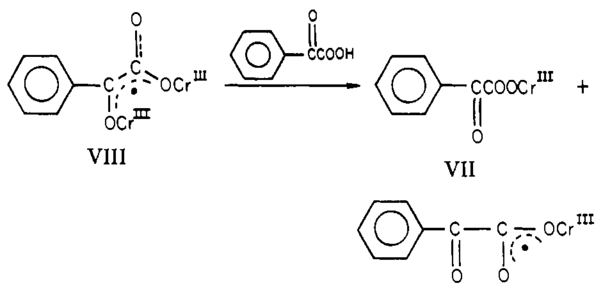
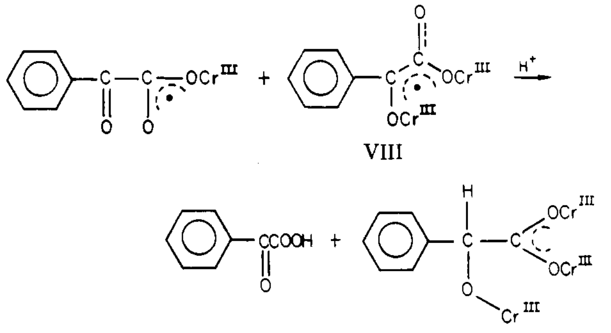
a period corresponding to the half-life for aquation (2.5 h), the slopes of the decay curves are diminished by half.[24]

Note, however, that the rate at which the keto acid is released from VII differs, by a large factor, from the rate at which pigment VIII disappears. When, for example, the pigment is generated from a 0.0014 M solution of the parent chromium(III) complex, it is found to disappear at the rate 1.5×10^{-6} M s^{-1}; but, under the same conditions, phenylglyoxylic acid is released at a rate of only 1.1×10^{-7} M s^{-1}. One molecule of the keto acid then results in the loss of 13 units of radical cation VIII. Recyclic is thus occurring. For the overall bleaching process, we favor the sequence (8) and (9), in which the keto acid acts as a reversible Cr^{2+} carrier, transporting this cation from the poorly coordinating keto-like group of radical VIII to the more basic carboxyl-like site of another unit of VIII, restoring, in part, the keto absorbance at 254 nm and reducing one of the two radical cations to the hydroxy acid level (IX). Chain termination is not represented here but may be presumed to involve bimolecular reaction between two of the radical species to yield a pinacol derivative. The observed 2:1 (rather than 1:1) stoichiometry of the overall reduction indicates, however, that the latter process plays only a minor role.



(8)



(9)

In sum, our results demonstrate the extraordinary ease with which bound phenylglyoxylate undergoes 1e reduction by Cr^{2+}, leading to Cr^{3+}-bound radical species. When this ligand is Co(III) bound, the radical collapses as internal electron transfer occurs. When, however, it is Cr(III) bound, the keto group of the ligand ultimately suffers 2e reduction via a chainlike process that appears to be unique to this ligand.

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[24] To carry out time-delay experiments of this type, it is necessary to destroy the keto acid formed during the delay period (using Eu^{2+} or Cr^{2+}) before generating the green radical cation by addition of further Cr^{2+}.

Contribution from the Department of Chemistry,
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Reaction between Permanganate Ion and Chlorine(III): Kinetics and Mechanism of the Initial Reaction and Dissociation of Chlorous Acid[1]

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and JOHN H. ROMANOW

Received August 18, 1983

In the pH range 1.3–5.0, chlorine(III) and permanganate react rapidly, yielding mixtures of products and unexpended reactants that are stable for approximately 10 s to 1 min, before the further occurrence of slower reactions leading to higher chlorine oxidation states. At 25.0 ± 0.5 °C and ionic strength 1.0 M ($NaClO_4$), the spectrophotometrically determined stoichiometry of this initial reaction is $MnO_4^- + 5ClO_2^-$ (or $5HClO_2$) $+ 8H^+$ (or $3H^+$) $= Mn^{2+} + 5ClO_2 + 4H_2O$. Under the same conditions the rate law is $^1/_5 d[ClO_2]/dt = -d[MnO_4^-]/dt = k_{app}[MnO_4^-][Cl(III)]$. It was found that the $[H^+]$ dependence of the pseudo-first-order rate constant $k = k_{app}[Cl(III)]$ is given by $k = (a + b[H^+])/(1 + c[H^+])$. A mechanism consisting of the rapidly established chlorous acid–chlorite protolytic equilibrium, $K_a = [H^+][ClO_2^-]/[HClO_2]$, and the two rate-limiting steps $MnO_4^- + ClO_2^- = MnO_4^{2-} + ClO_2$ (k_1) and $MnO_4^- + HClO_2 = MnO_4^{2-} + ClO_2 + H^+$ (k_2) leads to the following rate parameter values: $1/c = K_a = (2.70 \pm 0.45) \times 10^{-3}$ M, $a = k_1 = 24.4 \pm 2.0$ M^{-1} s^{-1}, $b/c = k_2 = 92 \pm 29$ M^{-1} s^{-1}. No significant variation of k_{app} with ionic strength was observed in the range 0.01–0.10 M ($NaClO_4$); a slight increase is observed in the range 0.1–2.0 M ($NaClO_4$). Variation of specific ions showed no observable change in k_{app} when Li^+, or $(CH_3)_4N^+$, replaces Na^+. The kinetically measured value of K_a at ionic strength 1.0 M, though smaller than other experimentally determined or extrapolated values, is considered more reliable than static determinations, since the latter are impaired by decomposition of chlorous acid. The experimental k_1 and k_2 greatly exceed the values predicted by the outer-sphere Marcus cross-reaction theory, and we find $k_2 > k_1$ while the Marcus theory predicts $k_1 > k_2$. Therefore, the rate-limiting steps are better described by an inner-sphere mechanism.

Introduction

The system acidic chlorite–iodide is capable of oscillating in a continuous-stirred tank reactor, behavior that may persist when oxidant or reductant is added. In an effort to determine whether such systems represent new oscillators or are perturbations on the fundamental $ClO_2^-–I^-$ system, more complex mixtures of the type $ClO_2^-–I^-–X$, where X = oxidant or reductant, were studied.[2] The $ClO_2^-–I^-–MnO_4^-$ system possesses a third stable steady state in addition to the two bistable states of $ClO_2^-–I^-$ and oscillates in a narrower pH range than

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[1] Systematic Design of Chemical Oscillators. 18. Part 17: Alamgir, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1983**, *105*, 2500.

[2] Orbán, M.; Dateo, C.; De Kepper, P.; Epstein, I. R. *J. Am. Chem. Soc.* **1982**, *104*, 5911.

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Table I. Determination of the Stoichiometry of the Initial Reaction of Chlorine(III) with Permanganate (23-26 °C)

pH	λ, nm	10^4 × $[MnO_4^-]$,[a] M	10^4 × [Cl(III)],[a] M	A_f[b]	$\Delta[MnO_4^-]/\Delta[Cl(III)]$
1.33	525	1.03	0.50	0.204	0.222
		1.33	2.50	0.183	0.220
		2.03	2.50	0.357	0.204
		2.89	1.67	0.590	0.228
					0.218 ± 0.007 (av)
3.05	525	2.03	2.50	0.373	0.177

pH	λ, nm	10^4 × $[MnO_4^-]$,[a] M	10^4 × [Cl(III)],[a] M	A_f[b]	$\Delta[MnO_4^-]/\Delta[ClO_2]$
3.05	360	0.050	2.50	0.313	0.202
		0.038	2.50	0.256	0.187
		0.033	2.50	0.248	0.170
		0.067	2.50	0.429	0.196
					0.189 ± 0.010 (av)

[a] Analytical concentrations after mixing. [b] Experiments were repeated 5-10 times; averages (av) are reported.

Table II. Order of Initial Reaction of Chlorine(III) with Permanganate (25 °C)[a]

pH	10^4 × $[MnO_4^-]$, M	[Cl(III)], M	k_{app}, M^{-1} s^{-1}
1.1	8.8	2.2×10^{-4}	139 ± 10
	8.8	4.3×10^{-4}	139 ± 8
1.75	4.3	2.0×10^{-1}	78.5 ± 0.5
	2.2	2.0×10^{-1}	78.5 ± 3.0
	2.2	1.0×10^{-1}	79.6 ± 1.5
	2.2	5.0×10^{-2}	76.4 ± 3.0

[a] Three trials.

Table III. Observed and Calculated Pseudo-First-Order Rate Constants[a]

pH	no. of trials	k, s^{-1}	k_{calcd},[b] s^{-1}
1.42	3	4.56 ± 0.02	4.40
1.63	3	4.41 ± 0.08	4.27
1.91	3	3.84 ± 0.14	4.02
2.02	3	3.66 ± 0.24	3.87
2.32	3	3.24 ± 0.15	3.40
2.50	3	3.07 ± 0.15	3.05
2.66	2	2.92 ± 0.12	2.73
2.88	3	2.54 ± 0.07	2.34
2.99	4	2.09 ± 0.03	2.15
3.10	3	1.96 ± 0.03	2.00
4.57	3	1.48 ± 0.04	1.25
4.79	4	1.20 ± 0.07	1.24
5.00	3	0.99 ± 0.03	1.23

[a] $[MnO_4^-] = 8.8 \times 10^{-4}$ M; $[ClO_2^-] = 5.0 \times 10^{-2}$ M; $I = 1$ M ($NaClO_4$); 25 °C; [buffer] = 1.0×10^{-1} M. [b] Calculated from eq 2, with $a = 1.22$, $b = 1717$, and $c = 371$.

the parent ClO_2^-–I^- system. It was, therefore, concluded that addition of permanganate produces a new, or different, oscillator. Since a knowledge of the kinetics of the chlorite–permanganate reaction is essential to understanding this oscillator (the permanganate–iodide reaction has already been studied[3]), we are reporting such a study.

Experimental Section

Reagent or higher grade chemicals were used without further purification. All solutions were prepared with distilled, deionized water. During kinetics measurements the temperature was maintained at 25.0 ± 0.5 °C; the stoichiometric determinations were carried out at temperatures between 23 and 26 °C.

Potassium permanganate (Fisher) solutions were prepared and standardized as described by Kolthoff and Sandell[4] against sodium oxalate (Fisher), which had been dried under vacuum at 110 °C for over 24 h. Stock solutions were kept in the dark and restandardized periodically.

Sodium chlorite (MCB) stock solutions were kept in basic solution (10^{-3} M NaOH) to retard decomposition. Fresh solutions were prepared for each series of experiments and kept no longer than 2–3 days.

Buffer solutions were prepared by partial neutralization of sulfuric acid (Baker), glacial acetic acid (Baker), or chloroacetic acid (Fisher) for pH ranges 1.4–2, 2.3–3, and 4.5–5.0, respectively. Buffer concentrations were 0.1 M except as noted.

Ionic strength was fixed by using 1 M sodium perchlorate (Fisher) as supporting electrolyte throughout the pH dependence study. The effect of the electrolyte cation was investigated by using lithium perchlorate (Alfa) and tetramethylammonium perchlorate (G. F. Smith).

The stoichiometric determinations were carried out spectrophotometrically on a Perkin-Elmer PE552A at wavelengths of 525 nm (absorptivity coefficient 2350 M^{-1} cm^{-1}) for MnO_4^- or 360 nm (absorptivity coefficient 1260 M^{-1} cm^{-1}) for ClO_2. At these wavelengths there is no interference of one absorbing species with the other. Hydrogen ion concentration was determined empirically by using an Orion 91-04 combination-glass electrode that was calibrated with known analytical hydrogen ion concentrations at a fixed ionic strength of 1 M ($NaClO_4$) and standardized for each experimental series.

Kinetics measurements were made with a Gibson-type stopped-flow spectrophotometer,[5] modified to include stainless-steel drive syringe barrels in place of Pyrex. Disappearance of permanganate was monitored at 525 nm, or evolution of chlorine dioxide at 360 nm. In *all* cases pseudo-first-order kinetics were observed for the reaction, either MnO_4^- or ClO_2^- being in excess. Additional experiments verified that reaction products at concentrations below approximately 10^{-2} M had no influence on the observed rate.

At fixed pH, we found identical second-order rate constants, consistent with the determined stoichiometry of the reaction, regardless of whether permanganate disappearance or ClO_2 appearance was being followed.

Results

Permanganate reacts with chlorine(III) in aqueous acid, oxidizing it rapidly to state IV and more slowly to higher oxidation states.[6] In the pH range 1.3–5.0 mixtures of products and unexpended reactants are stable for approximately 10 s to 1 min before further reactions occur. Spectrophotometric studies (Table I) show that, in this time period, the only experimentally observed reaction is (I).

$$\begin{aligned} &MnO_4^- + 5ClO_2^- \text{ (or } 5HClO_2) + \\ &\qquad 8H^+ \text{ (or } 3H^+) = Mn^{2+} + 5ClO_2 + 4H_2O \qquad \text{(I)} \end{aligned}$$

A series of stopped-flow experiments were carried out to determine the order of reaction 1 at constant temperature and $[H^+]$. The results (Table II) lead to eq 1.

$$\tfrac{1}{5}d[ClO_2]/dt = -d[MnO_4^-]/dt = k_{app}[MnO_4^-][Cl(III)] \qquad (1)$$

Further experiments were carried out to determine $[H^+]$, ionic strength, and specific ion dependencies of the apparent pseudo-first-order rate constant $k = k_{app}[Cl(III)]$.

The $[H^+]$ dependence results collected in Table III are summarized in eq 2. The data in Table IV show that reaction velocity is essentially unaffected by ionic strength variation, since k does not change appreciably in the range 0.01–0.1 M ($NaClO_4$) and increases very slightly in the range 0.1–2.0 M ($NaClO_4$). No specific-ion effect was observed when Li^+ or

$$k = (a + b[H^+])/(1 + c[H^+]) \qquad (2)$$

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Table IV. Ionic Strength Effects on the Reaction of Chlorine(III) with Permanganate[a]

$[NaClO_4]$, M	no. of trials	k, s^{-1}
0.18	3	0.71 ± 0.03
0.28	3	0.65 ± 0.02
0.68	3	0.60 ± 0.02
1.18	4	0.62 ± 0.01
1.18	3	0.64 ± 0.02
2.18	4	0.72 ± 0.02
0.016	2	0.076 ± 0.01
0.056	3	0.076 ± 0.02
0.096	4	0.081 ± 0.03

[a] Conditions: (top) 25 °C, pH 5.21, $[Cl(III)] = 5.0 \times 10^{-2}$ M, $[MnO_4^-] = 4.0 \times 10^{-4}$ M; (bottom) 25 °C, pH 3.99, $[Cl(III)] = 2.5 \times 10^{-3}$ M, $[MnO_4^-] = 4.0 \times 10^{-5}$ M.

Scheme I

$$K_a = [H^+][ClO_2^-]/[HClO_2] \quad \text{very rapid}$$

$$\left.\begin{array}{ll} MnO_4^- + HClO_2 = MnO_4^{2-} + ClO_2 + H^+ & k_1 \\ MnO_4^- + ClO_2^- = MnO_4^{2-} + ClO_2 & k_2 \end{array}\right\} \text{rate limiting}$$

$$8H^+ \text{ (or } 4H^+) + MnO_4^{2-} + 4ClO_2^- \text{ (or } 4HClO_2) \rightarrow Mn^{2+} + 4ClO_2 + 4H_2O \quad \text{rapid}$$

$(CH_3)_4N^+$ was substituted for Na^+.

Mechanism

One-electron transfer from chlorine(III) to permanganate is thermodynamically unfavorable: $E°(Mn(VII)/Mn(VI)) = 0.56$ V;[6] $E°(Cl(IV)/Cl(III)) = 1.09$ V.[7] However, since there is no evidence for possibly thermodynamically favorable two-electron transfer leading to Mn(V), we interpret the results as rate-limiting one-electron transfer from $HClO_2$ or ClO_2^- to permanganate (Scheme I), followed by rapid processes completing reaction I.

The rate and equilibrium constants in Scheme I are related to the kinetic parameters in eq 2 as follows: $a = k_1$, $1/c = K_a$, $b/c = k_2$. A nonlinear least-squares fit of Scheme I to the data fixing c at the literature value $K_a = 2.19 \times 10^{-2}$ M[8,9] produces unsatisfactory agreement; however, a satisfactory fit is obtained when c is allowed to vary (Figure 1). The resulting kinetically determined rate and equilibrium constants are $k_1 = 24.4 \pm 2.0$ M^{-1} s^{-1}, $k_2 = 92 \pm 29$ M^{-1} s^{-1}, and $K_a = (2.70 \pm 0.45) \times 10^{-3}$ M.

Discussion

It was found that permanganate inhibits the chlorite–iodide oscillator at pH 1 but produces oscillation at pH 2–3.5.[2] The inhibition was explained by proposing that permanganate oxidizes chlorine(III) too rapidly to allow iodide to be oxidized by chlorine(III). Occurrence of oscillation was explained by proposing that the permanganate–chlorine(III) reaction continues to dominate but is sufficiently slowed down to feed back into other major iodide, iodine, and chlorine(III) processes. The results of this study support these hypotheses. The permanganate–chlorine(III) reaction (116 M^{-1} s^{-1}) is faster than the competing chlorine(III)–I^- reaction (11 M^{-1} s^{-1})[10] at pH 1 but is sufficiently slow at pH 2–3.5 (Table III) to couple to other reactions in the system.

Two features of the stoichiometry stand out: Mn^{2+}, and not MnO_2, is produced; ClO_2 is a stable, though transitory, intermediate on the path to more highly oxidized chlorine species. Reduction of permanganate to Mn^{2+} has been observed in the acidified permanganate–iodide reaction[3,4] and in the permanganate–octacyanomolybdate(IV) reaction.[11] Production of ClO_2 implies that permanganate is acting as a 1-equiv oxidizing agent in the rate-determining step.

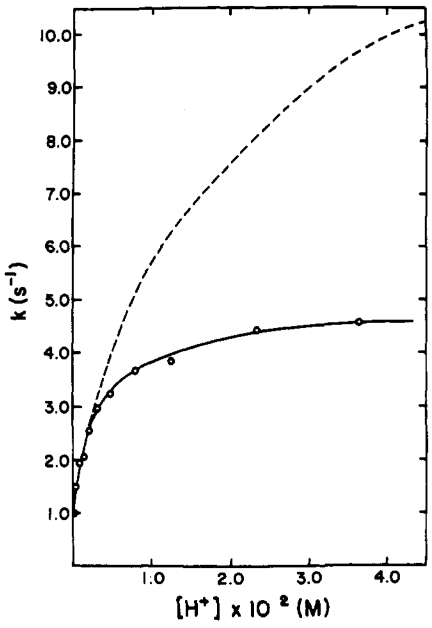

Figure 1. Observed pseudo-first-order rate constant, k (s^{-1}), vs. $[H^+]$ (M). Rate constant was calculated from eq 2 with either $c = 46$ M^{-1} (– –) (ref 8 and 9) or $c = 371$ M^{-1} (—) (this study). ○ indicates experimental values with conditions $[Cl(III)] = 5.0 \times 10^{-2}$ M, 25.0 °C, and 1 M $NaClO_4$.

Data leading to the classification of permanganate reactions as 1 or 2 equiv has been summarized by Stewart.[12] The oxidation of chlorine(III) falls into the 1-equiv category for two main reasons. First, a *direct* transfer of two electrons from chlorine(III) to permanganate results in ClO_3^-. No evidence for this process was found in the time period under investigation. We are left with the possibility that a 2-equiv oxidation is the result of a sequence of one-electron transfers producing 2 mol of ClO_2 and 1 mol of MnO_4^{3-} per mol of MnO_4^- consumed. Such a sequence could be followed by the rapid reaction[12] $MnO_4^{3-} + MnO_4^- \rightarrow 2MnO_4^{2-}$. This mechanism would be inconsistent with the observed rate law if, as has been observed, MnO_4^{2-} reactions are slower than MnO_4^- reactions, for a fourth-order reaction would then result. The proposed mechanism accounts for the stoichiometry (I), since the disproportionation of MnO_4^{2-} is extremely rapid in acidic solution[12] and leads to manganese species capable of oxidizing chlorine(III) to ClO_2. Our k_{app} of about 90 M^{-1} s^{-1} at low pH, though relatively large, is well within the wide range of values observed for permanganate reactions in acid; for example, it is greater than that for CN^- oxidation, $k_{app} < 10^{-2}$ M^{-1} s^{-1}, but less than $k_{app} = 3.8 \times 10^3$ M^{-1} s^{-1} for $Mo(CN)_8^{4-}$ oxidation.[13]

From this mechanism, it is possible to determine K_a, the dissociation constant of chlorous acid, kinetically. Our value of 2.7×10^{-3} is somewhat smaller than most previously determined K_a's of about 10^{-2} or larger for this reaction.[14] However, it is closer to the average value of 1.6×10^{-3} for oxo acids of formula H_nXO_m, $(m - n = 1)$, predicted by Pauling.[15] Apparently, the static studies, though seeking to avoid errors due to decomposition of chlorous acid in acidic media, fail to do so rigorously.

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A one-electron-transfer scheme suggests that the Marcus cross-reaction theory can be applied to the rate-determining step to determine whether it proceeds via an inner- or outer-sphere mechanism.[16] Some reactions of permanganate have been shown to be outer sphere by application of this theory.[11,17] There have been fewer studies of chlorine(III) reactions; however, a study of the kinetics of the reversible reaction between tris(1,10-phenanthroline)iron(III) and chlorine(III) was consistent with outer-sphere electron transfer.[18]

In Marcus theory, rate constants k_1 and k_2 are referred to as cross-reaction rate constants and are designated k_{12}. They can be calculated from eq 3. In this equation, k_{11} is the

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \tag{3}$$

self-exchange rate constant for the Cl(IV)/Cl(III) couple ($\gtrsim 10^2$ M^{-1} s^{-1});[19] k_{22} is the corresponding rate constant for MnO_4^-/MnO_4^{2-} (4×10^3 M^{-1} s^{-1});[20] K_{12} is the equilibrium constant for the reaction; $\ln f_{12}$ and W_{12} can be calculated from self-exchange rate and equilibrium constants and from electrostatic work terms.[16] Dodgen and Taube established a lower limit on k_{11}, which they found to be essentially independent of $[H^+]$ in the pH range 0–5. The values of K_{12} for the two different reactions, permanganate–$HClO_2$ and permanganate–ClO_2^-, were calculated from the standard potential,[7] and our kinetically determined pK_a, with the assumption that equilibration $HClO_2^+ \rightleftharpoons H^+ + ClO_2$ is rapid. Then, with distances of closest approach 1.5 Å for ClO_2/ClO_2^-,[18] 3.3 Å for MnO_4^-/MnO_4^{2-},[15] and 2.4 Å for ClO_2^-/MnO_4^-, we calculate (at $[H^+] = 10^{-5}$ M) $k_1 = 0.34$ M^{-1} s^{-1} and (at $[H^+] = 1$ M) $k_2 = 1.4 \times 10^{-2}$ M^{-1} s^{-1}. This calculation predicts values lower than those observed by factors of approximately 70 and 6600, respectively, and a trend in $[H^+]$ dependence opposite to that observed experimentally. It therefore seems likely that rate-limiting steps in the permanganate–chlorine(III) reaction proceed through an inner-sphere mechanism.

The stable[12] ions MnO_4^{2-} and MnO_4^{3-} are generated by feeding electrons into unoccupied antibonding orbitals on MnO_4^-.[21] Since at least a pair of electrons can be accepted, we picture the inner-sphere mechanism as taking place by attachment of a chlorine lone pair to manganese followed by electron transfer. Either permanganate or chlorite ions react as an ion pair, explaining the lack of ionic strength dependence. Only H^+ exerts a specific effect on the rate, acting as an accelerator, perhaps by stabilizing the active complex through H bonding between permanganate and chlorous acid oxygens.

Acknowledgment. This work was supported in part by Research Grant GM-08893-20 from the NIH and in part by Grant 79-05911 from the NSF. J.H.R. was supported in part by the Brandeis University Undergraduate Research Fund.

Registry No. MnO_4^-, 14333-13-2; ClO_2^-, 14998-27-7; $HClO_2$, 13898-47-0.

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Some Reactions of (Fluoroimido)tetrafluorosulfur[1]

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Received August 4, 1983

(Fluoroimido)tetrafluorosulfur undergoes a number of reactions with strong electrophiles, involving addition to the sulfur–nitrogen double bond. It also reacts readily with fluoride ion, forming the reactive nucleophile SF_5NF^-. Chlorine(I) fluorosulfate, bromine(I) fluorosulfate, and peroxydisulfuryl difluoride add to $F_4S{=}NF$, forming the respective cis adducts. The ^{19}F NMR spectra of these adducts provide the first examples of magnetic nonequivalence induced in an octahedral system by an adjacent chiral center. The anion SF_5NF^-, generated in situ from $F_4S{=}NF$ and KF, reacts readily with Br_2, forming SF_5NBrF, and with acyl fluorides, forming $RCONFSF_5$. The SF_5NF^- ion also reacts with $F_2C{=}NF$ to form $(SF_5NF)FC{=}NF$, which is isomerized to the unusual azo compound $F_5SN{=}NCF_3$ in the presence of CsF. Self-reaction of $F_4S{=}NF$ in the presence of KF does not produce the expected dimer $(SF_5NF)F_3S{=}NF$. Instead, extensive decomposition is observed, along with a low yield of the unusual amine $(SF_5)_2NF$.

Introduction

Compounds of sulfur, nitrogen, and fluorine containing multiple N–S bonds are well-known and have led to much unique and interesting chemistry. Among these compounds are examples containing triple (e.g., $N{\equiv}SF$, $N{\equiv}SF_3$, and $N{\equiv}SF_2(CH_3)$) and double (e.g., $F_4S{=}NR$, $(R)F_3S{=}NR$, $XX'F_2S{=}NR$, $XX'S({=}NR)_2$, $O_2S{=}NR$, and $(O)F_2S{=}NR$) bonds.[2] Despite the long and chemically productive history of this general class of compounds, reports of the synthesis and chemistry of imidotetrafluorosulfur compounds, $F_4S{=}NR$, have been few. Among the compounds of this class so far reported are $F_4S{=}NCF_3$,[3] $F_4S{=}NCH_3$,[4] and $F_4S{=}NSF_5$;[5] of these three compounds, extensive chemical investigations have been reported only for $F_4S{=}NSF_5$.[5] Some chemistry of a (perfluoroalkyl)(trifluoroimido)sulfur compound, $(CF_3)F_3S{=}NCF_3$,[6] has also been reported.

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[1] Work done in part at Kansas State University.

[2] For recent reviews of this area, see: (a) Glemser, O.; Mews, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 530. (b) Mews, R. *Adv. Inorg. Chem. Radiochem.* **1976**, *19*, 185. (c) Glemser, O.; Mews, R. *Ibid.* **1972**, *14*, 333.

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