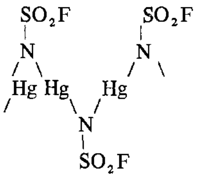
extended Roesky's method to include dimercury(I) *N,N'*-bis(fluorosulfuryl)ureide.

The new compounds are white solids which are stable at room temperature but slowly lose CH_3CN when held under reduced pressure. Upon heating under high vacuum, CH_3CN is lost more rapidly, but in the case of $Hg[N(SO_2F)C(O)NSO_2F] \cdot CH_3CN$ removal of the solvated CH_3CN is accompanied by decomposition *via* elimination of FSO_2NCO at temperatures below 100°. This result may be due to the high stability of $HgNSO_2F$ compared to Ag_2NSO_2F for which no evidence of formation was observed.

Infrared spectral data provide evidence for the proposed structure of the new compounds although some of the bands were broad, and exact assignment of some absorption frequencies is uncertain. In all cases, strong absorption bands appear in the region of 1400-1150 cm^{-1} indicating that the sulfuryl group ($-SO_2-$) is present.[14] Strong bands near 800 cm^{-1} indicate the presence of the S-F linkage.[14] For $Hg[N(SO_2F)C(O)NSO_2F] \cdot CH_3CN$ and $Ag_2[N(SO_2F)C(O)NSO_2F] \cdot CH_3CN$ strong absorptions at 1615 and 1560 cm^{-1}, respectively, are assigned to the amide I band.[13] The spectra of these substances also exhibit strong, sharp bands near 2300 cm^{-1} (ν(CN)) which indicates coordination of acetonitrile to the central Hg atom through the lone pair of electrons on nitrogen.[15] Sharp bands at 965 and 942 cm^{-1} (ν(C-C)), respectively, support this conclusion. However, in the case of $HgNSO_2F \cdot CH_3CN$, it appears that coordination of acetonitrile through the lone pair on nitrogen is either very weak or absent. The strongest band in the $-C{\equiv}N$ stretching region appears at 2255 cm^{-1} which is close to that reported for free CH_3CN (2250, 2251 cm^{-1}).[16-18] Another weaker absorption at 2290 cm^{-1} may be a combination band ($\nu_3 + \nu_4$) of free CH_3CN.[18] The presence of a weak third band at 2195 cm^{-1} is not understood. These results are in agreement with the observation that prolonged pumping at 100° results in removal of about 80% of the CH_3CN from $Hg[NSO_2F] \cdot CH_3CN$.

In view of the tendency for N-Hg-N bonds to be linear,[19] it is probable that unsolvated $HgNSO_2F$ exists as a chain polymer with a backbone formed of linear N-Hg-N bonds



A similar structure has been proposed[20,21] for the related compound $Na[SO_3NHg]$. The results of a vibrational and X-ray spectroscopic study performed by Breitinger, *et al.*,[13] suggested that dimercury(I) *N,N'*-bis(fluorosulfuryl)ureide exists in a polymeric chain structure in the solid state. It is likely that unsolvated $Hg[N(SO_2F)C(O)NSO_2F]$ also exists in a chain structure. However, if CH_3CN is coordinated to Hg, as the infrared spectral data appear to indicate, the N-Hg-N bond system would not be linear. Further work will be necessary to determine whether this is the case.

The ^{19}F nmr spectra of $Hg[N(SO_2F)C(O)NSO_2F]$ and $Ag[N(SO_2F)C(O)NSO_2F]$ in CH_3CN solution exhibit a singlet resonance in the region expected for fluorine on sulfur in a fluorosulfuryl group.[14] This result agrees with the proposed structure of the *N,N'*-bis(fluorosulfuryl)ureide group which contains two equivalent F atoms. ^{19}F nmr spectra for $HgNSO_2F$ were not obtained due to the insolubility of the substance.

The new compounds react vigorously with chlorine to produce mainly the metal chloride and *N,N*-dichlorofluorosulfurylamine according to the equations

$$HgNSO_2F + 2Cl_2 \rightarrow HgCl_2 + Cl_2NSO_2F$$

$$Hg[N(SO_2F)C(O)NSO_2F] + 2Cl_2 \rightarrow HgCl_2 + Cl_2NSO_2F + FSO_2NCO$$

$$Ag_2[N(SO_2F)C(O)NSO_2F] + 2Cl_2 \rightarrow 2AgCl + Cl_2NSO_2F + FSO_2NCO$$

The weight of the solid residue remaining in the reaction vessel was slightly greater than that expected for complete conversion to the metal chloride for the first two reactions listed above. This result suggests the occurrence of side reactions or incomplete reaction of Cl_2 with the substrate.

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Registry No. $HgNSO_2F \cdot CH_3CN$, 52500-56-8; $Hg[N(SO_2F)C(O)NSO_2F] \cdot CH_3CN$, 52555-16-5; $Ag_2[N(SO_2F)C(O)NSO_2F] \cdot CH_3CN$, 52555-15-4; HgO, 21908-53-2; Ag_2O, 12249-86-4; FSO_2NCO, 1495-51-8; $Ag_2[N(SO_2F)C(O)NSO_2F] \cdot 2CH_3CN$, 52555-17-6.

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Contribution from the Department of Chemistry,
Swarthmore College, Swarthmore, Pennsylvania 19081

Kinetics of Ligand Substitution on Ferric Horse Heart Myoglobin

D. A. Sweigart* and Caryn Bern

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Numerous kinetic studies of ligand interactions with ferric myoglobin have been reported.[1-3] Blanck, *et al.*,[1] studied the kinetics of anation and aquation of ferric myoglobin, reaction 1. The ligand L was CN^-, N_3^-, OCN^-, SCN^-, NO_2^-, etc. The kinetics were followed at 21-23° in phosphate-borate buffers covering the pH range 6-9.

$$Mb\text{-}OH_2 + L \rightleftharpoons Mb\text{-}L + H_2O \qquad (1)$$

The mechanism of these anation and aquation reactions is generally considered to be dissociatively activated,[3] as is the

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case with most octahedral metal complexes. If the usual dissociative interchange mechanism is operating, one expects ligand substitution to proceed by aquation followed by anation. This means that Blanck's results would be sufficient to allow one to predict the rate of ligand substitution. Accordingly we report here a study of reaction 2 where

$$\text{Mb-L} + \text{Y} \rightleftharpoons \text{Mb-Y} + \text{L} \tag{2}$$

the (L, Y) combinations are (SCN^-, N_3^-), (OCN^-, N_3^-), (SCN^-, CN^-), and (NO_2^-, SCN^-). We shall show that all these reactions proceed by aquation followed by anation.

Experimental Section

Horse heart ferric myoglobin was purchased from Sigma Chemical Co. All ligands were purchased from standard sources and were of the highest purity available. The substitution reactions were followed at 21 ± 0.5° with a Durrum stopped-flow apparatus. The medium was pH 7.5 phosphate buffer[4] (ionic strength 0.1 *M*). The myoglobin concentration was approximately 3×10^{-5} *M* and the entering and leaving group concentrations were kept in pseudo-first-order excess. Spectra of the myoglobin derivatives agreed with those previously reported.[5]

Results and Discussion

Figures 1 and 2 show the results for azide replacing thiocyanate and cyanate. For the replacement of thiocyanate with cyanide, the experimental error was large enough to cause some scatter, but k_{obsd} was approximately first order in cyanide with an intercept close to zero. The absorbance change for thiocyanate replacing nitrite was small. However, the value of k_{obsd} was definitely found to *decrease* with increasing [SCN^-] (fixed [NO_2^-]) and to increase with increasing [NO_2^-] (fixed [SCN^-]).

The common mechanism for ligand substitution at a six-coordinate center is aquation followed by anation, as depicted in eq 3 and 4. Invoking the steady-state approximation for Mb leads to eq 5. It is understood that solvent water

$$\text{Mb-L} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{Mb} + \text{L} \tag{3}$$

$$\text{Mb} + \text{Y} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \text{Mb-Y} \tag{4}$$

$$k_{\text{obsd}} = \frac{k_1k_3[\text{Y}] + k_2k_4[\text{L}]}{k_3[\text{Y}] + k_2[\text{L}]} \tag{5}$$

is involved in (3) and (4) so that the intermediate Mb contains coordinated water. An intermediate of formula Y-Mb-L is never formed, the only important species being Mb-L, Mb-Y, and Mb (*i.e.*, Mb-OH_2). All of the rate constants in eq 5 can be taken from the work of Blanck, *et al.*,[1] and we should therefore be able to predict quantitatively the rates if the postulated mechanism is correct. For this reason our reaction conditions (concentrations, temperature, etc.) were very similar to those used by Blanck, *et al.*[1]

For azide replacing thiocyanate (Figure 1) the predicted behavior correlates well with the observed. From Blanck's work k_{obsd} is predicted to be $(1.25 \times 10^5[\text{Y}] + 1.5 \times 10^3[\text{L}])/(5 \times 10^3[\text{Y}] + 5 \times 10^3[\text{L}])$. For $[\text{L}] \gg [\text{Y}]$ this reduces to $0.3 + 25[\text{Y}]/[\text{L}]$. Hence the intercept and limit in Figure 1 are predicted to be 0.3 and 25 sec^{-1}. The observed intercept is 0.2. For [SCN^-] = 0.05 *M* the predicted slope is 500; for [SCN^-] = 0.2 *M* the predicted value is 125. The observed values are 325 and 118, respectively.

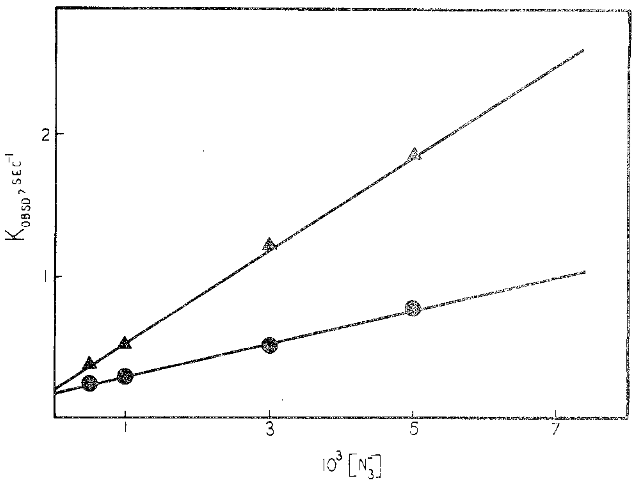

Figure 1. Plot of k_{obsd} *vs.* [N_3^-] for the reaction $\text{Mb-SCN} + N_3^- \rightarrow \text{Mb-N}_3 + SCN^-$. Values of [$SCN^-$]: ▲, 0.05 *M*; ●, 0.02 *M*.

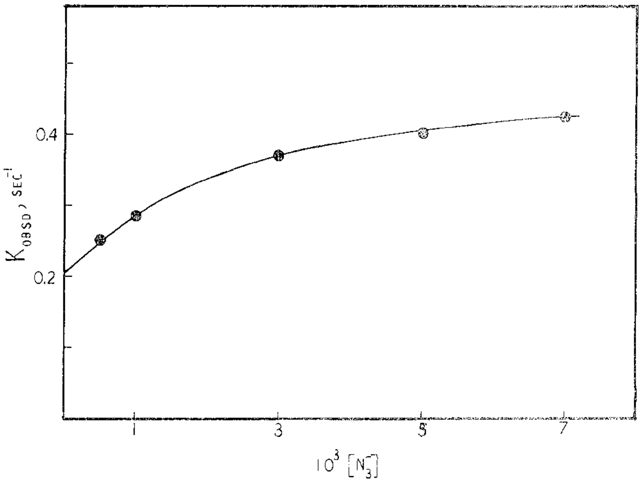

Figure 2. Plot of k_{obsd} *vs.* [N_3^-] for the reaction $\text{Mb-OCN} + N_3^- \rightarrow \text{Mb-N}_3 + OCN^-$. For all points, [$OCN^-$] = 0.05 *M*.

The reaction of azide replacing cyanate presents an interesting contrast to the thiocyanate system. Again the predicted and observed k_{obsd} values are in reasonably close agreement. In this case the plot of k_{obsd} *vs.* [Y] is nonlinear (Figure 2). The predicted rate constant is $(5 \times 10^3[\text{Y}] + 6 \times 10[\text{L}])/(5 \times 10^3[\text{Y}] + 2 \times 10^2[\text{L}])$. This predicts an intercept ([N_3^-] = 0) of 0.3, and a limiting value of k_{obsd} = 1.0. The observed intercept is 0.2 and estimated limit is 0.7.

As mentioned above, the system involving replacement of thiocyanate with cyanide exhibited greater experimental uncertainty than the previous two systems. The predicted k_{obsd} is $(5 \times 10^3[\text{Y}] + 10[\text{L}])/(2 \times 10^2[\text{Y}] + 5 \times 10^3[\text{L}])$ where [Y] means total cyanide. This equation reduces to $1/500 + [\text{Y}]/[\text{L}]$ for our conditions ([L] = 0.02 *M*, [Y] = ($3\text{-}15 \times 10^{-3}$)). The intercept and slope are predicted to be about zero and 50, respectively. We found the intercept to be 0 ± 0.05 and the slope to be 60 ± 10.

The final system studied, replacement of nitrite by thiocyanate, was experimentally difficult because of a small absorbance change. In addition rather high concentrations of Y and L were needed. The predicted results for this system are sufficiently interesting, however, to warrant a close investigation. The predicted k_{obsd} is $(2.5 \times 10^4[\text{Y}] + 8 \times 10^3[\text{L}])/(5 \times 10^3[\text{Y}] + 3 \times 10^2[\text{L}])$. This expression predicts an intercept of 27 and a limit, as [Y] gets large, of 5.0.

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(5) Reference 3, p 44; D. W. Smith and R. J. P. Williams, *Struct. Bonding (Berlin)*, **7**, 1 (1970).

In other words the rate constant should *decrease* with increasing nucleophile concentration. In addition k_{obsd} should increase with increasing nitrite concentration. This behavior was observed. For $[\mathrm{NO_2^-}]$ fixed at 0.025 M, k_{obsd} decreases from 6.3 (at $[\mathrm{SCN^-}] = 0.02\ M$) to 4.9 (at $[\mathrm{SCN^-}] = 0.1\ M$). For $[\mathrm{NO_2^-}] = 0.1\ M$, the k_{obsd} values are higher but still decrease with increasing $[\mathrm{SCN^-}]$, from 10.1 ($[\mathrm{SCN^-}] = 0.02\ M$) to 5.9 ($[\mathrm{SCN^-}] = 0.1\ M$). The possibility that this rate decrease was the result of increasing ionic strength due to the $\mathrm{SCN^-}$ was ruled out on the basis of the following experiment. The kinetic data for $[\mathrm{NO_2^-}] = 0.1\ M$ were collected at two ionic strengths, 0.25 M (data above) and 1.0 M ($\mathrm{KNO_3}$). The higher ionic strength caused not a decrease but an increase in k_{obsd} of about 40%. Thus the decrease in rate with increasing $[\mathrm{SCN^-}]$ cannot be an ionic strength effect.

We feel that our results are in good agreement with that predicted from the data of Blanck, *et al.*,[1] especially when small differences in ionic strength and temperature are considered. The conclusion is that the rates of ligand substitution on ferric myoglobin can be quantitatively predicted from a knowledge of aquation and anation rates. A species such as Y-Mb-L never becomes important during the reaction. For anation and aquation one expects the usual dissociative interchange mechanism to hold and the results for ligand substitution presented herein clearly support this.

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Registry No. Horse heart myoglobin, 12585-26-1; $\mathrm{Fe^{3+}}$, 20074-52-6; $\mathrm{SCN^-}$, 302-04-5; $\mathrm{N_3^-}$, 14343-69-2; $\mathrm{OCN^-}$, 661-20-1; $\mathrm{NO_2^-}$, 14797-65-0; $\mathrm{CN^-}$, 57-12-5.

Contribution from the Departments of Chemistry,
Texas A&M University, College Station, Texas 77843, and
the University of Rochester, Rochester, New York 14627

Photoelectron Spectra of the Rhenium Pentacarbonyl Halides

Gerald P. Ceasar,*[1a] Paul Milazzo,[1a] John L. Cihonski,[1b,c]
and Robert A. Levenson*[1b]

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HeI ultraviolet photoelectron spectroscopy (UPS) of the manganese pentacarbonyl halides $\mathrm{Mn(CO)_5X}$ (X = Cl, Br, I) has recently received considerable attention.[2-5] From experimental[2,5] and theoretical[3,4] considerations it has been shown that, in contrast to the situation normally observed in transition metal complexes, the highest occupied molecular orbital is primarily of ligand character. The most recent interpretation of UPS is that of Lichtenberger, Sarapu, and Fenske, who proposed, partly on the basis of theoretical calculations, that the energy ordering of the four highest filled molecular orbitals is $\mathrm{X}_\pi > \mathrm{X}_\sigma > \mathrm{e}(\mathrm{d}_{xz}, \mathrm{d}_{yz}) > \mathrm{b}_2(\mathrm{d}_{xy})$.[2] The X_π and X_σ levels are of symmetry e and a_1, respectively, but the X_π and X_σ notation will be used exclusively in this paper.

The present paper describes our investigations of the low-energy photoelectron spectra of the $\mathrm{Re(CO)_5X}$ series. This study was of interest since UPS has been used in a relatively limited number of transition metal complexes with noncubic symmetry and since an interpretation of the electronic spectra of the $\mathrm{Mn(CO)_5X}$ species has been based on the orbital ordering obtained from UPS results.[6] By contrasting the ionization potentials obtained for the Re series with those of the Mn complexes, we wished to determine the changes which take place in orbital structure with variation of the central metal atom and to see whether these data are consistent with previous interpretations. Our results now lead us to propose a new energy level ordering which we believe is appropriate for both the Mn and Re complexes.

Experimental Section

The rhenium pentacarbonyl halides were synthesized by methods analogous to those used to prepare the corresponding Mn complexes.[7,8] HeI spectra were recorded on a Vacuum Generators ESCA-2 photoelectron spectrometer operating at 35-MeV resolution. The iodide complex was sufficiently volatile to allow gas-phase spectra to be obtained at room temperature. For $\mathrm{Re(CO)_5Cl}$ and $\mathrm{Re(CO)_5Br}$ it was necessary to heat the ionization chamber to 70° before spectra could be obtained.

Results

The ultraviolet photoelectron spectra of the $\mathrm{Re(CO)_5X}$ series are shown in Figure 1 for the critically important 8-12-eV region and compared with the results on the Mn analogs[2] in Table I. (In constructing Table I, the position of bands split by spin-orbit coupling is taken as the average of the two components.) For the purpose of the discussion which follows ionization potentials are labeled I-IV with the lowest ionization being I.

The $\mathrm{Re(CO)_5X}$ spectra are characterized by several features which distinguish them from those of the Mn complexes. First, band II is seen for all X (Cl, Br, I) whereas it is not directly observed in $\mathrm{Mn(CO)_5I}$. Second, band I, assigned as an ionization from a degenerate level on intensity grounds,[2] exhibits more pronounced spin-orbit splitting in the case of $\mathrm{Re(CO)_5I}$ than in $\mathrm{Mn(CO)_5I}$ and even shows splitting for $\mathrm{Re(CO)_5Br}$ whereas none is seen in $\mathrm{Mn(CO)_5Br}$. These results suggest that the highest occupied molecular orbital, which we assign as being primarily of halogen parentage (*vide infra*), has a not insignificant amount of metal character. The presence of metal character in this level would then increase the observed spin-orbit splitting since the spin-orbit coupling constant for Re is much larger than that of Mn (0.3 *vs.* 0.03 eV). An alternative explanation for the larger splitting in the Re complexes is that the X_π level is more nearly pure halogen in character than in the Mn species. Third, band III for $\mathrm{Re(CO)_5Br}$ is split into two peaks separated by 0.12 eV while the chloride and iodide show no apparent splitting for this level. According to the arguments made above, band III, which is primarily of metal character (*vide infra*), should show some doublet splitting. Its absence in the chloride and iodide derivatives may result from changes in the amount of metal character due to halogen or carbonyl π mixing[2] or possibly from inductive changes in the effective charge on the metal, since the spin-orbit coupling

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[1] (a) University of Rochester. (b) Texas A&M University. (c) This research constitutes partial fulfillment of the Ph.D. degree requirements of J. L. C.

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