characterize these systems. Values of ΔH^* were obtained from slopes of plots of log k/T *vs.* $1/T$.

Discussion

Reactions of Cr^{2+} with $Co(NH_3)_5X^{2+}$ proceed by means of an "inner-sphere" transition state,[3,5] since the chromium(III) product is invariably CrX^{2+}. In many reactions of $Co(CN)_5^{3-}$ a product criterion based on the inertness of the cobalt(III) product also establishes an inner-sphere mechanism.[6] Unfortunately, this clear-cut criterion is not available with most reducing agents, since their oxidized forms are substitution labile.

In these instances the relative reaction rates of the azido and thiocyanato complexes may provide a more useful criterion indicating operation of an inner-sphere mechanism.[3,11] Provided nitrogen-bonded thiocyanate ion is the stable product, an inner-sphere mechanism should show a great preference for the symmetrical N_3^- over NCS^-. The available data are summarized in Table III. This criterion would place iron(II) ion in the inner-sphere category. The mechanism for vanadium(II) and europium(II) remains undecided by this criterion, as the lower ratios in these cases may be due to an inner-sphere reaction *via* the sulfur end of the thiocyanate ion or to outer-sphere reaction. Other arguments have been advanced, however, to suggest that vanadium(II) reacts by an outer-sphere pathway.[4,12] The reducing agent $Co(CN)_5^{3-}$, for which the inner-sphere path has been clearly established[6] (the product criterion is valid in this instance), would appear to be exceptional. Actually, this is due to sulfur-bonded thiocyanate ion being the stable configuration of the $Co(CN)_5SCN^{3-}$ product, as the work of Burmeister has established.[13]

TABLE III

RELATIVE RATES OF REDUCTION AT 25° OF AZIDO AND THIOCYANATO COMPLEXES

Oxidizing agent	Reducing agent	$k_{N_3^-}$-k_{NCS^-}	Ref.
$Co(NH_3)_5X^{2+}$	Cr^{2+}	10^4	4
$Co(NH_3)_5X^{2+}$	V^{2+}	27	4
$Co(NH_3)_5X^{2+}$	Eu^{2+}	300	4
$Co(NH_3)_5X^{2+}$	Fe^{2+}	$\geq 3 \times 10^3$	This work
$Co(NH_3)_5X^{2+}$	$Cr(dipy)_3^{2+}$	4	4
$Co(NH_3)_5X^{2+}$	$Co(CN)_5^{3-}$	1.6	6
$Cr(OH_2)_5X^{2+}$	Cr^{2+}	4×10^4	3, 11

The relative reaction rates of the halide ion complexes $Co(NH_3)_5X^{2+}$ with Fe^{2+} studied in this work provide an interesting comparison with earlier work. These rate constants decrease with increasing atomic number of X^-. These values trend in the same direction as those for europium(II) ion as the reducing agent, but are just opposite to those observed for chromium(II) as a reactant in the same series.[4] As these authors pointed out, this does not imply, however, that a mechanism involving an inner-sphere transition state is not operating here, and the azide–thiocyanate criterion suggested above may provide a better indication of mechanism.

There is the additional point that applies to the iron(II) reactions studied here: it is an unjustified assumption to assert that a given reducing agent reacts with each member of a series of related complexes along similar pathways, for there are instances where this is certainly not the case.[4,6]

The rate equation for the reaction of $Co(NH_3)_5C_2O_4H^{2+}$ and Fe^{2+} written in terms of the predominant species takes the form $k'[Co(NH_3)_5C_2O_4H^{2+}][Fe^{2+}]/[H^+]$. This rate law is consistent with bimolecular reaction of $Co(NH_3)_5C_2O_4^+$ and Fe^{2+}; k' is identified as the product of this bimolecular rate constant and the acid dissociation quotient of the binoxalato complex.[14] The reason the basic oxalato form reacts preferentially may lie in the nature of the reaction product. Since chelated $FeC_2O_4^+$ is the stable configuration, it is energetically profitable, in forming the bridged transition state, for both coordinating positions on the oxalate ion to be available to the incoming iron(II) ion.

An alternative pathway for this reaction, kinetically indistinguishable from that suggested previously, is provided by reaction of $Co(NH_3)_5C_2O_4H^{2+}$ and $FeOH^+$. Since the stable iron(III) product in solutions at these acid concentrations is Fe^{3+} and not $FeOH^{2+}$, this path appears to offer no particular energetic advantage for facilitating the electron-transfer process.

Acknowledgment.—The author wishes to express his appreciation to Professors A. Haim, J. Halpern, E. L. King, and H. Taube for helpful discussions concerning this work.

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[11] R. Snellgrove and E. L. King, *Inorg. Chem.*, **3**, 288 (1964).

[12] A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961).

[13] J. L. Burmeister, *Inorg. Chem.*, **3**, 919 (1964).

[14] Were the acid dissociation quotient Q_a of the binoxalato complex known, the true second-order rate constant for reaction of $Co(NH_3)_5C_2O_4^+$ and Fe^{2+} would be calculable. Although the numerical value of Q_a is not known, it is sufficiently small that in the range of $[H^+]$ studied here, 0.1–0.3 *M*, the protonated form of this cobalt(III) complex predominates.

CONTRIBUTION FROM THE GORGAS LABORATORY, ROHM & HAAS
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The Preparation of N,N-Difluorosulfamide

BY ROBERT A. WIESBOECK AND J. K. RUFF

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The successful fluorination of urea with elementary fluorine to difluorourea in aqueous media[1] prompted a study of the fluorination of sulfamide under similar conditions. It was found that at 0 to −5° N,N-difluorosulfamide was produced when an unbuffered aqueous solution of sulfamide was subjected to fluorination.

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[1] V. Grakauskas, paper presented before the Division of Industrial and Engineering Chemistry, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1961.

$$2F_2 + NH_2SO_2NH_2 \longrightarrow 2HF + NF_2SO_2NH_2$$

The progress of the reaction could be easily followed by the periodic determination of the oxidizing equivalent of the solution, and the fluorination was generally discontinued when 3.0 to 3.5 moles of iodide ion was oxidized per mole of sulfamide originally present. Small amounts of volatile material were also obtained. They consisted primarily of nitrogen trifluoride and carbon dioxide.

The acidic reaction mixture was not stable above $\simeq 5°$ and hydrolysis of the N,N-difluorosulfamide to difluoramine occurred on warming. Removal of the solvent from the cold mixture also resulted in decomposition of the product. The N,N-difluorosulfamide could be extracted in high yield from the reaction mixture with either diethyl ether or ethyl acetate, but attempts to isolate it from the organic phase were not successful. However, the product could be stored in a solution of ether at $-78°$ for several weeks without apparent decomposition.

Addition of triphenylphosphine oxide to the ethereal solution of N,N-difluorosulfamide resulted in the formation of the complex $(C_6H_5)_3PO \cdot NH_2SO_2NF_2$, which could be isolated as a white crystalline solid, m.p. 96–97°. The complex was moderately stable at ambient temperature in a dry atmosphere. However, slow decomposition was observed after 2 days. Other Lewis bases such as triphenylarsine oxide and trimethylamine N-oxide appeared to give similar 1:1 adducts but their lack of stability made complete characterization impossible.

The formation of the product as the unsymmetrical difluorosulfamide derivative rather than the other isomer is based on F^{19} n.m.r. evidence. Only a single band at $-37.7\ \phi$ was observed in the ethereal extract of the reaction mixture indicating the presence of a $-NF_2$ group. If the symmetrical isomer had been obtained coupling between the proton and fluorine in the $-NHF$ group would be expected. The F^{19} n.m.r. spectrum of the triphenylphosphine complex consisted of a single band at $-38.7\ \phi$. The observed field position is close to that assigned to the NF_2 group in difluoraminosulfuryl fluoride ($-41.6\ \phi$).[2] The infrared spectrum of the complex $(C_6H_5)_3PO \cdot NH_2SO_2NF_2$ contained bands at 3.19, 7.21, 8.27, 8.68, 9.31, 10.50, and 11.55 μ in addition to those found in the spectrum of triphenylphosphine oxide. The P–O stretching frequency found at 8.40 μ in the uncomplexed phosphine oxide was missing. Since the symmetrical S–O stretching mode in sulfamide is centered at 8.75 μ, definite assignment of the two bands observed at 8.27 and 8.68 μ cannot be made. It is probable that they arise from the P–O and S–O stretching modes, but it is not possible to distinguish which is which. It is felt that the two bands at 10.50 and 11.55 μ are attributable to NF stretching modes since neither band appears in the spectrum of sulfamide.

Several reactions of N,N-difluorosulfamide in solution were explored. Strong acids such as phosphoric acid or sulfuric acid greatly increased the rate of hydrolysis of the sulfamide to difluoramine and sulfamic acid.

$$NF_2SO_2NH_2 + H_2O \xrightarrow[<5°]{H^+} HNF_2 + HOSO_2NH_2$$

However, if concentrated sulfuric acid was employed some tetrafluorohydrazine in addition to difluoramine was also observed. The formation of tetrafluorohydrazine is believed to arise from oxidation of the difluoramine, produced by hydrolysis, by the sulfuric acid,[3] although further work will be necessary to substantiate this. Treatment of the complex $(C_6H_5)_3PO \cdot NH_2SO_2NF_2$ with dilute sulfuric acid also gave difluoramine in equally good yield. The acid hydrolysis of N,N-difluorosulfamide thus appears to be similar to that reported for N,N-difluorourea.[1] The hydrolysis of N,N-difluorosulfamide with 5 *N* sodium hydroxide, however, produced nitrogen as the only volatile material and no evidence for the formation of any species containing nitrogen–fluorine bonds was observed.

When a frozen aqueous solution of hypochlorous acid and the frozen reaction mixture containing N,N-difluorosulfamide were allowed to melt together chlorodifluoramine was obtained in good yield. If low temperatures ($<5°$) are not maintained during the course of reaction some nitrogen is also formed which results in lower yields of chlorodifluoramine. Sodium hypochlorite in neutral solution may also be employed with similar results. In fact the reaction between $(C_6H_5)_3PO \cdot NH_2SO_2NF_2$ and sodium hypochlorite produced chlorodifluoramine in good yield. The reaction between hypochlorite and N,N-difluorosulfamide as an alternate preparation of chlorodifluoramine[4–6] will perhaps be of some synthetic utility.

$$H_2NSO_2NF_2 + OCl^- \longrightarrow ClNF_2 + {}^-OSO_2NH_2$$

Experimental

N,N-Difluorosulfamide.—A solution of 9.6 g. (0.1 mole) of sulfamide in 50 ml. water was placed in a 250-ml. three-neck flask equipped with a magnetic stirrer, a thermometer, and a gas inlet tube. After cooling to 0° fluorine, diluted by 90 vol. % helium, was introduced at a rate of 1 l. of fluorine/hr. As soon as some fluorine was absorbed the temperature of the reactor was lowered as much as possible without freezing the mixture. The major portion of the reaction was carried out at about $-10°$. At certain intervals a 1-ml. sample was drawn from the reactor and added to an acidic aqueous iodide solution to determine the oxidizing titer by titration of the liberated iodine. These samples had to be heated to 50° under nitrogen for at least 30 min. in order to achieve complete reaction. The fluorination was discontinued as soon as 0.006 to 0.007 mole of iodide ion was consumed per ml. of sample. Difluorosulfamide was extracted with two 50-ml. portions of cold ether or ethyl acetate which removed 90–95% of the oxidizer. The extracts were stored at $-78°$. An attempt to remove the ether by distillation resulted in decomposition of the product. The oxidizing titer as determined by iodometric titration was used to determine approximately the concentration of N,N-difluorosulfamide in solution. Since close to 3.6 moles of iodide ion reacted with 1

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(2) M. Lustig, C. Bumgardner, F. A. Johnson, and J. K. Ruff, *Inorg. Chem.*, **3**, 1165 (1964).

(3) K. Martin, private communication.

(4) R. C. Petry, *J. Am. Chem. Soc.*, **82**, 2400 (1960).

(5) D. M. Gardner, W. W. Knipe, and C. J. Mackley, *Inorg. Chem.*, **2**, 413 (1963).

(6) T. W. Austin and R. Mason, *ibid.*, **2**, 646 (1963).

mole of $(C_6H_5)_3PO \cdot NH_2SO_2NF_2$ to produce 1.8 moles of iodine, it was assumed that the same stoichiometry held for the uncomplexed sulfamide.

Triphenylphosphine Oxide Complex of N,N-Difluorosulfamide.—A solution containing 33.4 g. (0.12 mole) of triphenylphosphine oxide in 100 ml. of benzene was added to 15.9 g. (0.12 mole) of N,N-difluorosulfamide in 100 ml. of ether. The mixture was frozen and, after addition of dry magnesium sulfate, was allowed to warm to room temperature. After stirring for 1 hr. the drying agent was removed by filtration. Slow evaporation of the solvent under vacuum precipitated a white crystalline compound which was filtered off and recrystallized from a mixture of 10% benzene in ether. The compound melted at 96–97° and was soluble in alcohol and methylene chloride.

Anal. Calcd. for $(C_6H_5)_3PO \cdot H_2NSO_2NF_2$: C, 52.68; H, 4.17; N, 6.82; F, 9.64. Found: C, 53.10; H, 4.22; N, 6.71; F, 9.27.

Acid Hydrolysis.—A 10-ml. sample of the fluorination mixture containing 0.517 g. (3.91 mmoles) of $NH_2SO_2NF_2$ was placed in a flask and attached to the vacuum line. After evacuating the system, 20 ml. of 1 *N* phosphoric acid (1 *N* sulfuric acid can also be used) was slowly added to the cold (<5°) reaction mixture. The off gases passed through two −78° traps and into a −126° trap.[7] After stirring the reaction mixture for 1 hr. the contents of the −126° trap were refractionated through a −78° and a −126° trap and then analyzed by infrared and mass spectrometry. Difluoramine, 0.155 g. (2.92 mmoles), was obtained essentially pure. Hydrolysis of the fluorination mixture occurred on standing 8 hr. at 25° without the addition of acid to produce difluoramine in 62% yield.

Preparation of Chlorodifluoramine.—An aqueous solution of 13.2 g. (0.10 mole) of N,N-difluorosulfamide, prepared as described above, was evacuated on the vacuum line and frozen in a −78° bath. Then 5.8 g. (0.11 mole) of hypochlorous acid in 400 ml. of water was added slowly while the reactor was still immersed in the Dry Ice bath. On warming slowly, chlorodifluoramine was liberated and was collected in a −196° trap after passing through two −78° traps. After refractionation, a total of 6.2 g. (0.071 mole) of chlorodifluoramine was obtained; yield 71%. Identification of the product was accomplished by infrared spectroscopy[4] and vapor density molecular weight (calcd. 87.5; found 85, 86.).

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[7] *Caution!* Do not trap difluoramine in a liquid nitrogen bath since we have experienced numerous explosions when such traps were allowed to warm.

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Unsymmetrical Cleavage of Diborane by Dimethyl Sulfoxide[1]

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It is well recognized that the bridge system of diborane appears to be cleaved symmetrically by amines, phosphines, ethers, and sulfides to form BH_3 adducts.[2,2a] At the present time, only two examples of apparent unsymmetrical cleavage exist in the literature. These are the reactions of diborane with ammonia to produce the diammoniate of diborane, $[BH_2(NH_3)_2]^+BH_4^-$,[3] and the reaction of amide ion with diborane to produce aminoborane, $(BH_2NH_2)_x$.[4] Perhaps the best documented example is the diammoniate of diborane. We wish to report the first documented example of apparent unsymmetrical cleavage of the bridge system of diborane by other than a nitrogen base.

A tensiometric investigation in dichloromethane at −78° revealed that diborane and dimethyl sulfoxide react in the mole ratio $0.5B_2H_6:(CH_3)_2SO$. On the basis of evidence provided below, the following reaction is proposed.

$$B_2H_6 + 2(CH_3)_2SO \longrightarrow BH_2[OS(CH_3)_2]_2{}^+BH_4{}^-$$

Low-temperature (−40 to −50°) Raman spectra of the solid product and of a solution of the product in dichloromethane were essentially identical in the B–H stretching region. A microphotometer trace of this region is compared with traces from the corresponding region in the Raman spectra of BH_3NH_3[5] and $[BH_2(NH_3)_2]^+BH_4^-$[6] in Figure 1. The number, shapes, and positions of the envelopes in the spectrum of the dimethyl sulfoxide–diborane reaction product most clearly match those of $[BH_2(NH_3)_2]^+BH_4^-$, indicating that diborane is cleaved unsymmetrically to give BH_2^+ and BH_4^-. Borane (BH_3) adducts in general present very simple spectra in the region under discussion, usually showing only two characteristic frequencies attributed to BH_3 in the B–H stretching region.[7,8]

Treatment of the dimethyl sulfoxide–diborane reaction product with HCl produced the reaction

$$BH_2[OS(CH_3)_2]_2{}^+BH_4{}^- + HCl \longrightarrow BH_2[OS(CH_3)_2]_2{}^+Cl^- + H_2 + {}^1/{}_2\,B_2H_6$$

A Raman spectrum of the resulting solution after H_2 and B_2H_6 had been distilled away revealed that only the absorptions assigned to $(DMSO)_2BH_2^+$ were present.

Low-temperature (−40 to −50°) n.m.r. studies in dichloromethane lend credence to the ionic formulation. The spectrum shows a quintet which is attributed to BH_4^-. The spin–spin coupling constant, 86 c.p.s., and chemical shift, 38 p.p.m., relative to $(C_2H_5)_2O \cdot BF_3$ are in good agreement with values observed for BH_4^-.[9] A well-defined spectrum of BH_2^+ could not be observed, but appeared to just overlap the low-field side of the BH_4^- quintet. No evidence was observed for a quartet which could be attributed to BH_3.

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[1] Presented before the Inorganic Division at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964.

[2] H. I. Schlesinger and A. B. Burg, *Chem. Rev.*, **31**, 1 (1942); F. G. A. Stone, *Advan. Inorg. Chem. Radiochem.*, **2**, 279 (1960).

[2a] NOTE ADDED IN PROOF.—We have found, very recently, that diborane can be cleaved unsymmetrically by methylamine and dimethylamine.

[3] R. W. Parry, D. R. Schultz, S. G. Shore, and P. R. Giradot, *J. Am. Chem. Soc.*, **80**, 1 (1958); R. W. Parry, G. Kodama, and D. R. Schultz, *ibid.*, **80**, 24 (1958).

[4] G. W. Schaeffer and L. J. Basile, *ibid.*, **77**, 331 (1955).

[5] R. C. Taylor, "The Chemistry of Boron Hydrides and Related Hydrides," WADD Technical Report 59-207 (1959).

[6] R. C. Taylor, D. R. Schultz, and A. R. Emery, *J. Am. Chem. Soc.*, **80**, 27 (1958).

[7] R. C. Taylor, "The Chemistry of Boron Hydrides and Related Hydrides," WADD Technical Report 60-262 (1960).

[8] R. C. Taylor, private communication.

[9] T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).