_3$, and 10.0 mL of acetone. The mixture was stirred for 4 h and filtered, and the filtrate was distilled. The product, 5.50 mmol of SF$_5$CBr=CHBr, was formed in 36% yield; bp 55 ± 1 °C (48 mmHg).

The infrared spectrum of the liquid had the following bands (cm^{-1}); 3149 (w), 3100 (mw), 1573 (m), 1253 (w), 1244 (w), 916 (s with sh at 928), 860 (vs, b), 814 (s), 760 (vw), 716 (m), 679 (w), 659 (m), 600 (m), 584 (m), 539 (mw), 527 (vw), 480 (w). The ^{19}F NMR spectrum (AB$_4$) contained a doublet of multiplets at ϕ 62.0 (SF$_4$) and a multiplet at ϕ 76.0 (SF) (peak areas 3.9 (SF$_4$) and 1.0 (SF)). The ^{1}H NMR spectrum showed a singlet at δ 7.83 and a pentet at δ 7.07 (coupling constants J_{SF_4-F} = 149 Hz and J_{SF_4-CH} = 3.0 Hz). The following two isomers are present:

pentet   singlet
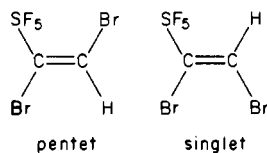
This assignment is based on the greater coupling expected for trans nuclei

relative to that for cis groups. This is analogous to the assignments made for the similar dichloro isomers.[2] The mass spectrum for SF$_5$CBr=CH-Br (70 eV) had the following m/e peaks: 314, 312, 310, (SF$_5$C$_2$H^{79,81}Br$_2$)$^+$; 233, 231, (SF$_5$C$_2$H^{79,81}Br)$^+$; 187, 185, 183, (C$_2$H^{79,81}Br$_2$)$^+$; 127, (SF$_5$)$^+$; 106, 104, (C$_2$H$_2$^{79,81}Br)$^+$; 89, (SF$_3$)$^+$; 79, 81, (Br)$^+$; 70, (SF$_2$)$^+$; 45, (SCH)$^+$; 44, (SC)$^+$; 32, (S)$^+$. Anal. Calcd: C, 7.70; H, 0.32; F, 30.5. Found: C, 7.96; H, 0.35; F, 30.1.

Preparation of SF$_5$C≡CH from SF$_5$CBr=CHBr. A three-necked round-bottomed Pyrex vessel, equipped with a Teflon stirring bar, a separatory funnel, a nitrogen-inlet tube, and a reflux condenser that was connected to a trap cooled to −78 °C (or −196 °C) and protected from the atmosphere by a mercury bubbler, was used for the debromination reaction. To this vessel were added 20 mL of diglyme and 33.0 mmol of zinc. The mixture was heated to 140 °C, and 8.97 mmol of SF$_5$C-Br=CHBr was added over a 0.5-h period. Heating at 140 °C was continued for 1 h under a slow nitrogen flow. The product, 6.05 mmol of SF$_5$C≡CH, was formed in 67% yield. The infrared spectrum agreed with that previously reported.[2]

Preparation of SF$_5$C≡CH from SF$_5$CH=CHBr. In the reaction vessel used for the debromination of SF$_5$CBr=CHBr, 80 mL of petroleum ether (90–120 °C fraction) was heated to reflux, and 205 mmol of KOH was added. SF$_5$CH=CHBr (85.8 mmol) was added slowly over a period of 0.8 h, and 305 mmol of additional KOH was added during this period. The mixture was heated at reflux for 2 h under a slow nitrogen flow. The product, 42.0 mmol of SF$_5$C≡CH, was collected in a trap cooled to −196 °C (yield 49%).

The infrared spectrum had the following bands (cm^{-1}); 3338 (ms), 2118 (m), 1613 (vw), 1506 (vw), 1344 (w with sh at 1338), 893 (vs, b), 730 (w), 720 (w), 674 (ms), 620 (m), 590 (ms). ^{19}F NMR spectrum: ϕ 71.8 (SF), ϕ 80.3 (SF$_4$) (multiplets; J_{SF_4-F} = 151.8 Hz). ^{1}H NMR spectrum: δ 2.76 (pentet; J_{F-H} = 3.15 Hz).

Registry No. SF$_5$CH=CHBr, 58636-82-1; SF$_5$Br, 15607-89-3; HC≡CH, 74-86-2; SF$_5$CHBrCHBr$_2$, 87224-28-0; (*E*)-SF$_5$CBr=CHBr, 98050-05-6; (*Z*)-SF$_5$CBr=CHBr, 98103-43-6; SF$_5$C≡CH, 917-89-5.

Kinetics and Mechanism of the Uncatalyzed and Silver(I)-Catalyzed Oxidation of Hydrazine with Peroxodiphosphate in Acetate Buffers

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A kinetic study of the title reaction (i) was made in acetate buffers by estimating peroxodiphosphate (pdp) iodometrically. Silver(I)

$$2H_nP_2O_8{}^{n-4} + N_2H_5{}^+ \rightarrow 4H_2PO_4{}^- + N_2 + (2n-3)H^+ \tag{i}$$
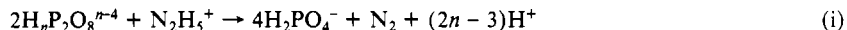
catalysis occurs through its complexation with pdp or $N_2H_5{}^+$. The empirical rate law (ii) holds where K_3 is the acid dissociation

$$-d[\text{pdp}]/dt = k_{\text{uncat}}[\text{pdp}][N_2H_5{}^+] + \frac{(A + B[^-O_2CCH_3])[\text{Ag(I)}][\text{pdp}][N_2H_5{}^+]}{([H^+] + K_3)(1 + K[^-O_2CCH_3])} \tag{ii}$$

constant of $H_2P_2O_8{}^{2-}$ and K is the complex formation constant of $Ag(O_2CCH_3)$. A and B are complex rate constants equal to 3.0×10^{-4} M^{-1} s^{-1} and 1.5×10^{-2} M^{-1} s^{-1}, respectively, at 40 °C and $I = 1.0$ M. K_3 was found to be 4.4×10^{-5} M under the same conditions. k_{uncat} is the second-order rate constant for the uncatalyzed reaction and is given by (iii) where k_1' and k_2' are

$$k_{\text{uncat}} = (k_1'[H^+] + k_2'K_3)/([H^+] + K_3) \tag{iii}$$

the rate constants for the $(H_2P_2O_8{}^{2-} + N_2H_5{}^+)$ and $(HP_2O_8{}^{3-} + N_2H_5{}^+)$ reactions and were found to be 2.25×10^{-3} M^{-1} s^{-1} and 7.5×10^{-3} M^{-1} s^{-1}, respectively, at 40 °C and $I = 1.0$ M.

We reported[1] silver(I)-catalyzed oxidation of water with peroxodiphosphate (pdp) as a sequel to the study of the mechanism of silver(I) catalysis in pdp oxidations. A few investigations[2,3] in our laboratory have revealed that there is no kinetic evidence

for a Ag(I)/Ag(II) cycle in Ag(I)-catalyzed reactions. A complex of Ag(I) with either the oxidant or reductant appears to be more reactive. This mechanism is different from that found in peroxodisulfate (pds) oxidations.[4] We thought a few more reactions should be investigated to substantiate the above conclusion about the mechanism.

Toward this aim, hydrazine appeared to be an attractive choice, not only because the reaction of hydrazine and higher valent silver

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(4) House, D. A. *Chem. Rev.* **1962**, *62*, 185.

is fast[5] but also because there is likelihood of a direct reaction[6] between hydrazine and silver(I), and thus the role of Ag(I) catalysis may perhaps be described in terms of a Ag(I)/Ag(0) cycle. Another reason for making this choice was that hydrazine is a strong reducing and complexing agent and its redox chemistry, though complicated, is well understood.[7,8]

A paper[9] describes the oxidation of hydrazine with pdp in acid solutions. However, it is now well-known that no direct reaction with pdp occurs in acid solutions, and it is peroxomonophosphate (pmp), a hydrolytic product of pdp, that oxidizes hydrazine. The oxidation of hydrazine with pmp is much faster than the hydrolysis of pdp, and the latter step is rate controlling in acid solutions. Hence, the present investigation was made in acetate buffers.

Experimental Section

General Procedures and Materials. Tetrapotassium peroxodiphosphate was a gift sample from the FMC Corp., and was used without further purification and standardized iodometrically.[10] All other materials and methods have been described previously.[1] The kinetics were followed by determining pdp iodometrically in the aliquots. The kinetic data were initially treated for the calculation of the initial rates by the plane-mirror method[11] for the determination of order with respect to pdp, and subsequently pseudo-first-order plots were made. The results were reproducible to ±3%. Hydrazinium perchlorate was used for hydrazine.

Preliminary Investigations. Since pdp oxidizes[1] water in the presence of Ag(I) at 50 °C, it was necessary to know whether any such reaction occurs at the temperature of study. It was noted that, with the concentrations of the order of 10^{-3} and at pH 3.42 and 40 °C, 8% decomposition of pdp occurs in 1 h. It will be seen later that the kinetic results do not show any oxidation of water in the presence of hydrazine and that the latter is exclusively oxidized.
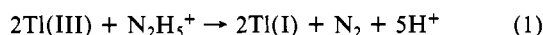
Further study showed that uncatalyzed oxidation of hydrazine also occurs, and later this was confirmed in the catalyzed study. Hence, first a few reactions were carried out without Ag(I) to obtain the pertinent data and to know the mechanism of the uncatalyzed reaction.

Reaction of Ag(I) with hydrazine has been reported,[6] and Ag(0) is formed if the pH > 5. The black precipitate of Ag(0) soon disappears on the addition of pdp. Thus it appears that as long as pdp is present and the pH < 5, no Ag(0) would accumulate or be visible in the system.

A dark brown solution or precipitate is obtained[1] on mixing solutions of pdp and AgNO₃ if the pH > 5.5. This has been said to be a complex of Ag(II)/Ag(III) and pdp, and this oxidizes water if no reducing substance is present. Also, phosphate is one of the products of reaction, and silver(I) phosphate is precipitated if the pH > 6. Thus to avoid all these difficulties and the hydrolysis of pdp, a suitable range of pH for study was found to be 3–5.

Results

Stoichiometry. In the presence of Ag(I) and excess pdp, the latter was determined iodometrically, and 2 mol of pdp was found to react with 1 mol of hydrazine. Stoichiometry could not be determined when excess hydrazine was present since Ag(I) interfered in the determination of unconsumed hydrazine. Stoichiometry was also determined in the absence of Ag(I) when excess hydrazine was present. Reaction mixtures with excess hydrazine were allowed to react till pdp, tested iodometrically, was consumed. The unreacted hydrazine was determined by adding the reaction mixture to a known excess of thallic perchlorate and back-titrating excess Tl(III) iodometrically. Tl(III) reacts with hydrazine according to reaction I[12] in acid perchlorate medium. The results

$$2Tl(III) + N_2H_5^+ \rightarrow 2Tl(I) + N_2 + 5H^+ \qquad (1)$$

of stoichiometry conform to eq 2.

$$2H_nP_2O_8^{n-4} + N_2H_5^+ \rightarrow 4H_2PO_4^- + N_2 + (2n-3)H^+ \qquad (2)$$

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Table I. pH Dependence of Uncatalyzed Reaction of Peroxodiphosphate and Hydrazine[a]

pH	$10^4[H^+]/M$	$10^4k_0'/s^{-1}$	$10^8k_0' \times$ $(K_3 + [H^+])$
3.29	5.13	1.05	5.85
3.45	3.54	1.15	4.58
3.60	2.51	1.24	3.66
3.84	1.44	1.39	2.62
4.39	0.41	1.82	1.55

[a] [pdp] = 3.4×10^{-3} M; [N₂H₅⁺] = 4.0×10^{-2} M; [⁻O₂CCH₃] = 4.5×10^{-2} M; I = 1.0 M; 40 °C. k_0' is the pseudo-first-order rate constant, and K_3 is 4.4×10^{-5} determined experimentally.
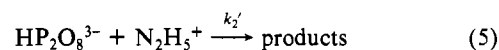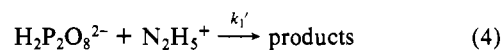
(a) Uncatalyzed Reaction. (1) Peroxodiphosphate and Hydrazine Dependences. The concentration of pdp was varied in the range 1.91×10^{-3} to 1.15×10^{-2} M, and the pseudo-first-order rate constant was found to be $(1.72 + 0.04) \times 10^{-4}$ s⁻¹ at [N₂H₅⁺] = 6.0×10^{-2} M, [⁻O₂CCH₃] = 4.5×10^{-2} M, pH 3.36, I = 1.0 M, and 40 °C. The order in hydrazine was also found to be 1 in the concentration range of $(2.0–8.0) \times 10^{-2}$ M, and the second-order rate constant at [⁻O₂CCH₃] = 4.5×10^{-2} M, pH 3.36, I = 1.0 M, and 40 °C was found to be $(2.85 \pm 0.15) \times 10^{-3}$ M⁻¹ s⁻¹.

(2) Acetate and Hydrogen Ion Dependences. Acetate ion concentration was varied in the range $(1.2–9.0) \times 10^{-2}$ M at pH 3.80, but there was no effect on the rate. The variation of H⁺ was done with the help of HClO₄, and the rate increased with the decrease of [H⁺]; the results are shown in Table I.

(3) Mechanism. A discussion[1] of pdp species under various conditions of pH has already been made, and H₂P₂O₈²⁻ and HP₂O₈³⁻ are the predominant species present[13] in the pH range studied; the equilibrium concerned is shown in (3). Hydrazine[14]

$$H_2P_2O_8^{2-} \overset{K_3}{\rightleftharpoons} HP_2O_8^{3-} + H^+ \qquad (3)$$
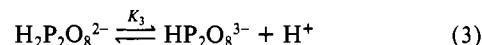
would predominantly be present as N₂H₅⁺ in such solutions. The following mechanism may be proposed for the uncatalyzed reaction:

$$H_2P_2O_8^{2-} + N_2H_5^+ \overset{k_1'}{\longrightarrow} \text{products} \qquad (4)$$

$$HP_2O_8^{3-} + N_2H_5^+ \overset{k_2'}{\longrightarrow} \text{products} \qquad (5)$$

Reactions 3–5 lead to the rate law (6). A plot of k_{uncat} ([H⁺]

$$-d[pdp]/dt = \frac{(k_1'[H^+] + k_2'K_3)[pdp][N_2H_5^+]}{[H^+] + K_3} \qquad (6)$$

+ K_3) vs. [H⁺] yielded a straight line with nonzero intercept in conformity with eq 7. From this, k_1' and $k_2'K_3$ were found to

$$k_{uncat} = (k_1'[H^+] + k_2'K_3)/([H^+] + K_3) \qquad (7)$$

be 2.25×10^{-3} M⁻¹ s⁻¹ and 3.25×10^{-7} s⁻¹, respectively.

An alternative mechanism with H₂P₂O₈²⁻, N₂H₅⁺, and N₂H₄ as the reactive species can also be given, and the same rate law (7) would be obtained, $k_2'K_3$ being replaced by $k_2'K_d$ where K_d is the acid dissociation constant of N₂H₅⁺.

Catalyzed Reaction. Peroxodiphosphate and Hydrazine Dependences. pdp was varied in the concentration range of $(1.45–5.66) \times 10^{-3}$ M at [N₂H₅⁺] = 2.0×10^{-2} M, [Ag(I)] = 2.0×10^{-3} M, [⁻O₂CCH₃] = 4.5×10^{-2} M, pH 3.36, I = 1.0 M, and 40 °C. The pseudo-first-order rate constant k_0 was found to be $(1.24 \pm 0.03) \times 10^{-4}$ s⁻¹. [N₂H₅⁺] was varied from 2.0×10^{-2} to 9.0×10^{-2} M at pH 2.92 and 3.30 (Supplementary Table I). A plot of k_0 vs. [N₂H₅⁺] yielded a straight line passing through the origin. The order in hydrazine is thus 1. The second-order rate constant was found to be $(5.76 \pm 0.06) \times 10^{-3}$ M⁻¹ s⁻¹ at pH 3.30. This value from the pdp study was found to be 6.2×10^{-3} M⁻¹ s⁻¹, which is slightly larger since the pH in the pdp variation was 3.36.

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Table II. Values of k_0, k_{uncat}, k_{cat}(exptl), and k_{cat}(calcd) at Different pH and $[^-O_2CCH_3]$ Values in the Ag(I)-Catalyzed pdp–$N_2H_5^+$ Reaction[a]

$10^2[N_2H_5^+]/$ M	$10^2[^-O_2CCH_3]/$ M	pH	$10^4k_0/$ s^{-1}	$10^3k^b/$ $M^{-1}s^{-1}$	$10^3k_{uncat}^c/$ $M^{-1}s^{-1}$	k_{cat}(exptl)/ $M^{-1}s^{-1}$	k_{cat}^d(calcd)/ $M^{-1}s^{-1}$
6.0	0.6	3.36	2.68	4.47	2.86	0.805	0.81
6.0	1.2	3.36	2.87	4.80	2.86	0.96	0.96
6.0	1.8	3.36	3.07	5.10	2.86	1.12	1.1
6.0	2.4	3.36	3.26	5.43	2.86	1.28	1.2
6.0	3.0	3.36	3.45	5.75	2.86	1.44	1.4
6.0	3.6	3.36	3.83	6.38	2.86	1.76	1.6
6.0	4.5	3.36	3.83	6.38	2.86	1.76	1.7
6.0	1.2	3.60	3.83	6.38	3.10	1.64	1.6
6.0	2.4	3.60	4.27	7.03	3.10	1.96	2.0
6.0	3.6	3.60	4.79	7.98	3.10	2.44	2.4
6.0	4.5	3.60	5.18	8.63	3.10	2.75	2.7
6.0	6.0	3.60	5.75	9.58	3.10	3.2	3.1
6.0	7.2	3.60	6.33	10.55	3.10	3.7	3.4
6.0	8.4	3.60	6.52	10.9	3.10	3.9	3.7
6.0	9.0	3.60	6.90	11.5	3.10	4.2	3.8
6.0	2.4	3.97	7.29	12.1	3.82	4.1	4.1
6.0	4.8	3.97	9.27	15.3	3.82	5.7	5.5
6.0	7.2	3.97	10.7	17.9	3.82	7.0	6.7
6.0	9.6	3.97	11.5	19.2	3.82	7.7	7.7
6.0	12.0	3.97	12.7	21.1	3.82	8.6	8.5
6.0	14.4	3.97	13.4	22.4	3.82	9.3	9.2
6.0	16.8	3.97	14.6	24.3	3.82	10.2	9.9
6.0	18.0	3.97	15.3	25.5	3.82	10.8	10.1
2.0	4.5	3.30	1.20	6.60	2.86	1.57	1.5
2.0	9.0	3.80	3.07	15.3	3.64	5.8	5.5
2.0	18.0	4.05	5.60	28.0	4.08	11.9	11.5
2.0	21.0	4.10	6.14	30.7	4.17	13.2	13.2
2.0	24.0	4.20	7.29	36.5	4.30	16.0	15.9
2.0	27.0	4.26	8.44	42.2	4.40	18.9	18.0
2.0	33.0	4.37	9.59	48.0	4.48	21.7	21.8
2.0	36.0	4.44	10.7	53.5	4.55	24.5	24.2
2.0	42.0	4.64	13.1	65.5	4.60	30.3	30.2
2.0	48.0	4.74	16.8	84	4.67	39.6	39.3
2.0	3.0	3.36	1.10	5.5	2.86	1.3	1.3
2.0	3.0	3.68	1.68	8.4	3.37	2.5	2.6
2.0	3.0	4.17	3.26	16.3	4.25	6.0	5.9
2.0	3.0	4.37	3.83	19.1	4.55	7.3	7.6
2.0	3.0	4.57	4.98	24.9	4.85	10	9.3
2.0	3.9	3.26	1.27	6.3	2.86	1.7	1.6
2.0	3.9	3.68	1.85	9.25	3.37	2.9	2.9
2.0	3.9	3.98	2.81	14.0	3.82	5.1	5.0
2.0	3.9	4.17	3.45	17.2	4.25	6.5	6.6
2.0	3.9	4.37	4.22	21.1	4.55	8.3	8.6
2.0	3.9	4.57	5.37	26.8	4.85	10.8	10.4
2.0	4.5	3.37	1.40	7.0	2.86	2.15	2.0
2.0	4.5	3.68	2.04	10.2	3.37	3.4	3.2
2.0	4.5	3.98	3.07	15.3	3.82	5.7	5.3
2.0	4.5	4.17	3.83	19.1	4.25	7.4	7.2
2.0	4.5	4.37	4.60	25.0	4.55	9.2	9.2

[a] [pdp] = 1.80×10^{-3} M; [Ag(I)] = 2.0×10^{-3} M; I = 1.0 M; 40 °C. [b] k is the second-order rate constant for the overall reaction. [c] A few values were obtained experimentally, and other values were obtained graphically from a plot of k_0' vs. pH. [d] Calculated from the rate laws (19) and (20) with $K_3 = 4.4 \times 10^{-5}$, $A = 3.0 \times 10^{-4}$, and $B = 1.5 \times 10^{-2}$.

Silver(I) Dependence. The concentration of Ag(I) was varied in the range $(1.0–9.0) \times 10^{-3}$ M at pH 2.92, 3.30, and 3.68 (Supplementary Table II). A plot of k_0 vs. [Ag(I)] yields straight lines with nonzero intercepts at pH 3.30 and 3.68, but at pH 2.92 a straight line passing through the origin is obtained. The catalyzed reaction has been studied at pH >3; hence, the rate law (8) should hold from Ag(I) dependence. The uncatalyzed reaction

$$-d[pdp]/dt = (k_{uncat} + k_{cat}[Ag(I)])[pdp][N_2H_5^+] \quad (8)$$

is very slow at pH <3, and there is insignificant contribution from the first term of eq 9; hence, at pH 2.92, a plot of k_0 vs. [Ag(I)] yields a straight line passing through the origin. The intercepts at pH 3.30 and 3.68 yield values of 2.6×10^{-3} and 3.37×10^{-3} M^{-1} s^{-1} for k_{uncat} at the same two pHs. The rate law (8) therefore holds.

Acetate Ion Dependence. The acetate ion concentration was varied at three fixed values of pH 3.36, 3.60, and 3.97. The results given in Table II show that k_0 significantly increases with the increase in the acetate ion concentration.

Hydrogen Ion Dependence. The pH was varied in such a way that acetate ion concentration remained constant. The results given in Table II show that k_0 increases with increasing pH. The pH was varied also when acetate ion concentration changed, and these results are also given in the same table. As a matter of fact, the main interest in this reaction seemed to be the hydrogen ion dependence of k_{cat}, and this was known in the following way. One can write (8) also as (9) or (10). The values of k_{uncat} are known

$$k_0 = (k_{uncat} + k_{cat}[Ag(I)])[N_2H_5^+] \quad (9)$$

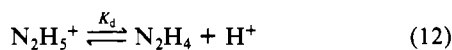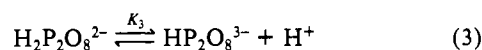$$k_{cat} = \frac{(k_0/[N_2H_5^+]) - k_{uncat}}{[Ag(I)]} \quad (10)$$

from the uncatalyzed study, and hence k_{cat} could be calculated at any pH. A plot of $(k_{cat})^{-1}$ vs. $[H^+]$ was found to be a good straight line with a nonzero intercept, and such plots at three different $[^-O_2CCH_3]$ values are shown in Figure 1. Hence, the

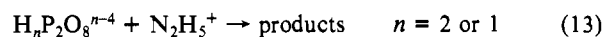form of the experimental rate law is (11) at fixed $[^-O_2CCH_3]$. A is a constant.

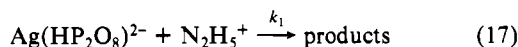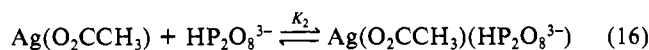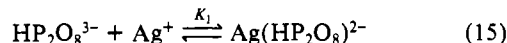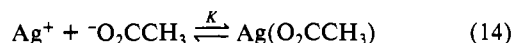$$k_0 = k_{uncat} + \frac{k_{cat}[Ag(I)]}{[H^+] + A} \tag{11}$$

Discussion

A discussion about the species pdp and hydrazine has already been made. Silver(I) can form a complex[15] with acetate ion with a formation constant of 5.4. Ag(I) can form a complex[6] with N_2H_4, too. The formation of Ag(0) on mixing Ag(I) and N_2H_4 and its quick dissolution on the addition of pdp strongly suggest a Ag(I)/Ag(0) cycle operating in the system. Similarly, formation of a dark brown solution (Ag(III)) on mixing pdp and Ag(I) and its quick disappearance on the addition of N_2H_4 strongly suggest a Ag(I)/Ag(III) cycle for the mechanism. However, the rate is not independent of either pdp or $N_2H_5^+$, and hence there is no kinetic evidence for a Ag(I)/Ag(0) or Ag(I)/Ag(II) cycle. The catalytic role of Ag(I) appears to be through its complexation with pdp. Peroxodiphosphate is reported[7] to form weak complexes with Na^+, K^+, and Li^+, and such a complex between pdp and Ag^+ cannot be ruled out. On the basis of this discussion and kinetic results, the following mechanism may be proposed for the reaction:

$$H_2P_2O_8^{2-} \underset{}{\overset{K_3}{\rightleftharpoons}} HP_2O_8^{3-} + H^+ \tag{3}$$

$$N_2H_5^+ \underset{}{\overset{K_d}{\rightleftharpoons}} N_2H_4 + H^+ \tag{12}$$

(a) Uncatalyzed Path:

$$H_nP_2O_8^{n-4} + N_2H_5^+ \rightarrow products \qquad n = 2 \text{ or } 1 \tag{13}$$

(b) Catalyzed Path. If one considers $HP_2O_8^{3-}$ and $N_2H_5^+$ as the reactive species, the following mechanism may be proposed:

$$Ag^+ + {}^-O_2CCH_3 \overset{K}{\rightleftharpoons} Ag(O_2CCH_3) \tag{14}$$

$$HP_2O_8^{3-} + Ag^+ \overset{K_1}{\rightleftharpoons} Ag(HP_2O_8)^{2-} \tag{15}$$

$$Ag(O_2CCH_3) + HP_2O_8^{3-} \overset{K_2}{\rightleftharpoons} Ag(O_2CCH_3)(HP_2O_8{}^{3-}) \tag{16}$$

$$Ag(HP_2O_8)^{2-} + N_2H_5^+ \overset{k_1}{\longrightarrow} products \tag{17}$$

$$Ag(O_2CCH_3)(HP_2O_8)^{3-} + N_2H_5^+ \overset{k_2}{\longrightarrow} products \tag{18}$$

Rate law 19 is then obtained. Other mechanisms considering

$$-d[pdp]/dt = k_{uncat}[pdp][N_2H_5^+] +$$
$$\frac{(k_1K_1 + k_2K_2K[^-O_2CCH_3])[Ag(I)][pdp][N_2H_5^+]}{([H^+] + K_3)(1 + K[^-O_2CCH_3])} \tag{19}$$

$H_2P_2O_8^{2-}$ and N_2H_4 as the reactive species or considering complexation between Ag^+ and $N_2H_5^+/N_2H_4$ can also be proposed, but all the mechanisms have the same form of the general rate law (20). A plot of k_{cat}^{-1} vs. $[H^+]$ was made (Figure 1), yielding

$$k_{cat} = \frac{A + B[^-O_2CCH_3]}{([H^+] + K_3)(1 + K[^-O_2CCH_3])} \tag{20}$$

a straight line with the intercept and slope of forms (21) and (22), respectively. From the ratio of intercept to slope, a value of 4.4

$$intercept = \frac{K_3(1 + K[^-O_2CCH_3])}{A + B[^-O_2CCH_3]} \tag{21}$$

$$slope = \frac{1 + K[^-O_2CCH_3]}{A + B[^-O_2CCH_3]} \tag{22}$$

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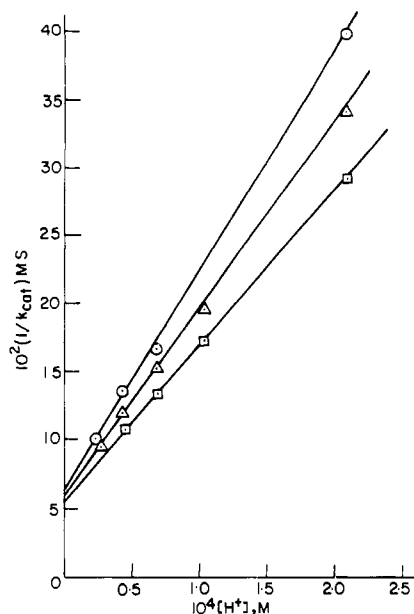(16) Crutchfield, M. N.; Edwards, J. O. *J. Am. Chem. Soc.* **1966**, *82*, 3533.

Figure 1. Plot of $1/k_{cat}$ vs. $[H^+]$. $[^-O_2CCH_3]_T = 3.0 \times 10^{-2}$ M (O), 3.9×10^{-2} M (△), 4.5×10^{-2} M (□); $[Ag(I)] = 2.0 \times 10^{-3}$ M; $I = 1.0$ M; 40 °C.
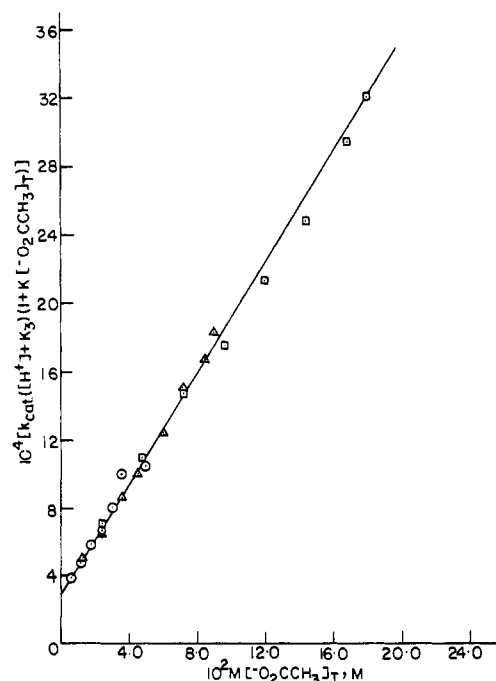

Figure 2. Plot of $[k_{cat}([H^+] + K_3)(1 + K[^-O_2CCH_3]_T)]$ vs. $[^-O_2CCH_3]_T$. $I = 1.0$ M; pH 3.36 (O), 3.60 (△), 3.97 (□); 40 °C; $K_3 = 4.4 \times 10^{-5}$.

$\times 10^{-5}$ for K_3 was obtained. This is quite similar to the value of 4.36×10^{-5} determined[17] pH-metrically at 40 °C. Equations 21 and 22 can be rearranged to (23) and (24), respectively. A plot

$$\frac{1 + K[^-O_2CCH_3]}{intercept} = \frac{A}{K_3} + \frac{B[^-O_2CCH_3]}{K_3} \tag{23}$$

$$\frac{1 + K[^-O_2CCH_3]}{slope} = A + B[^-O_2CCH_3] \tag{24}$$

of $(1 + K[^-O_2CCH_3])/$intercept vs. $[^-O_2CCH_3]$ using $K = 5.4$ yielded a straight line with a nonzero intercept that gave $A = 3.3 \times 10^{-4}$ M^{-1} s^{-1} and $B = 1.54 \times 10^{-2}$ M^{-1} s^{-1}. Similarly, a plot of $(1 + K[^-O_2CCH_3])/$slope vs. $[^-O_2CCH_3]$ also yielded a straight

(17) Gupta, B. Ph.D. Thesis, Rajasthan University, 1984; p 119.

line with a nonzero intercept. The values of A and B from this plot were found to be 3.0×10^{-4} M^{-1} s^{-1} and 1.5×10^{-2} M^{-1} s^{-1}. Thus, the values of A and B obtained from different plots are in good agreement. With the latter values of A and B and of K_3 so obtained and with k_{uncat} from the uncatalyzed study, k_{cat} can be calculated by making use of eq 19. These values along with the experimental values are shown in Table II, and the agreement among them is more than satisfactory.

Rate law 20 was verified in one more way. It can be rearranged as (25), and thus a plot of left side of eq 25 vs. [$^-O_2CCH_3$] can

$$k_{cat}([H^+] + K_3)(1 + K[^-O_2CCH_3]) = A + B[^-O_2CCH_3] \quad (25)$$

be made (Figure 2). A straight line with nonzero intercept resulted, yielding values of $A = 3.0 \times 10^{-4}$ M^{-1} s^{-1} and $B = 1.5 \times 10^{-2}$ M^{-1} s^{-1} at 40 °C, and $I = 1.0$ M. Thus, in all cases the values of A and B are similar, and rate law 19 holds for the Ag(I) catalyzed oxidation of hydrazine with peroxodiphosphate.

It appears that Ag(I) may have the catalytic role in all peroxodiphosphate reactions as in the case of peroxodisulfate reactions, but the two differ in their mechanisms. In the case of pds oxidations of most of the inorganic species like hydrazine,[5] cerium(III),[18] manganese(II),[5,19] water,[20] vanadyl ion,[21] thallium(I),[22]

etc., the rates are similar, and the reaction between pds and Ag(I) is rate controlling. Thus a Ag(I)/Ag(II) cycle operates. The second-order rate constant was found to be ~0.45 M^{-1} s^{-1} at 35 °C and $I = 1.0$ M and was independent of acid concentration (0.1–2.0 M). In the case of pdp, the oxidations so far studied are those of water,[1] arsenic(III),[2] antimony(III),[2] and phosphite,[3] and all of them have different rates under similar conditions. Thus, the reducing substance has also a role in controlling the rate. Although, in the case of pdp, Ag(I) catalysis has been explained through complexation with pdp, the point of interest is whether Ag(0) or Ag(II)/Ag(III) is formed or not. A reaction of Ag(I) and N$_2$H$_4$ forming Ag(0) has been reported,[6] and Ag^{II} or Ag^{III} is also obtained from pdp–Ag(I) reaction.[1] There is absolutely no kinetic evidence for either of these two situations, though one may be tempted to suggest a mechanism involving Ag(0) or Ag(II)/Ag(III). In view of the two observations in connection with the formation of different oxidation states of silver, the question of details of mechanism seems still open and perhaps a fresh study of the direct reactions of Ag(II) and hydrazine and of Ag(I) and hydrazine may be helpful in shedding light on the mechanism of the catalyzed reaction.

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Complexes of Thiosulfate and Disulfanemonosulfonate with *cis*-Bis(ethylenediamine)cobalt(III)

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The preparation and characterization of the anionic thiosulfato complexes *cis*-[(en)$_2$Co(SO$_3$)(S$_2$O$_3$)]$^-$ and *cis*-[(en)$_2$Co(S$_2$O$_3$)$_2$]$^-$ and of the molecular complex *cis*-[(en)$_2$Co(NO$_2$)(S$_2$O$_3$)] are reported. The structures of the latter and of the salt [(en)$_2$Co-(S$_2$O$_3$)]$^+$ClO$_4^-$, containing the chelating thiosulfato-*O,S* ligand, have been determined by single-crystal X-ray diffraction. Both compounds crystallize in the monoclinic class: the salt in space group $P2_1/c$ with 4 formula units in a unit cell of dimensions $a = 9.335$ (5) Å, $b = 9.423$ (4) Å, $c = 15.339$ (2) Å, and $\beta = 90.43$ (4)° and the molecular nitrito-*N* complex in space group $P2_1$ with 2 formula units in a unit cell of dimensions $a = 6.706$ (2) Å, $b = 13.223$ (3) Å, $c = 6.776$ (1) Å, and $\beta = 102.72$ (2)°. The molecular nitrito-*N* complex and the bis(thiosulfato) anion are each readily oxidized by aqueous I$_2$ to produce respectively *cis*-[(en)$_2$Co(NO$_2$)(S$_3$O$_3$)] and the substitution-labile *trans*-[(en)$_2$Co(H$_2$O)(S$_3$O$_3$)]$^+$ ion, two notably photoreactive Co(III) complexes of the unstable ligand disulfanemonosulfonate, S$_3$O$_3^{2-}$.

Introduction

Although thiosulfato complexes of bis(ethylenediamine)cobalt(III) with the trans configuration are well-known and have been extensively characterized,[3,4] those with the cis configuration have been less widely reported,[4-6] owing presumably to the trans-labilizing character of the thiosulfato group.[3] We report here an improved preparation and characterization of the previously reported[6] bis(thiosulfato) anion [(en)$_2$Co(S$_2$O$_3$)$_2$]$^-$ and the preparation and characterization of two new complexes in this

cis-bis(ethylenediamine) Co(III) series, the (thiosulfato)(sulfito) complex *cis*-[(en)$_2$Co(SO$_3$)(S$_2$O$_3$)]$^-$ and the (thiosulfato)(nitrito-*N*) complex *cis*-[(en)$_2$Co(NO$_2$)(S$_2$O$_3$)]. The single-crystal X-ray structural determinations of the latter and of the salt [(en)$_2$Co(S$_2$O$_3$)]$^+$ClO$_4^{-5}$ are reported and confirm the monodentate S-bonded thiosulfato ligand in the former and the chelated thiosulfato-*O,S* ligand in the latter.

The reactivity of the bis(thiosulfato) anion with aqueous I$_2$ to produce Co(III) complexes of the disulfanemonosulfonato ligand, S$_3$O$_3^{2-}$, has been reported.[7] Coordination to Co(III) confers some kinetic stability to this ligand that, as the free anion, rapidly reacts with H$_2$O.[8] This coordination stabilization led us to investigate the reactivity of aqueous I$_2$ with other thiosulfato complexes, and we have isolated and characterized a new complex in this series, *cis*-[(en)$_2$Co(NO$_2$)(S$_3$O$_3$)]. Both this complex and the previously reported *trans*-[(en)$_2$Co(H$_2$O)(S$_3$O$_3$)]$^+$ are photoreactive in the

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