$$CrCl^{2+} + Cr^{2+} + Cl^- \rightleftarrows cis\text{-}CrCl_2^+ + Cr^{2+} \qquad (k_7) \qquad (7)$$

$$CrCl^{2+} + Cr^{2+} + Cl^- \rightleftarrows trans\text{-}CrCl_2^+ + Cr^{2+} \qquad (k_8) \qquad (8)$$

k_8 have the values 0.44 and 0.56 M^{-2} sec^{-1} at 0°.[20] Again the ratio of $k_7/k_8 = 0.79$ is significantly smaller than the statistically expected value of 4.0. Moreover, a comparison of the value $k_7 + k_8 = 1.0\ M^{-2}$ sec^{-1} (0°) with the value $k_9 = 9\ M^{-1}$ sec^{-1} (0°) for reaction 9[21] il-

$$*CrCl^{2+} + Cr^{2+} \rightleftarrows CrCl^{2+} + *Cr^{2+} \qquad (k_9) \qquad (9)$$

lustrates once more the small effect of added chloride ion on the rate of inner-sphere reactions.

It is instructive to recast the chloride ion effects on the electron-transfer reactions considered above in the form of equilibrium constants involving transition states. Calculations have been previously carried out for acid dissociation constants[22,23] and can be generalized to many other formal reactions of transition states.[24] As an example, it can be seen that the proper combination of eq 10, 11, and 12 leads to eq 13 and a calculated value of $Q_{13} = 5.8 \times 10^6\ M^{-1}$.

$$Co(NH_3)_5OH_2^{3+} + Cr^{2+} \rightleftarrows [(NH_3)_5Co(OH_2)Cr^{5+}]^\ddagger \qquad (k_{10} = 0.50\ M^{-1}\ \mathrm{sec}^{-1}) \qquad (10)$$

$$Co(NH_3)_5Cl^{2+} + Cr^{2+} \rightleftarrows [(NH_3)_5CoClCr^{4+}]^\ddagger \qquad (k_{11} = 2.6 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}) \qquad (11)$$

$$Co(NH_3)_5OH_2^{3+} + Cl^- \rightleftarrows Co(NH_3)_5Cl^{2+} + H_2O \qquad (Q_{12} = 1.11\ M^{-1}) \qquad (12)$$

$$[(NH_3)_5Co(OH_2)Cr^{5+}]^\ddagger + Cl^- \rightleftarrows [(NH_3)_5CoClCr^{4+}]^\ddagger + H_2O \qquad (13)$$

Calculated values of Q for the formal reactions of the transition states of interest in the present note are summarized in Table II. Although no new information is obtained by recasting the chloride ion effects in terms of the equilibrium constants listed in Table II, the approach provides a useful summary of these effects. For example, comparisons of eq A with B and C and of eq D with E and F clearly illustrate the enormous difference between the effect of chloride ion in bridging as compared to nonbridging positions. Reactions A and D feature the substitution of a bridging water by chloride ion, and are seen to be extremely favorable ($Q > 10^5$). In contrast, reactions B, C, E, and F, which feature the substitution of a *cis* or *trans* nonbridging water by chloride ion, are relatively unfavorable (Q = 0.05–0.1). Moreover, the values Q = 1.0 and 0.8 for reactions G and H, respectively, when compared with the statistically expected value of 4.0, clearly demonstrate the increased stability of the transition states containing *trans* chloride ions. Interestingly, an entirely similar observation regarding the relative stabilities of *cis* and *trans* isomers was previously made for the $CrCl_2^+$ system.[13,14]

TABLE II

FORMAL EQUILIBRIUM CONSTANTS FOR SUBSTITUTION OF WATER BY CHLORIDE ION IN CHROMIUM-CONTAINING TRANSITION STATES

	Reactions	Q, M^{-1} [a]	Ref
A.	$[(NH_3)_5Co(OH_2)Cr^{5+}]^\ddagger + Cl^- \rightleftarrows [(NH_3)_5CoClCr^{4+}]^\ddagger + H_2O$	5.8×10^6	*b, c, d*
B.	$[(NH_3)_5CoClCr^{4+}]^\ddagger + Cl^- \rightleftarrows [cis\text{-}(NH_3)_5CoClCrCl^{3+}]^\ddagger + H_2O$	0.1	This work
C.	$[(NH_3)_5CoClCr^{4+}]^\ddagger + Cl^- \rightleftarrows [trans\text{-}(NH_3)_5CoClCrCl^{3+}]^\ddagger + H_2O$	0.1	This work
D.	$[(H_2O)_5Cr(OH_2)Cr^{5+}]^\ddagger + Cl^- \rightleftarrows [(H_2O)_5CrClCr^{4+}]^\ddagger + H_2O$	$>10^5$	*e, f, g*
E.	$[(H_2O)_5CrClCr^{4+}]^\ddagger + Cl^- \rightleftarrows [cis\text{-}(H_2O)_5CrClCrCl^{3+}]^\ddagger + H_2O$	0.05	*f, h, i*
F.	$[(H_2O)_5CrClCr^{4+}]^\ddagger + Cl^- \rightleftarrows [trans\text{-}(H_2O)_5CrClCrCl^{3+}]^\ddagger + H_2O$	0.06	*f, h, i*
G.	$[trans\text{-}(NH_3)_5CoClCrCl^{3+}]^\ddagger \rightleftarrows [cis\text{-}(NH_3)_5CoClCrCl^{3+}]^\ddagger$	1.0	This work
H.	$[trans\text{-}(H_2O)_5CrClCrCl^{3+}]^\ddagger \rightleftarrows [cis\text{-}(H_2O)_5CrClCrCl^{3+}]^\ddagger$	0.8	*f, h, i*

[a] Values for reactions A–C and G at 25°. Values for reactions D–F and H at 0°. [b] A. M. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **81**, 1288 (1959). [c] Reference 12. [d] D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *Inorg. Chem.*, **6**, 1027 (1967). [e] A. Anderson and N. A. Bonner, *J. Am. Chem. Soc.*, **76**, 3826 (1954). [f] Reference 21. [g] C. F. Hale and E. L. King, *J. Phys. Chem.*, **71**, 1779 (1967). [h] Reference 10. [i] Reference 14.

CONTRIBUTION FROM THE OLIN RESEARCH CENTER,
CHEMICALS GROUP, NEW HAVEN, CONNECTICUT 06504

Reaction of Chlorine Monofluoride with Some Group VI Elements and Derivatives

BY JAMES J. PITTS AND ALBERT W. JACHE

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As a fluorinating agent, chlorine monofluoride has been placed approximately below F_2, ClF_3, BrF_5, and IF_7 in reactivity.[1,2] The available information for such an assignment is mostly qualitative. For example, relatively little is known about the reactivity of chlorine monofluoride with group VI elements. Sulfur is said to react slowly and without flame, but no products are specified.[3] With SF_4 at 350°, chlorine monofluoride is said to react as a chlorofluorinating agent to yield SF_5Cl.[4]

Acting as a moderate fluorinating agent, chlorine monofluoride should have a number of attractive synthesis applications. This paper describes the investigation of reactions between chlorine monofluoride

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(20) Espenson and Slocum[10] reported the values 0.22 and 0.28, respectively. However, they failed to recognize that the observed[6] rate constant of 0.50 needs to be multiplied by 2 to account for the fact that only half of the forward events in reactions 7 and 8 lead to chloride exchange. The reported[10] values of Q_{2c} and Q_{2t} also must be multiplied by 2 to correct for the statistical effect.

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and the group VI elements sulfur, selenium, molybdenum, tungsten, and several of their derivatives.

Experimental Section

Materials.—Chlorine monofluoride was obtained from the Ozark-Mahoning Co. and was determined to be 99.4% pure by vapor-phase chromatography. Separation, using a column of Kel-F No. 1 oil on Fluoro-Pak support media in Teflon tubing, showed 0.4% CF_4 (undoubtedly present in the starting fluorine) and 0.2% Cl_2 as impurities. The presence of CF_4 in the infrared spectrum of ClF was also confirmed by its strong sharp band at 1283 cm^{-1}.[5]

The group VI elements and derivatives were obtained from a number of sources: tungsten (assay 99.9%), molybdenum (assay 99.7%), molybdenum disulfide, lead molybdate, and lead tungstate, K & K Laboratories, Inc.; selenium, molybdic anhydride (assay 99.5%), sodium molybdate, and sodium tungstate, Fisher Scientific Co.; tungstic anhydride, Fansteel Metallurgical Corp.; potassium molybdate, Amend Drug and Chemical Co., Inc.; sulfur (precipitated USP grade, assay 99.5%, Baker and Adamson label), Allied Chemical Corp.

All reagents were used as received with the exception of the dihydrated sodium molybdate and tungstate which were dried for several hours under vacuum at 120° to remove the water.

Apparatus.—The vacuum system used in this work consisted of a 0.25-in. o.d. copper tubing manifold equipped with Imperial Eastman Hi-Duty brass fittings and Hoke M327 Monel needle valves. Attached to the manifold were several Hoke high-pressure 4HSM150 Monel cylinders which served as the reaction vessel and for collection and storage of the gaseous products. The cylinders were fitted with the same type of Monel needle valves, the threaded joints being sealed with "Strip Teeze" brand Teflon pipe joint tape. The pressure within the vacuum system was recorded on an Ashcroft 1082AC test gauge which was calibrated to give a reading to within ±3 mm.

Infrared Spectra.—The infrared spectra of the gaseous products were obtained on a Perkin-Elmer Infracord spectrophotometer using an Isomet Corp. 5-cm Monel-body gas cell with AgCl windows sealed with Teflon gaskets. Extreme care was taken initially to pacify both the ir cell and the metal-transfer line with ClF. Failure to do so resulted in spectra showing ClO_2[6] and ClO_2F[7] as impurities.

Identification (both qualitative and quantitative) of the gaseous reaction products was made by comparison to known spectra appearing in the literature and included the references cited here: ClF,[8] SF_4,[9,10] SOF_2,[10,11] SO_2ClF,[10] SF_6,[12,13] SOF_4,[14] S_2F_{10},[15] SF_5Cl,[16,17] SeF_4,[18] SeF_6,[19] WF_6,[13,20] WF_5Cl,[21] MoF_6,[20] SiF_4,[22] CF_3Cl,[23,24] COF_2,[25] and COClF.[25]

The presence of nonabsorbing chlorine was established by its diluent effect on the intensity of the absorption bands of the other gaseous products. Further confirmation was made by the 100 mm vapor pressure exhibited by liquid chlorine at −78°.

Reaction with Sulfur.—A 150-ml Monel cylinder was first pacified with chlorine monofluoride and then charged with 1.0 g of pharmaceutical grade powdered sulfur. A Monel needle valve was attached and the cylinder evacuated on the vacuum line described above. Chlorine monofluoride was then introduced stepwise into the reaction cylinder from a storage cylinder until an equilibrium pressure of 1 atm was attained. The infrared spectrum of a 200-mm sample of the gaseous products revealed a number of compounds resulting from impurities in the sulfur. The main product proved to be SF_4 exhibiting its characteristic bands at 1744 vvw, 1281 w, 889 vvs, 738 vvs, 728 vvs, and 715 vs cm^{-1} with lesser amounts of SO_2ClF at 1475 m and 1230 m cm^{-1}, SOF_4 at 928 s cm^{-1}, and SiF_4 at 1030 m cm^{-1}.

The reaction system was then evacuated of all gaseous products; more chlorine monofluoride was introduced and again an infrared spectrum of the gaseous products was taken. This step was repeated until the system was "pacified" and the infrared spectrum was free from the effect of oxygen-containing impurities. At this point SF_4 was the only product observed in the infrared spectrum. From band intensity *vs.* pressure measurements it was apparent that the SF_4 was diluted with a nonabsorbing gas by an approximate 1:2 ratio thus strongly suggesting chlorine from the stoichiometry. Further confirmation was made by the approximate 100 mm vapor pressure exhibited by the gaseous products when cooled to −78° in a trichloroethylene–Dry Ice slush bath.

The products above were allowed to warm to room temperature and additional chlorine monofluoride was introduced to a pressure of 5 psi. The reaction cylinder was then suspended in a fluidized sand bed and heated at 200° for 2 hr. After cooling to room temperature, the infrared spectrum of a 250-mm sample of the gaseous products showed the presence of SF_6 at 940 vvs, possibly S_2F_{10} at 827 vvw, CF_4 at 1283 s, CF_3Cl at 1206 vs and 1105 vvw, COClF at 1095 ms, and COF_2 at 1248 s cm^{-1}. The latter four impurities are no doubt a result of interaction of the Teflon thread tape on the cylinder valve.

Reaction with Selenium.—In the same manner as above for sulfur, chlorine monofluoride was introduced into 0.5 g of powdered metallic selenium. The infrared spectrum of a 200-mm sample of the gaseous products showed the characteristic bands for SeF_4 at 745 s and 735 vs cm^{-1} "diluted" in intensity approximately 1:2 by the presence of chlorine. The chlorine was removed from the SeF_4 by vacuum distillation at 0° leaving solid SeF_4 which melted at room temperature and exhibited a vapor pressure of 12 mm. This was further confirmed by the infrared spectrum of this vapor which showed SeF_4 in high purity.

Additional chlorine monofluoride was introduced (to a pressure of 5 psi) onto the liquid SeF_4 and the reaction cylinder was heated at 200° in a fluidized sand bed for 2 hr. The infrared spectrum of the gaseous products showed no SeF_6 at either 1484 or 1438 cm^{-1}, only unreacted ClF and SeF_4.

Reaction of Tungsten and Its Derivatives.—Chlorine monofluoride, 1 g (15.5 mmol), was introduced onto 1 g (5.5 mg-atom) of powdered tungsten in the same procedure as described previously for sulfur and selenium. After reaction, the cylinder was cooled to −78° in a trichloroethylene–Dry Ice bath. The product liquid chlorine, as shown by its vapor pressure of about 100 mm, was then removed by pumping for several hours at −78°. On warming to room temperature the infrared spectrum of the remaining gaseous products showed pure WF_6 at 1480 m, 1380 m, 795 s, and 712 vvs cm^{-1}, but there was no indication for WF_5Cl.

Following the procedure above, 2.0 g (31.0 mmol) of ClF was allowed to react with 1.5 g (6.5 mmol) of tungstic anhydride, WO_3. After distilling off the chlorine formed at −78°, the infra-

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red spectrum of the remaining gaseous products showed ClO_2F at 1258 vs and 1100 s cm^{-1} in addition to the WF_6.

As above 1.0 g (15.5 mmol) of chlorine monofluoride was allowed to react with 0.5 g (1.1 mmol) of lead tungstate, $PbWO_4$, at room temperature. However, only a trace of WF_6 was formed as evidenced in the infrared spectrum of the product gases which showed mostly unreacted ClF. The reaction cylinder was then suspended in a vertical electric furnace, heated at 300° for 2 hr, and allowed to cool to room temperature. At this point the gaseous products were separated as before and proved to be WF_6, ClO_2F, and chlorine. The cylinder was opened under a blanket of dry nitrogen and a pale yellow solid was recovered and transferred immediately into a nitrogen-filled Nalgene Teflon (FEP) 1600 bottle. The solid was found to hydrolyze rapidly in air turning brown and suggesting that it was PbF_4. *Anal.* Calcd for PbF_4: F, 26.8. Found: F, 26.1.

The reaction of 1.0 g (15.5 mmol) of ClF with 0.5 g (1.7 mmol) of anhydrous sodium tungstate again yielded only a trace of free WF_6 at room temperature. After heating at 300° for 2 hr the only gaseous products proved to be ClO_2F and chlorine with again only a trace of WF_6 showing up in the infrared region. A white solid was recovered from the reactor under a blanket of nitrogen. It was suspected to be the known $2NaF \cdot WF_6$ complex.[26] Crushed ice was added to a weighed amount of the solid in a Teflon bottle and the bottle was capped. Hydrolysis of the material gave a clear acidic solution. The "active fluorine" in the product was determined by titrating the acidity generated from the hydrolysis with 0.5 *N* NaOH. *Anal.* Calcd

$$2NaF \cdot WF_6 + 3H_2O \longrightarrow WO_3 + 2Na^+ + 6H^+ + 8F^-$$

for $2NaF \cdot WF_6$: active F, 29.9. Found: active F, 28.0.

Reaction of Molybdenum and Its Derivatives.—In a manner similar to the procedure used above for sulfur, selenium, and tungsten, 1.5 g (22.3 mmol) of chlorine monofluoride was allowed to react with 1.0 g (10.4 mg-atom) of powdered molybdenum at room temperature. The reaction cylinder was cooled to −78° and the liquid chlorine formed in the reaction was pumped off as before. The infrared spectrum of the gaseous products remaining showed the presence of high-purity MoF_6 at 1475 vvw, 1385 vvw, and 741 vvs cm^{-1}.

Reaction of 1.5 g (22.3 mmol) of chlorine monofluoride with 0.5 g (3.1 mmol) of MoS_2 yielded, in addition to chlorine and MoF_6, SF_4 as evidenced by its infrared absorption at 889 vs, 738 sh, 728 sh, and 715 s cm^{-1}.

In addition to the gaseous products described, traces of blue-green solids were recovered from the two reactions above and, when exposed to moist air, rapidly hydrolyzed to dark blue inks. This suggests lower molybdenum fluorides which are known to hydrolyze to the blue oxyfluorides.[27]

Chlorine monofluoride, 1.5 g (22.3 mmol), was added to 0.5 g (2.1 mmol) of potassium molybdate utilizing the same general procedure. At room temperature chlorine and ClO_2F proved to be the only major gaseous products with only a trace of MoF_6 observed in the infrared spectrum. The reaction cylinder was placed in the electric furnace and heated at 300° for 2 hr. Then, after cooling the cylinder in a −78° trichloroethylene–Dry Ice bath, the product chlorine and a trace of unreacted ClF were pumped off. The infrared analysis of the remaining trace of gaseous products showed high-purity MoF_6 at 1475, 1385, and 741 cm^{-1}. After the cylinder was completely evacuated of all gases at room temperature, a pale gray solid remained. This appeared to be the known $2KF \cdot MoF_6$ complex,[28] and the hydrolysis in ice water gave an acidic solution which was titrated with 0.5 *N* NaOH for "active fluorine." *Anal.* Calcd for

$$2KF \cdot MoF_6 + 3H_2O \longrightarrow MoO_3 + 2K^+ + 6H^+ + 8F^-$$

$2KF \cdot MoF_6$: active F, 35.0. Found: active F, 34.8.

The reaction of ClF with anhydrous sodium molybdate proved virtually identical with the reaction of ClF with K_2MoO_4. The reaction of 2.0 g (31.0 mmol) of ClF with 0.5 g (2.4 mmol) of Na_2MoO_4 at 300° resulted in gaseous chlorine, ClO_2F, and a light gray-brown solid again suggesting the known complex $2NaF \cdot MoF_6$.[26] *Anal.* Calcd for $2NaF \cdot MoF_6$: F, 55.7. Found: F, 55.1.

Results and Discussion

The reaction of chlorine monofluoride with sulfur and selenium was found to proceed quite smoothly at room temperature to yield only the respective tetrafluorides

$$S + 4ClF \xrightarrow{25°} SF_4 + 2Cl_2$$

$$Se + 4ClF \xrightarrow{25°} SeF_4 + 2Cl_2$$

The complete absence of SF_5Cl in the products from the reaction at 200° between SF_4 and ClF in the presence of chlorine does prove to be somewhat of an enigma.

$$SF_4 + 2ClF \xrightarrow[2Cl_2]{200°} SF_6 + Cl_2$$

Nyman and Roberts[4] have claimed that chlorine monofluoride prepared *in situ* reacts with SF_4 to form SF_5Cl in 90% yield

$$3SF_4 + Cl_2 + ClF_3 \xrightarrow{350°} 3SF_5Cl$$

The reaction of SF_4 and cesium fluoride with chlorine has also been reported to yield SF_5Cl[29]

$$SF_4 + Cl_2 + CsF \xrightarrow{60°} SF_5Cl + CsCl$$

The failure of chlorine monofluoride to fluorinate SeF_4 further to the hexafluoride even up to 200° is also somewhat surprising but perhaps indicative of its more moderate reactivity as a fluorinating agent.

With elemental tungsten and molybdenum, as well as molybdenum disulfide, fluorination to the respective hexafluorides proceeded smoothly at room temperature

$$W + 6ClF \xrightarrow{25°} WF_6 + 3Cl_2$$

$$Mo + 6ClF \xrightarrow{25°} MoF_6 + 3Cl_2$$

$$MoS_2 + 14ClF \xrightarrow{25°} MoF_6 + 2SF_4 + 7Cl_2$$

The reaction of sodium and potassium molybdates and sodium tungstate with ClF at 300° yielded the $2MF \cdot MoF_6$ and $2MF \cdot WF_6$ type of complexes. However, with $PbWO_4$ the products were PbF_4 and WF_6. The failure of a similar $PbF_4 \cdot WF_6$ complex to form is best explained on the basis of the more polarizing character of Pb^{4+} *vs.* Na^+ or K^+.

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