Polyatomic Cations of Tellurium and Selenium in Chloroaluminate Salts. A Study of the Systems M–(MCl₄ + 4AlCl₃)[1]

BY DAVID J. PRINCE, JOHN D. CORBETT,* AND BRUCE GARBISCH

The formation of reduced polyatomic cations of tellurium and of selenium has been examined in the binary sections M–(MCl₄ + 4AlCl₃) using phase equilibrium, X-ray, and infrared techniques. Phases found with tellurium have the empirical compositions $TeAlCl_{3.5}$, Te_2AlCl_4, and Te_3AlCl_4. Infrared data suggest (and subsequent X-ray structural results have confirmed) the occurrence of the square Te_4^{2+} cations in the first two (plus $Al_2Cl_7^-$ and $AlCl_4^-$ anions, respectively). The analogous selenium system forms the compounds Se_xAlCl_4, $x = 2$ and 4 only. Infrared data for the first suggest the formulation $Se_4^{2+}(AlCl_4^-)_2$, and the latter has been shown to be $Se_8^{2+}(AlCl_4^-)_2$. Vapor phase transport reactions in both systems and solution studies of the tellurium compounds in $NaAlCl_4$ are also noted. No evidence could be obtained for the formation of solid $TeCl_2$.

Introduction

Previous studies have shown that the ion Bi_9^{5+} can be isolated from the Bi–BiCl₃ system[2] and that tetrachloroaluminate salts of Bi_5^{3+} and Bi_8^{2+} are evidently obtained from reactions of bismuth metal with the salt mixture $BiCl_3 + 3AlCl_3$.[3] Consideration of the factors which may be important in the stability of such ions led to the conclusion that a large s–p separation in the valence state, *i.e.*, a substantially "inert s pair," is evidently necessary for stable bonding in these particular structures.[4] A search for further examples of polyatomic cations with elements possessing large s–p separations in the valence state has led us to an examination of the pertinent chemistry of tellurium and selenium, recognizing of course that maintenance of reasonably low ion charges would likely mean that these elements should form new types of cations with different electronic structures rather than analogs of the bismuth series. The present paper reports the preparation and properties of five compounds containing homopolyatomic cations of tellurium or selenium which are formed in the corresponding M–(MCl₄ + 4AlCl₃) systems.

During the course of our investigations Gillespie and coworkers[5-9] have described the identification of the species Se_4^{2+}, Se_8^{2+}, Te_4^{2+}, and Te_n^{n+} both in fluorosulfuric acid solvent and in some salts obtained therefrom, and Bjerrum and Smith[10] have identified Te_{2n}^{n+} (*n* probably equal to 2) in fused $NaAlCl_4$. Lundkvist[11]

has also suggested positively charged ions Se_n^{2+}, Se_n^+, etc., are responsible for the conductivity of solutions of selenium in $SeCl_2$ (although chloride would likely carry most of the current in any case). Some of the cations present in phases described here are evidently the same as found in solutions or in solid compounds prepared by these other workers.

Experimental Section

Elemental selenium and tellurium stated to be 99.999% in purity were purchased from American Smelting and Refining and from United Mineral and Chemical, respectively. The tetrachlorides were prepared by the reaction of the element with chlorine diluted with argon. The TeCl₄ and commercial AlCl₃ were purified by vacuum sublimation, and SeCl₄, by sublimation in a stream of chlorine. All reactions, purifications, transfers, and storages were carried out using customary vacuum and drybox techniques. Many of these, as well as thermal analysis methods, were as previously described for bismuth.[3] Infrared data were secured on a Beckman Model IR-11 instrument.

The densities of the pure phases identified in this work were estimated from the weight and dimensions of cast rods. The appropriate composition was sealed in 0.7-cm. i.d. tubing, melted, solidified rapidly, heated until only a few crystals remained, and then cooled slowly. This technique is of course successful only when the compounds studied melt congruently.

Single crystals of all reduced phases were mounted in capillaries in an argon-filled glove box and were studied by Weissenberg or precession techniques in sufficient detail to identify unit cell dimensions and probable space groups.

Results

The investigation of the reduced tellurium and selenium systems was carried out in the pseudo-binary systems M–(MCl₄ + 4AlCl₃), the proportions of the two starting salts being chosen so that all chloride from MCl₄ would be potentially bound as $AlCl_4^-$ on reduction. According to the reported data[12] on the MCl₄–AlCl₃ binary systems the 1:4 proportion employed gives a mixture of 3AlCl₃ plus the compound MCl₄·AlCl₃ (the latter may be $MCl_3^+AlCl_4^-$[13]). However, the present study indicates AlCl₃ is no longer present as a separate phase once reduction proceeds to the first compound and that chlorine in MCl₄ is indeed con-

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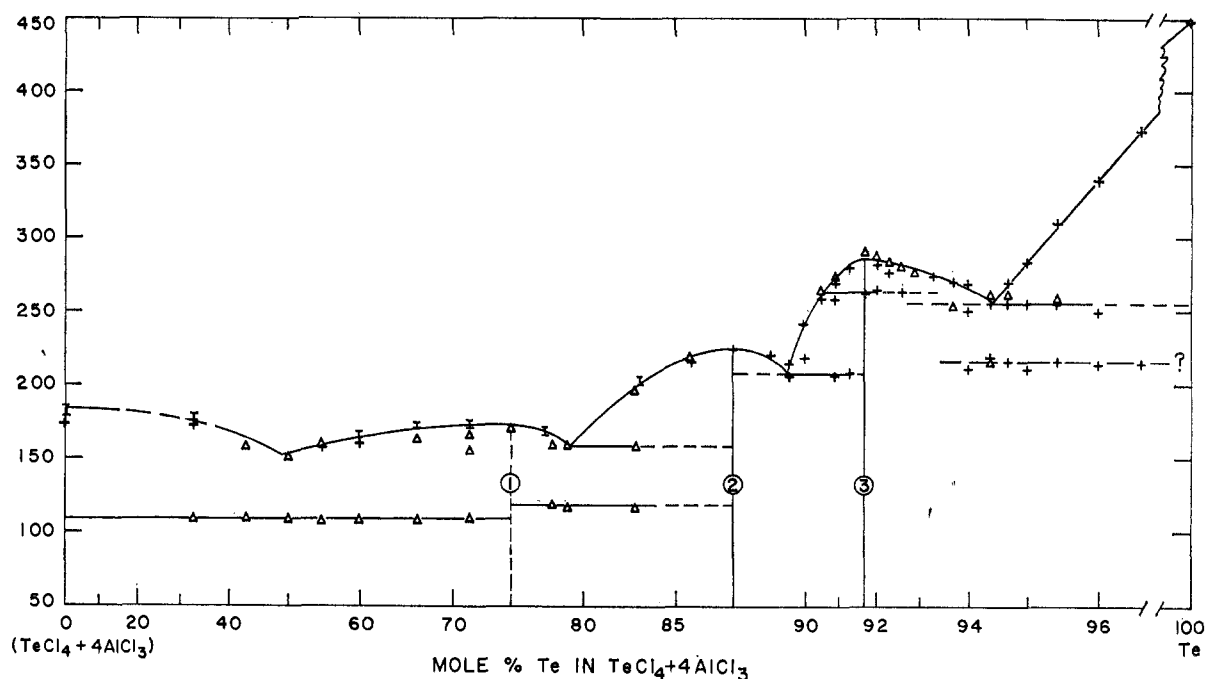(11) M. Lundkvist, *Acta Chem. Scand.*, **22**, 287 (1968).

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Figure 1.—Phase diagram for the system $(TeCl_4 + 4AlCl_3)$–Te: $+$, cooling; $\triangle$, heating; I, liquidus determined by visual inspection following equilibration. The abscissa is logarithmic in mole fraction of the mixture $(TeCl_4 + 4AlCl_3)$.

verted to tetrachloroaluminate so that the more reduced compounds and the element form a series of binary systems in the $(MCl_4 + 4AlCl_3)$–M section. The first tellurium compound formed on reduction is an exception, however, as will be explained shortly.

Thermal analysis and X-ray powder pattern data were found to provide the best criteria for the deduction of the composition of a new phase although neither was highly satisfactory by usual standards. The reduced compounds give relatively poor diffraction patterns, evidently not only because of high absorption but also because of large thermal parameters for the heavy atoms. Simple cooling for thermal analysis usually results either in large supercooling, $\geq 100°$ in some regions, or in glass formation. Consequently, in some parts of the systems only the liquidus could be located at all well and this from heating rather than cooling data. In the extreme, the liquidus could only be approximately bracketed by a series of visual inspections following equilibrations at known temperatures which had been approached from below with crystals present. In some regions eutectic or other subliquidus arrests aided in the deduction of the compound's composition, but in general the kinetic difficulties associated with transitions in the systems made the assignment of most solidus effects impractical.

Tellurium.—The parts of the $TeCl_4 + 4AlCl_3$–Te phase diagram which were delineated are shown in Figure 1. These together with X-ray data suggest that three reduced phases of the type Te_xAlCl_4 are formed with x being close to 1, 2, and 3, which correspond to 75.0, 87.5, and 91.7 mol % tellurium in $TeCl_4 + 4AlCl_3$, respectively.

For the first compound formed on reduction the combination of the relatively imprecise liquidus and

solidus data shown with X-ray powder data for mixtures suggest that the product has the approximate composition $Te_{1.0\pm0.1}AlCl_4$ (75 $\pm$ 2.5% Te). However, a subsequent single-crystal X-ray structural determination[14] has shown the compound is short on chloride and is actually $TeAlCl_{3.5}$. Since only the adjacent phases $TeCl_4 \cdot AlCl_3$ and $TeAlCl_{3.5}$ are necessary to describe the mixture "$TeAlCl_4$," its composition properly lies at the liquidus maximum in Figure 1 and serves as a terminus for the ternary eutectics shown at 109° (with $AlCl_3$) and 118° (with Te_2AlCl_4). (The latter lie outside of the section shown.) In other terms $TeCl_4 \cdot AlCl_3$, "$TeAlCl_4$," and $TeAlCl_{3.5}$ all lie within the 50% $AlCl_3$ section of the ternary $TeCl_4$–$AlCl_3$–Te system. The compound $TeAlCl_{3.5}$ and the composition $TeAlCl_4$ are moderately close to one another in the ternary system since they correspond to 43.75 and 37.5% Te. The characteristic crystals of $AlCl_3$ properly disappear from mixtures on reduction to about the $TeAlCl_4$ composition.

On further reduction a maximum melting point of 225° is found next at a composition of $Te_{2.0\pm0.15}AlCl_4$. Bjerrum and Smith[9] have reported 228° for the melting point of a phase of the same composition. Heating data continue to be the more useful means of characterization and these give the composition of the next phase as $Te_{3.0\pm0.12}AlCl_4$. The arrest at 262° in this region appears to be a polymorphic transition in the compound since no X-ray evidence whatsoever could be obtained for the presence of yet another phase. In this region the pattern for Te_2AlCl_4 predominates to 90% Te and by 93.5% that of Te_3AlCl_4 has diminished and that for the element is more important. The thermal effect at 215° for systems containing 94–97% Te could not be

(14) T. W. Couch and J. D. Corbett, to be submitted for publication.

TABLE I

PROPERTIES OF POLYTELLURIUM AND -SELENIUM CHLOROALUMINATES

Empirical compn	Mp, °C	Color	Density, g cm^{-3}	Crystallographic data
TeAlCl$_{3.5}$	>173	Rose purple	2.6 ± 0.2	Monoclinic, $a = 9.11$, $b = 11.15$, $c = 13.10$ Å, $\beta = 90.17°$, space group $P2_1/c$, $Z = 8$
Te$_2$AlCl$_4$	225	Purple	3.04 ± 0.02	Orthorhombic, $a = 10.74$, $b = 14.13$, $c = 11.83$ Å, space group $Pbca$, $Z = 8$
Te$_3$AlCl$_4$	285–290	Black	3.5 ± 0.2	Hexagonal, $a \approx 9.5$, $c \approx 12.8$ Å, space group $P6cc$ or $P6/mcc$, $Z \approx 4$
Te$_3$AlCl$_4$·NaAlCl$_4$	?	Black	...	Hexagonal, $a \approx 24.8$, $c \approx 10.1$ Å
Se$_2$AlCl$_4$	203 ± 2	Orange	...	Orthorhombic, $a \approx 12.8$, $b \approx 12.7$, $c \approx 9.1$ Å, space group $Pbam$ or $Pba2_1$
Se$_4$AlCl$_4$	192	Black	3.2 ± 0.2	Orthorhombic, $a = 14.92$, $b = 10.67$, $c = 13.22$ Å, space group $Pca2_1$, $Z = 8$

associated with the appearance of any new X-ray data and its source is unknown. The powder pattern data for these three compounds together with those for the initial components nicely account for all the X-ray data obtained. All three phases are diamagnetic as measured on rod cast "neat" for density estimates.

Crystals of the most reduced phase (and of Te) can be grown by vapor-phase transport, probably via TeCl$_2$(g). Under 5 cm of argon a starting composition near Te$_3$-AlCl$_4$ in a 290/150° gradient produces only tellurium metal, but with a 290/225° gradient black crystals of Te$_3$AlCl$_4$ are obtained. The Te$_3$AlCl$_4$ compound is hexagonal and a very poor diffractor. The less reduced phases were formed in transport reactions only as purple droplets. Rectangular plates of Te$_2$AlCl$_4$ can be grown on cooling its solution in NaAlCl$_4$, especially after reheating so that a few crystals remain for nucleation. Crystals of TeAlCl$_{3.5}$ are obtained from a slowly cooled melt of about the same composition, but they have not yet been grown from NaAlCl$_4$. Well-formed, shiny black hexagonal needles were obtained from attempts to recrystallize Te$_3$AlCl$_4$ from NaAlCl$_4$. Weissenberg photographs showed a very large hexagonal cell; although these were reasonable diffractors, multiple and broadened spots suggest an order–disorder problem may be present. Both annealing and quenching treatments indicated these black needles are not just a polymorph of the starting material although the tellurium in them has approximately the same oxidation state as in Te$_3$AlCl$_4$. These properties suggest a double salt with NaAlCl$_4$ is formed, and subsequent powder pattern examination of different mixtures of Te$_3$AlCl$_4$ and NaAlCl$_4$ after fusion indicates the composition is near 1:1, *i.e.*, NaTe$_3$(AlCl$_4$)$_2$. Yet another phase poorer in NaAlCl$_4$ may be formed since such mixtures give X-ray data not totally explicable in terms of presently indentified phases.

Some cryometric measurements on (Te$_2$AlCl$_4$)$_n$ were carried out in NaAlCl$_4$. The value of $n = 2.0 \pm 0.5$ from heating data is consistent with other melt studies.[10]

Properties of the polytellurium and -selenium salts obtained are collected Table I.

Selenium.—A parallel but brief phase study of the corresponding selenium system was also carried out. Since supercooling and glass formation are substantial problems here visual observations at equilibrium accordingly played a larger role in defining the liquidus

curve, and the result is necessarily less precisely determined.

Data for the composition range studied, 80–96.7 mol % selenium in SeCl$_4$ + 4AlCl$_4$, are shown in Figure 2;
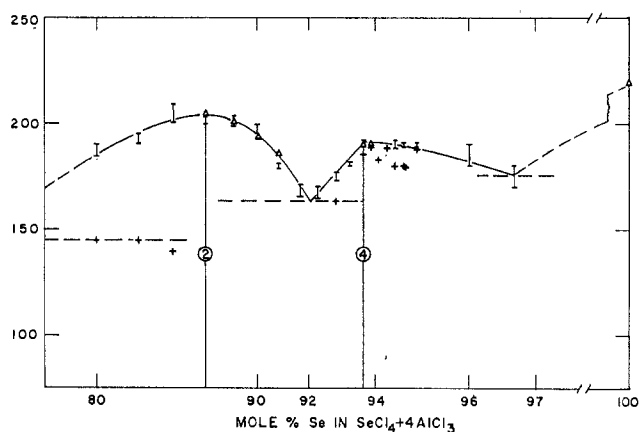

Figure 2.—Partial phase diagram for the system (SeCl$_4$ + 4AlCl$_3$)-Se. The symbols and abscissa scale are the same as in Figure 1.

note that the temperature scale is expanded relative to Figure 1. Orange, brick-shaped crystals are the first reduction product, and the melting point is a maximum at Se$_{2.0\pm0.25}$AlCl$_4$. Crystals of the phase are transported readily to cooler portions of sealed tubes containing samples with about 80–92% selenium. The relationship $a \approx b \approx \sqrt{2}c$ (Table I) gives the powder pattern the appearance of that of a cubic phase.

Visual observation of different mixtures showed a black phase also exists which is more reduced than the lowest tellurium product. The phase is transported to the cool end of a tube held in a 195/140° gradient. Although the melting point data alone would make it difficult to establish the composition of the black phase any better than $4.0 \leq$ Se:AlCl$_4 \leq 5.0$, a crystal structure determination[15] has established that the lower limit, Se$_4$AlCl$_4$, is correct.

Powder pattern data for all reduced mixtures can be accounted for very well in terms of only those for the components and of those calculated and observed for the two new phases. There may be more than the 1:1 adduct in the SeCl$_4$-AlCl$_3$ binary system, however.

Infrared data for the reduced tellurium and sele-

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Table II

INFRARED FREQUENCIES FOR SOME
TETRACHLOROALUMINATE PHASES[a]

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Compound	$\nu_3(AlCl_4^-)$, cm^{-1}	$\nu_4(AlCl_4^-)$ cm^{-1}	Probable $\nu(M-M)$, cm^{-1}	Other bands[b]
Te$_2$AlCl$_4$	482 vs	184 s	133 m	
	462 sh	168 sh	124 w, sh	
	515 sh			
Te$_3$AlCl$_4$	483 vs	179 s	128 vs, br (?)	
	464 sh			
	520 sh			
Te$_3$AlCl$_4$·	480 vs, br	185 s, br	115 m, br	
NaAlCl$_4$		213? vw	95 m, br	
		195? sh		
Se$_2$AlCl$_4$	550 s	192 m	329 m	
	485 m	182 s	310? w	
	455 m	173 sh		
Se$_4$AlCl$_4$	480 vs	183 s, sym	250–330[c] vw	50–80 w, br
	460 sh			
NaAlCl$_4$	494 vs	204 m		
	480 vs	173 m		103 mw, br

[a] Abbreviations: s, strong; m, medium; w, weak; v, very; br, broad; sh, shoulder; sym, symmetrical. [b] Probably lattice modes. [c] A number of bands were observed which were barely above background.

nium tetrachloroaluminate and for NaAlCl$_4$ with a known structure[16] are collected in Table II.

Discussion

Four compounds have been found of empirical formula M$_x$AlCl$_4$, with M = Se, x = 2 or 4, and with M = Te, x = 2 or 3, plus one more phase with a different anion, TeAlCl$_{3.5}$. Only the compounds M$_2$AlCl$_4$ are common to both systems. The diamagnetism of the tellurium phases plus the general observation that most stable polyatomic compounds have an even number of electrons suggests that the empirical formulas should in all cases be at least doubled or that the cations should have even charges, i.e., M$_{2x n}^{2n+}$(AlCl$_4^-$)$_{2n}$. The infrared data generally support the existence of AlCl$_4^-$ ions, and two recent structural determinations have established the presence of discrete ions with dipositive cations (n = 1), namely, Se$_8^{2+}$(AlCl$_4^-$)$_2$[15] and Te$_4^{2+}$-(AlCl$_4^-$)$_2$.[17]

In Table II the infrared spectra are assigned according to the probable origin of the vibrations. The characteristic infrared-active vibrations of AlCl$_4^-$, ν_4 and ν_3 (both of f$_2$ symmetry in the tetrahedral ion), occur close to the reported frequencies of 183 and 495 cm^{-1} [18] (or 488 cm^{-1} [13]), respectively. The fact that the observed bands are generally split is reasonable in view of probable low site symmetry for the AlCl$_4^-$ ion. The symmetry known for the anion in NaAlCl$_4$, Se$_8$(AlCl$_4$)$_2$, and Te$_4$(AlCl$_4$)$_2$ would lift the threefold degeneracy of the f$_2$ mode to give 2a′ + a″ modes. As an example of the static distortions involved the range of variations from T_d in the anions in the last salt are ±0.03 Å in distances and ±2.6° in bond angles.

Bands in the region 135–95 cm^{-1} are assigned to Te–

Te vibrations in the tellurium compounds since the bands have reasonable intensity and are rather high for lattice modes in such heavy compounds. The presence of an infrared band at 133 cm^{-1} with a shoulder at 124 cm^{-1} in Te$_4$(AlCl$_4$)$_2$ compares with the observation of a polarized Raman band at 139 cm^{-1} for the Te$_4^{2+}$ ion in fluorosulfuric acid.[6] In the crystal the Te$_4^{2+}$ ion occurs at a special position with only C_i symmetry although within experimental error the ion has at least D_{2h} symmetry.[17] The distortion of the ion from regular D_{4h} symmetry is expected to lead to splitting of the e$_u$ mode into b$_{2u}$ + b$_{3u}$(D_{2h}) or to 2a$_u$(C_i) as is evidently observed.

Of the selenium compounds, only Se$_2$AlCl$_4$ gave reasonable vibrational spectra in the 250–300-cm^{-1} region where Se–Se vibrations are expected,[19] namely, a band at 329 cm^{-1} together with a weaker one at 310 cm^{-1}. Barr, et al.,[7] found bands in almost identical positions which they assigned to the Se$_4^{2+}$ ion, and so we conclude that the analogous square cation Se$_4^{2+}$ is present in a compound formulated Se$_4^{2+}$(AlCl$_4^-$)$_2$. Molecular orbital calculations[20] for the hypothetical polonium congener of Se$_4^{2+}$ and Te$_4^{2+}$ indicate that a square-planar ion with electronic configuration a$_{1g}^2$b$_{2g}^2$e$_u^4$-a$_{2u}^2$e$_g^4$ is expected with 14p electrons. The bicyclo ion Se$_8^{2+}$ has only an approximate mirror plane[15] and 18 infrared-active modes are expected. The observed spectrum contains a number of very weak features in the region 330–250 cm^{-1} which may arise from cation vibrations.

No evidence has been found in the chloroaluminate system for a salt of the yellow ion Te$_n^{n+}$ ($n \geq 4$) which has been deduced in HSO$_3$F. Although the salt TeAlCl$_{3.5}$ has a similar composition, it turns out to be another salt of Te$_4^{2+}$, namely, Te$_4^{2+}$(Al$_2$Cl$_7^-$)$_2$.[14] In this case an unsplit vibration frequency of 130 cm^{-1} is found for the cation; the probable anion data presently available are inconclusive.

There is no precedent or clear analogy for an ion Te$_{6n}^{2n+}$. On the basis of approximate density measurements the unit cell accommodates 12 tellurium atoms so n may be only 1 or 2 (for an ordered structure). Inter- or intramolecular bonding of six-membered tellurium rings may be involved, analogous to Se$_8^{2+}$. A six-membered ring configuration has been suggested for S$_4$N$_2$,[21] which is isoelectronic with Te$_6^{2+}$ in terms of valence electrons.

Although reports of the preparation of solid TeCl$_2$ occur in the literature,[22,23] three separate attempts in this laboratory to obtain such a phase from Te–TeCl$_4$ reactions under a variety of conditions have met with absolutely no success. Although good thermal analysis results are extremely difficult to procure, there appears to be only a single eutectic between the components, and all X-ray evidence indicates no new phase what-

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soever is formed. In retrospect the report of the preparation of TeCl₂ by reaction of the element and C₂Cl₂F₂[23] in general did not clearly distinguish the assigned product from either the glassy or the finely crystalline mixture of Te and TeCl₄ one evidently gets on cooling the one-phase melt of the composition TeCl₂. The tetrachloroaluminate derivative Te(AlCl₄)₂ does not exist either.

Inner-Sphere Mechanisms of Oxidation. Stoichiometry and Kinetics of the Cobalt(III) Oxidation of Oxalic Acid in Acid Perchlorate Solution

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The stoichiometry and kinetics of the reaction 2Co(III)ₐq + H₂C₂O₄ → 2Co(II)ₐq + 2CO₂ + 2H⁺ have been investigated in perchloric acid–sodium perchlorate solutions. The stoichiometry was measured using standard analytical procedures and the kinetics were followed at ionic strength 3.0 *M* using stopped-flow and conventional spectrophotometry. Any intermediate complexes formed between the reactants could not be detected by kinetic or spectrophotometric means. The acid dissociation constants of H₂C₂O₄ were measured as a function of temperature and the results were used in an analysis of the empirical acidity dependence of the rate law. A comparison of the relative rate constants for the CoOHₐq²⁺ reactions with H₂C₂O₄ and HC₂O₄⁻ and of the individual rate constants themselves with those for other reductants suggests that intermediate complex formation is rate determining. The observed enthalpies and entropies of activation of a series of cobalt(III) oxidation reactions are consistent with this interpretation.

Introduction

The rate law for second-order redox reactions of cobalt(III) in aqueous perchloric acid solution generally takes the form $k_{obsd} = k_1 + k_2 K_h/[H^+]$, where the rate constants k_1 and k_2 are defined by the reactions

$$Co_{aq}^{3+} + B \xrightarrow{k_1} products$$

$$CoOH_{aq}^{2+} + B \xrightarrow{k_2} products$$
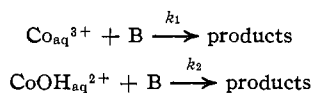
Here B is the reductant and K_h is the acid dissociation constant of Co_{aq}^{3+}.[2,3] When B is H₂O₂, HNO₂, Br⁻, or SCN⁻ the rate of the redox reaction appears to be controlled by the rate of substitution of the reductant in the inner coordination sphere of the cobalt(III).[4] By contrast, when B is hydroquinone or I⁻ the rates of oxidation are much higher and substitution on cobalt(III) is no longer rate determining.[4]

When cobalt(III) and oxalic acid are mixed in aqueous perchloric acid a redox reaction takes place at a notably higher rate than those observed with typical organic reductants.[2] In this paper we report a study of the stoichiometry and kinetics of this reaction. The stoichiometry was determined by standard analytical methods and the kinetics were studied at ionic strength 3.0 *M* using both conventional and stopped-flow spectrophotometry.

Experimental Section

Reagents.—All reagents used were of analytical grade and triply distilled water was used throughout. Solutions of cobalt(III) were prepared and standardized as described previously.[3,4] Sodium perchlorate solutions were prepared[5] by neutralization of sodium carbonate with perchloric acid and were standardized gravimetrically. Sodium oxalate was dried at 110–120° for 2 hr, allowed to cool in a desiccator, and then made up into stock solutions which were standardized by titration with manganese(VII) at 60°.

Determination of Acid Dissociation Constants of Oxalic Acid.—Solutions containing (1–4) × 10⁻² *M* sodium oxalate and 3.0 *M* sodium perchlorate were titrated with perchloric acid at constant temperature under nitrogen using a Radiometer Model 4 pH meter fitted with a Type G200B glass electrode and a Type K100 calomel electrode in which the potassium chloride had been replaced with saturated sodium chloride solution.[5] The solutions were maintained at constant temperature to within ±0.1° over the range 1.5–47.8° in a jacketed titration vessel through which water was circulated from a thermostat. At least 1 hr was allowed for equilibration and pH measurements were obtained to within ±0.002 unit. The system was calibrated in the range $[H^+]$ = (0.02–1) × 10⁻¹ *M* by titration of 3.0 *M* sodium perchlorate solution with perchloric acid at the appropriate temperatures. Preliminary estimates of the acid dissociation con-

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