Perhaloalkyl Hypochlorites and Pentafluorosulfur Hypochlorite. I. Preparation and Properties

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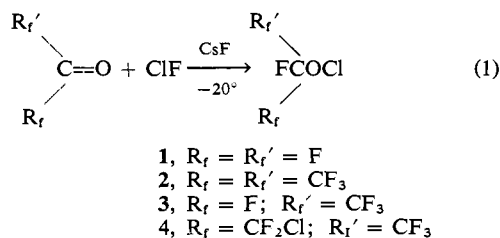
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Abstract: The preparation and properties of the new hypochlorites CF_3OCl, C_2F_5OCl, i-C_3F_7OCl, $CF_2ClCF(CF_3)OCl$, $ClO(CF_2)_5OCl$, and SF_5OCl are described. The first five are most conveniently prepared through the cesium fluoride catalyzed addition of chlorine monofluoride to the appropriate carbonyl compound at low temperature. Pentafluorosulfur hypochlorite is prepared through an analogous reaction in which F_4SO is used rather than a carbonyl compound. The new perhaloalkyl hypochlorites appear to be much more stable than the corresponding primary and secondary alkyl hypochlorites.
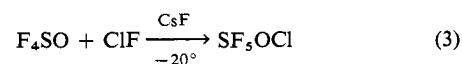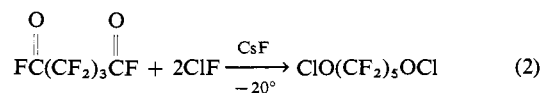
W̲e have recently prepared and characterized several members of a new class of chemical compounds, the perhaloalkyl hypochlorites. In addition to these, we have also prepared the closely analogous pentafluorosulfur hypochlorite.

These compounds are superficially similar to the corresponding fluoroxyperfluoroalkyl[1-5] and fluoroxypentafluorosulfur[6] compounds (often called "hypofluorites"). There are, however, some rather distinct differences in the chemical behavior of the two compound classes. These differences may result from the different relative electronegativities of oxygen and halogen in R_fOCl as compared to R_fOF. The polarity of the halogen–oxygen bond in the hypochlorites will therefore be the reverse of what it is in the fluoroxy compounds. In order to draw attention to this distinction, we have chosen to refer to R_fOCl species as "hypochlorites," whereas R_fOF species are designated as "fluoroxy" compounds. We have explored the chemistry of the hypochlorites in some detail and will present our findings in subsequent papers.[7]

The new perhaloalkyl hypochlorites are easily prepared in high yields by the metal fluoride catalyzed reaction of perhaloalkyl carbonyl compounds with chlorine monofluoride as shown in eq 1.

$$\underset{R_f}{\overset{R_f'}{\diagdown}}C{=}O + ClF \xrightarrow[-20°]{CsF} \underset{R_f}{\overset{R_f'}{\diagdown}}FCOCl \qquad (1)$$

1, $R_f = R_f' = F$
2, $R_f = R_f' = CF_3$
3, $R_f = F$; $R_f' = CF_3$
4, $R_f = CF_2Cl$; $R_f' = CF_3$

The chlorofluorination technique appears to be quite general and was also used to prepare the difunctional compound decafluoropentane-1,5-dihypochlorite (eq 2) as well as the inorganic pentafluorosulfur hypochlorite

$$\overset{O}{\underset{\parallel}{FC}}(CF_2)_3\overset{O}{\underset{\parallel}{CF}} + 2ClF \xrightarrow[-20°]{CsF} ClO(CF_2)_5OCl \qquad (2)$$

$$F_4SO + ClF \xrightarrow[-20°]{CsF} SF_5OCl \qquad (3)$$

(eq 3). The use of "positive" chlorine reagents other than ClF also appears promising, since dichlorine monoxide was found to be a convenient reagent for the preparation of trifluoromethyl hypochlorite (eq 4).

$$F_2CO + Cl_2O \xrightarrow[-20°]{CsF} CF_3OCl + [CsOCl] \qquad (4)$$
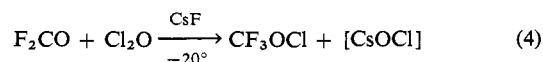
Quite unexpectedly, carbon dioxide is unreactive with chlorine monofluoride in the presence of cesium fluoride over a wide temperature range. By way of contrast, the analogous fluorination proceeds quite readily at temperature as low as $-80°$.[8-10] Evidently there are quite distinct differences between the reaction types.

Experimental Section

Materials and Equipment. Chlorine monofluoride and thionyl tetrafluoride were obtained from Ozark-Mahoning Co. and were used without further purification. Hexafluoroacetone and chloropentafluoroacetone, obtained from the Specialty Chemicals Division of Allied Chemical Corp., were also used as received. Carbonyl fluoride, trifluoroacetyl fluoride, oxalyl fluoride, and perfluoroglutaryl fluoride were prepared by heating the corresponding acyl chlorides with an alkali metal fluoride in the absence of a solvent and purified by vacuum-line fractionation. Chlorine monoxide was prepared by the reaction of chlorine with mercuric oxide at low temperature.[11] Cesium fluoride (American Potash and Chemical Corp.) was dried before use *in vacuo* at 140° and finely ground with a Spex Mixer/Mill Model 8000 using a tungsten carbide capsule and ball.

Vacuum manipulations were carried out in a nickel–Monel system with Kel-F U traps. Infrared spectra were obtained with a Perkin-Elmer Model 137B spectrophotometer using a Monel infrared cell equipped with silver chloride windows. The ^{19}F nmr spectra were recorded at 56.4 MHz with a Varian Model V-4302 spectrometer.

(1) K. B. Kellogg and G. H. Cady, *J. Am. Chem. Soc.*, **70**, 3986 (1948).

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(4) M. Lustig, A. R. Pitochelli, and J. K. Ruff, *ibid.*, **89**, 2841 (1967).

(5) P. G. Thompson and J. H. Prager, *ibid.*, **89**, 2263 (1967).

(6) J. K. Ruff and M. Lustig, *Inorg. Chem.*, **3**, 1422 (1964).

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(10) R. L. Cauble and G. H. Cady, *ibid.*, **89**, 1962 (1967).

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Table I. Infrared and Nmr Spectra of the Perhaloalkyl Hypochlorites and Pentafluorosulfur Hypochlorite

	Ir, cm^{-1}	^{19}F nmr (rel to CFCl$_3$)[a]
CF$_3$OCl	1262 (s), 1220 (sh), 1205 (s), 925 (m), 650 (m)	+71.9 (singlet)
C$_2$F$_5$OCl	1380 (m), 1240 (s), 1220 (m), 1190 (s), 1100 (s), 760 (w), 735 (w)	+78 (unresolved, area 3.16) +87 (unresolved, area 2.0)
i-C$_3$F$_7$OCl	1320 (s), 1250 (s), 1215 (m), 1190 (m), 1155 (s), 1005 (s), 795 (w), 755 (m), 728 (m), 665 (w)	+81.3 (unresolved) +143 (unresolved)
CF$_2$ClCF(CF$_3$)OCl	1315 (s), 1250 (s), 1200 (s), 1161 (s), 1115 (s), 1052 (m), 1025 (m), 926 (ms), 893 (m), 755 (w), 728 (m)	+68.1 (unresolved, area 2.0) +79.5 (unresolved, area 2.9) +139 (unresolved, area 1.0)
ClO(CF$_2$)$_5$OCl[b]		+86.4 (unresolved, area 4.0) +123 (unresolved, area 6.0)
SF$_5$OCl[c]	926 (s), 890 (s), 720 (mw)	AB$_4$ pattern $\phi = -60.2$ $\phi^a = -57.7$ $J_{ab}{}^b = 161.5$ Hz

[a] The nmr spectra were obtained on nonspinning pure samples, and chemical shifts were determined by substitution. Spin-spin couplings between fluorine atoms on adjacent carbon atoms were not observed since, under the conditions of our experiments, couplings of less than 3 Hz would not be resolved. The aforementioned vicinal couplings are normally somewhat less than this (cf. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, 1966, p 875). [b] The gas-phase infrared spectrum of ClO(CF$_2$)$_5$OCl was not obtained owing to its low volatility. Although fluorine atoms are in three different environments in this molecule, only two distinct resonance signals were observed. This probably results from the very similar environments of the fluorine atoms bonded to carbon atoms 2, 3, and 4. A similar situation occurs in CF$_3$(CF$_2$)$_5$CF$_3$, where no distinction in chemical shift is found between the fluorine atoms bonded to carbon atoms 3, 4, and 5 (cf. Emsley, Feeney, and Sutcliffe, footnote a, p 893; See also ref 4). [c] The calculations of the nmr spectrum for the AB$_4$ model were accomplished by the use of a generalized seven-spin program written for the IBM 360/50 computer. An excellent fit of the theoretical and experimental plots indicated that the calculated parameters were accurate.

Preparation of the Hypochlorites. All of the hypochlorite preparations (except that of decafluoropentane 1,5-dihypochlorite) were performed in essentially the same manner. In a drybox operation, a 30-ml stainless steel cylinder was charged with a small amount (0.5-2.0 g) of dry, finely ground CsF. The cylinder was then capped with a valve and removed to the vacuum system. Conventional vacuum techniques were used to condense the appropriate carbonyl compound (or F$_4$SO) into the cylinder. This was followed by the addition of a slight excess of ClF and storage at $-20°$. Reactions were normally allowed to proceed overnight, although 2-3 hr is sufficient for completion. The absence of the characteristic carbonyl absorption in the infrared spectra of the products indicated the formation of the new hypochlorites. The hypochlorite products were always transferred to the vacuum system for infrared analysis or separation without allowing the reaction cylinder to warm to room temperature.

Conventional vacuum-line fractionation was used to free the hypochlorites from excess ClF and minor impurities. In all cases, the product yield was essentially quantitative.

The infrared and nmr data for the new compounds are summarized in Table 1.

Trifluoromethyl Hypochlorite. The procedure outlined above was followed using carbonyl fluoride (8 mmol) and ClF (10 mmol). Fractionation of the product between -140 and $-196°$ traps led to the isolation of pure CF$_3$OCl in the $-140°$ trap. *Anal.* Calcd for CF$_3$OCl: C, 9.96; F, 47.30; Cl, 29.46. Found: C, 9.50; F, 45.9; Cl, 29.22.

The molecular weight was determined by the gas density method: calcd for CF$_3$OCl, 120.5; found, 120.7.

The vapor pressure between -131 and $-54°$ obeys the equation

$$\log P_{mm} = 7.413 - \frac{1.025 \times 10^3}{T(°K)}$$

The normal boiling point calculated from this equation is $-47°$, and the latent heat of vaporization is 4684 cal mole^{-1}, corresponding to a Trouton constant of 20.7 cal deg^{-1} mol^{-1}. The melting point is $-164°$.

Pentafluoroethyl Hypochlorite. The above preparative procedure was followed using trifluoroacetyl fluoride (10 mmol) and ClF (13 mmol). Fractionation between -111 and $-196°$ led to the isolation of pure C$_2$F$_5$OCl in the $-111°$ trap. *Anal.* Calcd for C$_2$F$_5$OCl: C, 14.52; F, 53.88; Cl, 20.44. Found: C, 14.08; F, 55.72; Cl, 20.82. Vapor pressures were not measured, but the

distribution of C$_2$F$_5$OCl during fractionation suggests a boiling point of about $-10°$.

Heptafluoroisopropyl Hypochlorite. The usual preparative procedure was followed using hexafluoroacetone (10 mmol) and ClF (10 mmol). Fractionation of the product between -95 and $-196°$ led to the isolation of pure i-C$_3$F$_7$OCl in the $-95°$ trap. *Anal.* Calcd for i-C$_3$F$_7$OCl: C, 16.33; F, 60.32; Cl, 16.10. Found: C, 16.40; F, 58.88; Cl, 16.35.

The molecular weight was determined by the gas density method: calcd for i-C$_3$F$_7$OCl, 220.5; found, 220.4.

The vapor pressure between -77 and $13.5°$ obeys the equation

$$\log P_{mm} = 7.6149 - \frac{1.3956 \times 10^3}{T(°K)}$$

The normal boiling point calculated from this equation is 22°, and the latent heat of vaporization is 6378 cal mol^{-1} corresponding to a Trouton constant of 21.6 cal deg^{-1} mol^{-1}.

1-(Chlorodifluoromethyl)tetrafluoroethyl Hypochlorite. The above preparative procedure was followed using chloropentafluoroacetone (3 mmol) and ClF (3 mmol). Fractionation of the product between -78 and $-196°$ led to the isolation of pure CF$_2$ClCF(CF$_3$)OCl in the $-78°$ trap. *Anal.* Calcd for CF$_2$ClCF(CF$_3$)OCl: Cl, 29.96. Found: Cl, 29.14.

Pentafluorosulfur Hypochlorite. The normal preparative procedure as previously outlined for the preparation of the perhaloalkyl hypochlorites was followed with F$_4$SO (10 mmol) and ClF (11 mmol) as reactants. The reaction products were fractionated between -111 and $-196°$ traps. Essentially pure SF$_5$OCl containing a trace of SOF$_4$ was retained in the $-111°$ trap. *Anal.* Calcd for SF$_5$OCl: S, 17.96; F, 53.22; Cl, 19.86. Found: S, 17.11; F, 51.30; Cl, 19.09.

Decafluoropentane 1,5-Dihypochlorite. The usual preparative procedure for the hypochlorites was modified somewhat in that a U-trap reactor was constructed of $^3/_8$-in. Kel-F tubing. One side of the "U" was left unchanged while the upper portion of the other limb was bent downward until it formed an angle of about 30° with the sides of the "U." This was then heat-sealed to $^3/_{16}$-in. Kel-F tubing which was closed at the bottom.

The reactor was charged with CsF in the drybox as before, making certain that it was retained within the bottom of the "U" but did not plug the tubing. The open side of the reactor was then connected through a "Nupro" all-Teflon valve to the vacuum system. Perfluoroglutaryl fluoride (2 mmol) and ClF (4 mmol)

were then condensed into the "U" portion of the reactor. The mixture was allowed to warm to $-20°$ and remain at that temperature overnight. After this time, the reactor was tipped to allow the liquid hypochlorite to be decanted from the cesium fluoride into the $^3/_{16}$-in. portion of the reactor which was then inserted into the probe of the nmr spectrometer. After obtaining the nmr spectrum, the sample was frozen and the tubing cut so that the entire sample fell into a basic solution for hydrolysis. Weights were determined by difference through weighing the entire apparatus and sample before hydrolysis and the separate pieces afterward. Standard analytical techniques were then used to determine chlorine. *Anal.* Calcd for $ClO(CF_2)_5OCl$: Cl, 20.11. Found: Cl, 18.3. Although the chlorine analysis (because of handling difficulties) is not especially good, the nmr evidence leaves little doubt that $ClO(CF_2)_5OCl$ was formed.

Thus, in another reaction, monitored by nmr spectroscopy, the $FC(O)(CF_2)_3C(O)F$ spectrum (absorptions at -24.5, $+118$, and $+123.5$ ppm) disappeared on treatment with ClF and new absorptions consistent with $ClO(CF_2)_5OCl$ appeared. These absorptions are given in Table I.

Alternative Preparation of Trifluoromethyl Hypochlorite. The usual preparative procedure was followed using carbonyl fluoride (2 mmol) and Cl_2O (2 mmol). CF_3OCl was shown to be present through a comparison of the infrared spectrum of the product gases with the spectrum of an authentic sample of CF_3OCl. No attempt was made to identify CsOCl among the solids after reaction.

Attempted Preparation of $ClOCF_2CF_2OCl$. The usual preparative procedure was followed using oxalyl fluoride (5 mmol) and ClF (10 mmol). At $-20°$, the only volatile products found were COF_2 and CF_3OCl but in insufficient quantities for complete material balance. A repetition of this experiment, carried out at $-78°$, led only to COF_2, CF_3OCl, and unreacted $(COF)_2$.
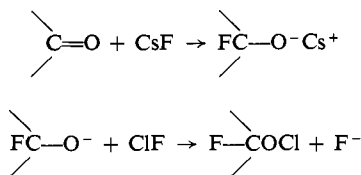
No evidence for $ClOCF_2CF_2OCl$ was found from the reaction at $-20°$. After remaining for several days at $-20°$, the products were reinvestigated and found to contain a yellow, relatively high-boiling product. This material exploded violently upon warming to room temperature and thus could not be characterized.

Attempted Preparation of $CF_2(OCl)_2$. The usual preparative procedure was followed using carbon dioxide (7 mmol) and ClF (14 mmol). This failed to produce the desired $CF_2(OCl)_2$. Variation of the temperature over the range from -78 to $+80°$ failed to produce any reaction between these materials.

Discussion

The preparation of the new perhaloalkyl hypochlorites and pentafluorosulfur hypochlorite represents a further extension of the metal fluoride catalyzed reactions between fluoride ion acceptors and various oxidizing agents to produce new and rather unusual compounds. For example, Ruff and coworkers have used elemental fluorine to oxidize compounds containing carbonyl or thionyl functions (over CsF) to fluoroxy compounds.[3,6] We have recently reported the use of oxygen difluoride as an oxidant in a metal fluoride catalyzed system to produce good yields of bis(trifluoromethyl) trioxide.[12]

In all these cases, the products can be rationalized as arising from preliminary formation of a fluoroanion which then reacts with the oxidant to form the final product. Thus, for the preparation of the perhaloalkyl hypochlorites, the reaction is presumed to proceed according to the following sequence.
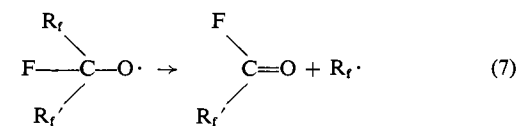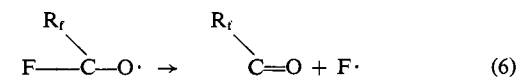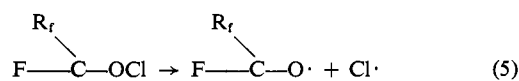
$$\overset{\diagdown}{\underset{\diagup}{C}}=O + CsF \rightarrow F\overset{\diagdown}{\underset{\diagup}{C}}-O^-Cs^+$$

$$F\overset{\diagdown}{\underset{\diagup}{C}}-O^- + ClF \rightarrow F\overset{\diagdown}{\underset{\diagup}{C}}OCl + F^-$$

In support of this, it is known that most of the carbonyl compounds used form stable adducts with cesium fluoride,[13-17] and we have successfully demonstrated that the reaction of preformed $CsOCF_3$ with ClF does lead to trifluoromethyl hypochlorite.

The various hypochlorites decompose on storage at elevated temperatures for prolonged periods. In particular, CF_3OCl decomposes slowly at $150°$. The other hypochlorites are, in general, less stable (or more reactive) than CF_3OCl with the order of stability given by the series $CF_3OCl > C_2F_5OCl \sim i\text{-}C_3F_7OCl > SF_5OCl$. Insufficient data have been obtained for $CF_2ClCF(CF_3)OCl$ and $ClO(CF_2)_5OCl$ to permit ranking them in this series.

The new hypochlorites appear to be much more stable than the corresponding alkyl hypochlorites, some of which are so unstable as to be practically nonisolable.[18] The new compounds provide an excellent example of fluorine substituents stabilizing an unusual and highly reactive molecular structure.

The decomposition reactions of the hypochlorites, when they do occur, can be rationalized as follows.

$$F\overset{R_f}{\underset{R_f'}{\diagdown C \diagup}}OCl \rightarrow F\overset{R_f}{\underset{R_f'}{\diagdown C \diagup}}O\cdot + Cl\cdot \tag{5}$$

$$F\overset{R_f}{\underset{R_f'}{\diagdown C \diagup}}O\cdot \rightarrow \overset{R_f}{\underset{R_f'}{\diagdown C \diagup}}=O + F\cdot \tag{6}$$

$$F\overset{R_f}{\underset{R_f'}{\diagdown C \diagup}}O\cdot \rightarrow \overset{F}{\underset{R_f'}{\diagdown C \diagup}}=O + R_f\cdot \tag{7}$$

$$R_f\cdot + Cl\cdot \rightarrow R_fCl \tag{8}$$

R_f and R_f' can each be F or CF_3

Therefore, in the case of C_2F_5OCl, the decomposition products are COF_2, CF_3Cl, $CF_3C(O)F$, and ClF. In the case of $i\text{-}C_3F_7OCl$, they are $CF_3C(O)F$, CF_3Cl, $(CF_3)_2CO$, and ClF.

A striking example of the importance of the previously mentioned reversal of the chlorine–oxygen bond polarity, as compared to the fluorine–oxygen bond polarity, is provided by the reactions of Cl_2O and OF_2, respectively, with carbonyl fluoride. The products are not analogous but in each case may be presumed to result from initial reaction of the trifluoromethoxide ion with the most positive atom in the halogen oxide. With Cl_2O this process leads to CF_3OCl, whereas with OF_2 the initial product is probably CF_3OOF.[12]

(12) (a) L. R. Anderson and W. B. Fox, *J. Am. Chem. Soc.*, **89**, 4313 (1967); (b) I. Solomon, private communication.

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(14) M. E. Redwood and C. J. Willis, *Can. J. Chem.*, **43**, 1893 (1965).
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(17) F. W. Evans, M. H. Litt, A-M. Weidler-Kubanek., and P. P. Avonda, *J. Org. Chem.*, **33**, 1837 (1968).
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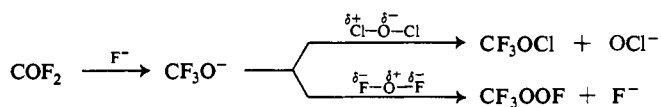
We expect to explore further the differences between fluorinations and chlorofluorinations and to compare the new hypochlorites chemically with the fluoroxy compounds.

Caution: While we have experienced no explosive decomposition of the simple hypochlorites, an explosion did occur during attempts to isolate the products from the chlorofluorination of oxalyl fluoride. All the hypochlorites are powerful oxidizing agents and may react violently with certain reducing agents. In addition, all the new hypochlorites are expected to be quite toxic. Adequate safety shielding and ventilation should be used at all times when handling these compounds.

Reactions Involving Copper(I) in Perchlorate Solution. Kinetics and Mechanism of the Copper(II) Catalysis of Vanadium(III) Reductions of Cobalt(III) Complexes[1a-c]

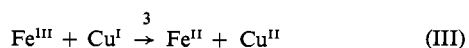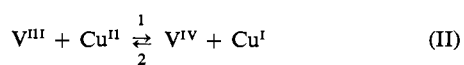## O. Jerry Parker and James H. Espenson[1d]

Contribution from the Department of Chemistry and the Institute for Atomic Research, Iowa State University, Ames, Iowa 50010. Received October 3, 1968

Abstract: Copper(II) catalyzes the oxidation of V^{3+} to VO^{2+} by the cobalt(III) complexes $Co(NH_3)_5Br^{2+}$, $Co(NH_3)_5Cl^{2+}$, and *trans*-$Co(en)_2Cl_2^+$. The rate equation is $-d[V^{3+}]/dt = (g + h/[H^+])[Cu^{2+}][V^{3+}]$, independent of $[Co(III)]$. At 25.0° and $\mu = 3.00\ M$ ($LiClO_4$), the values are $g = 0.018 \pm 0.002\ M^{-1}sec^{-1}$ and $h = 0.336 \pm 0.001\ sec^{-1}$. The activation parameters for h are $\Delta H^{\ddagger} = 19.4 \pm 0.1$ kcal mole^{-1} and $\Delta S^{\ddagger} = 4.4 \pm 0.4$ eu. The rate was also studied with $NaClO_4$ as the added electrolyte and at $\mu = 1.00\ M$ ($LiClO_4$). The rate-determining step is proposed to be the rapid reaction of V^{3+} and Cu^{2+}, followed by the rapid reoxidation of the Cu^+ so formed by $Co(III)$. The role of $Cu(I)$ in the catalytic cycle is discussed, and some "direct" measurements of the $V^{3+} + Cu^{2+}$ rate are presented. The relation of the present results to those on the reverse reaction, $VO^{2+} + Cu^+$, is considered. Arguments are advanced for a mechanism in which the inner-sphere reaction of VOH^{2+} and Cu^{2+} is the main rate-determining step.

The oxidation–reduction reaction between hydrated V^{3+} and Cu^{2+} cations in dilute perchloric acid solution is given by reaction I. This process has been considered in three previous studies.[2-4] One of these was

$$V^{3+} + Cu^{2+} + H_2O = VO^{2+} + Cu^+ + 2H^+ \quad (I)$$
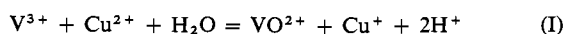
the study of the reaction of Fe(III) and V(III), for which Higginson and Sykes[2] proposed the following two-step mechanism[5] to account for the catalytic effect of Cu^{2+}.

$$V^{III} + Cu^{II} \underset{2}{\overset{1}{\rightleftarrows}} V^{IV} + Cu^{I} \quad (II)$$

$$Fe^{III} + Cu^{I} \overset{3}{\to} Fe^{II} + Cu^{II} \quad (III)$$

Since the rate expression for catalysis was first order with respect to V(III) and Cu(II), the first step of the sequence

was presumed to be rate determining and the catalytic rate constant thereby identified as k_1. In addition, the reaction of VO^{2+} and Cu^+, the reverse of the process presumed responsible for the catalysis, has been studied.[3] The work of Ramsey, *et al.*,[4] established the catalytic effect of Cu^{2+} on the oxidation of V^{3+} by molecular oxygen in perchloric acid solution. They proposed the rate-determining step was reaction II, followed by the rapid reaction of Cu(I) with O_2.

In the present study we have considered further the reaction of V^{3+} and Cu^{2+} to study its kinetics and mechanism in the absence of the complications present in the earlier work, where substantial corrections had to be made for the uncatalyzed reaction. Since equilibrium in reaction I lies largely toward the left, a direct study of $Cu^{2+} + V^{3+}$ is not possible except under a very special and limited set of circumstances.

We have used a procedure similar to the earlier catalytic work,[2] except that used as an oxidizing substrate in place of Fe^{3+} or O_2 was a substance for which the spontaneous oxidation of V^{3+} in the absence of Cu^{2+} does not occur to an appreciable extent. The materials used have been Co(III) complexes, which are known[6] to react rapidly with Cu(I). The three complexes $Co(NH_3)_5Br^{2+}$, $Co(NH_3)_5Cl^{2+}$, and *trans*-$Co(en)_2Cl_2^+$ were studied in

(1) (a) Work performed under the auspices of the U. S. Atomic Energy Commission, Contribution No. 2427; (b) based on the Ph.D. Thesis of O. J. Parker, Iowa State University, Aug 1968; (c) presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968; (d) Fellow of the Alfred P. Sloan Foundation.
(2) W. C. E. Higginson and A. G. Sykes, *J. Chem. Soc.*, 2841 (1965).
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