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Chemical and Physical Properties of Some Xenon Compounds

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Useful preparative reactions for several xenon compounds can be systematized as acid–base chemistry. The hydrolysis of XeF_4 and ammonolysis of XeF_6 have been investigated. The melting point of XeO_4 and the melting point and vapor pressure of XeO_3F_2 are presented, along with negative-ion mass spectra for molecular xenon compounds.

Introduction

During the early development of xenon chemistry it was discovered[1] that the hydrolysis of xenon tetrafluoride resulted in fixation of part of the xenon in the form of a water-soluble compound (which turned out to be xenon trioxide). It remains to this day rather obscure how it happens that Xe(IV) becomes Xe(VI) and why the yield of xenon trioxide is about half that possible. The investigation herein reported does not completely solve the problem but does provide clarification and redefinition.

The discovery that the two higher xenon fluorides undergo hydrolysis to produce a xenon oxide obviously suggested ammonolysis. Unfortunately, no evidence was obtained for the formation of a xenon nitride, but reactions were observed that could be compared to other parts of xenon's descriptive chemistry.

During several years of preparation (and attempted preparation) of new xenon compounds, it became clear that many reactions could be systematized on an acid–base basis and that this systematization could be used to choose particular reactions for compound syntheses.

Experimental Section

Reaction products were observed by a Bendix time-of-flight mass spectrometer fitted with a Kel-F system of tubing and valves for admission of volatile materials to the source of the machine. A system of Kel-F is far superior to one of metal for use with highly reactive fluorinating agents.

This system was used to study the relative amounts of xenon trioxide and xenon difluoride produced by hydrolysis of xenon tetrafluoride. Xenon tetrafluoride was distilled into a Kel-F tube fitted with a Kel-F valve and was weighed. Then small increments of water were distilled in by using liquid nitrogen. After each increment the tube was allowed to warm to ambient temperature and the vapors in the tube were examined with the mass spectrometer. The procedure was repeated until the tube no longer contained xenon tetrafluoride. Product xenon difluoride was distilled away from xenon trioxide. Both compounds were then taken up in water and titrated iodometrically.

The same system was used to study the reaction of ammonia with xenon difluoride, xenon tetrafluoride, and xenon hexafluoride. The xenon fluoride and ammonia were distilled by liquid nitrogen into a Kel-F tube fitted with a Kel-F valve. The valve was closed, the tube was allowed to warm to ambient temperature, and gaseous products were examined with the mass spectrometer. The solid formed by reaction of ammonia with excess xenon hexafluoride could be caused to explode by thermal shock (50 °C). The gases produced were analyzed with the mass spectrometer and the N/Xe ratio was obtained by comparison with a standard mixture admitted to the mass spectrometer in the same fashion (Kel-F valve) as the mixture produced by explosion.

Xenon tetraoxide was prepared[2] by reaction of sodium perxenate with boiled concentrated sulfuric acid. That which was used for determination of its melting point was trapped several times at dry-ice temperature and subjected to high vacuum to free it of carbon dioxide and silicon tetrafluoride. These contaminants derive from the procedure used for making sodium perxenate: hydrolysis of xenon hexafluoride to produce xenon trioxide solution and ozonolysis of the latter in aqueous sodium hydroxide.

Absence of the contaminants was verified by mass spectrometry. Xenon dioxide difluoride[3] and xenon trioxide difluoride[4] were prepared as previously described. The sample of xenon tetrafluoride used in this work was furnished by Felix Schreiner of Argonne National Laboratory.[5]

Hydrolysis of Xenon Tetrafluoride

When xenon tetrafluoride is hydrolyzed to make xenon trioxide, it is reasonable to use an excess of water to absorb the heat of reaction. When this is done, about one-third of the xenon becomes xenon trioxide, whereas redox stoichiometry alone would allow a maximum of two-thirds. Appelman and Malm[6] suggested the reaction sequence

$$3XeF_4 + 6H_2O \rightarrow 2XeO + XeO_4 + 12HF$$

$$2XeO \rightarrow 2Xe + O_2$$

$$XeO_4 \rightarrow XeO_3 + {}^1/_2O_2$$

The formation and decomposition of XeO_4 serve to reduce the yield from the 50% that would be produced by a simple Xe(IV) → Xe(VI) + Xe(II) disproportionation.

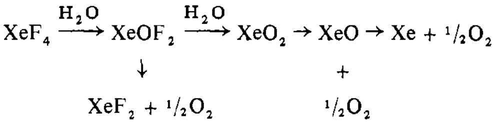
Mass spectrometric examination of the gaseous products of the reaction of xenon tetrafluoride with water showed no xenon tetraoxide but did show xenon difluoride. Whenever water was used in limited amounts, as described in the Experimental Section, more xenon difluoride was produced than xenon trioxide. In the experiment that gave the maximum recovery of xenon, 12.9% was recovered as xenon trioxide and 38.9% as xenon difluoride, making a total of 51%.

However, when a large excess of water was used and added to the xenon tetrafluoride all at once, the yield of xenon trioxide predominated over that of xenon difluoride and was close to one-third. For example, in one such experiment 33.2% of the xenon was recovered as xenon trioxide and only 1.8% as xenon difluoride.

Ogden and Turner[7] have reacted water with xenon tetrafluoride at -80 °C and observed infrared bands that they ascribed to $XeOF_2$, and the formation at -80 °C of this unstable compound has been confirmed by Jacob and Opferkuch.[8] It seems reasonable to assume that the observed xenon difluoride produced in the hydrolysis experiments reported here came from decomposition of this compound

$$2XeOF_2 \rightarrow 2XeF_2 + O_2$$

and that $XeOF_2$ is the initial product of attack by water on xenon tetrafluoride



$$\begin{tikzcd}
XeF_4 \arrow[r, "H_2O"] & XeOF_2 \arrow[r, "H_2O"] \arrow[d] & XeO_2 \arrow[r] & XeO \arrow[r] & Xe + {}^1/_2O_2 \\
 & {} & & + & \\
 & XeF_2 + {}^1/_2O_2 & & {}^1/_2O_2 &
\end{tikzcd}$$

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(1) Chernick, C. L., et al. *Science* **1962**, *138*, 136.

(2) Huston, J. L.; Studier, M. H.; Sloth, E. N. *Science* **1964**, *143*, 1161.

(3) Huston, J. L. *J. Phys. Chem.* **1967**, *71*, 3339.

(4) Claassen, H. H.; Huston, J. L. *J. Chem. Phys.* **1971**, *55*, 1505.

(5) Osborne, D. W.; Schreiner, F.; Flotow, H. E.; Malm, J. G. *J. Chem. Phys.* **1972**, *57*, 3401.

(6) Appelman, E. H.; Malm, J. G. *J. Am. Chem. Soc.* **1964**, *86*, 2141.

(7) Ogden, J. S.; Turner, J. J. *Chem. Commun.* **1966**, 693.

(8) Jacob, E. J.; Opferkuch, R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 158.

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Table I. Acid-Base Reactions

	acid	base	
1	$XeOF_4$	+ XeO_3	→ $2XeO_2F_2$
2	XeF_6	+ $2XeO_3$ (excess)	→ $3XeO_2F_2$
3	$2XeF_6$ (excess)	+ XeO_3	→ $3XeOF_4$
4	XeF_6	+ XeO_2F_2	→ $2XeOF_4$
5	XeF_4	+ XeO_3 (excess)	→ XeO_2F_2, XeF_2
6	XeF_4 (excess)	+ XeO_3	→ XeO_2F_2, $XeOF_4$, XeF_2
7	XeF_4	+ XeO_2F_2	→ $XeOF_4$, XeF_2
8	XeF_2	+ XeO_2F_2	→ no reaction
9	XeF_2	+ XeO_3	→ no reaction
10	XeF_6	+ Na_4XeO_6	→ XeO_3F_2, XeO_4
11	$XeOF_4$	+ Na_4XeO_6	→ XeO_4
12	XeO_2F_2	+ Na_4XeO_6	→ XeO_4
13	XeF_6	+ XeO_4	→ XeO_3F_2 + $XeOF_4$
14	$XeOF_4$	+ XeO_4	→ no reaction
15	XeF_6	+ XeO_3F_2	→ XeO_2F_4 + $XeOF_4$
16	XeO_3F_2	+ XeO_2F_2	→ $XeOF_4$ + XeO_4
17	XeO_3F_2	+ XeO_3	→ XeO_2F_2 + XeO_4
18	XeF_4	+ Na_4XeO_6	→ XeF_2, XeO_4 (small)
19	XeF_4	+ XeO_3F_2	→ no reaction
20	XeF_2	+ Na_4XeO_6	→ no reaction

and decomposes to XeF_2 when the amount of water is limited. But a large amount of water can facilitate the formation of XeO_2 and XeO, which *may* then cause formation of Xe(VIII). One can write equations for possible reactions by which this may happen, for example:

$$XeOF_2 + XeO_2 \rightarrow XeO_2F_2 + XeO$$

$$XeO_2F_2 + H_2O \rightarrow XeO_3 + 2HF$$

The second of these is a known reaction, which has been observed by exposing XeO_2F_2 to water vapor. The first is hypothetical.

Since xenon difluoride is known to be reasonably stable and to have a well-developed redox chemistry in water solution,[9] it seemed that it might be the oxidizing agent by which Xe(IV) is converted to Xe(VI). But the addition of xenon difluoride to xenon tetrafluoride before hydrolysis gave no increase in the yield of xenon trioxide. Any definitive explanation of the formation of xenon trioxide will require more exact knowledge of the intermediates involved. Use of oxidant traps such as aryl sulfonic acids might help provide such knowledge. But any mechanism for the formation of xenon trioxide should also account for the larger formation of xenon difluoride when the amount of water is limited.

Acid-Base Reactions

Xenon hexafluoride is a thermodynamically stable but extremely reactive substance. Its ability to remove oxide ions from other compounds, inserting fluoride ions in their place, can be considered an acid-base process in the Lux-Flood[10] sense. While this reactivity of xenon hexafluoride toward moisture and other sources of oxide ions can be a nuisance and can require extensive conditioning of apparatus, it has proved to be synthetically useful.

The acid-base reactions of Table I can be systematized by a sequence of descending acidity, $XeF_6 > XeO_2F_4 > XeO_3F_2 > XeO_4 > XeOF_4 > XeF_4 > XeO_2F_2 > XeO_3 \approx XeF_2$, wherein any acid (oxide acceptor) can react with any base (oxide donor) beneath it to produce an intermediate acid. Xenon dioxide difluoride was first isolated[3] by reaction 1 but subsequent isolations were based on reactions 2–4, which were more convenient since they used xenon hexafluoride rather than xenon oxide tetrafluoride and avoided one synthetic step.[4]

When xenon tetrafluoride was used in place of xenon hexafluoride (reactions 5–7), the reactions were slower and in all three cases xenon difluoride was produced. It appears, as with the hydrolysis of xenon tetrafluoride, that xenon difluoride is produced from intermediate $XeOF_2$.

Xenon difluoride is too weak an acid to react with XeO_2F_2 or XeO_3 (Table I, entries 8 and 9).

Attempts were made to fluorinate xenon tetraoxide by using F_2, KrF_2, SbF_5, ClF_3, ClF_5, IF_5, and IF_7; in no case could a fluorinated compound of Xe(VIII) be made. Initial experiments using xenon hexafluoride also failed, and the first preparation of xenon trioxide difluoride (in minute amount) came from reaction 10,[11] where xenon hexafluoride discharges XeO_4 from its salt and also attacks the evolved gas. Xenon oxide tetrafluoride (reaction 11) and xenon dioxide difluoride (reaction 12) are sufficiently acidic to discharge XeO_4 but not sufficiently acidic then to attack it.

Reinvestigation showed that xenon hexafluoride does indeed react with xenon tetraoxide to produce xenon trioxide difluoride (reaction 13)[4] and with the latter to produce xenon dioxide tetrafluoride (reaction 15)[12] but it is essential that an excess of xenon hexafluoride not be used. It seems the failure to obtain these compounds with excess reagent may be due to the sequence

$$XeF_6 + XeO_2F_4 \rightarrow XeOF_4 + XeOF_6$$

$$XeOF_6 \rightarrow XeF_6 + {}^{1}/{}_{2}O_2$$

amounting to decomposition of XeO_2F_4 to $XeOF_4$, catalyzed by XeF_6. XeO_2F_4 decays more rapidly to $XeOF_4$ and O_2 than XeO_3F_2 decays to XeO_2F_2 and O_2; it seems likely that $XeOF_6$ (which could not be detected) should be very unstable.

Reactions 16 and 17 were predicted from the acidity sequence and then observed. Reaction 18 shows the acidity of xenon tetrafluoride, weak relative to that of xenon hexafluoride, and its tendency to form xenon difluoride when presented with oxide ions. A predicted reaction that could not be demonstrated

$$XeO_2F_4 + XeO_4 \rightarrow 2XeO_3F_2$$

was thwarted by the instability of XeO_2F_4.

Reaction 1 is demonstrably reversible: (1) prolonged pumping on purified XeO_2F_2 yields a little of the more volatile $XeOF_4$ in the distillate; (2) exhaustive pumping also gives a residue of XeO_3(s); (3) when XeO_2F_2 is dissolved in liquid hydrogen fluoride, a small amount of XeO_3(s) precipitates; (4) tracer fluorine shows exchange between $XeOF_4$ and XeO_2F_2;[13] (5) if XeO_2F_2 is heated over 100 °C in a fluorinated metal container, it decomposes to $XeOF_4$, Xe, and O_2. This can be due to this reversibility and the instability of XeO_3

$$2XeO_2F_2 \rightleftarrows XeOF_4 + XeO_3$$

$$XeO_3 \rightarrow Xe + {}^{3}/{}_{2}O_2$$

The most thermally stable molecular compound containing a Xe–O bond is $XeOF_4$. A sample heated for 1 h at 240 °C in a well-fluorinated container showed no decomposition. At 300 °C decomposition to xenon tetrafluoride and oxygen was just apparent. At 400 °C there was extensive decomposition to xenon tetrafluoride, xenon difluoride, oxygen, and fluorine.

A sample of xenon oxide tetrafluoride was heated with 500 atm of fluorine. It showed no attack at 200 °C but began to form xenon hexafluoride at 260 °C.

Ammonolysis of Xenon Hexafluoride

The hydrolysis of xenon hexafluoride with excess water produces xenon trioxide.[14] The reactions of the xenon fluorides with ammonia were studied in an attempt to prepare a xenon nitride.

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(9) Appelman, E. H.; Malm, J. G. *J. Am. Chem. Soc.* **1964**, *86*, 2297.
(10) Moeller, T. "Inorganic Chemistry"; Wiley: New York, 1952; p 321.
(11) Huston, J. L. *Inorg. Nucl. Chem. Lett.* **1968**, *4*, 29.
(12) Huston, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 5255.
(13) Frame, H. D.; Huston, J. L.; Sheft, I. *Inorg. Chem.* **1969**, *8*, 1549.
(14) Dudley, F. B.; Gard, G.; Cady, G. H. *Inorg. Chem.* **1963**, *2*, 228.

As expected, xenon difluoride, xenon tetrafluoride, and xenon hexafluoride show increasing reactivity toward ammonia. The reactivity of xenon difluoride was sufficiently low so that it was possible for the mass spectrometer to "see" the two reactants simultaneously. Xenon tetrafluoride could not be "seen" simultaneously with ammonia. Regardless of which reagent was in excess, these two xenon fluorides produced xenon, nitrogen, hydrogen fluoride, and ammonium fluoride. Xenon tetrafluoride also showed reduction to xenon difluoride. In no case was any evidence obtained for formation of a compound containing both xenon and nitrogen.

The products of the reaction of xenon hexafluoride with ammonia depend on reagent proportions. With excess ammonia the products are the same as when xenon tetrafluoride is used. But the reaction of ammonia with excess xenon hexafluoride produces an explosive white solid, which contains nitrogen, hydrogen, xenon, and fluorine. It is even more easily detonated by either mechanical or thermal shock than is xenon trioxide but does seem to explode with less violence. Because of its tendency to explode, most observations were made with the solid at 0 °C.

If this solid was subjected to vacuum, excess xenon hexafluoride could be removed in 1 or 2 min. Then followed an emission of xenon hexafluoride sufficiently prolonged (1 h or more) to indicate that it was being produced by chemical decomposition of the solid.

After the emission of xenon hexafluoride, the solid emitted (for several hours) nitrogen, xenon, hydrogen fluoride, and *elemental fluorine*. As the decomposition products became less copious the residual solid became less explosive and finally, when no more gases were being emitted, a small residue of ammonium fluoride (or ammonium hydrogen fluoride) remained.

Eighteen experiments were terminated by causing the solid to explode by thermal shock, and the resulting gas mixtures were analyzed by mass spectrometry. The N/Xe ratio averaged 1.89 and tended to increase with time as the decomposition proceeded. Most were in the range 1–2, the smallest being 1.0 for a sample that exploded spontaneously shortly after initial removal of excess XeF_6. The various observations on the explosive white solid can be explained as follows: Unlike xenon difluoride or xenon tetrafluoride, xenon hexafluoride is capable of acting as a fluoride ion acceptor to form alkali metal salts such as $CsXeF_7$ and Cs_2XeF_8.[15] The former, on heating, loses xenon hexafluoride to form the latter. This suggests the reaction sequence

$$XeF_6 + 2NH_3 \rightarrow Xe + N_2 + 6HF$$

$$HF + NH_3 \rightarrow NH_4F$$

$$NH_4F + XeF_6(g) \rightarrow NH_4XeF_7(s)$$

$$2NH_4XeF_7 \rightarrow XeF_6(g) + (NH_4)_2XeF_8(s)$$

The evolution of elemental fluorine in the latter stages of decomposition requires the formation of a lower oxidation state of xenon or xenon gas. A *possible* example might be

$$(NH_4)_2XeF_8 \rightarrow (NH_4)_2XeF_4 + 2F_2$$

$$(NH_4)_2XeF_4 \rightarrow 2NH_4F + XeF_2$$

which relieves the crowding around Xe in XeF_8^{2-}. The evolution of fluorine suggests comparison to the decomposition of K_2UF_8 to K_2UF_7 and F_2 at 300 °C.[16]

The validity of the assumption that the explosive solid is formed by reaction of ammonium fluoride with excess xenon hexafluoride was tested by exposing ammonium fluoride to the vapor of xenon hexafluoride, with results similar to those reported above. Further characterization of the solid was prevented by its instability. The only evidence for existence of a Xe–N bond has been obtained by LeBlond and DesMarteau[17] in $FXeN(SO_2F)_2$. With this exception all xenon compounds that can be made and worked with at "ordinary" temperatures contain only Xe–F and Xe–O covalent bonds.

Table II. Negative-Ion Mass Spectra (in Approximate Order of Diminishing Intensity)

XeF_2:	XeF^-, (XeF_3^-)[a]
XeF_4:	XeF^-, XeF_2^-
XeF_6:	XeF_2^-, XeF_3^-, XeF_4^-, XeF^-, XeF_6^-, (XeF_5^-), (XeF_7^-)
$XeOF_4$:	XeF_2^-, XeF^-, XeF_3^-, XeF_4^-, $XeOF_3^-$
XeO_2F_2:	XeF^-, XeF_2^-, $XeOF^-$
XeO_3F_2:	XeF^-, XeF_2^-, $XeOF^-$, XeO_2F^-
XeO_2F_4:	XeF_2^-, XeF^-, XeF_3^-, $XeOF_3^-$, XeF_4^-, $XeOF^-$
XeO_3:	XeO^-, (XeO_2^-)
XeO_4:	XeO_2^-, XeO^-, XeO_3^-, (XeO_4^-)

[a] Parentheses indicate very faint intensities; some may be due to ion/molecule reactions.

Melting Points and Vapor Pressures

Xenon tetraoxide is a high explosive with an especial tendency to detonate when the solid is caused to melt. But by depositing small crystals (by distillation) on the inside of a thin-walled glass bulb, the melting point was obtained without mishap. It is −35.9 ± 0.2 °C.

The melting point of xenon trioxide difluoride was obtained with a sample contained in a small Kel-F tube fitted with a Kel-F valve. It is −54.1 ± 0.5 °C.

A Helicoid gauge was used for vapor-pressure measurements with this sample. The following were obtained (torr): −50.4 °C, 4; −50.8 °C, 5; −36.9 °C, 12; −36.8 °C, 10; −29.3 °C, 22; −28.0 °C, 24.

These correspond to a heat of vaporization of 33.0 kJ/mol, $\sigma = 3.0$. Within experimental error this cannot be distinguished from the heat of vaporization of xenon tetraoxide, calculated from published data.[18] But the extrapolated normal boiling points of xenon trioxide difluoride and xenon tetraoxide are about 40 and 85 °C, respectively.

It was not possible to make sufficient xenon dioxide tetrafluoride for measurement of its melting point or vapor pressure. But mass spectrometric observation of its distillation made clear that it is more volatile than xenon trioxide difluoride and is therefore the most volatile known xenon compound. Xenon tetraoxide is the most volatile molecular tetraoxide, and volatility increases with progressive substitution of its oxygen by fluorine to form oxide fluorides. A similar sequence of increasing volatility for compounds of xenon(VI) can be observed with xenon trioxide, xenon dioxide difluoride, and xenon oxide tetrafluoride.

Negative-Ion Mass Spectra

Positive-ion mass spectra of xenon molecular compounds usually show molecular ions and all expected fragment ions. (The molecular ion of xenon hexafluoride is observed only with great difficulty.)[19] Table II lists negative-ion mass spectra for these compounds. Curiously, only for xenon hexafluoride is the molecular ion observed with ease. For the four oxide fluorides, fluorine-containing fragments are more often observed than oxygen-containing fragments. Fragments always are observed containing all fluorine atoms in the molecule, but not all oxygen atoms. For instance, the spectrum of XeO_2F_2

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(15) Peacock, R. D.; Selig, H.; Sheft, I. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2561.

(16) Bougon, R.; Charpin, P.; Desmoulin, J. P.; Malm, J. G. *Inorg. Chem.* **1976**, *15*, 2532.

(17) LeBlond, R. D.; DesMarteau, D. P. *J. Chem. Soc., Chem. Commun.* **1974**, 555.

(18) Selig, H.; Claassen, H. H.; Chernick, C. L.; Malm, J. G.; Huston, J. L. *Science* **1964**, *143*, 1322.

(19) Studier, M. H.; Sloth, E. N. In "Noble Gas Compounds"; Hyman, H. H., Ed.; University of Chicago Press: Chicago, 1963; p 49.

contains XeF_2^- but not XeO_2^- or XeO_2F^-. These observations are consistent with the greater electronegativity of fluorine.

If the spectra of oxide fluoride molecules containing a certain number of fluorine atoms are compared, it can be seen that an increase in the number of oxygen atoms tends to increase the number of oxygen-containing fragments and their intensities relative to fragments containing only xenon and fluorine. This can be seen from the spectra of XeO_4 and XeO_2F_4.

Pictures of the negative-ion spectra of xenon oxide tetrafluoride[19] and xenon dioxide difluoride[3] have previously been published.

Acknowledgment. I thank Evan Appelman and John Malm for helpful discussion and Felix Schreiner for a sample of xenon tetrafluoride.

Registry No. XeF_4, 13709-61-0; XeF_6, 13693-09-9; XeO_4, 12340-14-6; XeO_3F_2, 15192-14-0.

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Base Hydrolysis of Pentaamminecobalt(III) Complexes of Urea, Dimethyl Sulfoxide, and Trimethyl Phosphate

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The base hydrolysis of the $[(NH_3)_5CoL]^{3+}$ ions (where L is $(NH_2)_2C{=}O$, $(CH_3)_2S{=}O$, and $(CH_3O)_3P{=}O$) and the $[(NH_3)_5CoOSO_3]^+$ ion has been studied over a range of conditions. Trace studies (with $^{18}OH_2$) show that the three 3+ ions cleave very largely (>97%) by Co–O bond rupture with rate laws of the form $-d[(NH_3)_5CoL^{3+}]/dt = k[(NH_3)_5CoL^{3+}][OH^-]$. In the presence of azide ion, both $[(NH_3)_5CoOH]^{2+}$ and $[(NH_3)_5CoN_3]^{2+}$ are produced. The ratio of these products is constant among the 3+ substrates but differs from that observed with the $[(NH_3)_5CoOSO_3]^+$ ion and with complexes of the type $[(NH_3)_5CoX]^{2+}$, where X includes a variety of anions. The results support the conjugate base dissociative (S_N1cB) mechanism where the short-lived intermediate five-coordinate species captures the atmosphere of its immediate precursor. Some results obtained with the neutral competitor methanol are reported, and the evidence for the mechanism is reviewed.

Introduction

Studies on a variety of $[Co(NH_3)_5X]^{2+}$ complexes have accumulated evidence in support of a conjugate base dissociative (S_N1cB) mechanism for hydrolysis under basic conditions.[2-4] The evidence derives from kinetic studies,[5] competition studies using the isotopes of water[6] and anions,[7] stereochemical studies,[4,8] and the examination of sterically crowded molecules,[9] all of which indicate the existence of an intermediate of reduced coordination number. In many cases it has been demonstrated that deprotonation at a coordinated amine center precedes hydrolysis of the cobalt–ligand bond. In most of the anion competition studies, the leaving group has been anionic, usually with unit charge. This paper explores the competition properties further for the neutral leaving groups urea, dimethyl sulfoxide, and trimethyl phosphate, with selected anionic (azide, acetate, and thiocyanate ions) and neutral (methanol) competitors. In order to determine the dependence of anion competition (with N_3^-) on the charge of the substrate, we have also examined the base hydrolysis of the $[Co(NH_3)_5OSO_3]^+$ ion, where the leaving group is a dianion.

For each of the 3+ complexes, the possibility existed that O-coordination to Co(III) might enhance the susceptibility of the ligand to nucleophilic attack by hydroxide ion and that this pathway might be competitive with cobalt–oxygen bond fission. Hydroxide ion dependent hydrolysis of the $[(NH_3)_5CoOCH{\cdot}NMe_2]^{3+}$ ion has been observed to give $[(NH_3)_5CoOOCH]^{2+}$ and $NHMe_2$. It occurs at a rate ~10^4-fold faster than the hydrolysis of the uncoordinated ligand.[10] A similar reaction of hydroxide ion with the $[(NH_3)_5CoOC(NH_2)_2]^{3+}$ ion would, for example, produce either NH_3 and $[(NH_3)_5CoO_2CNH_2]^{2+}$ or free urea and $[(NH_3)_5CoOH]^{2+}$, in which the oxygen atom derived from urea, depending on the leaving group from the tetrahedral (at carbon) intermediate. If ammonia were the leaving group, the reaction could model the chemistry of jack bean urease, the nickel metalloenzyme[11] which produces ammonium carbamate as the initial product of the hydrolysis of urea.[12] The $[(NH_3)_5CoO_2P(OMe)_2]^{2+}$ ion could be produced from $[(NH_3)_5CoOP(OMe)_3]^{3+}$ by an analogous route. Oxygen-18 tracer studies have been used to determine the positions of bond cleavage, and the kinetics of base hydrolysis of the complexes are described.

Experimental Section

Visible spectra were recorded with Cary 14 or Cary 118C spectrophotometers. ^1H NMR spectra were measured with JEOL Minimar (100MHz) or Varian T60 spectrometers using Me_2SO-d_6

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(1) (a) The Australian National University. (b) University of New South Wales.

(2) Tobe, M. L. *Acc. Chem. Res.* **1970**, *3*, 377 and references therein.

(3) Sargeson, A. M. *Pure Appl. Chem.* **1973**, *33*, 527 and references therein.

(4) Jackson, W. G.; Sargeson, A. M. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed; Academic Press: New York, 1980; Vol. 2, pp 321–335 and references therein.

(5) Ahmed, E.; Tucker, M. L.; Tobe, M. L. *Inorg. Chem.* **1975**, *14*, 1 and references therein.

(6) Green, M.; Taube, H. *Inorg. Chem.* **1963**, *2*, 948.

(7) Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1966**, *88*, 5443.

(8) Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1967**, *89*, 5129.

(9) Buckingham, D. A.; Foxman, B. M.; Sargeson, A. M. *Inorg. Chem.* **1970**, *9*, 1790.

(10) Buckingham, D. A.; Harrowfield, J. MacB.; Sargeson, A. M. *J. Am. Chem. Soc.* **1974**, *96*, 1726.

(11) Dixon, N. E.; Gazzola, C.; Blakely, R. L.; Zerner, B. *J. Am. Chem. Soc.* **1975**, *97*, 4131. Dixon, N. E.; Blakely, R. L.; Zerner, B. *Can. J. Biochem.* **1980**, *58*, 469. Dixon, N. E.; Gazzola, C.; Asher, C. J.; Lee, D. S. W.; Blakely, R. L.; Zerner, B. *Ibid.* **1980**, *58*, 474.; **1980**, *58*, 481.

(12) Blakely, R. L.; Hinds, J. A.; Kunze, H. E.; Webb, E. C.; Zerner, B. *Biochemistry* **1969**, *8*, 1991. Dixon, N. E.; Riddles, P. W.; Gazzola, C.; Blakely, R. L.; Zerner, B. *Can. J. Biochem.* **1980**, *58*, 1335.