

One might expect that since the excited state involves a substantial change in the dipole moment of the molecule, some aspect of the dielectric properties of the solvent should be important in defining the Stokes shift. We find evidence of this if we perform dual-parameter fitting procedures on the Stokes shift data. The correlation coefficient improves from the value of 0.884 found for pure acceptor number (excluding water) to 0.973 if the solvent dielectric continuum¹² parameter ($1/n^2 - 1/Ds$) is used in a dual-parameter fit along with acceptor number. The improvement in the fit is illustrated in Figure 2B. An improvement of nearly equal magnitude is obtained if the dipole-solvation solvent parameter $(1 - Ds)/(2Ds + 1)$ due to Onsager is used.¹³

Experimental Section

$\text{Ru}(\text{bpy})_2(\text{CN})_2$ was synthesized according to the method outlined by Demas and co-workers. MLCT band maxima and extinction coefficients were found to be in good agreement. All solvents were reagent grade or better and were stored over activated 3-Å molecular sieves for at least 8 h prior to use.

The electrochemical data were collected on an IBM 225 EC instrument by differential-pulse polarography vs an SCE. Absorption measurements were made on a Perkin-Elmer 330 spectrophotometer, and emission measurements were made on a Hitachi 650 recording fluorimeter thermostated to 23 ± 1 °C. Emission spectra were corrected for instrument response by using the standard dye 4-(dimethylamino)-4'-nitrostilbene.

Acknowledgment. Thanks are gratefully expressed to the Research Corp. for its generous support of this work.

Registry No. $(\text{bpy})_2\text{Ru}^{\text{II}}(\text{CN})_2$, 58356-63-1; $(\text{bpy})_2\text{Ru}^{\text{III}}(\text{CN})_2^+$, 58356-64-2.

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Convenient Synthesis of Xenon Oxide Tetrafluoride

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Received December 1, 1987

Xenon oxide tetrafluoride, XeOF_4 , is generally prepared by partial hydrolysis of XeF_6 using either dynamic or static methods. In the static methods XeF_6 is reacted with either H_2O or SiO_2 .¹ These reactions, particularly on a larger scale, are very hazardous and, unless great care is exercised, can result in violent explosions due to the localized formation of highly explosive XeO_3 . This hazard of the static methods can be diminished somewhat by the dynamic method of bleeding air saturated with water vapor into a circulating loop filled with XeF_6 vapor and monitoring the XeF_6 consumption by infrared spectroscopy.² The main drawback of this dynamic method is the requirement for complex hardware. A third method, involving the reaction of XeF_6 with SeO_2F_2 ,³ avoids the explosion hazard and appears scalable, but the SeO_2F_2 starting material is a highly toxic gas and is not readily available.⁴

Therefore, a safer and more convenient synthesis, using readily available reagents and lending itself to an easy scaleup, was highly desirable.

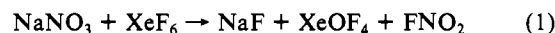
Experimental Section

Materials and Apparatus. NaNO_3 (J. T. Baker, 99.5%) was dried in a vacuum oven at 120 °C prior to its use. Xenon hexafluoride was prepared from Xe and F_2 and purified by complexing with NaF and subsequent vacuum pyrolysis of the adduct.^{5,6} Volatile materials were manipulated in a stainless steel vacuum line equipped with Teflon-FEP U-traps, 316 stainless steel bellows-seal valves, and a Heise Bourdon tube-type pressure gauge.⁷ Chlorine trifluoride was used for the passivation of the vacuum line, reactors, and any connections between them. Nonvolatile materials were handled in the dry N_2 atmosphere of a glovebox. Raman spectra were recorded on a Spex Model 1403 spectrophotometer using the 647.1-nm exciting line of a Kr ion laser. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer using a 5-cm path length Teflon cell with AgCl windows for gases and AgCl disks, pressed in an Econo press (Barnes Engineering Co.), for solids.

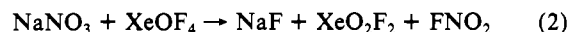
Preparation of XeOF_4 . In a typical experiment, finely powdered NaNO_3 (3.09 mmol) was loaded inside the glovebox into a prepassivated 10-mL stainless steel cylinder equipped with a stainless steel valve. The cylinder was connected to the vacuum line, and XeF_6 (3.41 mmol) was added at -196 °C. The cylinder was allowed to warm to room temperature and was then placed into a 70 °C oven for 10 h. It was reconnected to the vacuum line and cooled to -196 °C, and the volatile products were separated on warmup of the cylinder to ambient temperature by fractional condensation through two U-traps kept at -78 and -196 °C, respectively. The -78 °C trap contained pure XeOF_4 (2.54 mmol, 82% yield based on the limiting reagent NaNO_3), which was identified by its vapor pressure,² infrared spectrum as a gas,⁸ and Raman spectrum as a liquid.⁸ The -196 °C trap contained FNO_2 (3.01 mmol). The white solid residue in the cylinder (338 mg; weight calculated for 3.01 mmol of $\text{NaF} + 0.08$ mmol of $\text{NaNO}_3 + 0.63$ mmol of $\text{XeF}_6 + 0.24$ mmol of $\text{XeO}_2\text{F}_2 = 333$ mg) was spectroscopically identified as NaF and contained larger amounts of NaXeF_7 and Na_2XeF_8 ⁹ and smaller amounts of XeO_2F_2 ¹⁰ and NaNO_3 .

Results and Discussion

The reaction of NaNO_3 with a slight excess of XeF_6 provides a convenient, one-step synthesis of XeOF_4 according to



The use of an excess of NaNO_3 should be avoided to suppress the secondary reaction



The extent of (2) was less than 10% when a 10% excess of XeF_6 was used in (1). The reaction conditions for (1) were chosen in such a manner that the NaF byproduct complexes the excess XeF_6 by forming the NaXeF_7 and Na_2XeF_8 salts,^{9,11} thus allowing easy product separation. The NaXeF_7 and Na_2XeF_8 salts, NaF , and XeO_2F_2 are all nonvolatile at ambient temperature, and the only volatile products, XeOF_4 and FNO_2 , can be readily separated by fractional condensation through two traps kept at -78 and -196 °C, respectively. The yield of XeOF_4 is about 80% based on the limiting reagent NaNO_3 . The excess of XeF_6 , complexed with NaF , could easily be recovered by vacuum pyrolysis, if desired.

Compared to the previously used methods,¹⁻³ the above synthesis offers the following advantages: (i) elimination of the explosion hazard associated with the hydrolysis of XeF_6 , (ii) scalability, (iii)

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the use of a low-cost, nontoxic, commercially available starting material, and (iv) a simple, one-step process giving a pure product in high yield.

Acknowledgment. We are indebted to Dr. C. J. Schack and R. D. Wilson for their help and to the Office of Naval Research for financial support.

Registry No. XeOF₄, 13774-85-1; NaNO₃, 7631-99-4; XeF₆, 13693-09-9.

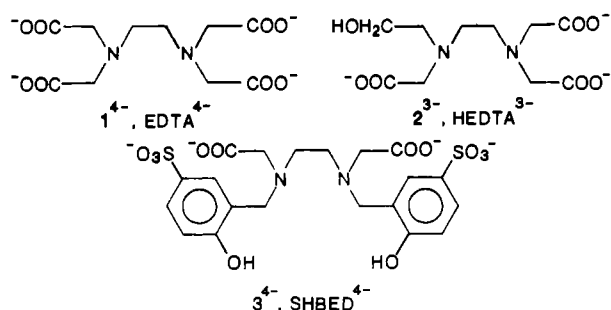
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Ferrous Chelates of EDTA, HEDTA, and SHBED

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Received December 9, 1987

In the course of investigating the kinetics of reduction of several dioxygen complexes by iron(II) chelates of EDTA (1, ethylenediamine-*N,N'*-tetraacetic acid), HEDTA (2, *N*-(hydroxyethyl)-ethylenediamine-*N,N'*-triacetic acid) and SHBED (3, *N,N'*-bis-(2-hydroxy-5-sulfobenzyl)ethylenediamine-*N,N'*-diacetic acid),



it was found that the reduction potentials of the ferrous chelates of EDTA and HEDTA do not vary with p[H] in the manner predicted by the equilibrium data in the literature. The hydrolysis constants of Fe(II)-EDTA reported by Schwarzenbach and Heller¹ (pK = ca. 9.1), together with the well-known hydrolysis constant of Fe(III)-EDTA² (pK = ca. 7.5) indicate that in a pH range where the monohydroxo forms of both Fe(II) and Fe(III) chelate compounds exist, the reduction potential should not vary very much with p[H]. The fact that this was found not to be the case led to the idea that the equilibrium data for Fe(II)-EDTA may be in error. This interpretation is reinforced by the fact that the hydrolysis constants published for the formation of Fe(OH)L³⁻ and Fe(OH)₂L⁴⁻ have no counterpart with the accepted equilibrium constants for the adjacent metal ions, Mn²⁺ and Co²⁺. A hydrolysis constant of similar magnitude reported for Fe(II)-HEDTA³ (pK = ca. 8.8) indicates that some of the other early work might also be in error. It was therefore decided to investigate these two ferrous chelate systems, along with the ferrous chelate of another ligand, SHBED, which is also being employed in our studies of the reduction of dioxygen complexes, to be reported separately.

Experimental Section

SHBED, obtained from Lyndal Chemical, was recrystallized from water acidified with acetic acid; the EDTA, HEDTA, and FeSO₄·7H₂O employed were of reagent grade quality and were used without further purification. Purity of all ligands was verified by titration with standard carbonate-free KOH. Carbonate-free 0.1 M potassium hydroxide solutions were prepared from Baker Dilut-It ampules with boiled distilled water and were standardized by titration with potassium hydrogen phthalate to a phenolphthalein end point. Gran's method⁴ was used to

Table I. Protonation and Fe(II) Chelate Formation Constants of EDTA, HEDTA, and SHBED

equilibrium quotient	formation constant		
	EDTA (H ₄ L)	HEDTA (H ₃ L)	SHBED ²⁻ (H ₄ L ²⁻)
[HL]/([L][H])	10.17 ^a	9.82	12.27 ^b
[H ₂ L]/([HL][H])	6.11 ^a	5.31	10.25 ^b
[H ₃ L]/([H ₂ L][H])	1.95 ^a	2.55	8.05 ^b
[H ₄ L]/([H ₃ L][H])	1.5 ^a		4.50 ^b
[H ₃ L]/([H ₄ L][H])			2.59 ^b
[H ₆ L]/([H ₅ L][H])			1.80 ^b
[ML]/([M][L])	14.94 ^c	12.58 ^c	19.75 ^c
[MHL]/([ML][H])	2.06 ^c	2.36 ^c	6.25 ^c
[MH ₂ L]/([MHL][H])			4.73 ^c

^aReferences 2 and 7. ^bReference 8. ^cThis work.

confirm the absence of carbonate in the potassium hydroxide standard solution and the absence of atmospheric contamination of the sample during the course of potentiometric equilibrium measurements.

Equilibrium Measurements. Potentiometric measurements were performed in a jacketed, airtight glass titration cell equipped with O-ring fittings for glass and saturated calomel electrodes and for gas inlet and outlet tubes. A Teflon adapter was used to attach a microburet to this vessel.

All solutions were adjusted to 0.100 M ionic strength by addition of potassium nitrate. The temperature was maintained at 25.00 ± 0.01 °C by circulating thermostated water through the outer jacket of the cell. Solutions were kept under an atmosphere of argon that was passed through alkaline pyrogallol scrubbers to remove oxygen and carbon dioxide and then equilibrated with water vapor by passage through a 0.100 M potassium nitrate solution.

Measurements were made with a Corning Model 130 pH meter calibrated with standard acid and base so that [H⁺] concentration was measured directly. For the purpose of this paper the term p[H] designates the negative log of the hydrogen ion concentration.

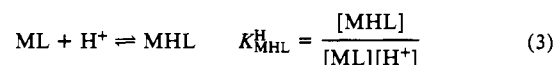
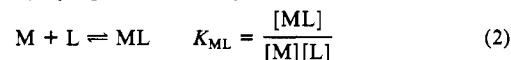
Ligand protonation constants, K_Hⁿ, as defined by

$$H_{n-1}L^{x+} + H^+ \rightleftharpoons H_nL^{(x+1)+} \quad K_H^n = \frac{[H_nL^{(x+1)+}]}{[H^+][H_{n-1}L^{x+}]} \quad (1)$$

were verified by potentiometric equilibrium measurements of 1.0 × 10⁻³ M solution of the acid form of each ligand in the absence of metal ions. These equilibrium constants were calculated by the computer program PKAS.⁵

Acid forms of organic ligands have often been found to contain nonstoichiometric amounts of water. By a systematic variation of the molecular weight so as to minimize the difference between observed and calculated p[H] values, corrected ligand concentrations were calculated.

Equilibria in the 1:1 metal-ligand systems were found to be represented adequately by eq 2-4. The experimental solutions contained



approximately 1 × 10⁻³ M Fe(II) and 1 × 10⁻³ M ligand. Potentiometric data were analyzed and the equilibrium constants were calculated with the aid of the computer program BEST.⁶

Results and Discussion

Careful potentiometric equilibrium p[H] measurements of 1:1 Fe²⁺-EDTA and Fe²⁺-HEDTA solutions with rigorous exclusion of oxygen gave p[H] profiles showing no indication of hydrolysis up to p[H] 12. Calculation of the equilibrium constants of these systems by the methods previously described,^{5,6} gave only the formation constants of the simple 1:1 chelates and constants for the formation of monoprotonated species at low p[H]. The equilibrium constants for these complexes and the corresponding

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