resonances a–f, which are expected assuming the solid-state geometry (Figure 1 and **3**), are resolved. Two distinct dynamic processes are apparent which cause coalescence of peaks c–f at ca. −20 and +42 °C. Peaks a and b do not necessarily coalesce but possibly become accidently degenerate at ca. 80 °C; however, at higher temperatures (100 °C) the resonances do not again show nonequivalence, as might be expected for accidental degeneracy. Since the barrier to C=N bond rotation in the thiocarboxamido ligand is expected to be much higher than for $S_2C{=}N$ bond rotation[19,20] and because of the overall coalescence pattern and intensities, peaks a and b are assigned to the η^2-$SCNMe_2$ ligand. Additionally, the −20 °C coalescence is most likely due to $S_2C{=}N$ bond rotation[20] while the 42 °C coalescence probably results from fast Me_2dtc scrambling via a metal-centered rearrangement process. The complexes $RuX(R_2dtc)_3$, where X = Cl (**1**) or I, are nonrigid at −90 °C such that all R_2dtc ligands appear equivalent. Possible mechanisms for this process have been discussed.[3] It is certainly possible that a similar ligand scrambling occurs in **3**; however, it is not clear why the presence of the η^2-$SCNMe_2$ ligand significantly increases the barrier to this rearrangement. The coalescence of peaks a and b at ca. 80 °C must result from C=N bond rotation in the η^2-$SCNMe_2$ ligand; however, the possibility of accidental degeneracy cannot be eliminated (vide supra).

Acknowledgment. This research was supported by the National Science Foundation. We are grateful to Dr. Arild Christensen and to Syntex Analytical Instruments for carrying out the X-ray analysis. We thank Engelhard Industries for a loan of $RuCl_3$.

Registry No. **3**, 68200-83-9; $Ru(Me_2dtc)_3$, 43190-67-6; $RuCl(S_2CNEt_2)_2(SCNEt_2)$, 68200-84-0.

Supplementary Material Available: A table of observed and calculated structural factor amplitudes (19 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Part 1: G. L. Miessler, G. Stuk, T. P. Smith, K. W. Given, M. C. Palazzotto, and L. H. Pignolet, *Inorg. Chem.*, **15**, 1982 (1976). (b) Part 2: G. L. Miessler, E. Zoebisch, and L. H. Pignolet, *ibid.*, **17**, 3636 (1978).

(2) K. W. Given, B. M. Mattson, M. F. McGuiggan, G. L. Miessler, and L. H. Pignolet, *J. Am. Chem. Soc.*, **99**, 4855 (1977).

(3) K. W. Given, B. M. Mattson, and L. H. Pignolet, *Inorg. Chem.*, **15**, 3152 (1976).

(4) A. R. Hendrickson, J. M. Hope, and R. L. Martin, *J. Chem. Soc., Dalton Trans.*, 2032 (1976).

(5) G. L. Miessler, M. F. McGuiggan, and L. H. Pignolet, paper in preparation.

(6) See for example: (a) A. W. Gal, Ph.D. Thesis, University of Nijmegen, Toernooiveld, Nijmegen, The Netherlands, 1977; (b) A. W. Gal, A. F. J. M. van der Ploeg, F. A. Vollenbroek, and W. Bosman, *J. Organomet. Chem.*, **96**, 123 (1975); (c) W. K. Dean and D. G. van der Veer, *ibid.*, **144**, 65 (1978); (d) G. R. Clark, T. J. Collins, D. Hall, S. M. James, and W. R. Roper, *ibid.*, **141**, C5 (1977), and references cited therein.

(7) M. R. Churchill, R. A. Lashewycz, and F. J. Rotella, *Inorg. Chem.*, **16**, 265 (1977).

(8) Data collection was carried out by Dr. Arild Christensen of Syntex Analytical Instruments, Cupertino, Calif.

(9) Data were reduced to net intensities (I) and their esd's ($\sigma(I)$) according to the equations $I = \mathrm{CT} - \tau(B_1 + B_2)$ and $\sigma(I) = [\mathrm{CT} + \tau^2(B_1 + B_2)]^{1/2}$, where CT is the count during the scan, τ is the ratio of scan time to background time (=1 in the present case) and B_1 and B_2 are the initial and final backgrounds.

(10) "Syntex XTL Operations Manual", 2nd ed., Syntex Analytical Instruments, Cupertino, Calif., 1976.

(11) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; the numerator of R_2 was the function minimized; the weights were $w = [\sigma(|F_o|)]^{-2}$, where $\sigma(F_o)^2 = \sigma(I)/Lp$. Atomic scattering factors were taken from "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974. Anomalous dispersion corrections from the same source were used for Ru, Cl, and S.

(12) B. M. Mattson and L. H. Pignolet, *Inorg. Chem.*, **16**, 488 (1977).

(13) S. H. Wheeler, B. M. Mattson, G. L. Miessler, and L. H. Pignolet, *Inorg. Chem.*, **17**, 340 (1978).

(14) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, p 260.

(15) W. K. Dean, R. S. Charles, and D. G. van der Veer, *Inorg. Chem.*, **16**, 3328 (1977).

(16) W. P. Bosman and A. W. Gal, *Cryst. Struct. Commun.*, **5**, 703 (1976).

(17) W. P. Bosman and A. W. Gal, *Cryst. Struct. Commun.*, **4**, 465 (1975).

(18) L. Ricard, J. Estienne, and R. Weiss, *Inorg. Chem.*, **12**, 2182 (1973).

(19) W. K. Dean, *J. Organomet. Chem.*, **135**, 195 (1977), and references cited therein.

(20) B. L. Edgar, D. J. Duffy, M. C. Palazzotto, and L. H. Pignolet, *J. Am. Chem. Soc.*, **95**, 1125 (1973); L. H. Pignolet, *Top. Curr. Chem.*, **56**, 91 (1975).

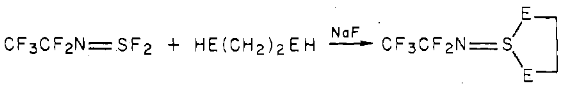
Contribution from the Anorganisch-Chemisches Institut der
Universität, Göttingen, West Germany

$CF_3CF_2N{=}SF_2$—A Precursor of Five- and Six-Member Heterocycles

O. Glemser and Jean'ne M. Shreeve*[1]

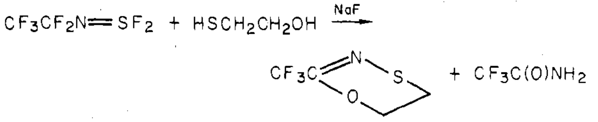
Received August 31, 1978

While taking advantage of the facile route for the synthesis of five-member heterocycles which contain three-coordinate sulfur(IV) via the reaction of pentafluoroethyliminosulfur difluoride with amines[2,3] and diols, viz.



E = NCH_3; O

we observed that the reaction with 2-mercaptoethanol did not produce an analogous product. Instead a slightly volatile colorless liquid, in addition to solid $CF_3C(O)NH_2$, was formed at room temperature and was removed under dynamic vacuum (eq 1). Since traces of CF_3CN were known to be present in the $CF_3CF_2N{=}SF_2$, we examined the reaction of the 2-mercaptoethanol with this nitrile. None of the 2-trifluoromethyl-1,4,3-oxathiazine was formed. It was shown subsequently that carefully purified $CF_3CF_2N{=}SF_2$ behaves as in (1).



(1)

The formation of $CF_3\overline{C{=}NSCH_2CH_2O}$ is unexpected. It was separated from the $CF_3C(O)NH_2$ by repeated sublimations. When the solid residue from the reaction was extracted with anhydrous CH_2Cl_2, and the solid remaining, after evaporation of CH_2Cl_2, was heated at 60°C under high vacuum, a slightly volatile liquid and solid were distilled off. These products were not separated. The most distinguishing feature seen in the infrared spectrum of the mixture is a very intense band at 1787 cm^{-1} which likely arises from $\nu_{C=O}$. Additional bands fall in the O–H, C–H, and C–F stretching regions.

Spectral data are very useful in assigning the correct structure for these new heterocycles, particularly for the unexpected oxathiazine. In the infrared spectrum of $CF_3\overline{C{=}NSCH_2CH_2O}$, a strong band at 1657 cm^{-1} is assigned to $\nu_{C=N}$. There is no activity in the ν_{N-H} region. A molecule ion is observed in the mass spectrum, and a peak assigned to CF_3CO^+ supports a structure with C–O and N–S bonding. In the nuclear magnetic resonance spectra, a singlet CF_3 resonance and two proton resonances of equal area, which can be assigned to CH_2O and CH_2S, are found.

Experimental Section

All gases, volatile liquids, and sublimable solids were handled in a conventional glass vacuum apparatus. Pentafluoroethyliminosulfur difluoride was prepared by standard literature methods. The other reagents were standard shelf items and were used after drying over molecular sieves in the case of liquids and at 150 °C for NaF.

Products were purified by sublimation, trap-to-trap separation, or prolonged exposure to dynamic vacuum. Infrared spectra were obtained by using a liquid film between KBr plates or solids as KBr disks. The ^{19}F and ^{1}H nuclear magnetic resonance spectra were measured at 60 MHz with CCl_3F and $(CH_3)_4Si$ as internal references. Mass spectra were obtained at 70 eV. Elemental analyses were completed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

In a typical reaction, 5–10 mmol of $CF_3CF_2N{=}SF_2$ and an excess of the amine, diol, or mercaptoethanol at −196 °C were added to a 50-mL Pyrex glass vessel equipped with a Teflon stopcock and containing 30–40 mmol of anhydrous NaF. The vessel was allowed to warm to and remain at room temperature while being stirred magnetically for several days. The product was purified by fractional condensation or, if solid, by sublimation.

New Compounds

$CF_3CF_2N{=}SN(CH_3)CH_2CH_2N(CH_3)$. A 62% yield was obtained from the reaction of 8 mmol of $CF_3CF_2NSF_2$ with 18 mmol of $HN(CH_3)CH_2CH_2N(CH_3)H$ (excess NaF). The compound is a sublimable, colorless solid which melts at 59 °C. IR (KBr disk): 2970 (w), 2930 (w), 2895 (m), 2820 (w), 2765 (w), 1650 (s, br), 1528 (w), 1472 (w), 1450 (w), 1372 (m), 1208 (sh), 1193 (s), 1168 (s), 1140 (s), 1100 (m), 1055 (m), 1015 (w), 982 (w), 915 (m), 872 (w), 820 (m), 763 (m), 680 (s), 523 (w), 458 (w) cm^{-1}. Mass spectrum (*m/e*): M^+, 251; $C_2F_5NSN(CH_3)CH_2^+$, 208; $M - CF_3^+$, 182; $F_2CNSN(CH_3)CH_2^+$, 139; $NSN(CH_3)CH_2CH_2N^+$, 117. ^{19}F NMR: $\phi(CF_3)$ −86.4, $\phi(CF_2)$ −75.0. ^{1}H NMR: $\delta(CH_3)$ 5.8, $\delta(CH_2)$ 7.2. Anal. Calcd: C, 28.76; H, 4.25; N, 16.92. Found: C, 28.69; H, 3.98; N, 16.73.

$CF_3CF_2N{=}SOCH_2CH_2O$. A 70% yield was obtained from the reaction of 5.5 mmol of $CF_3CF_2NSF_2$ with 12.6 mmol of $HOCH_2CH_2OH$ (excess NaF). The compound is a slightly volatile, colorless liquid which was purified by fractional distillation. IR (capillary film): 2985 (w), 2920 (w), 1472 (w), 1390 (m), 1265 (vs), 1210 (vs), 1105 (vs), 1025 (sh), 1010 (s), 915 (s), 768 (m), 732 (s), 663 (s), 603 (m), 545 (w), 445 (m) cm^{-1}. Mass spectrum (*m/e*): M^+, 225; $M - F^+$, 206; $C_2F_5NS^+$, 165; $C_2F_4NSO^+$, 162; $C_2F_5^+$, 119; CF_2NSO^+, 112. ^{19}F NMR: $\phi(CF_3)$ −87.4(t), $\phi(CF_2)$ −83.7 (br), $J_{CF_3-CF_2} = 0.9$ Hz. ^{1}H NMR $\delta(CH_2)$ 4.5 (mult). Anal. Calcd: C, 21.04; H, 1.76; N, 6.14. Found: C, 21.33; H, 1.78; N, 6.22.

$CF_3C{=}NSCH_2CH_2O$. A 15% yield was found from the reaction of 13 mmol of $CF_3CF_2NSF_2$ with 21 mmol of $HOCH_2CH_2SH$ (excess NaF). The compound is a slightly volatile liquid at 22 °C and was separated with great difficulty from the other volatile product, $CF_3C(O)NH_2$ (20% yield), by repeated sublimations. IR (capillary film): 2960 (w), 2910 (w), 1750 (w), 1657 (s), 1467 (w), 1423 (w), 1387 (s), 1337 (s), 1293 (s), 1210 (s), 1145 (s, sh), 1125 (s), 995 (w), 970 (m), 868 (m), 833 (m), 746 (m), 719 (m), 702 (w), 595 (w), 525 (w), 508 (w), 400 (m) cm^{-1}. Mass spectrum (*m/e*): M^+, 171; $M - F^+$, 152; $M - C_2H_4^+$, 143; $C_4H_2FNS^+$, 115; $M - CF_3^+$, 102; CF_3CO^+, 97; $OC_2H_4S^+$, 76. ^{19}F NMR: $\phi(CF_3)$ −74.4. ^{1}H NMR $\delta(CH_2O)$ 4.57 (mult), $\delta(CH_2S)$ 3.17 (mult). Anal. Calcd: C, 28.07; H, 2.42. Found: C, 28.01; H, 2.34.

Acknowledgment. J.M.S. is grateful to the Alexander von Humboldt Stiftung for a United States Senior Scientist Award.

Registry No. $CF_3CF_2N{=}SN(CH_3)CH_2CH_2N(CH_3)$, 68297-70-1; $CF_3CF_2N{=}SOCH_2CH_2O$, 68297-71-2; $CF_3C{=}NSCH_2CH_2O$, 68297-72-3; $CF_3CF_2NSF_2$, 4101-37-5; $HN(CH_3)CH_2CH_2N(CH_3)H$, 110--3; $HOCH_2CH_2OH$, 107-21-1; $HOCH_2CH_2SH$, 60-24-2.

References and Notes

(1) Correspondence should be directed to this author at the Department of Chemistry, University of Idaho, Moscow, Idaho 83843.

(2) W. C. Smith, C. W. Tullock, R. D. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 551 (1960).

(3) T. Kitazume and J. M. Shreeve, *J. Fluorine Chem.*, **8**, 437 (1976).

Contribution from the Departments of Chemistry,
Concordia University, Montreal, Quebec, Canada, H3G 1M8,
and Boston University, Boston, Massachusetts 02215

Temperature Dependence of the Photoaquation of Tris(2,2′-bipyridine)chromium(III) Ion in Alkaline Solution[1]

Mary A. Jamieson,[2a] Nick Serpone,*[2a] Marian S. Henry,[2b] and Morton Z. Hoffman*[2b]

Received May 18, 1978

Detailed examinations of the thermal[3,4] and photochemical aquation[5] of $Cr(bpy)_3^{3+}$ (bpy = 2,2′-bipyridine) in alkaline solution (reaction 1) have led to the conclusion that both

$$Cr(bpy)_3^{3+} \xrightarrow[h\nu,\ kT]{H_2O,\ OH^-} Cr(bpy)_2(OH)_2^+ + bpy \qquad (1)$$

reactions occur via the direct association of the $^4A_2$ ground state or ^2E excited state with H_2O to form the same seven-coordinate intermediate. Evaluation of the rate constant for the thermal reaction at pH 9.8 as a function of temperature (e.g., 4.7×10^{-7} s^{-1} at 11 °C) has resulted in the following activation parameters:[3] $E_a = 22.9 \pm 0.6$ kcal mol^{-1}, $\Delta H_{298}^{\ddagger} = 22.3 \pm 0.6$ kcal mol^{-1}, $\Delta S_{298}^{\ddagger} = -8.8 \pm 1.9$ eu.

Inasmuch as the same seven-coordinate intermediate is believed to be formed from both $^4A_2$ and ^2E electronic states via equivalent reaction paths, $Cr(bpy)_3^{3+}$ offers the unusual opportunity to compare directly the kinetic parameters of ground- and excited-state reactivities of the same species. In this paper we report the temperature dependence of the photochemical aquation of $Cr(bpy)_3^{3+}$ and make such a comparison.

Experimental Section

The $[Cr(bpy)_3](ClO_4)_3{\cdot}{}^1/_2H_2O$ sample was prepared according to the procedure described previously;[3] however, oxidation was carried out with chlorine gas. All chemicals and solvents used were reagent grade and the water was distilled.

Continuous photolyses were carried out at 313 nm with an Oriel 1000-W Hg–Xe lamp and a 0.25-m Bausch and Lomb grating monochromator (bandwidth 22 nm). To improve the spectral purity of the incident light, the beam was passed through an 8-cm path of cooled distilled water.[6] The intensity of the incident light ($\sim 1 \times 10^{-6}$ einstein min^{-1}) was measured by ferrioxalate actinometry.[7] Constant temperature (±0.1 °C) during irradiation was maintained with a jacketed cell holder and a constant-temperature water bath. Absorption spectra were recorded with an Aminco-Bowman DW-2 spectrophotometer.

Solutions were prepared and handled in dim red light. Quantum yields of bpy release, Φ, were determined in the temperature range 6.3–36.3 °C at pH 9.8 (Britton-Robinson buffer,[8] 0.008 M); the ionic strength was adjusted to 1.0 M with NaCl. Exactly 3.00 mL of $Cr(bpy)_3^{3+}$ ($\sim 1 \times 10^{-3}$ M) solution in a 1-cm quartz cell fitted with a stopcock was deoxygenated with prepurified N_2 for 25 min in the thermostated cell holder and then irradiated at 313 nm for 85–180 s at the desired temperature. A sample of the solution was kept in the dark in the water bath to measure the thermal component of the aquation reaction (2–43% of the total reaction). During irradiation, the solution was stirred with a stream of N_2. Immediately after irradiation, a 2.00-mL aliquot of the irradiated solution was taken for the determination of the concentration of free bpy (±15%) according to the extraction procedure described previously.[3,4] The irradation time was chosen so that no more than 10% of the $Cr(bpy)_3^{3+}$ was photolyzed. Values of Φ represent the average of two to four determinations (standard deviation is ±0.01).

The details of the flash photolysis determination of the decay kinetics of the ^2E state of $Cr(bpy)_3^{3+}$ have been reported.[5]

Results and Discussion

The value of the rate constant of the decay of the ^2E state of $Cr(bpy)_3^{3+}$ (k_0) is pH independent (−0.4 to +13.0)[5] but