Finally, by difference, 40% of the CT excitation energy is dissipated directly to the ground state, without passing through the LF energy levels.

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Registry No. *trans*-$[Cr(NH_3)_4(CN)Cl]ClO_4$, 116301-75-8; *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$, 19544-03-7; NH_3, 7664-41-7; CN^-, 57-12-5; Cl^-, 16887-00-6.

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Protolytic Properties of Perxenic Acid

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Spectra and protolytic properties of aqueous perxenic acid in the pH range −0.2 to 13 were studied by conventional and stopped-flow spectrophotometry. The following p*K* values and limits were found (25.0 °C): $pK_{H_4XeO_6} < 0$, $pK_{H_3XeO_6^-} = 4.29 \pm 0.03$; $pK_{H_2XeO_6^{2-}} = 10.81 \pm 0.04$. The enthalpy of dissociation (25.0 °C) of $H_3XeO_6^-$ is 0 ± 5 kJ mol^{-1}; that of $H_2XeO_6^{2-}$ is 3 ± 2 kJ mol^{-1}.

Introduction

Because of the rapid decomposition of perxenates by acids[1,2]

$$HXeO_6^{3-} + 3H^+ \rightarrow XeO_3 + 2H_2O + \tfrac{1}{2}O_2 \qquad (1)$$

little is known of the equilibrium properties of perxenic acid in acid aqueous solution. It has been pointed out, however, that perxenic acid may possess unusual protolytic properties.[3] Raman spectra of aqueous alkaline perxenate solutions show that the Xe(VIII) species present in these solutions are octahedrally coordinated,[4] which implies the formula H_4XeO_6 for the perxenic acid itself. This accords with the crystal structure of alkali-metal perxenates.[5]

Protonation of perxenate to $H_3XeO_6^-$ and H_4XeO_6 has not heretofore been observed because of the rapidity of reaction 1. A p*K* value of 10.5 has been measured for the acid dissociation of $H_2XeO_6^{2-}$,[3] and a lower p*K* limit of 14 has been set for the dissociation of $HXeO_6^{3-}$.[4] Assumption of a 4–5 unit difference between successive pK's suggests $pK_1 \sim 2$ for the acid dissociation of H_4XeO_6, in disagreement with Pauling's empirical rules,[6] which predict a value between −2 and −3 for pK_1 of such an acid. In the present investigation we have determined the protolytic equilibria of perxenic acid in the pH range −0.2 to 13 by time-resolved spectrophotometric measurements.

Experimental Section

Time-resolved absorbance measurements of perxenate solutions were made at pH <7 with an Aminco-Marrow stopped-flow apparatus[7] and at pH >7 with a Cary 219 spectrophotometer. A cell length of 1 cm was used with both instruments. The temperature was kept constant to within 0.1 °C. A few experiments were made with a nonthermostated SF-51 High-Tech stopped-flow spectrophotometer with an optical path of 0.2 cm. The temperature in these experiments was ambient (23 ± 2 °C).

Absorbance readings on the Aminco-Marrow instrument were calibrated against readings on the Cary instrument in the wavelength range $200 < \lambda < 300$ nm, using a 10^{-4} mol dm^{-3} periodate solution at pH 11, which has a spectrum similar to that of perxenate solutions (vide infra). The error of absorbance readings on the stopped-flow instruments was typically 1–2%. A source of error in the present stopped-flow measurements was a slow decomposition of the perxenate stock solution when kept in the storage syringe of the Aminco-Marrow instrument. Correction for the decomposition was obtained by repeating the measurements in the opposite order with fresh solutions.

The solution studied resulted from mixing a perxenate stock solution, which contained 10^{-2} mol dm^{-3} NaOH and 10^{-4} to 3×10^{-3} mol dm^{-3} Na_4XeO_6, with an equal volume of a solution containing a buffer or an acid. Perxenate stock solutions were prepared by dissolving an appropriate quantity of sodium perxenate, weighed on a Cahn Electrobalance, in 5 or 10 mL of 10^{-2} mol dm^{-3} NaOH solution. Ionic strength was adjusted with sodium perchlorate. The pH of the mixed solution at zero time after the mixing was set equal to the pH of a solution that resulted from mixing with the buffer or acid a solution of the same composition as the stock solution but in which sodium perxenate was replaced by an appropriate quantity of sodium hydroxide. The pH was measured with a Radiometer pH M 64 Research pH meter using a Radiometer G 202 C glass electrode and a Radiometer K 701 calomel electrode. The pH calibration was made with Radiometer type S 1316 and S 1326 standard buffers.

Scheme I

$$H_4XeO_6 = H_3XeO_6^- + H^+ \qquad (2)$$

$pK_1 < 0^a$

$$H_3XeO_6^- = H_2XeO_6^{2-} + H^+ \qquad (3)$$

$pK_2 = 4.29 \pm 0.03;^a\ \Delta H_2° = 0 \pm 5$ kJ mol^{-1} ^{a,d}

$$H_2XeO_6^{2-} = HXeO_6^{3-} + H^+ \qquad (4)$$

$pK_3 = 10.75 \pm 0.02,^b\ 10.8,^b\ 10.81 \pm 0.04;^{a,d}\ \Delta H_3°, = 3 \pm 2$ kJ mol^{-1} ^{a,d}

$$HXeO_6^{3-} = XeO_6^{4-} + H^+ \qquad (5)$$

$pK_4 > 14^c$

[a] This work. [b] Data from ref 3 extrapolated to zero ionic strength. [c] Reference 4. [d] Error estimated.

Acids were titrated with sodium hydroxide solutions standardized against potassium hydrogen phthalate. Sodium perxenate was prepared as described previously.[3] The molar weight was 380. Perchloric acid and sulfuric acid were Merck Suprapur. Water was triply distilled. All other chemicals were Merck p.a.

Results and Discussion

Protolytic Properties. Scheme I shows protolytic equilibria among perxenate species at 25.0 °C. (Unless stated otherwise, the errors given are standard deviations obtained by least-squares treatment).

The spectra of perxenate solutions in the pH regions −0.2 to 2, 6 to 8, and 12 to 13, which we assign to $H_3XeO_6^-$, $H_2XeO_6^{2-}$, and $HXeO_6^{3-}$, respectively, are shown in Figure 1.

The spectra of $HXeO_6^{3-}$, $H_2XeO_6^{2-}$, and XeO_3 agree with spectra measured previously.[3] Molar absorption coefficients determined here of $HXeO_6^{3-}$ at 239 nm (max), of $H_2XeO_6^{2-}$ at

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(1) Malm, J. G.; Appelman, E. H. *At. Energy Rev.* **1969**, *No. 3*.
(2) Appelman, E. H.; Anbar, M. *Inorg. Chem.* **1965**, *4*, 1066.
(3) Appelman, E. H.; Malm, J. G. *J. Am. Chem. Soc.* **1964**, *86*, 2141.
(4) Downey, G. D.; Claassen, H. H.; Appelman, E. H. *Inorg. Chem.* **1971**, *10*, 1817.
(5) Zalkin, A.; Forrester, J. D.; Templeton, D. H.; Williamson, S. M.; Koch, C. W. *J. Am. Chem. Soc.* **1964**, *86*, 3569. Ibers, J. A.; Hamilton, W. C.; Mac Kenzie, D. R. *Inorg. Chem.* **1964**, *3*, 1412. Zalkin, A.; Forrester, J. D., Templeton, D. H. *Inorg. Chem.* **1964**, *3*, 1417.
(6) Pauling, L. *General Chemistry*, 3rd ed.; W. H. Freeman: San Francisco, CA, 1970. (The correlation was originally presented in the 1st edition of 1940.)
(7) Kläning, U. K.; Sehested, K.; Holcman, J., *J. Phys. Chem.* **1985**, *89*, 760.

0020-1669/88/1327-3760$01.50/0

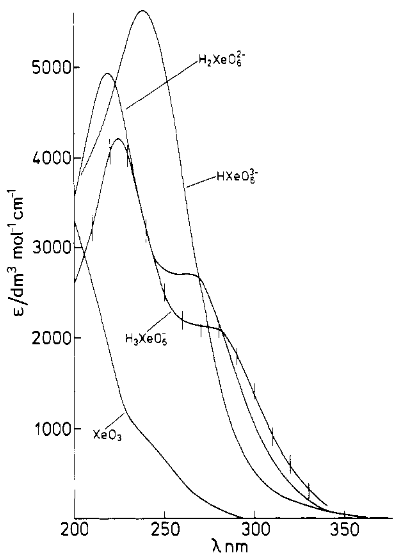

Figure 1. Spectra of XeO_3, $H_3XeO_6^-$, $H_2XeO_6^{2-}$, and $HXeO_6^{3-}$. (The vertical bars on the $H_3XeO_6^-$ curve indicate uncertainties.)

219 nm (max), and of XeO_3 at 200 nm are 5620, 4920, and 3350 $dm^3\ mol^{-1}\ cm^{-1}$, respectively. The corresponding values previously determined are 5600, 4950, and 3300 $dm^3\ mol^{-1}\ cm^{-1}$.[3] The spectra shown in Figure 1 are normalized to the latter values. The spectrum of $H_2XeO_6^{2-}$ was obtained from optical densities of perxenate solutions in 10^{-2} mol dm^{-3} phosphate buffers at pH 7-8 measured at 1-min intervals and extrapolated to zero time after preparation of the solution.

The stoichiometry of reaction 1 under the present conditions was verified by measuring the absorption spectrum before and after acidifying a perxenate solution that was originally at pH 12.5.

The spectrum of $H_3XeO_6^-$ was obtained from stopped-flow spectrophotometric measurements by observing the absorbance change, ΔOD, after mixing of perxenate solutions with solutions of perchloric acid or sulfuric acid. Assuming that ΔOD is caused by the reaction

$$H_3XeO_6^- + H^+ \rightarrow XeO_3 + 2H_2O + \tfrac{1}{2}O_2 \qquad (6)$$

we determined the molar absorption coefficient of $H_3XeO_6^-$, $\epsilon_{H_3XeO_6^-}$, from the relation $\Delta OD = (\epsilon_{H_3XeO_6^-} - \epsilon_{XeO_3})lc$ and the molar absorption coefficient of XeO_3, ϵ_{XeO_3} measured in the present work. l is the length of the optical cell, and c is the initial concentration of $H_3XeO_6^-$.

The kinetics of reaction 6 are complex and appear to be irreproducible at low perxenate concentration.[8] However, in the present measurements the uncertainty of the extrapolation of ΔOD to zero time necessitated by the dead-time of the instrument (3×10^{-3} s) was not larger than 2-3%.

No change of the molar absorption coefficients of $H_3XeO_6^-$ and $H_2XeO_6^{2-}$ was observed upon changing the perxenate concentration from 5×10^{-5} to 5×10^{-3} mol dm^{-3} and the temperature from 15 to 30 °C and 0 to 30 °C, respectively.

The present assignment of spectra leads to an upper limit of zero for pK_1. A value of pK_2 was determined from stopped-flow measurements of ΔOD at 265 nm, extrapolated to zero time after mixing at 10^{-2} mol dm^{-3} NaOH solution containing 4×10^{-4} mol dm^{-3} sodium perxenate with an equal volume of a solution containing 0.2 mol dm^{-3} of an acetate or a phosphate buffer. The ionic strength was adjusted to 0.1 mol dm^{-3} by addition of sodium perchlorate to the buffer solution. ΔOD at zero time should be related to the measured pH by

$$pH = pK_2 - \log(f^-/f_2^-) - \log((\Delta OD_{pH7} - \Delta OD)/(\Delta OD - \Delta OD_{pH2})) \qquad (7)$$

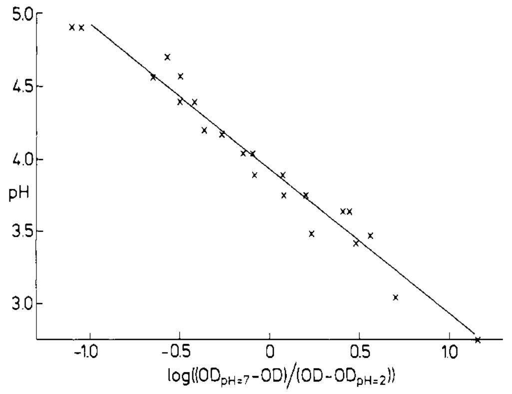

Figure 2. pH of perxenate solutions containing acetate or phosphate buffers versus log $((\Delta OD_{pH7} - \Delta OD)/(\Delta OD - \Delta OD_{pH2}))$. ΔOD is the absorbance change at 265 nm caused by reaction 6 and is measured by stopped-flow spectrophotometry.

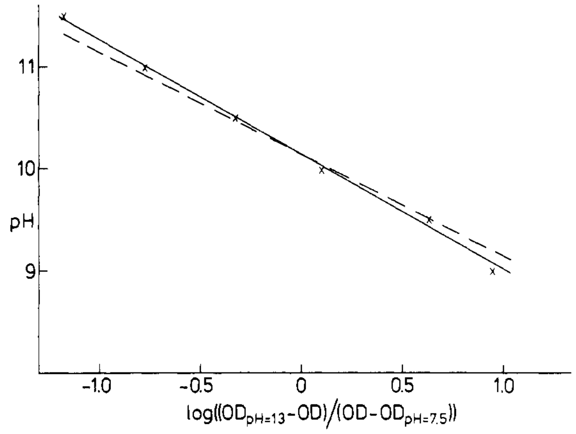

Figure 3. pH of perxenate solutions containing borate or phosphate buffers versus log $((OD_{pH13} - OD)/(OD - OD_{pH7.5}))$. OD is the optical density at 245 nm of the perxenate solution, extrapolated to zero time after preparation of the solution. Data are taken from ref 3 and unpublished addenda thereto. The stippled line is drawn with the theoretical slope of −1.

in which f^- and f_2^- are activity coefficients of singly and doubly charged ions, respectively. The findings agree with eq 7. The data are plotted in Figure 2. The straight line through the points represents a least-squares fit of pH to a linear function of log $((\Delta OD_{pH7} - \Delta OD)/(\Delta OD - \Delta OD_{pH2}))$. The slope is -0.99 ± 0.06, and the intercept is 3.92 ± 0.03. With f^- and f_2^- calculated by Güntelberg's formula for activity coefficients,[9] we find $pK_2 = 4.29 \pm 0.03$ (25 °C).

From the observation that the quantity $(\Delta OD_{pH7} - \Delta OD)/(\Delta OD - \Delta OD_{pH2})$ measured in acetate buffer at pH 4.02 was constant between 20 and 30 °C and the fact that the enthalpy of dissociation of acetic acid[9] is small over the same temperature range, we estimate the enthalpy of dissociation of $H_3XeO_6^-$: $\Delta H_2^\circ = (0 \pm 5)$ kJ mol^{-1} at 25.0 °C.

A pK value of 10.5 for the dissociation of $H_2XeO_6^{2-}$ at an ionic strength of 0.02 mol dm^{-3} was obtained previously by an electrometric titration of an alkaline sodium perxenate solution with perchloric acid.[3] With the use of Güntelberg's formula for calculating coefficients,[9] this value leads to $pK_3 = 10.8$ at zero ionic strength. We applied a least-squares treatment similar to that above to previously measured molar absorbancies of perxenate in various buffer solutions[3] at $7.5 < pH < 13$ and obtained a pK value of 10.13 ± 0.02 at an ionic strength of 0.1 mol dm^{-3}. By the use of Güntelberg's formula for activity coefficients, this corresponds to $pK_3 = 10.75 \pm 0.02$ at zero ionic strength.

Note, however, from Figure 3 that the slope of the straight line determined by the least-squares treatment deviates significantly

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(8) Kläning, U. K.; Bjergbakke, E.; Sehested, K., to be submitted for publication.

(9) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed. (revised); Butterworths: London, 1970.

Table I. p*K* Values and Standard Gibbs Energies of Formation, $\Delta_f G°$, of Perxenic Acid and Perxenate Anions at 25.0 °C

	H_4XeO_6	$H_3XeO_6^-$	$H_2XeO_6^{2-}$	$HXeO_6^{3-}$	XeO_4^{4-}
p*K*	−3 to 0[a]	4.29 ± 0.03	10.81 ± 0.04	>14	
$\Delta_f G°$/kJ mol^{-1}	260 ± 10[b]*	250 ± 20*	275 ± 20*	335 ± 20*	>420

[a] Lower limit, Pauling's rule; upper limit, this work. [b] Reference 1; an asterisk denotes errors estimated.

from the theoretical value of −1. Moreover, because of the high charge of the perxenate anions, Güntelberg's formula for activity coefficients may not be valid at the present ionic strength. To obtain a more realistic value for pK_3 we have measured

$$K = [CO_3^{2-}][H_2XeO_6^{2-}]/[HXeO_6^{3-}][HCO_3^-] \qquad (8)$$

for the equilibrium

$$HXeO_6^{3-} + HCO_3^- = H_2XeO_6^{2-} + CO_3^{2-} \qquad (9)$$

at $[HCO_3^-] \sim [CO_3^{2-}]$ varying between 2.5×10^{-3} and 2.5×10^{-2} mol dm^{-3}, and with the perxenate concentration adjusted to $10^{-2} \times [CO_3^{2-}]$.

The ratio $Q = [H_2XeO_6^{2-}]/[HXeO_6^{3-}]$ was measured as

$$Q = (OD_{pH12.7} - OD)/(OD - OD_{pH7.9}), \qquad (10)$$

where $OD_{pH12.7}$, $OD_{pH7.9}$, and OD are optical densities of perxenate solutions containing 5×10^{-2} mol dm^{-3} NaOH, 5×10^{-2} mol dm^{-3} phosphate buffer, and carbonate–hydrogen carbonate, respectively. Perxenate solutions containing carbonate and hydrogen carbonate in almost equal concentrations were prepared by mixing a sodium hydroxide solution containing perxenate with an equal volume of a solution containing $NaHCO_3$ in a concentration twice that of the sodium hydroxide.

The concentrations of CO_3^{2-} and HCO_3^-, corrected for the hydrolysis of CO_3^{2-} and reactions with perxenate, were found from the relations: $[CO_3^{2-}] = [NaOH] + [Na_4XeO_6] + [H_2XeO_6^{2-}] - [OH^-]$ and $[HCO_3^-] = [NaHCO_3] - [CO_3^{2-}]$, where [NaOH], $[Na_4XeO_6]$, and $[NaHCO_3]$ denote concentrations of added substances. $[OH^-]$ was determined by pH measurements and $[H_2XeO_6^{2-}]$ from measurements of Q, and $[Na_4XeO_6] = [H_2XeO_6^{2-}] + [HXeO_6^{3-}]$.

In Figure 4 log K at 25 °C is plotted against the square root of the ionic strength, $\sqrt{\mu}$. The points indicate a negative curvature. The straight line represents a least-squares fit of the data, excluding the point at $\mu = 0.1$ mol dm^{-3}. A value pK_3 = 10.82 ± 0.02 was obtained by extrapolating log K to zero ionic strength and taking $pK_{HCO_3^-} = 10.33$ for the dissociation of HCO_3^-.[10] By extrapolating linearly from the value of log K at $\sqrt{\mu} \sim 0.1$ to zero ionic strength, taking the slope as equal to that of the Debye-Hückel limiting law, we obtain pK_3 = 10.81. We estimate the error not to be larger than ±0.04.

The enthalpy of dissociation of $H_2XeO_6^{2-}$ at 25.0 °C, $\Delta H_3°$, was estimated from measurement of K at varying temperatures

$$\Delta H_3° = \Delta H°_{HCO_3^-} - RT^2(\partial(\ln K)/\partial T)_p \qquad (11)$$

$(\partial(\ln K)/\partial T)_p$ was approximated by $\Delta(\ln Q + \ln \sum_i f_i)/\Delta T$. Q was measured at $\mu = 0.1$ mol dm^{-3}. At 20.4, 25.2, and 29.5 °C, we find ln Q = −0.03, 0.05, and 0.11 with the estimated errors of ±0.02. Accordingly, we take $\Delta(\ln Q)/\Delta T = (1.5 \pm 0.3) \times 10^{-2}$ K^{-1}. The term $\Delta(\ln \sum_i f_i)/\Delta T$ is small compared to $\Delta(\ln Q)/\Delta T$. From the straight line in Figure 4, we find $\Delta(\ln \sum_i f_i) = 2.3\alpha\sqrt{\mu}$ ln 10, where α is the constant of the Debye–Hückel limiting law for activity coefficients, f_i. We take $\Delta(\ln \sum_i f_i)/\Delta T = 2.3\sqrt{\mu}$ ln 10 dα/dT. With $\mu = 0.1$ mol dm^{-3} and dα/dT = 10^{-3} K^{-1},[10] $\Delta(\ln \sum_i f_i)/\Delta T = 1.7 \times 10^{-3}$ K^{-1}. Taking $\Delta H°_{HCO_3^-} = 15.1$ kJ mol^{-1},[10] we find $\Delta H_3° = (3 \pm 2)$ kJ mol^{-1}.

The present determination of acid dissociation constants leads to new estimates for the standard Gibbs energies of formation of the perxenate anions (Table I).

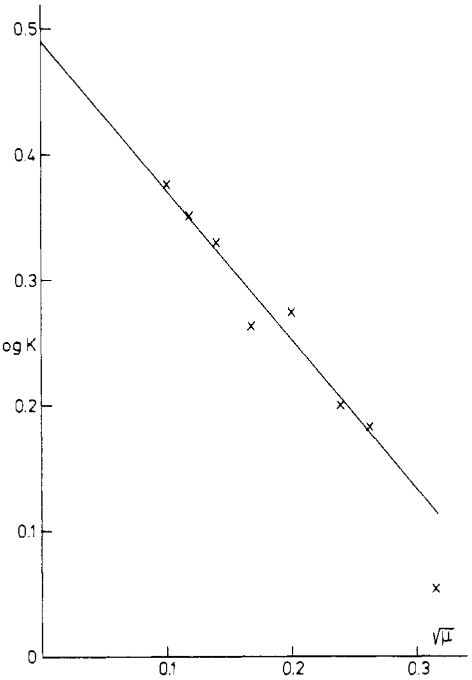

Figure 4. Logarithm of the equilibrium constant K for the equilibrium $HCO_3^- + HXeO_6^{3-} = CO_3^{2-} + H_2XeO_6^{2-}$, plotted against the square root of the ionic strength $\mu \sim 4[CO_3^{2-}]$.

Both Pauling's empirical correlation[6] and the more involved treatment by Ricci[11] predict that an acid of the formula H_4XeO_6 should have about the same ionization constant as sulfuric acid (p*K* between −2 and −3), while p*K* values for the subsequent ionization steps are expected to differ by 4–5 units. We see from Table I that the p*K* values for the second and third ionization of perxenic acid differ by about 6.5 units, and a comparable difference between the p*K*'s for the first and second ionizations is required if perxenic acid is, in fact, to be as strong as sulfuric acid. Such large differences between successive ionization constants of simple oxoacids, while unusual, are not unknown; they appear in such familiar acids as H_2CO_3 and H_2CrO_4.[12] Substantial deviations from Pauling's rules can also reflect changes in coordination or aggregation accompanying ionization, although in the present case the deviations do not appear to be of sufficient magnitude to warrant invoking such elaborate explanations.

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Registry No. H_4XeO_6, 14125-26-9.

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(10) Harned, H. S.; Owens, B. B. *The Physical Chemistry of Electrolytic Solutions*: Reinhold: New York, 1968.

(11) Ricci, J. E. *J. Am. Chem. Soc.* **1948**, *70*, 109.

(12) Perrin, D. D. *Ionisation Constants of Inorganic Acids and Bases in Aqueous Solution*, 2nd ed.; IUPAC Chemical Data Series No. 20; Pergamon: New York, 1982.