

Table IV. Results for Te(IV) Equilibria in KAlCl_4 Based on Spectrophotometric Measurements

Processes	pK regions in 0.10 F TeCl_4 soln
$\text{TeCl}_6^{2-} \rightleftharpoons \text{TeCl}_5^- + \text{Cl}^-$	0.17-1.06
$\text{TeCl}_5^- \rightleftharpoons \text{TeCl}_4 + \text{Cl}^-$	1.10-3.25
$\text{TeCl}_4 \rightleftharpoons \text{TeCl}_3^+ + \text{Cl}^-$	2.92-4.62

Discussion

As the measurements and calculations show, there seems to be a well-established case of stepwise chloro complex formation for Te(IV) in KAlCl_4 . In the present work it was impossible to detect any special trend in the calculated pK regions as a function of concentration. However, if it is assumed that the difference between the pK regions calculated at 0.10 and 0.30 F Te(IV) for the reaction $\text{TeCl}_6^{2-} \rightleftharpoons \text{TeCl}_5^- + \text{Cl}^-$ is due to a variation in the activity coefficient for K_2TeCl_6 , a change of ca. 17% in the activity coefficient will bring the mean values to coincide. This change is, as mentioned above, comparable to the maximum variation expected for the activity coefficient.

As an extension of the present work it would be important to perform measurements at pCl^- values higher than those used here. If linear extrapolation is valid for the pK values for the formation of TeCl_2^{2+} , a value of about 4.3 is obtained. This value is still much smaller than the pK found for the self-dissociation of KAlCl_4 mentioned above. There are therefore reasons to expect that TeCl_2^{2+} can be found in solutions. Contrary to this, Raman spectra of the $\text{AlCl}_3\text{-TeCl}_4$ system²⁰ do not indicate any formation of TeCl_2^{2+} , but it is of course possible that TeCl_2^{2+} is only present in

(20) F. W. Poulsen, N. J. Bjerrum, and O. F. Nielsen, to be submitted for publication.

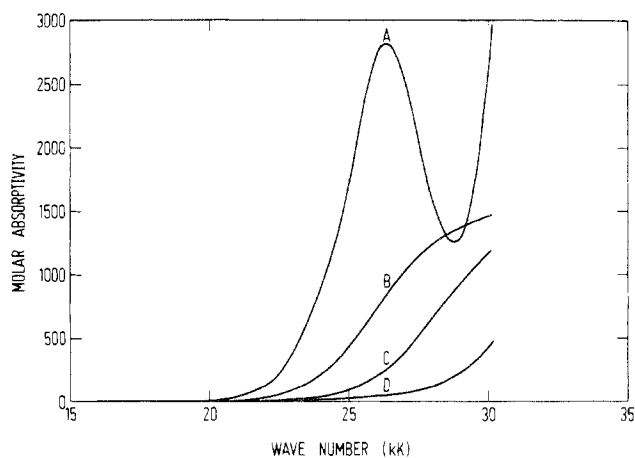


Figure 3. Calculated spectra: A, TeCl_6^{2-} ; B, TeCl_5^- ; C, TeCl_4 ; D, TeCl_3^+ . The solvent was KAlCl_4 at 300° . Each spectrum was calculated on the basis of nine measured spectra by use of the pK values of 0.71, 2.19, and 3.76 for the reactions $\text{TeCl}_6^{2-} \rightleftharpoons \text{TeCl}_5^- + \text{Cl}^-$, $\text{TeCl}_5^- \rightleftharpoons \text{TeCl}_4 + \text{Cl}^-$, and $\text{TeCl}_4 \rightleftharpoons \text{TeCl}_3^+ + \text{Cl}^-$, respectively.

small concentrations. In another experiment we intend to measure the values of the pK's as a function of the reciprocal value of the absolute temperature. Here a linear dependence would only be expected, if the above models are correct.

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Kinetic Study of the Reaction $\text{Np(VII)} + \text{V(IV)} \rightarrow \text{Np(VI)} + \text{V(V)}$ in Aqueous Perchloric Acid Media¹

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The title reaction has been investigated by the stopped-flow technique as a function of acidity, ionic strength, and temperature. At constant $[\text{H}^+]$ the empirical form of the rate law is $-\text{d}[\text{Np(VII)}]/\text{d}t = k''[\text{Np(VII)}][\text{VO}^{2+}]$ where k'' exhibits only a slight acid dependence most conveniently expressed as $\log k'' = \log k + n \log [\text{H}^+]$. At 25° and $\mu = 1.00$, with k'' expressed in units of $F^{-1} \text{sec}^{-1}$, $\log k = 3.159 \pm 0.005$ and $n = -0.112 \pm 0.076$. The temperature dependence of k over the range $2.7\text{-}25^\circ$ results in a value of 7.3 ± 0.9 kcal/mol for the Arrhenius activation energy. Rate parameters for the title reaction, which is of one-to-one stoichiometry, are compared to the corresponding parameters governing the two-to-one oxidation of Hg_2^{2+} by Np(VII) , as well as to the corresponding parameters governing the one-to-one oxidation of VO^{2+} by the relatively weak oxidant Mn(III) . While the relative rates of these reactions are reflected primarily in ΔH^* , the importance of considering S^* as well as ΔS^* values is pointed out. It is also qualitatively noted that of the reported oxidations of VO^{2+} , that by Np(VII) is the most rapid and Np(VII) is the most powerful oxidant.

Introduction

Our previous studies designed to characterize the chemistry and reaction dynamics of the extremely powerful 1-equiv

oxidant Np(VII) have utilized the multiequivalent reductants H_2O ,^{4a} Tl(I) ,^{4b} and Hg(I) .^{4c} These reactions proceed at rates

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(2) Participant in the Argonne National Laboratory Summer Faculty Research Participation Program.

(4) (a) J. C. Sullivan and A. J. Zielen, *Inorg. Nucl. Chem. Lett.*, **5**, 927 (1969); (b) R. C. Thompson and J. C. Sullivan, *J. Amer. Chem. Soc.*, **92**, 3028 (1970); (c) M. A. Thompson, J. C. Sullivan, and E. Deutsch, *ibid.*, **93**, 5667 (1971).

measurable by conventional kinetic techniques. Among the considerations prompting investigation of the title reaction was a desire to determine what effects result when the reductant requires only a single equivalent change. The expected, and observed, increased rate of Np(VII) oxidation of a 1-equiv reductant has necessitated use of the stopped-flow technique and development of Np(VII)-handling procedures appropriate to this technique. This investigation also provides an opportunity to assess the relevance of a large free energy change to kinetic parameters by comparison with results previously reported for the oxidation of V(IV) by a variety of reactants.⁵

Experimental Section

Reagents. The preparation and standardization of Np(VII), perchloric acid, and lithium perchlorate solutions have been previously summarized.⁴ The primary stock solution of vanadyl perchlorate was prepared⁶ from a perchloric acid solution of reagent grade vanadyl sulfate to which a 2% stoichiometric excess of reagent grade barium hydroxide was added. The barium sulfate was removed and the solution evaporated until incipient crystallization and then cooled. The resulting crystals were dissolved in triply distilled water (negative tests for Ba²⁺ and SO₄²⁻), recrystallized from 4 F perchloric acid, and then dissolved in triply distilled water. A second stock solution of vanadyl perchlorate was prepared from vanadyl sulfate utilizing an ion-exchange procedure similar to that previously described.^{5c} Both solutions were standardized using the molar extinction coefficient for V(IV) at 7650 Å, 17.9 F⁻¹ cm⁻¹,⁷ and the concentration of the primary stock solution was also confirmed by standard redox titrimetry.⁶

Equipment. A Durrum Model D-110 stopped-flow spectrophotometer equipped with a storage oscilloscope was used for the kinetic studies. The absorbance-time output of this instrument was digitalized at 1000 equally spaced time intervals and stored in a Biomation 802 Transient Recorder which was interfaced for on-line operation with a Xerox Sigma V digital computer. For determinations carried out at temperatures other than 25°, the Durrum storage syringes were jacketed by means of machined brass tubing fitted to the syringes with O rings and thermostated water was circulated through the jackets. A separate thermostating system kept the temperature of the Durrum reaction system (drive syringes, mixing chamber, cuvette, etc.) constant to ±0.1° for all temperatures investigated.

Procedures. An aliquot of the Np(VII) stock solution in 1.25 F NaOH was injected into a volumetric flask containing the requisite quantities of perchloric acid and lithium perchlorate which had been equilibrated at a temperature sufficiently lower than the working temperature to compensate for the heat of neutralization. The acidic Np(VII) and V(IV) reactant solutions, both at the same ionic strength maintained with lithium perchlorate, were then quickly placed in the storage syringes. The Durrum reaction system was then flushed several times with the reagents and replicate rate determinations were carried out at 4400 Å where the molar extinction coefficient of Np(VII) (ca. 410 F⁻¹ cm⁻¹) is much larger than that of Np(VI), V(IV), or V(V). At the beginning of a given series of kinetic experiments the concentration of Np(VII) in the storage syringe was usually about (1–2) × 10⁻³ F and the corresponding concentration of V(IV) was at least 15 times greater (the concentration of a reactant in the reaction mixture is half its concentration in the storage syringe). As time progressed, the concentration of Np(VII) in the storage syringe decreased, and the concentration of Np(VI) increased, due to the relatively slow Np(VII) oxidation of water.^{4a} This decay could be monitored by the decreasing optical density changes observed on the storage oscilloscope during a series of experiments. Data collection was discontinued once the concentration of Np(VII) in the storage syringe reached about 1 × 10⁻⁴ F. This continuous variation of initial Np(VII) and Np(VI) concentra-

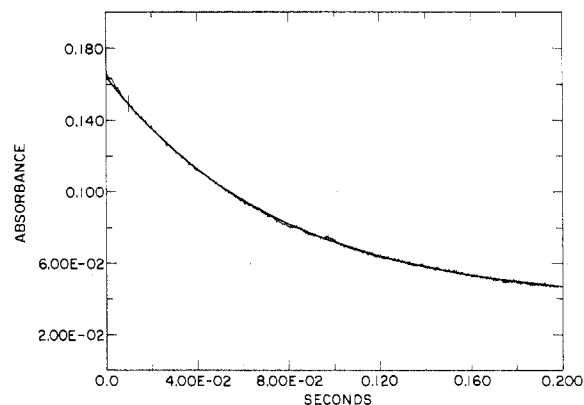


Figure 1. Graphical representation of a typical kinetic experiment: $[\text{Np(VII)}]_0 = 1.9 \times 10^{-4} F$, $[\text{VO}^{2+}]_0 = 9.20 \times 10^{-3} F$, $[\text{H}^+]_0 = 0.910 F$, $\mu = 1.00 F$ (LiClO₄), 25°. Smooth curve is the best fit OD-*t* line calculated by computer according to eq 1; wiggly line is the observed OD-*t* trace. For this experiment the best fit value of $k_{\text{obsd}} = 13.19 \pm 0.03 \text{ sec}^{-1}$.

tions during a given series of experiments had no effect on the values of the first-order rate constants observed during the series.

Data Analysis. All kinetic experiments were analyzed for periods up to a least 90% of completion. Initial estimates of the rate parameters were obtained from the display on the storage oscilloscope. Exact values for the individually observed rate parameters, k_{obsd} , were then obtained from a least-squares adjustment of the optical density-time data (800–950 OD-*t* data points per experiment) within the first-order rate expression⁸

$$\text{OD}_t = (\text{OD}_0 - \text{OD}_\infty)e^{-k_{\text{obsd}}t} + \text{OD}_\infty \quad (1)$$

The standard deviation for a given experiment is defined in the usual manner as

$$\sigma_{\text{exptl}} = [(\text{OD}_t^{\text{obsd}} - \text{OD}_t^{\text{calcd}})^2 / (N - 3)]^{1/2} \quad (2)$$

where *N* is the number of OD-*t* points and $\text{OD}_t^{\text{calcd}}$ is calculated from eq 1 utilizing the optimized values of OD_0 , OD_∞ , and k_{obsd} ; values of σ_{exptl} ranged from 2.9 to 11.6×10^{-4} with an average value of 7.0×10^{-4} optical density unit for the 166 determinations summarized in this paper. Since the total optical density change in any experiment was never less than 0.04 unit, these values of σ_{exptl} demonstrate that the functional form of eq 1 adequately describes the observed data. See Figure 1.

The precision obtained within a given set of determinations, *i.e.*, replicate measurements using the same reactant solutions in the storage syringes, is illustrated by the following data. At 25°, $\mu = 1.00 F$, using the primary vanadyl stock solution, $[\text{H}^+] = 0.065 F$, $[\text{VO}^{2+}]_0 = 9.2 \times 10^{-3} F$, and $1.91 \times 10^{-4} F < [\text{Np(VII)}]_0 < 4.94 \times 10^{-4} F$; consecutive values computed for k_{obsd} (sec⁻¹) and its standard deviation were 18.08 ± 0.03 , 17.74 ± 0.04 , 17.64 ± 0.02 , 18.07 ± 0.03 , 18.13 ± 0.03 , and 18.54 ± 0.03 . It is evident that there are other than random errors which limit the precision in the determination of k_{obsd} . Therefore the rate parameters that are reported in this paper are the mean values of k_{obsd} , \bar{k}_{obsd} , for a given set (at least five values in a set) along with their standard deviations from this mean, σ_m . The reproducibility of \bar{k}_{obsd} can be assessed by noting that in a second set of four determinations of k_{obsd} , under the same conditions and concentrations as above except starting with the secondary vanadyl stock solution, $\bar{k}_{\text{obsd}} = 17.8 \pm 0.3 \text{ sec}^{-1}$ which is in substantial agreement with the first determination of $\bar{k}_{\text{obsd}} = 18.0 \pm 0.3 \text{ sec}^{-1}$. This experiment also shows that there is no dependence of \bar{k}_{obsd} on the source of vanadyl perchlorate; all other results reported herein were obtained using the primary vanadyl stock solution.

Unless otherwise noted, all errors reported in this work are standard deviations.

Results and Discussion

The value estimated for the potential of the Np(VII)-

(8) The program for the on-line operation of the equipment and the least-squares adjustment of the data was developed by Mr. John Hines and Dr. A. J. Zielen of the Chemistry Division, Argonne National Laboratory.

(5) (a) D. R. Rosseinsky and M. J. Nicol, *J. Chem. Soc. A*, 1196 (1970), and references therein cited; (b) K. M. Davies and J. H. Espenson, *J. Amer. Chem. Soc.*, 92, 1889 (1970); (c) R. C. Thompson, *Inorg. Chem.*, 10, 1892 (1971); (d) W. S. Melvin and G. Gordon, *ibid.*, 11, 1912 (1972).

(6) The preparation and standardization of this vanadyl stock solution were carried out by Mr. Leon Asher, Department of Chemistry, University of Chicago.

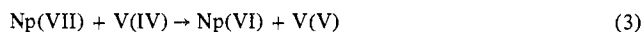
(7) E. H. Appelman and J. C. Sullivan, *J. Phys. Chem.*, 66, 442 (1962).

Table I. Dependence of \bar{k}_{obsd} on $[\text{V(IV)}]^a$

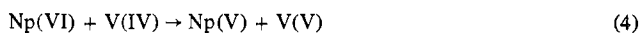
$10^3 [\text{V(IV)}]_0, F$	$10^{-1}(\bar{k}_{\text{obsd}} \pm \sigma_m), \text{sec}^{-1}$	$10^{-3}k'', F^{-1} \text{sec}^{-1}$	$10^3 [\text{V(IV)}]_0, F$	$10^{-1}(\bar{k}_{\text{obsd}} \pm \sigma_m), \text{sec}^{-1}$	$10^{-3}k'', F^{-1} \text{sec}^{-1}$
7.35	1.17 ± 0.02	1.59 ± 0.03	69.0	10.9 ± 0.4	1.58 ± 0.06
23.0	3.56 ± 0.06	1.55 ± 0.03	92.0	14.1 ± 0.9	1.53 ± 0.09
46.0	7.07 ± 0.07	1.54 ± 0.02			

^a Conditions: 25° , $\mu = 1.00 F$ (LiClO_4), $[\text{H}^+]_0 = 0.525 F$, $[\text{Np(VII)}]_0 = (0.53-4.98) \times 10^{-4} F$.

Np(VI) couple (+2.0 V)^{4a} along with that measured for the V(V)-V(IV) couple (+1.00 V)⁹ provides assurance that the reaction



should go to completion. Since the Np(VI)-Np(V) couple has a potential of +1.14 V,¹⁰ the subsequent reaction



is also thermodynamically feasible, but it is not of dynamic significance on the time scale of importance in the present study.¹⁰ Evidence that side reactions, such as the oxidation of water by Np(VII), do not interfere with the stoichiometry of reaction 3 is provided by the following results. At 25° , $\mu = 1.00 F$, $[\text{H}^+] = 0.09 F$, $[\text{Np(VII)}]_0 = 1.81 \times 10^{-3} F$, and $[\text{VO}^{2+}]_0 = 3.68 \times 10^{-3} F$; spectrophotometric determinations at 7650 Å yield a value of $\Delta[\text{VO}^{2+}]/\Delta[\text{Np(VII)}] = 1.03 \pm 0.05$.

Information provided in the Experimental Section showed that the rate law describing the disappearance of Np(VII) in reaction 3, when VO^{2+} is present in great excess, is first order in Np(VII) and zero order in Np(VI). Table I summarizes the dependence of \bar{k}_{obsd} on the concentration of VO^{2+} . A linear least-squares adjustment of the 33 data points summarized in this table results in values of $0.45 \pm 0.51 \text{ sec}^{-1}$ for the intercept and $(1.53 \pm 0.03) \times 10^3 F^{-1} \text{ sec}^{-1}$ for the slope. Since the intercept term is statistically insignificant, the empirical form of the rate law at constant hydrogen ion concentration based on these data is

$$-d[\text{Np(VII)}]/dt = k'' [\text{Np(VII)}] [\text{VO}^{2+}] \quad (5)$$

The variation of the second-order rate parameter, k'' , as a function of hydrogen ion concentration and temperature is summarized in Table II. It is seen that while k'' is dependent upon $[\text{H}^+]$, the magnitude of this dependence is too small to allow confident inference of an acid-dependent term in the rate law. Therefore at each temperature the data were correlated by the usual relation

$$\log k'' = \log k + n \log [\text{H}^+] \quad (6)$$

At 2.7, 13.6, and 25.0° respectively the values computed for $\log k$ and n were 2.724 ± 0.006 and -0.093 ± 0.006 , 2.899 ± 0.016 and -0.126 ± 0.017 , and 3.159 ± 0.005 and -0.112 ± 0.076 . The Arrhenius activation energy calculated from these values of $\log k$ and thus representing the activation energy at $[\text{H}^+] = 1.00 F$ is $7.3 \pm 0.9 \text{ kcal/mol}$.

An additional series of experiments in which the ionic strength was varied with lithium perchlorate (25° , $[\text{H}^+] = 0.035 F$, other constraints as in Table II) was conducted. At ionic strengths of 0.0875, 0.152, 0.471, 2.00, and 3.00 F , the respective values determined for $10^{-3}k''$ ($F^{-1} \text{ sec}^{-1}$)

(9) G. Charlot, A. Collumeau, and M. J. Marchon (IUPAC), "Selected Constants, Oxidation-Reduction Potentials of Inorganic Substances in Aqueous Solution," Butterworths, London, 1971, p 54.

(10) A preliminary estimate for the second-order rate parameter governing eq 4 of $13 F^{-1} \text{ sec}^{-1}$ at 25° and $2 F \text{ HClO}_4$ has been presented by J. C. Sheppard, *J. Phys. Chem.*, **68**, 1190 (1964).

Table II. Dependence of k'' on $[\text{H}^+]$ and Temperature^{a,b}

2.7°		13.6°		25.0°	
$[\text{H}^+], F$	$10^{-3}k'', F^{-1} \text{sec}^{-1}$	$[\text{H}^+], F$	$10^{-3}k'', F^{-1} \text{sec}^{-1}$	$[\text{H}^+], F$	$10^{-3}k'', F^{-1} \text{sec}^{-1}$
0.025	0.74 ± 0.01	0.025	1.21 ± 0.01	0.035	2.06 ± 0.01
0.077	0.67 ± 0.01	0.077	1.14 ± 0.03	0.120	1.92 ± 0.04
0.167	0.64 ± 0.01	0.167	1.01 ± 0.02	0.231	1.66 ± 0.02
0.386	0.58 ± 0.01	0.386	0.92 ± 0.02	0.525	1.53 ± 0.03
0.880	0.53 ± 0.02	0.880	0.77 ± 0.02	0.910	1.43 ± 0.03

^a Conditions: $\mu = 1.00 F$ (LiClO_4), $[\text{V(IV)}]_0 = (9.20-92.0) \times 10^{-3} F$, $[\text{Np(VII)}]_0 = (0.53-5.76) \times 10^{-4} F$. ^b Each entry is the average of at least five independent determinations.

were 1.09 ± 0.02 , 1.27 ± 0.02 , 1.69 ± 0.03 , 2.92 ± 0.09 , and 3.71 ± 0.04 .

The composition of the activated complex for the predominant, if not sole, path for reaction 3 consists of one V(IV) and one Np(VII) molecule. It is of interest to note (but does not provide substantiative evidence for a detailed mechanistic discussion) that there is no significant kinetic path dependent upon $[\text{H}^+]$, a result which is in marked contrast to those obtained in previous studies.⁴

A path independent of $[\text{H}^+]$ has also been reported for the oxidation of Hg(I) by Np(VII).^{4c} For that reaction path at 25° , $\mu = 1.00 F$, $k = 28 F^{-1} \text{ sec}^{-1}$, $\Delta H^* = 11.6 \pm 0.3 \text{ kcal/mol}$, and $\Delta S^* = -13 \pm 1 \text{ eu}$. When these values are compared to those obtained in the present study (same constraints, same units) of $k = 1.44 \times 10^3$, $\Delta H^* = 6.7 \pm 0.9$, and $\Delta S^* = -22 \pm 3$, it is evident that the 50-fold greater rate of oxidation of VO^{2+} relative to Hg_2^{2+} by the acid-independent path is reflected primarily in the ΔH^* term. Despite the similarity of the ΔS^* values for these paths the difference in the corresponding values of S^* is very large. Following Newton and Baker¹¹ $S^* = \Delta S^* + \Sigma S^\circ(\text{reactants}) - \Sigma S^\circ(\text{other products in net activation process})$ and using values of $S^\circ(\text{Hg}_2^{2+})$ and $S^\circ(\text{VO}^{2+})$ of +20 and -32 eu, respectively,¹² we calculate $S^*(\text{Np(VII)} \cdot \text{Hg}_2^{2+}) - S^*(\text{Np(VII)} \cdot \text{VO}^{2+}) = +61 \text{ eu}$. Since the two activated complexes presumably have the same formal charge, Z^* , this large difference in S^* is not expected from previously reported correlations of S^* with Z^* .^{11,13}

A major path for the oxidation of VO^{2+} by Mn(III) is independent of $[\text{H}^+]$ and has values of $\Delta H^* = 11.1 \pm 0.7 \text{ kcal/mol}$ and $\Delta S^* = -12 \pm 2 \text{ eu}$.¹⁴ When these results are compared with those obtained in the present study, it is again evident that the major difference is in the ΔH^* term. A similar comparison with the other reported oxidations of VO^{2+} is not feasible for reasons such as variation in formal charge of the oxidant, predominant paths dependent upon $[\text{H}^+]$, etc. Qualitatively it may be noted that the potential

(11) T. W. Newton and F. B. Baker, *Advan. Chem. Ser.*, No. 71, 268 (1967).

(12) *Nat. Bur. Stand. (U. S.), Tech. Note*, No. 270-4, 1 (1969); No. 270-5, 1 (1969).

(13) R. G. Linck in "Transition Metals in Homogeneous Catalysis," G. N. Schrauzer, Ed., Marcel Dekker, New York, N. Y., Chapter 7.

(14) D. R. Rosseinsky and M. J. Nicol, *J. Chem. Soc. A*, 1022 (1968).

for the Np(VIII)-Np(VI) couple is considerably more positive than that of the other reactants considered and the rate of oxidation of VO^{2+} by Np(VII) is also greater.

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Depolarized Light-Scattering Study of Isopolyvanadates in Alkaline Aqueous Solution

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Rayleigh depolarized scattering intensities have been measured at 6328 Å over a range of vanadate concentrations in alkaline aqueous salt solutions at 20°. Vanadates have been found to be highly anisotropic. On the basis of the scattering data it is possible to ascribe tetrahedral coordination to a HVO_4^{2-} monomer, a linear $\text{V}_2\text{O}_7^{4-}$ dimer, and a planar metavanadate species in agreement with Raman and nmr assignments. Evidence for association of HVO_4^{2-} ions has been presented and a polymerization mechanism involving the formation of hydrogen-bonded intermediates has been proposed.

Introduction

The pH-dependent polymerization of vanadium(V) in aqueous solution has been the subject of numerous chemical investigations¹⁻¹³ ranging from applications of cryoscopy¹ and diffusion² to more recent emf,^{3,4} ^{51}V nmr,^{9,10} and Raman spectroscopic studies.¹¹⁻¹³ The aggregation process has been described in some detail,^{3,4} pointing clearly to the stability of monomer and dimer species. There seems to be some doubt on the basis of emf work though, concerning whether or not the dimer condenses to form a trimer or a tetramer, or a mixture of the two.

Raman and ^{51}V nmr studies have provided strong evidence for a VO_4^{3-} ion in strongly alkaline solution followed in succession at lower pH by HVO_4^{2-} , H_2VO_4^- , $\text{V}_2\text{O}_7^{3-}$, and $\text{V}_3\text{O}_9^{3-}$ or $\text{V}_4\text{O}_{12}^{4-}$. Spectroscopic data do not support the existence of mixtures of trimeric and tetrameric metavanadates. As the pH is lowered from 14 to 8, VO_4^{3-} , HVO_4^{2-} , $\text{V}_2\text{O}_7^{4-}$, and the metavanadate appear to predominate in turn. Fundamental Raman vibrational frequencies for postulated VO_4^{3-} , $\text{V}_2\text{O}_7^{4-}$, and the metavanadate do not shift in heavy water even though oxygen and hydrogen exchange is rapid indicating that these species are not protonated.

Seemingly in contrast, crystal studies^{14,15} have shown the

importance of the VO_6 octahedron in the solid state, although a number of solids show coordination numbers 4 and 5^{16,17} as well. Because of the marked tendency of vanadium to expand its coordination number from 4 to 5 or 6 there has been a lingering concern that vanadates could be present in aqueous solution as five-coordinate (VO_2)- $(\text{OH})_3^{2-}$ rather than HVO_4^{2-} or even $(\text{VO}_2)\text{O}(\text{OH})_4^{4-}$ rather than $\text{V}_2\text{O}_7^{4-}$, etc. Uncertainty has been heightened because emf results cannot distinguish between such species and because kinetic results¹⁸ have been used as a basis for suggesting the existence of five-coordinate species.

This light-scattering depolarization study has been undertaken to choose between the postulated four- and five-coordinate structures. A choice should be possible on the basis of predicted substantially different molecular polarizability tensor components calculated for structures of given degree of polymerization. The assignments will be especially credible if calculations based on the optical bond model can be shown to explain the scattering data for all species present. Results will be valuable since they will complement extensive nmr and Raman data already available.

Experimental Section

Light-Scattering Photometer. Intensities of Rayleigh-scattered light were measured by means of a specially constructed photometer described elsewhere.¹⁹ A Spectra-Physics Model 122 cw laser was used to provide a vertically polarized light source of wavelength 6328 Å. All depolarization measurements were made using a 30 × 30 mm glass cell. The cell was painted on the outside, except for the entrance and exit slits, with a flat black paint to minimize reflection. The calibration of the photometer and a secondary glass standard was accomplished using aqueous solutions of 1,2-tungstosilicic acid. The procedure has been described elsewhere.²⁰ Solution refractive indices were measured by means of a Brice-Phoenix differential refractometer, Model BP-2000V.

Solution Clarification. Dust-free solutions were obtained by

- (1) P. Z. Dullberg, *Z. Phys. Chem., Stoechiom. Verwandtschaftslehre*, **45**, 129 (1903).
- (2) G. Jander and K. F. Jahr, *Z. Anorg. Allg. Chem.*, **212**, 1 (1933).
- (3) N. Ingri and F. Brito, *Acta Chem. Scand.*, **13**, 1971 (1959).
- (4) F. Brito, N. Ingri, and L. G. Sillen, *Acta Chem. Scand.*, **18**, 1557 (1964).
- (5) F. J. C. Rossotti and H. Rossotti, *Acta Chem. Scand.*, **10**, 957 (1956).
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