Registry No. $\mathrm{Ru(NH_3)_6^{2+}}$, 19052-44-9; $\mathrm{(NH_3)_5CoO_2Co(NH_3)_5^{5+}}$, 12259-09-5.

References and Notes

(1) H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

(2) (a) A. G. Sykes and R. N. F. Thorneley, *J. Chem. Soc. A*, 232 (1970); (b) D. Seewald, N. Sutin, and K. O. Watkins, *J. Am. Chem. Soc.*, **91**, 7307 (1969); (c) W. G. Movius and R. G. Linck, *ibid.*, **91**, 5394 (1969).

(3) (a) A. McAuley and J. Hill, *Q. Rev., Chem. Soc.*, **23**, 18–36 (1969); (b) K. Kustin and J. Swinehart, *Prog. Inorg. Chem.*, **13**, 101–158 (1970).

(4) When the gradient is unity, such correlations are consistent with the Marcus cross reaction equation with $f = 1$: R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964), and references therein.

(5) M. R. Hyde, R. S. Taylor, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 2730 (1973).

(6) P. R. Guenther and R. G. Linck, *J. Am. Chem. Soc.*, **91**, 3769 (1969).

(7) B. Grossman and A. Haim, *J. Am. Chem. Soc.*, **93**, 6490 (1971).

(8) K. L. Scott and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1832 (1972).

(9) J. C. Chen and E. S. Gould, *J. Am. Chem. Soc.*, **95**, 5539 (1973).

(10) See data obtained by D. H. Huchital, N. Sutin, and B. Warnqvist, *Inorg. Chem.*, **6**, 838 (1967), and illustration and comments in D. R. Rosseinsky, *Chem. Rev.*, **72**, 229 (1972).

(11) J. R. Pladziewicz, T. J. Meyer, J. A. Broomhead, and H. Taube, *Inorg. Chem.*, **12**, 639 (1973).

(12) An argon and not nitrogen atmosphere is essential: D. E. Harrison and H. Taube, *J. Am. Chem. Soc.*, **89**, 5706 (1967).

(13) R. Davies, M. Mori, A. G. Sykes, and J. A. Weil, *Inorg. Synth.*, **12**, 197 (1970).

(14) J. Simplicio and R. G. Wilkins, *J. Am. Chem. Soc.*, **91**, 1325 (1969).

(15) A. G. Sykes and J. A. Weil, *Prog. Inorg. Chem.*, **13**, 35 (1970).

(16) For details see, for example, K. L. Scott, M. Green, and A. G. Sykes, *J. Chem. Soc. A*, 3651 (1971).

(17) J. F. Endicott and H. Taube, *Inorg. Chem.*, **4**, 437 (1965).

(18) A. G. Sykes, *Trans. Faraday Soc.*, **59**, 1325 (1963).

(19) A. B. Hoffman and H. Taube, *Inorg. Chem.*, **7**, 1971 (1968).

(20) J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **86**, 1686 (1964).

(21) M. L. Hyde, Ph.D. Thesis, University of Leeds, 1973.

(22) Data for the $\mathrm{Cr^{2+}}$ and $\mathrm{V^{2+}}$ reductions of some 17 mononuclear, binuclear (including the μ-superoxo complex), and tetranuclear cobalt(III) complexes believed to be outer-sphere reactions give a linear plot of log k_V against log k_{Cr} from which the fit log $k_V = (1.02 \pm 0.04)$ log $k_{Cr} + (1.73 \pm 0.11)$ is obtained: K. L. Scott, personal communication.

(23) T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968).

(24) B. R. Baker, M. Orhanovic, and N. Sutin, *J. Am. Chem. Soc.*, **89**, 722 (1967).

(25) A. G. Sykes, *Adv. Inorg. Chem. Radiochem.*, **10**, 158 (1967).

(26) D. L. Toppen and R. G. Linck, *Inorg. Chem.*, **10**, 2635 (1971).

Contribution from the Department of Chemistry,
Manchester University, Manchester M13 9PL, England

Inorganic Compounds Containing the Trifluoroacetate Group. IV.[1] Preparation and Properties of Arsenic Tris(trifluoroacetate), $\mathrm{As(O_2CCF_3)_3}$, and Related Compounds

C. David Garner* and Barry Hughes

Received October 24, 1974 AIC40742F

Trifluoroacetato complexes of the group 5 elements which have been prepared previously included $\mathrm{Bi(O_2CCF_3)_3}$, $\mathrm{Na[Bi(O_2CCF_3)_4]}$, and $\mathrm{Na[AsO(O_2CCF_3)_2]}$ which were obtained by reaction of the corresponding oxide with trifluoroacetic anhydride.[2] Goel et al.[3,4] have prepared $\mathrm{R_3Sb(O_2CCF_3)_2}$ (where R = Me or Ph) and several other carboxylato derivatives by metathesis between $\mathrm{R_3SbX_2}$ (X = halide) and $\mathrm{AgO_2CCF_3}$ in MeOH (R = Me) or $\mathrm{C_6H_6}$ (R = Ph) solution and reported ir spectral, conductometric, and molecular weight data. The tris(carboxylato) complexes $\mathrm{As(O_2CCHF_2)_3}$[5] and $\mathrm{M(O_2CH)_3}$[6] (M = Sb or Bi) have been synthesized, the former by heating $\mathrm{Hg(CHF_2CO_2)_2}$ with As and the latter by refluxing $\mathrm{M_2O_3}$ with $\mathrm{HCO_2H}$. However, attempts to prepare $\mathrm{As(O_2CCH_3)_3}$ from $\mathrm{AsCl_3}$ and $\mathrm{CH_3CO_2H}$ produced a mixture of $\mathrm{(CH_3CO_2)_xAsCl_{3-x}}$ (where x = 1 or 2) derivatives which were not readily separable.[7] Cullen[8] has prepared $\mathrm{Me_2As(O_2CCF_3)}$ by the reaction of $\mathrm{Me_2AsCl}$ and $\mathrm{AgO_2CCF_3}$ and showed that, while the compound distilled at its boiling point (136°) under nitrogen, at 205° it decomposed giving some $\mathrm{Me_2AsCF_3}$. This note reports a study of the preparation and properties of $\mathrm{As(O_2CCF_3)_3}$ and an extension of this work to the corresponding P, Sb, and Bi compounds.

Experimental Section

All manipulations were carried out under an atmosphere of dried nitrogen. Anhydrous $\mathrm{CF_3CO_2H}$ (Koch-Light) and trifluoroacetic anhydride (Koch-Light) were used without further purification. Reagent grade $\mathrm{AsCl_3}$ and $\mathrm{PCl_3}$ were purified by distillation under reduced pressure and $\mathrm{SbCl_3}$ by sublimation under a dynamic vacuum at 65° (10^{-2} Torr); $\mathrm{BiCl_3}$ was purified by the addition of excess $\mathrm{SOCl_2}$ and refluxing for 2 hr, followed by the evaporation of excess $\mathrm{SOCl_2}$. $\mathrm{CH_2Cl_2}$ and $\mathrm{CHCl_3}$ were distilled from $\mathrm{CaH_2}$, and THF was distilled from Na wire, immediately prior to use. Ir spectra were recorded on Perkin-Elmer 225 and 457 spectrometers calibrated with polystyrene film, and mass spectra were obtained on an AEI MS12 instrument using a 70-eV beam. ^{1}H NMR spectra were measured on a Perkin-Elmer R12A instrument at 60 MHz using TMS as an internal standard, and ^{19}F NMR spectra, on a Varian HA-100 instrument at 100 MHz using $\mathrm{C_6H_5CF_3}$ as an internal standard.

Preparation of Arsenic Tris(trifluoroacetate), $\mathrm{As(O_2CCF_3)_3}$. $\mathrm{AsCl_3}$ (3.9 g, 21.5 mmol) was dissolved in $\mathrm{CH_2Cl_2}$ (50 ml), $\mathrm{AgO_2CCF_3}$[9] (14.9 g, 67.5 mmol) was added, and the mixture was stirred for 4 hr at room temperature. The precipitate of AgCl was then filtered off and the bulk of the $\mathrm{CH_2Cl_2}$ distilled from the filtrate at 40° (760 Torr) to afford a viscous, pale yellow oil. Fractional distillation under reduced pressure afforded as the least volatile fraction a transparent, crystalline, extremely hygroscopic solid, mp 45.5–46.0°, in 70% yield. Anal. Calcd for $\mathrm{C_6F_9O_6As}$: C, 17.4; F, 41.3; As, 18.1. Found: C, 17.1; F, 41.4; As, 18.1.

The mass spectrum of the compound was obtained by dissolving a sample of $\mathrm{CH_2Cl_2}$ and injecting a portion of the solution through a serum cap into the warmed inlet of the mass spectrometer. Peaks were observed at the following m/e values (with relative intensities) and assigned as 396 (25) $\mathrm{As_4O_6^+}$, 301 (30) $\mathrm{As(O_2CCF_3)_2^+}$, 300 (10) $\mathrm{As_4^+}$, 220 (10) $\mathrm{AsO_2(O_2CCF_3)^+}$, 207 (25) $\mathrm{AsF(O_2CCF_3)^+}$, 188 (50) $\mathrm{As(O_2CCF_3)^+}$, in addition to peaks corresponding to further fragmentation products, including m/e 91 (100) $\mathrm{AsO^+}$. Ir spectra were recorded for a sample sublimed as a thin film onto a NaCl window cooled to ca. −196° and contained in an ir gas cell (Table I) and also for samples dissolved in $\mathrm{CH_2Cl_2}$ and $\mathrm{CS_2}$ at room temperature. The ^{19}F NMR spectrum of the compound dissolved in $\mathrm{CHCl_3}$ consisted of a single resonance 76.8 ppm upfield of $\mathrm{CFCl_3}$, within the range 74–79 ppm upfield of $\mathrm{CFCl_3}$ typical[12] of trifluoroacetate compounds.

Preparation of Trivinylarsonium Trifluoroacetate, $\mathrm{[(H_2C{=}CH)_3AsH]O_2CCF_3}$. The reaction between $\mathrm{(H_2C{=}CH)_3As}$ and $\mathrm{CF_3CO_2H}$ was investigated as an alternative synthetic route to $\mathrm{As(O_2CCF_3)_3}$. $\mathrm{(H_2C{=}CH)_3As}$ (2.4 g) was prepared[10] by the reaction of $\mathrm{AsCl_3}$ and $\mathrm{(H_2C{=}CH)MgBr}$ in THF and was then added to a mixture of $\mathrm{CF_3CO_2H}$ (10 ml) and $\mathrm{(CF_3CO)_2O}$ (1 ml); this solution was refluxed for 3 hr. The excess solvent was then evaporated at ca. 72° (760 Torr), and the residue was extracted with $\mathrm{CH_2Cl_2}$ and filtered before distillation of solvent at ca. 40° (760 Torr). On allowing the resulting viscous solution to stand at −10° for 2 hr, large platelike crystals were deposited. These crystals were filtered and washed with pentane; traces of solvent were removed by pumping (10^{-3} Torr) at room temperature; yield 2.45 g, 65% based on $\mathrm{(H_2C{=}CH)_3As}$; mp 154–156° dec. Anal. Calcd for $\mathrm{C_8H_{10}AsF_3O_2}$: C, 35.5; H, 3.7; As, 27.8. Found: C, 35.2; H, 3.5; As, 27.6. The mass spectrum was recorded at 100° and contained peaks at m/e 157, 156, 129, 102, and 75, corresponding to the fragments $\mathrm{(H_2C{=}CH)_3AsH^+}$ and $\mathrm{(H_2C{=}CH)_nAs^+}$ (where n = 3, 2, 1, or 0), respectively, and at m/e 113, 97, 94, and 69 corresponding to $\mathrm{CF_3CO_2^+}$, $\mathrm{CF_3CO^+}$, $\mathrm{CF_2CO_2^+}$, and $\mathrm{CF_3^+}$ fragments, respectively. The ^{1}H NMR spectrum of $\mathrm{[(H_2C{=}CH)_3AsH](CF_3CO_2)}$ in $\mathrm{CDCl_3}$ solution consisted of a singlet at τ 6.9, assigned to the As–H hydrogen atom, and 12 resolved peaks centered at τ 3.5 which resemble those obtained for $\mathrm{(H_2C{=}CH)_4Sn}$ and $\mathrm{(H_2C{=}CH)_2Sn(O_2CCF_3)_2}$.[11]

Preparation of Arsenic Tris(trifluoroacetate)–2,2′-Bipyridyl, $\mathrm{As(O_2CCF_3)_3{\cdot}N_2C_{10}H_8}$. $\mathrm{As(O_2CCF_3)_3}$ (2.07 g, 5 mmol) was dissolved in $\mathrm{CHCl_3}$ (10 ml) and a solution of 2,2′-bipyridyl (0.78 g, 5 mmol) in $\mathrm{CHCl_3}$ (5 ml) was added; the resulting solution was stirred for 0.5

Table I. Ir Spectra of $M(O_2CCF_3)_3$ (M = P, As, Sb, or Bi)[a]

Assignment[b]	$P(O_2CCF_3)_3$ (liquid film, 25°)	$As(O_2CCF_3)_3$ (solid film, −196°)	$Sb(O_2CCF_3)_3$ (Nujol mull, 25°)	$Bi(O_2CCF_3)_3$ (Nujol mull, 25°)
COO asym str	1785 vs	1744 vs	1662 s	1641 s
COO sym str	1382 s	1355 vs	1435 m, b[c]	1452 m[c]
CF_3 str	1210 vs, b[d]	1205 vs, b	1200 vs, b	1215 vs, b
	1155 vs, b	1155 vs, b	1165 vs, b	1138 vs, b
C–C str	854 s	865 s	854 m	848 s
O–C–O def	802 s	773 s	794 s	808 m
CF_3 bend	726 s	735 vs	728 s	732 s

[a] Abbreviations: asym, asymmetric; sym, symmetric; str, stretch; def, deformation; vs, very strong; s, strong; m, medium; w, weak; vw, very weak. [b] Based on the studies of R. L. Redington and K. C. Lin, *Spectrochim. Acta, Part A*, **27**, 2445 (1971), and P. J. Miller, R. A. Butler, and E. R. Lippincott, *J. Chem. Phys.*, **57**, 5451 (1972). [c] Observed in hexachlorobutadiene mull. [d] P–O stretches probably obscured by these bands.

hr at 25°. Solvent was then removed at this temperature (10^{-2} Torr) until crystallization commenced and the product was obtained in 95% yield as fine white needles (mp 131–132°) by cooling to −10°. The sample was filtered, washed with pentane, and dried at room temperature under reduced pressure. Anal. Calcd for $C_{16}H_8N_2AsF_9O_6$: C, 33.7; H, 1.4; N, 4.9. Found: C, 33.6; H, 1.5; N, 5.2. The mass spectrum was virtually the same as that obtained for $As(O_2CCF_3)_3$ with the addition of an intense peak at *m/e* 156 corresponding to the parent ion of 2,2'-bipyridyl. Ir spectra of the compound mulled in Nujol and hexachlorobutadiene contained bands at 1681 (vs), 1440 (s), 1200 (vs, b), 1150 (vs, b), 853 (m), 789 (m), 771 (m), and 727 (m) cm^{-1} (the assignments of which follow from the data in Table I) in addition to absorbances characteristic of 2,2'-bipyridyl. The ^1H NMR spectrum was recorded in $CDCl_3$ solution and comprised a multiplet between τ 1.2 and 1.5 with a profile similar to that for pure 2,2'-bipyridyl.

Attempts were also made to prepare a pyridine adduct in a manner analogous to that described above. Although crystalline products were obtained, the analytical results obtained were not completely consistent with the composition $As(O_2CCF_3)_3(NC_5H_5)_2$.

Preparation of the Arsenic Tris(trifluoroacetate)–Boron Tribromide Adduct, $(CF_3CO_2)_3As\cdot BBr_3$. $As(O_2CCF_3)_3$ (0.77 g, 1.9 mmol) was dissolved in $CHCl_3$ (10 ml) and a solution of BBr_3 (2.64 g, 10.5 mmol) in $CHCl_3$ (5 ml) was added. A violent, exothermic reaction occurred immediately and the mixture was allowed to cool to room temperature before solvent was evaporated (10^{-2} Torr). The solution was set aside at −10° and the transparent needles which formed were filtered off and dried in vacuo; yield 0.84 g, 68% based on $As(O_2CCF_3)_3$. The compound decomposed explosively at 165° and such instability together with its extreme moisture sensitivity has precluded full characterization. Elemental analyses afforded As:Br ratios of 1:3; however, the actual values obtained were variable; typical data follow. Anal. Calcd for $C_6AsBBr_3F_9O_6$: As, 11.3; Br, 36.1; F, 25.7. Found: As, 10.4; Br, 36.1; F, 23.9. The mass spectrum of the compound was recorded at 80° in a manner analogous to that described for $As(O_2CCF_3)_3$. Peaks (of relative intensity) were obtained at the following *m/e* values (^{79}Br) and attributed to the fragments: 662 (10) $(CF_3CO_2)_3AsBBr_3^+$, 549 (15) $(CF_3CO_2)_2AsBBr_3^+$, 470 (20) $(CF_3CO_2)_2AsBBr_2^+$, 436 (10) $(CF_3CO_2)AsBBr_3^+$, 425 (25) $(CF_3CO_2)AsBr_3^+$, 357 (10) $(CF_3CO_2)AsBBr_2^+$, 346 (35) $(CF_3CO_2)AsBr_2^+$, 312 (100) $AsBr_3^+$, in addition to peaks corresponding to further fragmentation products.

Preparation of Phosphorus, Antimony, and Bismuth Tris(trifluoroacetates), $M(O_2CCF_3)_3$ (Where M = P, Sb, or Bi). The preparative route described above for the arsenic derivative, using MCl_3 (M = P, Sb, or Bi) and $Ag(O_2CCF_3)$ (>1:3) was employed, and in each case a quantitative amount of AgCl was filtered off. The filtrate was fractionally distilled under reduced pressure to yield a clear volatile liquid in the case of phosphorus, transparent rhombic crystals, mp 109–111°, in the case of antimony, and a white granular solid, mp 186–189°, in the case of bismuth. All of these materials were very moisture sensitive and reasonable analyses have only been obtained so far for the bismuth derivative. Anal. Calcd for $C_6F_9O_6Bi$: C, 13.1, F, 31.3. Found: C, 12.8; F, 31.8. The mass spectra of the phosphorus and antimony products exhibited peaks corresponding to the fragments $M_4O_6^+$, M_4^+, $M_2O_3^+$, MO^+, $CF_3CO_2^+$, and further decomposition products. The mass spectrum of the bismuth derivative contained peaks at *m/e* 466, 450, 322, 241, and 225 corresponding to the fragments $Bi_2O_3^+$, $Bi_2O_2^+$, $Bi(O_2CCF_3)^+$, BiO_2^+, and BiO^+, respectively. The infrared spectra recorded for these tris(trifluoroacetates) are given in Table I.

Discussion

The low melting point and appreciable volatility of $As(O_2CCF_3)_3$ imply that the compound is comprised of discrete molecular units. The simplicity of the ir spectrum (Table I) and the position of the asymmetric carboxylato stretching frequency (1744 cm^{-1}) suggest[12] that each trifluoroacetato group is coordinated to the arsenic in a unidentate manner. We therefore anticipate that the $As(O_2CCF_3)_3$ molecules have a three-coordinate pyramidal structure such as illustrated in Figure 1, with arsenic(III) possessing a stereochemically active lone pair. This structure is expected to persist in solution as essentially the same ir spectrum as that given in Table I was recorded for $As(O_2CCF_3)_3$ in CH_2Cl_2 and CS_2 solutions. The $As_4O_6^+$ and As_4^+ fragments observed in the mass spectrum of this compound presumably arise from recombination reactions in the mass spectrometer.

$AsCl_3$ is known to function as a Lewis base, to give, e.g., $AsCl_3\cdot 2,2'$-bipy,[13] or a Lewis acid, to give, e.g., $AsCl_3\cdot BX_3$ (X = Cl or Br).[14] $As(O_2CCF_3)_3$ also appears capable of functioning in both of these capacities. It is considered that $As(O_2CCF_3)_3\cdot 2,2'$-bipy contains a chelated (N,N) bipyridyl group in addition to three unidentate trifluoroacetato groups. Although the carboxylato stretching frequencies shift upon coordination of 2,2'-bipyridyl (1744 to 1681 and 1355 to 1440 cm^{-1}), these changes are considered to result primarily from a reduction in the polarization of the trifluoroacetato groups by the arsenic(III) when coordinated to additional donor atoms, rather than a change in coordination of these groups. As would be anticipated, $As(O_2CCF_3)_3\cdot 2,2'$-bipy is considerably less moisture sensitive than $As(O_2CCF_3)_3$. Full characterization of $As(O_2CCF_3)_3\cdot BBr_3$ has proved difficult largely because of its (sometimes explosive) instability and extreme moisture sensitivity. Nevertheless, its mass spectrum provides good evidence for the suggested formulation and a simple molecular unit containing a distorted tetrahedral (O_3B) coordination about As would be anticipated for this compound. The bromo arsenic peaks observed in the mass spectrum presumably arise from ion–molecule reactions in the mass spectrometer.

The information presently available concerning the tris(trifluoroacetates) of P, Sb, and Bi, in particular their volatility and carboxylato stretching frequencies (Table I), suggest that $P(O_2CCF_3)_3$ is composed of discrete molecules with the structure shown in Figure 1. The fragments $P_4O_6^+$, P_4^+, and $P_2O_3^+$ observed in the mass spectrum of this compound are presumed to arise from recombination reactions in the mass spectrometer. Structures composed of such molecules are also favored for the corresponding Sb and Bi derivatives. However, significant molecular associations via bridging trifluoroacetato groups are anticipated for these compounds, since they have reasonably high melting points and their asymmetric carboxylato stretching frequencies are low for unidentate trifluoroacetato groups bonded to such atoms but are consistent with a bridging mode of bonding for these ligands.[12]

The formation of $[(H_2C{=}CH)_3AsH](O_2CCF_3)$ by refluxing $(H_2C{=}CH)_3As$ with $CF_3CO_2H–(CF_3CO)_2O$ con-

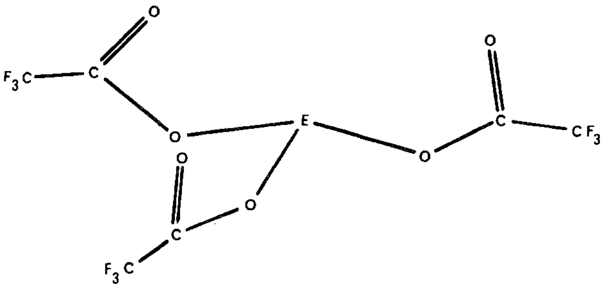

Figure 1. Suggested molecular structure of $E(O_2CCF_3)_3$ (E = P or As).

trasts with the reaction between $(H_2C{=}CH)_4Sn$ and CF_3CO_2H[11] and suggests that cleavage of vinyl atom bonds by trifluoroacetic acid is not a general route to trifluoroacetato complexes. The $(H_2C{=}CH)_3AsH^+$ ion does not appear to have been reported previously, although Forbes et al.[15] have prepared the related species $(H_2C{=}CH)AsEt_3^+$ and $(H_2C{=}CH)(C_{12}H_9)AsMe_2^+$.

Acknowledgment. We thank the S.R.C. for a research studentship to B.H.

Registry No. $P(O_2CCF_3)_3$, 54823-88-0; $As(O_2CCF_3)_3$, 3012-25-7; $Sb(O_2CCF_3)_3$, 54823-89-1; $Bi(O_2CCF_3)_3$, 37442-83-4; $[(H_2C{=}CH)_3AsH]O_2CCF_3$, 54823-90-4; $As(O_2CCF_3)_3{\cdot}N_2C_{10}H_8$, 54823-87-9; $(CF_3CO_2)_3As{\cdot}BBr_3$, 54823-91-5; $AsCl_3$, 7784-34-1; AgO_2CCF_3, 2966-50-9; CF_3CO_2H, 76-05-1; $(H_2C{=}CH)_3As$, 13652-20-5; 2,-2'-bipyridyl, 366-18-7; boron tribromide, 10294-33-4.

References and Notes

(1) Part III: C. D. Garner and B. Hughes, *J. Chem. Soc., Dalton, Trans.*, in press.
(2) P. V. Radheshwar, R. Dev, and G. H. Cady, *J. Inorg. Nucl. Chem.*, **34**, 3913 (1972).
(3) R. G. Goel and H. S. Prasad, *Can. J. Chem.*, **48**, 2488 (1970).
(4) R. G. Goel and D. R. Ridley, *J. Organomet. Chem.*, **38**, 83 (1972).
(5) M. A. Raksha and N. N. Yarovenko, *Zh. Obshch. Khim.*, **32**, 273 (1962).
(6) J. D. Donaldson, J. F. Knifton, and S. D. Ross, *Spectrochim. Acta*, **20**, 847 (1964).
(7) H. Gutbier and H. G. Plust, *Chem. Ber.*, **88**, 1977 (1955).
(8) W. R. Cullen and L. G. Walker, *Can. J. Chem.*, **38**, 472 (1960).
(9) D. W. A. Sharp, D. H. Brown, K. C. Moss, and M. J. Baillie, *J. Chem. Soc. A*, 3110 (1968).
(10) D. Seyferth and M. A. Weiner, *Chem. Ind. (London)*, 402 (1959).
(11) C. D. Garner and B. Hughes, *J. Chem. Soc., Dalton Trans.*, 1306 (1974), and references therein.
(12) C. D. Garner and B. Hughes, *Adv. Inorg. Chem. Radiochem.*, **17**, 1 (1975).
(13) C. D. Smulbach, *Inorg. Chem.*, **4**, 1232 (1965).
(14) N. N. Greenwood and P. G. Perkins, *Pure Appl. Chem.*, **2**, 55 (1961).
(15) M. H. Forbes, I. J. Miller, F. G. Mann, and D. M. Heinekey, *J. Chem. Soc.*, 2762 (1961).

Contribution from the Department of Chemistry,
Arizona State University, Tempe, Arizona 85281

Mechanism of the Titanium(III) Reduction of Azido- and Isothiocyanatopentaamminecobalt(III)[1]

James P. Birk

Received November 5, 1974 AIC407642

Although the reduction of substituted cobalt(III)–ammine complexes by various metal ions has received considerable attention in the past, titanium(III) has been largely ignored as a reducing agent. Some work was done in sulfate media,[2,3] where considerable kinetic complications were observed due to the presence of sulfate, or in perchlorate media[2,3] with the halo-, aquo-, and sulfatopentaamminecobalt(III) complexes. The latter studies are complicated by the fact that the $Ti^{III}-ClO_4^-$ reaction,[3-5] although slower than the $Ti^{III}-Co^{III}$ reactions, could be kinetically significant by virtue of a possible intervention of one of the intermediate oxidation states of chlorine. More recently, interest in $Ti^{III}-Co^{III}$ reactions has been reawakened, with some studies being carried out in tosylate media.[6,7] The latter study involved the reaction of Ti(III) with *cis*- and *trans*-$Co(en)_2(H_2O)_2^{3+}$ and evidence was presented to suggest an inner-sphere mechanism for these reactions.[7] However, the question of the mode of electron transfer has remained largely unanswered. Among the several approaches used to attempt to distinguish between inner-sphere and outer-sphere mechanisms for reduction of Co(III) is a comparison of azide and isothiocyanate as potential bridging ligands.[8-11] It is this approach that we wished to investigate for Ti(III), carrying out experiments in chloride media, which we have previously found to be convenient for the study of Ti(III) reactions.[12,13] This criterion is based on the supposition that if the metal centers are hard, preferring N bonding with NCS^-, and if the reactions are inner sphere, involving the transfer of a bridging ligand, then the reaction should proceed much faster when the bridging group is azide than when it is isothiocyanate. For an outer-sphere reaction, the rates of the two reactions are expected to be approximately the same. Although a detailed analysis of this criterion requires that differences in stabilities of precursor complexes be taken into account,[11] the presence of such precursor complexes is an indication of an inner-sphere mechanism, so it should be possible to apply this criterion without regard for whether the rate effects are due to thermodynamic or kinetic factors. We have in fact been able to obtain evidence in favor of an inner-sphere mechanism by applying this criterion and by observing a rate law which suggests the presence of steady-state quantities of a precursor complex in the azide reaction.

Experimental Section

The preparation, storage, handling, and analysis of titanium(III) chloride in aqueous HCl solutions and of HCl, $HClO_4$, LiCl, and $LiClO_4$ solutions have been previously described.[12,14] Thermostating arrangements and procedures for kinetic studies have been described.[14] Kinetic measurements were carried out with a Cary 14 or a Varian Techtron 635 recording spectrophotometer, primarily at 302 nm for $Co(NH_3)_5N_3^{2+}$ (results were identical at 320 and 340 nm) and at 305 or 495 nm for $Co(NH_3)_5NCS^{2+}$. During the long time periods in which measurements were made on the $Ti^{III}-Co(NH_3)_5NCS^{2+}$ solutions at 305 nm, photochemically induced oxidation of Ti(III) apparently occurred,[15] so solutions were stored in the dark between measurements. Reaction solutions were purged with purified nitrogen at least 15 min prior to addition of Ti(III) to prevent possible oxidation by oxygen.

Pseudo-first-order plots of ln $(D_t - D_\infty)$ vs. time (D = absorbance) were linear for at least 4–5 half-lives in solutions containing no ClO_4^-. When ClO_4^- was present, however, curvature was observed in proportion to the ClO_4^- concentration, due to the $Ti^{III}-ClO_4^-$ reaction.[3-5] The Guggenheim method[16] was used to treat the data in these experiments. Plots were linear for at least 3 half-lives.

The product of the reaction between Ti(III) and $Co(NH_3)_5N_3^{2+}$ was determined to be Co^{2+} by detection with NCS^- in mixed acetone–water solution.[17] No reaction between N_3^- or HN_3 and Ti(III) could be detected over periods long compared to normal reaction times when NaN_3 was added to a solution containing 0.047 M Ti(III) and 1.45 M HCl or to solutions of lower concentrations.

The complexes $[Co(NH_3)_5N_3]Cl_2$[18] and $[Co(NH_3)_5NCS]Cl_2$[19] were prepared according to published procedures. Stock solutions of these complexes were prepared fresh before each set of experiments.

Results

The kinetics of the $Ti^{III}-Co(NH_3)_5N_3^{2+}$ reaction were determined at 25.0° and 0.500 M ionic strength, maintained with LiCl and $LiClO_4$, over the concentration ranges $(0.5-4.0) \times 10^{-4}$ M Co(III), $(0.5-13) \times 10^{-3}$ M Ti(III), 0.034–0.50 M Cl^-, and 0.031–0.475 M H^+. Data presented in Table I