sumed in their kinetic analysis that the rate of hydrolysis of the chelated ester would be independent of $[ClO_4^-]$.

(5) Changing the solvent from H_2O to D_2O slows down hydrolysis for both complexes. At low ClO_4^- (0.8 *M* $NaClO_4$) this reduction is 1.5-2-fold but is more significant (~2.5) in 3.6 *M* $NaClO_4$. Thus the slower rates observed in the pmr experiments result from a solvent effect.

(6) The changes observed in the CH_3 signal derived from *cis*-$[Co(en)_2Br(glyOEt)](ClO_4)_2$ are idenitcal with those observed with $[Co(en)_2(glyOEt)](ClO_4)_3$ under the same conditions. The two sets of signals result from the chelate ester (1.27 ppm) and ethanol (1.10 ppm).

(7) The same CH_3 signals are observed, both initially, during the reaction and, finally, in the absence of added $NaClO_4$ (0.2 *M* $DClO_4$, 0.3 *M* $Hg(ClO_4)_2$, ~0.2 *M* complex) and in 3.6 *M* $NaClO_4$; only the rates of interconversion differ. This confirms that perchlorate does not alter the immediate products following loss of Br^-.

(8) The CH_3 signal of unreacted $[Co(en)_2Br(glyOEt)](ClO_4)_2$ is centered ~6.5 Hz *upfield* from that in the chelated ester and ~ 11 Hz *downfield* from ethanol. The assignment given by Nomiya and Kobayashi is incorrect.[9] The signal purported by them to result from unreacted $[Co(en)_2Cl(glyOEt)]^{2+}$ (Figure 3A)[1] and $[Co(en)_2(H_2O)(glyOEt)]^{3+}$ (Figure 3B)[1] is in fact due to the chelated ester $[Co(en)_2(glyOEt)]^{3+}$.

The above results demonstrate unequivocally that increasing the ClO_4^- concentration does not alter the mechanism for hydrolysis of the ester function in *cis*-$[Co(en)_2X(glyOEt)]^{2+}$ following treatment with Hg^{2+}; only the rate is altered. Also the data confirm that such hydrolyses proceed exclusively *via* the chelate ester intermediate $[Co(en)_2(glyOEt)]^{3+}$. This is in agreement with our own unpublished observations that aquo ester or aquoamide complexes of the type $[Co(en)_2(OH_2)(glyY)]^{3+}$ (Y = OR, NH_2) hydrolyze rapidly *via* an intramolecular process without formation of $[Co(en)_2(glyY)]^{3+}$ at an intermediate stage.

Registry No. *cis*-$[Co(en)_2Br(glyOEt)](ClO_4)_2$, 49567-52-4; $[Co(en)_2(glyOEt)](ClO_4)_3$, 52613-64-6; ClO_4^-, 14797-73-0.

(9) Comparison of the central peak separations in Figure 3 of Nomiya and Kobayashi[1] suggests that the CH_3 signal of EtOH (Figure 3A) is centered some 10 Hz upfield from the 1.20-ppm signal (which is wrongly assigned); that is at 1.10 ppm rather than at 1.16 ppm. This then agrees with Figure 3B and with our results.

Contribution from the Department of Chemistry,
Howard University, Washington, D. C. 20001, and the
Laboratory of Biochemistry, National Heart and Lung Institute,
National Institutes of Health, Bethesda, Maryland 20014

Metal-Porphyrin Interactions. IV. Electron-Transfer Kinetics between Dithionite and Manganese(III) and Cobalt(III) Porphyrins[1]

Peter Hambright* and P. B. Chock

Received May 10, 1974 AIC402970

There is much current interest in the mechanisms of electron transfer involving hemoproteins,[2-7] and it is thus surprising that so few studies have been done with the simpler prosthetic group porphyrins[8,9] themselves. To this end, we report the kinetics of reduction (to the divalent state) of a series of cobalt(III) and manganese(III) porphyrins by dithionite ($S_2O_4^{2-}$) in aqueous pyridine solutions. The results show that the kinetic and electrochemical stabilities parallel one another for both metalloporphyrin types. It is argued that the manganese results are consistent with an outer-sphere mechanism.

Experimental Section

The manganese(III) and cobalt(III) porphyrins were prepared by standard methods.[10,11] The dithionite concentration was determined by titration with $Fe(CN)_6^{3-}$, which gave similar results to the Methylene Blue procedure.[9,12] The kinetics were followed in the Soret region using a Durrum-Gibson stopped-flow apparatus. The reactions were run under pseudo-first-order conditions with at least 100-fold excess of total dithionite to total porphyrin (*ca.* 10^{-5} *M*). The first-order rate constant, k_0, was calculated in the usual manner,[13] from triplicate absorbance-time oscilloscope traces. The reactions were done under purified N_2 at 17°, in a distilled pyridine-0.1 *M* NaCl-0.05 *M* Hepes buffer media. Dithionite was analyzed before and after each reaction, and the difference was never more than 2%. This indicates the stability of the reductant under the reaction conditions. No reduction of the macrocycle by dithionite was found except for manganese(III) tetramethyltetrapyridylporphine and manganese(III) diacetyldeuteroporphyrin dimethyl ester. For the former, only ring reduction was found, while with the latter, metal reduction was much faster than ring reduction.

Results

Manganese(III) deuteroporphyrin IX dimethyl ester was the most thoroughly studied compound. In 4 *M* pyridine, the reaction was first order in porphyrin over 3 half-lives, and the observed rate constant, k_0, was independent of total porphyrin from 3×10^{-6} to 17×10^{-6} *M*. The observed rate was independent of pH from 7.4 to 8.1 and half order in total dithionite (see Table I). $k_0/[S_2O_4^{2-}]^{1/2} = 30 \pm 4\ M^{-1/2}\ sec^{-1}$. Table I shows that k_0 was fairly independent of pyridine concentration from 2.5 to 4.5 *M* pyridine. Data could not be taken over a greater range due to the insolubility of the porphyrin esters at lower concentrations and of dithionite at higher pyridine concentrations. This small pyridine range certainly limits the mechanistic conclusions that can be drawn, but it is the only way that such data on a wide range of compounds can be obtained. Table II shows the relative rates of reduction of a series of cobalt(III) and manganese(III) porphyrins which differ in their peripheral substituents.

The half-order dependence on dithionite is due to the $S_2O_4^{2-}$-$2SO_2\cdot^-$ equilibria, with the radical anion as the reductant. The equilibrium constant, K_D, has been esti-

---

* To whom correspondence should be addressed at Donner Laboratory and Donner Pavilion, University of California, Berkeley, California 94720.

(1) Part III: P. Hambright and P. B. Chock, *J. Amer. Chem. Soc.*, **96**, 3123 (1974).

(2) J. K. Yandell, D. P. Fay, and N. Sutin, *J. Amer. Chem. Soc.*, **95**, 1131 (1973).

(3) J. W. Dawson, H. B. Gray, R. A. Holwerda, and E. W. Westhead, *Proc. Nat. Acad. Sci. U. S.*, **69**, 30 (1972).

(4) C. E. Castro and H. F. Davis, *J. Amer. Chem. Soc.*, **91**, 5405 (1969).

(5) R. X. Ewall and L. E. Bennett, *J. Amer. Chem. Soc.*, **96**, 942 (1974).

(6) H. L. Hodges, R. A. Holwerda, and H. B. Gray, *J. Amer. Chem. Soc.*, **96**, 3132 (1974).

(7) C. Creutz and N. Sutin, *Proc. Nat. Acad. Sci. U. S.*, **70**, 1071 (1973).

(8) P. Hambright and E. B. Fleischer, *Inorg. Chem.*, **4**, 912 (1965).

(9) J. James and P. Hambright, *J. Coord. Chem.*, **3**, 183 (1973).

(10) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier, Amsterdam, 1964.

(11) L. J. Boucher, *Coord. Chem. Rev.*, **7**, 289 (1972).

(12) R. G. Rinker, T. P. Gordon, D. M. Mason, R. R. Sakaida, and W. R. Corcoran, *J. Phys. Chem.*, **64**, 573 (1960).

(13) H. Baker, P. Hambright, and L. Wagner, *J. Amer. Chem. Soc.*, **95**, 5942 (1973).

Table I. Dependence of k_0 on Dithionite Concentration for Manganese(III) Deuteroporphyrin IX Dimethyl Ester (17°)

k_0,[a,b] sec^{-1}	[py], M	$[S_2O_4^{2-}]_{TOT}$, M	$k_0/[S_2O_4^{2-}]_{TOT}^{1/2}$, $M^{-1/2}$ sec^{-1}
5.75	4.0	3.94×10^{-2}	29.0
3.62	4.0	1.85×10^{-2}	26.6
2.81	4.0	1.36×10^{-2}	24.2
1.98	4.0	3.24×10^{-3}	34.8
1.30	4.0	1.53×10^{-3}	33.2
2.74	2.5	1.22×10^{-2}	24.8
2.82	3.2	1.22×10^{-2}	25.5
2.69	4.5	1.22×10^{-2}	24.3

[a] 0.1 M NaCl–0.05 M Hepes buffer, pH 7.8. [b] [Porphyrin] = 9.1×10^{-6} M.

Table II. Reduction Rates of Cobalt(III) and Manganese(III) Porphyrins with Dithionite

Porphyrin[a]	pK_3[b]	$E_{1/2}$-(Cl-$Mn^{III}P$–$Mn^{II}P$),[c] V	$k_0/[S_2O_4^{2-}]^{1/2}$,[d] $M^{-1/2}$ sec^{-1} $Mn^{III}P$	$Co^{III}P$
Etioporphyrin III		−0.45	12.6	
Mesoporphyrin DME	5.8	−0.43	27.6	13.5×10^{-2}
Deuteroporphyrin DME	5.5	−0.38	30.0	29.6×10^{-2}
Hematoporphyrin DME		−0.37	187.0	
Protoporphyrin DME	4.8	−0.35	123.0	
Diacetyldeuteroporphyrin DME	3.3		$>10^3$	
Dibromodeuteroporphyrin DME	3.0			2.73
Tetrapyridylporphine			$\gg 10^3$	

[a] DME is dimethyl ester. [b] Acid dissociation constants for the monocation–free base porphyrin equilibria from ref 10. [c] $E_{1/2}$ *vs.* sce in aceotnitrile.[11,20] [d] $[S_2O_4^{2-}]_{Tot} = 1.22 \times 10^{-2}$ M, 17°, 4 M pyridine, 0.1 M NaCl, 0.05 M Hepes, pH 7.8.

mated[14] to be 1.6×10^{-10} M, at 25°. The cobalt(III) and cobalt(II) porphyrins are exclusively in their dipyridine forms in 4 M pyridine.[15] Electrochemical work shows that below 1 M picoline,[16,17] manganese(II) hematoporphyrin has *twice* as many moles of picoline complexed as the Mn(III) reactant, whereas above 1 M picoline, both the reduced and oxidized forms have the *same* number of ligands complexed. For hematoporphyrin, the Mn(II):Mn(III) ratio of the stability constants[16] for dipyridinate formation is 6.8 (25°). Manganese(II) mesoporphyrin has a stability constant of 38 M^{-2} (30°), for bis(pyridine) formation.[11] We can thus estimate a formation constant of *ca.* 5 M^{-2} for bis(pyridine) ligation to manganese(III) porphyrins.

This value is 50 times larger[18] than that determined for hydroxomanganese(III) mesoporphyrin: $K_1 = 5.9 \times 10^{-2}$ M^{-1}, $K_2 = 1.9$ M^{-1}, or $K_1K_2 = 0.112$ M^{-2} at 30°. The recent hematoporphyrin study[16] shows no evidence for a monopyridinate. The fact that the distinctive absorption spectra show that the X-Mn^{III}-P complexes (X = halides) in noncoordinating solvents change into the same species giving the same spectra in basic coordinating solvents[19] has been used as evidence for dipyridine formation. Thus K_1 is probably small (~0.1 M^{-1}), and with $K_1K_2 \simeq 5$ M^{-2}, $K_2 \simeq 50$ M^{-1}. The monopyridine formation constants in noncoordinating chloroform were shown to be independent of porphyrin type.[20]

Several reaction mechanisms can be postulated. The basic equilibria considered are

$$Mn^{III}P + py \rightleftharpoons py\text{-}Mn^{III}P \qquad K_1 \tag{1}$$

$$py\text{-}Mn^{III}P + py = (py)_2\text{-}Mn^{III}P \qquad K_2 \tag{2}$$

$$S_2O_4^{2-} = 2SO_2\cdot^- \qquad K_D \tag{3}$$

$$SO_2 + H_2O = 2H^+ + SO_3^{2-} \qquad \text{fast} \tag{4}$$

For an outer-sphere reaction, the rate-determining step would be

$$(py)_2\text{-}Mn^{III}P + SO_2\cdot^- \xrightarrow{k_{OUT}} (py)_2\text{-}Mn^{II}P + SO_2 \tag{5}$$

The observed rate constant would be

$$k_0 = \frac{k_{OUT}K_D^{1/2}[S_2O_4^{2-}]^{1/2}K_1K_2[py]^2}{1 + K_1[py] + K_1K_2[py]^2} \tag{6}$$

For an inner-sphere reaction

$$py\text{-}Mn^{III}P + SO_2\cdot^- \xrightarrow{k_{IN}} py\text{-}Mn^{II}P + SO_2 \tag{7}$$

the rate constant would be

$$k_0 = \frac{k_{IN}K_D^{1/2}[S_2O_4^{2-}]^{1/2}K_1[py]}{1 + K_1[py] + K_1K_2[py]^2} \tag{8}$$

We have argued above that $K_1K_2 \approx 5$ M^{-2} and $K_1 \approx 0.1$ M^{-1}. In either mechanism, under the experimental conditions, $K_1K_2[py]^2 \gg (1 + K_1[py])$. This would predict that the outer-sphere reaction (eq 6) should have a rate independent of pyridine ($k_0 = K_{OUT}K_D^{1/2}[S_2O_4^{2-}]^{1/2}$). The inner-sphere mechanism (eq 8) should have a rate inversely dependent on pyridine ($k_0 = k_{IN}K_D^{1/2}[S_2O_4^{2-}]^{1/2}K_2^{-1}[py]^{-1}$).

Discussion

Our kinetic results appear to be in agreement with an outer-sphere electron-transfer pathway. This is not a strong inference since (1) the stability constants on which the argument depends are not well known and (2) due to solubility considerations the reactions could not be run over a greater range of ligand concentrations. For example, if $K_1[py] \gg (1 + K_1K_2[py]^2)$, the conclusions would be exactly the opposite of what we have put forward (*i.e.*, the outer-sphere reaction would be first order in pyridine, while the inner-sphere process would be pyridine independent).

The reductions of porphyrins of Mn^{3+} and Fe^{3+} with Cr^{2+}, V^{2+}, Eu^{2+}, and $Cr(bipy)_3^{2+}$ were also of an uncertain mechanism in aqueous solution[8] due to the lability of the water molecules in the axial positions of the porphyrin. In noncoordinating solvents where the Fe–Cl bond was inert, the demonstration of the transfer of Cl^- to chromium during electron transfer suggested an inner-sphere process.[21]

It is noted that both metal ion adjacent and remote pathways[2,3,5-7] have been demonstrated in the reduction of ferricytochrome *c* with Cr^{2+}, $Ru(NH_3)_6^{2+}$, Fe(EDTA), and $S_2O_4^{2-}$. The reductant in the cytochrome case[6] was found to be $S_2O_4^{2-}$, while our results for Mn(III) are consistent with $SO_2\cdot^-$ as the reducing agent, as found with molecular oxygen.[12]

Compared with the aquo ion studies, polarographic measurements show that the porphyrin ring stabilizes the Mn(III)

---

(14) S. Lynn, R. G. Rinker, and W. H. Corcoran, *J. Phys. Chem.*, **68**, 2363 (1964).

(15) D. G. Davis and L. A. Truxillo, *Anal. Chim. Acta*, **64**, 55 (1973).

(16) D. G. Davis and J. G. Montalvo, Jr., *Anal. Lett.*, **1**, 641 (1968).

(17) D. G. Davis and J. G. Montalvo, Jr., *Anal. Chem.*, **41**, 1195 (1969).

(18) J. H. Taylor, *J. Biol. Chem.*, **135**, 569 (1940).

(19) L. J. Boucher, *J. Amer. Chem. Soc.*, **90**, 6640 (1968).

(20) P. Hambright, *Chem. Commun.*, 470 (1967).

(21) I. A. Cohen, *Ann. N. Y. Acad. Sci.*, **206**, 453 (1973).

state with respect to Mn(II), and electron-donating substituents on the porphyrin periphery further stabilize the oxidized form.[22] Table II compares the potentials of $\mathrm{ClMn^{III}P-Mn^{II}P}$ (measured in acetonitrile) with the rate of reduction of the manganese(III) porphyrins in 4 *M* pyridine. Since both $\mathrm{Mn^{II}P}$ and $\mathrm{Mn^{III}P}$ are high spin with or without nitrogen donor ligands,[11] no change in the relative order of the oxidation potentials is expected due to the differing types of solvents. Table II shows that the more negative the $\mathrm{ClMn^{III}P-Mn^{II}P}$ couple, the slower the rate of reduction to the divalent state by dithionite. Thus electrochemical and kinetic stabilities parallel one another in both the cobalt and the manganese porphyrin series. These are a number of cases where the driving force of a reaction contributes to its rate.[23]

Since K_D is unknown under the reaction conditions, the results are reported in terms of $(k_0/[\mathrm{S_2O_4}^{2-}]^{1/2})$. With $K_\mathrm{D}{}^{1/2}$ *ca.* 10^{-5} $M^{1/2}$, the rates for $\mathrm{Mn^{III}P}$ are *ca.* 10^6 M^{-1} sec^{-1} and those for Co(III) approximately 10^4 M^{-1} sec^{-1}. This can be explained in part by the greater ligand field stabilization energy of a formal d^6 Co^{3+} configuration *vs.* d^4 for Mn(III). In addition, bis(pyridine)manganese(III) hematoporphyrin is reduced at potentials 86 mV more positive[16] than hematoporphyrin of $\mathrm{(py)_2Co^{III}}$ in line with their relative reactivities toward dithionite.

Acknowledgments. We thank the USAEC, Contract No. AT-(40-1)-4047, for partial financial support, and the NIH for a special faculty fellowship (1 F 14 GM 56001-01 NPR) to P. H. during the course of this work.

Registry No. Etioporphyrin(III), 531-16-8; mesoporphyrin DME, 1263-63-4; deuteroporphyrin DME, 10589-94-3; hematoporphyrin DME, 33070-12-1; protoporphyrin DME, 5522-66-7; diacetyldeuteroporphyrin DME, 52760-90-4; dibromodeuteroporphyrin DME, 14196-91-9; tetrapyridylporphine, 16834-13-2; Mn(III), 14546-48-6; Co(III), 22541-63-5; $\mathrm{S_2O_4}^{2-}$, 14844-07-6.

(22) L. J. Boucher and H. K. Garber, *Inorg. Chem.*, 9, 2644 (1970).

(23) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964), and references therein.

Contribution from the Department of Chemistry,
Wake Forest University, Winston-Salem, North Carolina 27109

Reactions of Fluorosulfuryl Isocyanate With Metal Oxides[1]

Ronald E. Noftle* and James Crews

Received May 21, 1974 AIC40326V

Fluorosulfuryl isocyanate, $\mathrm{FSO_2NCO}$,[2,3] has been found to react with various metal fluorides to form addition products which were characterized as salts of (fluoroformyl)fluorosulfurylimide, $\mathrm{M^+[N(SO_2F)C(O)F]^-}$.[4,5] In these reactions which involved addition of fluoride ion, the carbon–nitrogen bond in $\mathrm{FSO_2NCO}$ remained intact. Therefore, it was of interest to examine reactions of $\mathrm{FSO_2NCO}$ with a stronger base which could effect cleavage of the carbon-nitrogen bond and lead to the synthesis of new sulfur-nitrogen compounds. $\mathrm{FSO_2NCO}$ was found to react with red mercury(II) oxide (HgO) and silver(I) oxide ($\mathrm{Ag_2O}$) *via* elimination of $\mathrm{CO_2}$ to form the compounds mercury(II) fluorosulfurylamide, mercury(II) *N,N'*-bis(fluorosulfuryl)ureide, and disilver(I) *N,N'*-bis(fluorosulfuryl)ureide which were isolated as the solvates from acetonitrile.

Experimental Section

Materials. $\mathrm{FSO_2NCO}$ was prepared by the method of Roesky and Hoff.[6] The infrared spectrum, $^{19}\mathrm{F}$ nmr spectrum, and vapor density (mol wt calcd, 125; found, 124) agreed with those previously reported.[6,7] HgO and $\mathrm{Ag_2O}$ were obtained from Baker and Adamson and Fisher Scientific, respectively. $\mathrm{CH_3CN}$ was Fisher Certified reagent grade and distilled from $\mathrm{CaH_2}$ prior to use.

Preparation of $\mathrm{HgNSO_2F\cdot CH_3CN}$. In a typical run, HgO (0.4474 g, 2.06 mmol) was placed in a preweighed 30-ml Pyrex bulb equipped with a Fischer and Porter Labcrest 4-mm bluntnose Teflon–glass valve. The reaction vessel was evacuated and flamed gently to remove residual moisture. $\mathrm{CH_3CN}$ (4.1888 g) was condensed into the reaction vessel under high-vacuum conditions from a reservoir which contained $\mathrm{CaH_2}$ to ensure that the solvent was dry. A stoichiometric amount of $\mathrm{FSO_2NCO}$ with respect to HgO (1:1) was measured out by volume and condensed into the reaction mixture. The actual amount of $\mathrm{FSO_2NCO}$ transferred (0.2661 g, 2.13 mmol) was determined by weighing. As the reaction mixture approached room temperature, a slow evolution of gas ($\mathrm{CO_2}$) was observed. The mixture was stirred for several days, and the orange color of HgO slowly disappeared as a white solid formed. $\mathrm{CO_2}$ was periodically removed from the reaction mixture by holding the vessel at −78° and condensing the material volatile at that temperature into a trap held at −196°. The volatile material obtained in this way was subjected further to fractional condensation at −78 and −196° to rid the $\mathrm{CO_2}$ of traces of $\mathrm{CH_3CN}$ that had condensed in the original separation. Infrared analysis showed that the material which had condensed in the trap held at −196° was pure $\mathrm{CO_2}$.[8] The molecular weight was obtained by vapor density measurements: calcd for $\mathrm{CO_2}$, 44.0; found, 43.7. Weight: calcd for $\mathrm{CO_2}$, 0.0906 g; found, 0.0880 g, 97.1% on basis of original amount of HgO. The solvent was removed from the solid residue by pumping on the reaction vessel through a trap cooled to −196°. Infrared analysis of the material which condensed at this temperature showed the presence of $\mathrm{CH_3CN}$ only.[9] The white solid which remained in the reaction vessel was pumped until the weight loss did not exceed several milligrams per hour and chemically analyzed. Weight: calcd for $\mathrm{HgNSO_2F\cdot CH_3CN}$, 0.6994 g; found, 0.6989 g. *Anal.* Calcd for $\mathrm{HgNSO_2F\cdot CH_3CN}$: C, 7.09; H, 0.89; N, 8.27; S, 9.45; F, 5.61. Found: C, 6.63; H, 0.88; N, 7.71; S, 8.73; F, 5.5.

If a molar ratio of $\mathrm{FSO_2NCO}$ to HgO greater than 1:1 was allowed to react, it was noticed in several instances that the weight of the white residue was higher than that calculated for $\mathrm{HgNSO_2F\cdot CH_3CN}$. This result suggested that reaction of HgO with 2 equiv of $\mathrm{FSO_2NCO}$ could occur and this hypothesis was verified. For a typical run, the composition of the product was calculated assuming that the excess $\mathrm{FSO_2NCO}$ reacted with $\mathrm{HgNSO_2F\cdot CH_3CN}$ to form $\mathrm{Hg[N(SO_2F)C(O)NSO_2F]\cdot CH_3CN}$. Amounts: HgO, 0.5276 g, 2.44 mmol; $\mathrm{FSO_2NCO}$, 0.3281 g, 2.62 mmol; $\mathrm{CO_2}$ produced, 0.1035 g, 2.35 mmol; calcd for mixture of 2.26 mmol of $\mathrm{HgNSO_2F\cdot CH_3CN}$ + 0.18 mmol of $\mathrm{Hg[N(SO_2F)C(O)NSO_2F]\cdot CH_3CN}$, 0.8487 g; found for same mixture, 0.8599 g. Other runs gave similar results.

Preparation of $\mathrm{Hg[N(SO_2F)C(O)NSO_2F]\cdot CH_3CN}$. The general procedure is described above. HgO (0.4065 g, 1.88 mmol) reacted with $\mathrm{FSO_2NCO}$ (0.2394 g, 1.92 mmol) in $\mathrm{CH_3CN}$ (2.8475 g) to produce $\mathrm{CO_2}$ (0.0819 g, 1.86 mmol) and a white solid ($\mathrm{HgNSO_2F}$) insoluble in the $\mathrm{CH_3CN}$ solvent. Another portion of $\mathrm{FSO_2NCO}$ (0.2429 g, 1.94 mmol) was added to the reaction vessel such that the overall ratio of $\mathrm{FSO_2NCO}$ to HgO was 2:1. When the reaction mixture was warmed to room temperature and stirred, the white solid immediately dissolved to give a clear colorless solution. No gases were evolved when this reaction took place. The solvent and excess $\mathrm{FSO_2NCO}$ were removed from the reaction vessel by pumping through a trap cooled to −196°. Infrared analysis revealed that only $\mathrm{CH_3CN}$[9]

---

[1] Presented in part at the 25th Southeast Regional Meeting of the American Chemical Society, Charleston, S. C., Nov 1973.

[2] H. Jonas and D. Voigt, *Angew. Chem.*, 70, 572 (1958).

[3] R. Appel and H. Rittersbacher, *Chem. Ber.*, 97, 849 (1964).

[4] J. A. Roderiguez and R. E. Noftle, *Inorg. Chem.*, 10, 1874 (1971).

[5] R. E. Noftle, J. W. Green, and S. K. Yarbro, paper presented at the 24th Southeast Regional Meeting of the American Chemical Society, Birmingham, Ala., Nov 1972.

[6] H. W. Roesky and A. Hoff, *Chem. Ber.*, **101**, 162 (1968).

[7] R. E. Noftle and J. M. Shreeve, *Inorg. Chem.*, 7, 687 (1968).

[8] R. H. Pierson, A. N. Fletcher, and E. St. C. Gantz, *Anal. Chem.*, 28, 1218 (1956).

[9] R. M. Badger and S. H. Bauer, *J. Amer. Chem. Soc.*, 59, 303 (1937).