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Nature of Vanadium(IV) in Basic Aqueous Solution[1]

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Strongly basic aqueous solutions of vanadium(IV) were studied by means of ESR, optical, and Raman spectroscopy. ESR spectra and pH titrations show that vanadium(IV) is monomeric with stoichiometry $VO(OH)_3^-$. Higher oligomers, if present at all, are of minor importance. A strong Raman absorption at 987 cm^{-1} confirms the presence of the vanadyl group in solution. ESR parameters for $VO(OH)_3^-$ are $\langle g \rangle = 1.970$, $\langle a \rangle = -96.1$ G, $g_\parallel - g_\perp = -0.020$, and $a_\parallel - a_\perp = -120$ G. The isotropic hyperfine splitting, unlike that of the aquovanadyl ion, is temperature independent. Electronic transitions were found at 12.8, 19.2, and 24.4×10^3 cm^{-1}. Comparison of the spectral data for $VO(OH)_3^-$ with those of $VO(H_2O)_5^{2+}$ suggests that the hydroxo complex is structurally related to the aquo ion by the ionization of three water protons and that the metal-to-ligand σ bonds are somewhat more covalent in $VO(OH)_3^-$ than in $VO(H_2O)_5^{2+}$.

Introduction

The chemistry of vanadium(IV) in acid solutions or in the presence of strongly coordinating ligands is reasonably well understood.[2] The nature of the 4+ state in neutral or basic solutions, on the other hand, has received relatively little study by modern techniques. The interest in oxo anions of vanadium(IV) began with Berzelius,[3] who isolated an oligomeric vanadate(IV) salt. Later analyses of salts from strongly basic solutions of vanadium(IV) by Crow[4] and by Koppel and Goldman[5] led to the formulation $M_2V_4O_9 \cdot xH_2O$ where M is Na, K, NH_4, or Ba/2. Crow[4] also claimed to have obtained $M_2V_2O_5 \cdot xH_2O$ where M is Ag or Pb/2.

Titration curves obtained by Britton[6] and by Ostrowetsky[7] were found to be consistent with the presence of the $V_4O_9^{2-}$ species in basic solution. Ostrowetsky[7] also examined the uv spectrum and found the shape of the charge-transfer band at ca. 325 nm to depend on base concentration in the pH range 13–14. Polarographic studies by three different groups[7-9] were inconclusive and apparently contradictory.

Although there was little reason to doubt the existence of an oligomeric vanadate(IV) in solution when we began our work, there was reason to expect that the description of the system was incomplete. Virtually all other amphoteric oxides are converted to monomeric anions in sufficiently strongly basic media.[10] That VO_2 does not behave similarly would at least be worth verifying. Thus the goal of this work was to characterize the species found in basic solutions of vanadium(IV) and to elucidate the equilibria connecting them. Only one species was found—a monomer—and no evidence was obtained for polymeric oxo anions in solution above pH 12.

Experimental Section

Acidic stock solutions of vanadyl perchlorate were prepared from Fisher vanadyl sulfate and analyzed by permanganate titration as described earlier.[11] Basic solutions of vanadium(IV) were prepared by rapid addition of the vanadyl perchlorate solution to a solution of sodium hydroxide with vigorous stirring under positive nitrogen pressure in a gastight cell. Nitrogen gas was bubbled through both solutions for about 30 min before mixing to remove dissolved oxygen.

pH titrations were carried out in a gastight titration vessel under nitrogen using a Coleman 30 pH meter and a Coleman 3-265 combination electrode, calibrated with Fisher BuffAR standards at pH 4.0 and 7.0. The titrant—NaOH or $HClO_4$ solutions—was added in 0.1-ml increments with a Hamilton syringe pipet.

X-Band ESR spectra were obtained with a Varian V-4502 spectrometer using 100-kHz field modulation. Spectra were obtained at ambient temperature with samples contained in a Varian aqueous sample cell which was part of a closed-loop flow system which included the titration vessel. This system allowed samples to be introduced into the spectrometer cavity without changing the position of the sample cell or exposing the sample to the atmosphere. At temperatures other than ambient, samples were contained in thin-walled capillaries which were filled in a nitrogen-filled glove bag. Temperature control was with a Varian variable-temperature accessory. The magnetic field was calibrated by proton resonance, and the microwave frequency was determined by observation of the electron resonance of a DPPH sample ($g = 2.0036$[12]) taped to the sample tube.

Optical spectra were recorded on a Cary 14 spectrophotometer using the closed-loop flow system including the titration vessel and a 10-cm absorption cell. Spectra were obtained in the 220–1000-nm range for basic solutions of vanadium(IV) varying in concentration from 0.12 to 1.5 m*M*.

Raman spectra of 5.0 m*M* solutions of vanadium(IV) in 1.0 *M* NaOH were obtained with a Jarrell-Ash 25-300 Raman spectrograph operating with laser excitation at 514.5 nm and covering the range 900–2000 cm^{-1}. Samples were prepared in a nitrogen-filled glove bag and transferred to a multiple reflectance cell for observation of the spectrum.

Results and Discussion

Stoichiometry of the Reaction of the Vanadyl Ion with Base. Titration of a 5 m*M* solution of $VO(ClO_4)_2$ in 1.0 *M* $NaClO_4$ with 1.00 *M* NaOH proceeded with precipitation of a gray solid—presumably hydrated VO_2—starting about pH 4. The precipitate increased in quantity until a clear colorless su-

Table I. ESR Parameters

pH	$\langle g \rangle$	$\langle a \rangle$,[a] G	Δg[b]	Δa,[b] G	$g_\parallel$[c]	$g_\perp$[c]	$a_\parallel$[d]	$a_\perp$[d]
2.0	1.964 ± 0.001	−116.4 ± 0.2	−0.043 ± 0.001	−129.5 ± 0.5	1.935	1.978	−203	−73
14.0	1.970 ± 0.001	−96.1 ± 0.3	−0.020 ± 0.001	−120.0 ± 1.0	1.957	1.977	−176	−56

[a] From isotropic room-temperature spectra. [b] From comparison of computer simulations with experimental spectra of frozen solutions. [c] Computed from $\langle g \rangle$ and Δg. [d] Computed from $\langle a \rangle$ and Δa.

Table II. Temperature Dependence of Hyperfine Splitting Constants

	$-\langle a \rangle$, G			$-\langle a \rangle$, G	
Temp, °C	pH 2.0	pH 14.0	Temp, °C	pH 2.0	pH 14.0
−3		96.0 ± 1.1	25	116.6 ± 0.3	96.1 ± 0.1
3	115.4 ± 0.3	95.7 ± 0.5	37	116.7 ± 0.3	96.2 ± 0.2
11	115.6 ± 0.5	96.1 ± 0.3	51	117.0 ± 0.3	96.3 ± 0.2
21	116.3 ± 0.8	96.1 ± 0.2	63	117.2 ± 0.2	96.2 ± 0.2

pernatant remained. Addition of further base caused partial redissolution of the precipitate leaving a brown solution. Unfortunately, however, equilibrium between the precipitate and the solution was attained very slowly, so that we were unable to obtain reproducible titration curves, even at 60°C. Thus the number of moles of base required completely to redissolve the gray precipitate could not be determined accurately. Time for equilibration was limited by the sensitivity of the system to oxygen. With our titration vessel, negligible oxidation occurred in times up to 1 hr, but a true equilibrium titration curve would probably require days, during which even very low levels of oxygen could seriously perturb the results.

Reverse titrations with 0.97 *M* $HClO_4$ of a clear brown solution, being 5.0 m*M* in vanadium(IV) and containing an excess of NaOH, gave an apparent equivalence point, accompanied by formation of the gray precipitate, when 2.90 ± 0.15 mol of base/mol of vanadium remained. This ratio is somewhat higher than observed by Britton and Welford[6] (about 2.2) or Ostrowetsky[7] (about 2.6). Again, the curves were found to be poorly reproducible when precipitate was present. These results are difficult to assess for two reasons: (1) the ratios quoted are the result of small differences in relatively large titers so that analytical errors are magnified; (2) the shape and position of the titration curves depend critically on the time allowed for equilibration after addition of acid or base. The equivalence points obtained are of somewhat doubtful significance.

In another approach to the problem of stoichiometry, larger amounts of base were added with rapid stirring to the initially clear blue solution. If at least 3.0 mol of base/mol of vanadium(IV) was added, formation of the gray precipitate could be avoided and a clear brown solution obtained. When 2.9 mol of base or less was added, varying amounts of the gray precipitate remained after equilibration. Addition of 3.0 mol of base/mol of vanadium gave a clear brown solution with a pH of about 11.4. Titration of this solution with further base gave a reproducible pH titration curve which was, however, virtually superimposable on the curve obtained when a solution of $NaClO_4$ at the same ionic strength was titrated with NaOH. Thus the vanadium(IV) species at pH ~12 results from the reaction of the aquovanadyl ion with not more than 3 mol of base.

Vibrational Spectra. The Raman spectrum of a solution 5.0 m*M* in $VO(ClO_4)_2$ and 1.0 *M* in NaOH showed a narrow (ca. 10 cm^{-1}) intense absorption band centered at 987 ± 5 cm^{-1}. The rather dilute solutions, necessitated by the low solubility of vanadium(IV) in basic solution, limited the signal-to-noise ratio rather severely and precluded the observation of any other spectral features attributable to the vanadium-containing species.

Oxovanadium(IV) complexes exhibit a strong narrow V–O stretching absorption, with most data falling in the range 950–1000 cm^{-1}.[2] The observed band at 987 cm^{-1} thus indicates that the vanadyl group is present in the basic solution species and suggests a V–O bond environment intermediate between that of the aquo ion ($\bar{\nu}$ 1001 cm^{-1})[13] and that of hydrated VO_2 ($\bar{\nu}$ 968 cm^{-1}).[14]

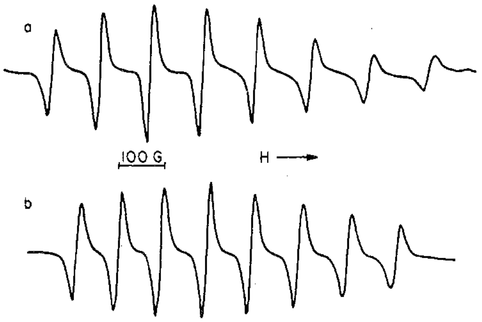

Figure 1. ESR spectra of 0.005 *M* vanadium(IV) in (a) 1.0 *M* $NaClO_4$ solution, pH 2.0, and (b) 1.0 *M* NaOH solution.

Electron Spin Resonance Spectra. Room-temperature ESR spectra of 5 m*M* vanadium(IV) in 1.0 *M* $NaClO_4$ (pH 2) and in 1.0 *M* NaOH solutions are shown in Figure 1. The isotropic *g* values and vanadium nuclear hyperfine splitting constants were obtained by means of a nonlinear least-squares fit to the exact solution of the Breit–Rabi equation.[15,16] The resulting parameters are given in Table I. Spectra recorded at various temperatures were also analyzed to determine the splitting constants given in Table II. (*g* values were not measured as a function of temperature.) The splitting constant of the aquo ion appears to have a small, but real, temperature dependence, whereas the splitting observed in strongly basic solution is temperature independent within experimental error.

Identical ESR spectra were obtained for samples prepared as described in the pH range 12–14 and for a solution obtained by dissolving solid $K_2V_3O_7 \cdot 2H_2O$[17] in base. An eight-line ESR spectrum implies that vanadium(IV) is monomeric in basic solutions. An alternative hypothesis—that the spin–spin coupling in a possible oligomer is so weak that each unpaired electron "sees" only one vanadium nucleus—seems untenable in the absence of any large ligands in the system. This result does not rule out the possibility that an ESR-active monomeric species is in equilibrium with an oligomer which either is diamagnetic or exhibits undetectably broad lines.

In order to test this possibility, ESR intensities for solutions of vanadium(IV) were measured as a function of concentration to obtain an ESR Beer's law plot. The ESR spectrum of a sample of $VO(ClO_4)_2$ in 1.0 *M* $NaClO_4$ (pH 2) was recorded, the sample removed through the closed-loop flow system and replaced with a solution having identical vanadium concentration, but in 1.0 *M* NaOH, and the spectrum then remeasured without any change in spectrometer parameters or position of the cell in the microwave cavity. This experiment was performed for concentrations ranging from 1.5 to 14 m*M*.

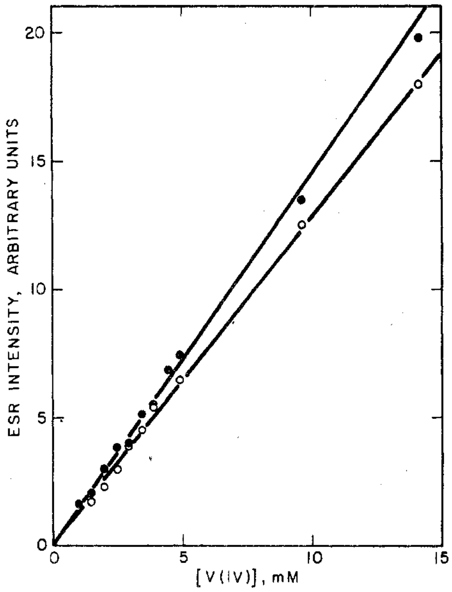

Figure 2. Intensities of ESR spectra of vanadium(IV) in 1.0 *M* $NaClO_4$ solution, pH 2.0 (closed circles), and in 1.0 *M* NaOH solution (open circles) as functions of vanadium concentration.

Intensities were computed by multiplying the derivative amplitude by the square of the width for each hyperfine line, averaging over the eight lines, and adjusting for differences in amplifier gain from one run to another. The results of these experiments are shown in Figure 2 where the measured intensities are plotted as functions of concentration. The slopes of the straight lines obtained are 1.45 ± 0.09 mM^{-1} for the acid solution spectra and 1.28 ± 0.04 mM^{-1} for the basic solution spectra. Because of difficulties in obtaining sufficiently rapid mixing to avoid formation of precipitate or perhaps because the solubility limit is about 15 m*M*, it was not possible to extend these data to higher concentrations in basic solution. Additional points up to 24 m*M* in acid solution were obtained, however; these fall on the same line and are included in the determination of the slope.

There are two explanations for the somewhat smaller slope found for the basic solution spectra. The method used to compute the ESR intensities assumes that the lines are strictly lorentzian. Because of unresolved proton hyperfine structure,[18-20] the lines are somewhat distorted; the effect is larger in the basic solution spectra,[20] so that these intensities are systematically underestimated.

The difference in slopes may also reflect a slightly lower spectrometer sensitivity for the basic solutions. The sensitivity of an ESR spectrometer is proportional to the cavity quality factor, Q_c, given by

$$Q_c^{-1} = Q_u^{-1} + \eta_\epsilon \epsilon'' + \eta_\chi \chi''$$

where Q_u is the unloaded cavity *Q*, η_ϵ and η_χ are the electric and magnetic filling factors, and ϵ'' and χ'' are the imaginary parts of the dielectric constant and the magnetic susceptibility, respectively.[21] From data on dielectric loss in solutions of $NaClO_4$[22] and NaOH[23] at microwave frequencies, we can estimate that ϵ'' for 1 *M* $NaClO_4$ at 10 GHz is about 40 whereas the corresponding value for 1 *M* NaOH solution is about 55. Since the filling factor depends only on geometry, we expect the ESR sensitivity to be somewhat greater for the $NaClO_4$ solutions than for the NaOH solutions. Thus both sources of systematic error would tend to reduce the Beer's law slope for the basic solution spectra.

The very similar Beer's law slopes for the acid and basic solution intensities, the fact that vanadium(IV) at pH 2 is known to be virtually entirely monomeric in the concentration range studied, and the very good straight line obtained for the basic solution intensities combine to convince us that vanadium(IV) in 1 *M* NaOH is monomeric, at least up to 14 m*M*. We cannot, of course, rule out a monomer–polymer equilibrium at lower pH.

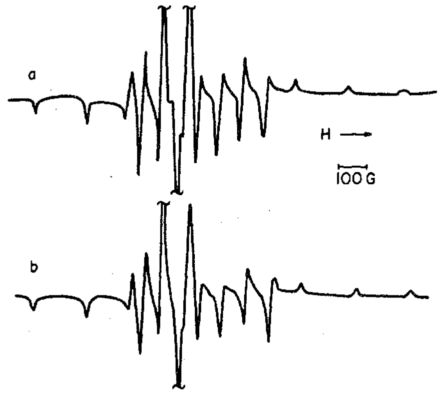

Figure 3. (a) Experimental and (b) computer-simulated ESR spectra of 0.005 *M* vanadium(IV) in frozen 1.0 *M* $NaClO_4$ solution, pH 2.0.

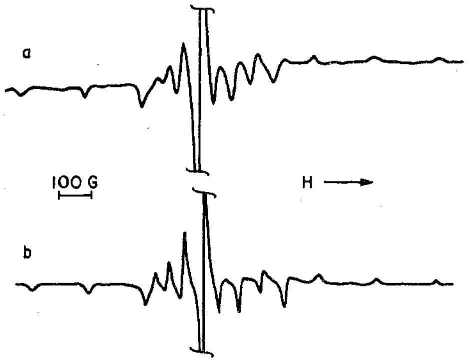

Figure 4. (a) Experimental and (b) computer-simulated ESR spectra of 0.005 *M* vanadium(IV) in frozen 1.0 *M* NaOH solution.

ESR spectra were measured for frozen solutions, 4.0 m*M* in vanadium(IV) at pH 2 and 14. The spectra are shown in Figures 3 and 4. Computer-simulated spectra, based on solutions of the spin Hamiltonian to second order in perturbation theory, were generated by the methods of Taylor and Bray[24] and compared with the experimental spectra in order to estimate the anisotropic parameters. In the simulations, the isotropic parameters, $\langle g \rangle = {}^1/_3(g_\parallel + 2g_\perp)$ and $\langle a \rangle = {}^1/_3(a_\parallel + 2a_\perp)$, were held constant and equal to the isotropic values given in Table I; the anisotropies, $\Delta g = g_\parallel - g_\perp$ and $\Delta a = a_\parallel - a_\perp$, were adjusted to match best the experimental spectra. Simulated spectra with the best fit parameters are also shown in Figures 3 and 4. As reflected by the estimated uncertainties given in Table I, the anisotropies were quite sharply determined by this procedure. We were unable to find evidence of departure from axial symmetry in either of the two spectra. From the anisotropies and the isotropic values given in Table I, the tensor components can be computed and are also given in Table I. Since the isotropic hyperfine splitting of the aquo ion is known to be temperature dependent (see Table II) and the *g* values may also vary with temperature, there is the possibility that these components may be somewhat in error.

Agreement with anisotropic parameters previously determined for the aquo ion in a dilute single crystal of zinc Tutton salt[25] and in frozen mineral acid solutions[26,27] is satisfactory as a whole, though there are small differences outside our experimental error which might be due to differing environments for the aquo ion.

Electronic Spectra. Basic solutions of vanadium(IV) are

Table III. Electronic Spectral Data

Transition	Acid soln[a]		Basic soln	
	$10^3\nu$, cm^{-1}	ϵ, cm^{-1} M^{-1}	$10^3\nu$, cm^{-1}	ϵ, cm^{-1} M^{-1}
$^2B_2 \rightarrow {}^2E$	13.1	17	12.8	18
$^2B_2 \rightarrow {}^2B_1$	16.0	8	19.2	16
$^2B_2 \rightarrow {}^2A_1$	44.8[b]		24.4	20

[a] From Ballhausen and Gray.[28] [b] Predicted band position.[28]

Table IV. Molecular Parameters

Species	$(\beta_1{}^*)^2$	$(\epsilon_\pi{}^*)^2$	P, cm^{-1}	κ
$VO_{aq}{}^{2+}$	0.54	0.63	0.0127	0.80
$VO(OH)_3{}^-$	0.44	0.65	0.0122	0.69

reddish brown due to three absorption bands which cover most of the visible region of the spectrum. Band maxima and extinction coefficients are given in Table III. The spectrum of the basic solution species differs from that of the aquo ion[28] in the shift to higher energy of the second d–d band and the shift to lower energy of the third band which is hidden under the charge-transfer band in the spectrum of the aquo ion. The extinction coefficient and position of the first band are almost unperturbed although the band is somewhat broader in the basic solution spectrum. Beer's law plots of the absorbances at the band maxima, as well as on the side of the charge-transfer band, are satisfactorily linear over the concentration range 0.6–2.0 m*M* for vanadium(IV) in basic solution.

Reproducibility of the spectra in the visible region was generally very good. In the charge-transfer region, however, extreme care was required to prevent oxidation; tiny amounts of vanadium(V) very seriously affect the uv spectrum. We suspect that it is this effect which caused the apparent variation in the charge-transfer band with pH reported by Ostrowetsky.[7]

Discussion of ESR Parameters. The components of the axially symmetric g tensor are given by[29]

$$g_\parallel = g_e - \frac{8\lambda(\beta_1{}^*\beta_2{}^*)^2}{\Delta E(^2B_2 \rightarrow {}^2B_1)}$$

$$g_\perp = g_e - \frac{2\lambda(\beta_2{}^*\epsilon_\pi{}^*)^2}{\Delta E(^2B_2 \rightarrow {}^2E)}$$

where $g_e = 2.0023$ is the free-electron g value, λ is the spin–orbit coupling constant, $\beta_2{}^*$, $\beta_1{}^*$, and $\epsilon_\pi{}^*$ are the coefficients of the metal d_{xy}, $d_{x^2-y^2}$, and d_{xz}, d_{yz} orbitals in the antibonding molecular orbitals $^2B_2$, $^2B_1$, and ^2E, respectively. Bramman et al.[30] suggested that the spin–orbit coupling constant for V^{4+}, $\lambda = 248$ cm^{-1}, is most appropriate for use in computing bonding parameters from the g tensor of a vanadyl complex. Using this value, together with the experimental energy differences, and assuming $\beta_2{}^* = 1.0$, values of $(\beta_1{}^*)^2$ and $(\epsilon_\pi{}^*)^2$ are computed for the two vanadium(IV) species and are given in Table IV. The most significant difference between the acid and basic solution parameters is the greater ligand character in the $B_1{}^*$ molecular orbital of the basic solution species. Thus the equatorial metal-to-ligand bonds are apparently somewhat more covalent than in the aquo complex. The similarity in the $\epsilon_\pi{}^*$ coefficients suggests that π bonding in the V═O group is similar in the two species.

The components of the hyperfine tensor may be written as[29]

$$A = -P[(\beta_2{}^*)^2(\kappa + {}^4/_7) + \Delta g_\parallel + {}^3/_7\Delta g_\perp]$$

$$A = -P[(\beta_2{}^*)^2(\kappa - {}^2/_7) + {}^{11}/_{14}\Delta g_\perp]$$

where $\Delta g_\parallel = g_e - g_\parallel$, $\Delta g_\perp = g_e - g_\perp$, κ is a measure of the Fermi contact interaction, and $P = g\beta g_N\beta_N\langle r^{-3}\rangle$. Assuming $\beta_2{}^* = 1.0$, the parameters P and κ are computed and are given in Table IV. The values of P found are comparable to those obtained for $VO(acac)_2$ and vanadyl tetraphenylporphyrin;[29] they are close to the value expected for V^{2+}, consistent with arguments advanced by Bramman et al.[30] The near constancy of P seems to confirm the assumption that $\beta_2{}^* = 1$.

The temperature dependence of the isotropic hyperfine splitting of the aquo ion—about 0.03 G/K—is on the same order of magnitude as that observed for $VO(acac)_2$ in benzene.[31] The temperature dependence of the copper splitting in $Cu(acac)_2$, of comparable magnitude but opposite sign, was ascribed to partial population of an excited vibrational state having a smaller splitting constant.[32] A similar explanation could be applied in the present case, though the contact interaction would have to be greater in the excited state. It is interesting that the basic solution species exhibits no detectable variation of the hyperfine splitting constant with temperature, possibly reflecting stiffer bonds and consequent lesser population of excited vibrational states.

Structure of the Basic Solution Species. Given that the basic solution species is a monomer formed by the reaction of the aquovanadyl ion with not more than 3 mol of base, the only possible stoichiometry is

$$VO^{2+} + 3OH^- \rightarrow VO(OH)_3{}^-$$

One might imagine at least three possible structures for $VO(OH)_3{}^-$, differing in the degree of hydration and ranging in coordination number from 4 to 6.

Four-coordinate $VO(OH)_3{}^-$ with a distorted tetrahedral structure or five-coordinate $VO(OH)_3(H_2O)^-$ with a distorted trigonal-bipyramidal structure would have a threefold axis of rotation. One would expect from simple ligand field theory arguments[33] an ordering of the vanadium d levels: $(d_{xy}, d_{x^2-y^2}) < (d_{xz}, d_{yz}) < d_{z^2}$. Thus a degenerate ground state is predicted which would cause the ESR spectrum, if observable, to be quite different from that of the aquo ion. Further, only two d–d bands would be expected and considerably larger extinction coefficients might be anticipated. For these reasons, we discard these two alternatives.

The similarity of the optical and ESR spectra of the basic solution species to those of the aquo ion suggests rather strongly that $VO(OH)_3{}^-$ is structurally similar to the aquo ion. Assuming a distorted octahedral structure, the ligand trans to the vanadyl oxygen would most likely be a loosely bound water, leaving the three hydroxide ligands, together with another water, in the equatorial plane.

Ligand field theory arguments,[33] in which it is assumed that hydroxide ligands exert a stronger ligand field than do water ligands, predict a red shift and splitting (or broadening) of the first d–d band, a blue shift of the second band, and a red shift of the third band from the positions in the spectrum of the aquo ion. Although the observed red shift of the first band is much smaller than might have been expected, the other predictions are fulfilled.

The complex would possess at most a single mirror plane of symmetry and one might expect the anisotropic ESR spectrum to reflect this with $g_x \neq g_y$ and $a_x \neq a_y$. The anisotropies $g_x - g_y$ and $a_x - a_y$ are related to the splitting of the first d–d band.[30] That band was somewhat broadened in the basic solution spectrum, but even assuming that the unresolved splitting was as large as 10^3 cm^{-1}, the ESR anisotropies would be too small for resolution in the experimental spectrum.

The discovery that vanadium(IV) exists in basic solution as a monomer does not necessarily invalidate the earlier work[3–5] showing that oligomeric solids are obtained, although it now appears that the potassium salt is best formulated as $K_2V_2O_7 \cdot 2H_2O$.[17,34] Vanadium(IV) complexes are known to be labile and have often been found to exhibit different structures in solution and in the solid state. If the solution species is $VO(OH)_3{}^-$ and the solid-state species is $V_3O_7{}^{2-}$, however, proton transfer must accompany molecular rearrangement in the crystallization process.

Summary

pH titrations of the aquovanadyl ion, while inconclusive with respect to the exact stoichiometry of the basic solution species, place an upper limit of 3 mol of base/mol of vanadium(IV). An eight-line ESR spectrum shows the species to be monomeric, and ESR-inactive oligomers are ruled out by the linearity of an ESR Beer's law plot and the similarity of the slope of the plot to that for the aquovanadyl ion. Thus the basic solution species must be $VO(OH)_3^-$. Analysis of the Raman spectrum which shows the presence of the vanadyl group, V=O, and interpretation of the ESR and optical parameters show that $VO(OH)_3^-$ is structurally similar to the aquo ion $VO(H_2O)_5^{2+}$ with somewhat more covalent, and perhaps stiffer, equatorial V–O bonds. It thus appears that the two species are related by the ionization of three water protons, i.e.

$$VO(H_2O)_5^{2+} + 3OH^- \rightarrow VO(OH)_3(H_2O)_2^- + 3H_2O$$

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Registry No. $VO(OH)_3(H_2O)_2^-$, 56586-21-1; $VO(H_2O)_5^{2+}$, 15391-95-4.

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Kinetics and Mechanism of the Oxidation of Uranium(III) by Cobalt(III) in Perchlorate Media

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The kinetics of the oxidation of U(III) by Co(III) has been studied in perchlorate media. The rate law of the reaction was found to be given by the expression $-d[Co(III)]/dt = k_1[Co(III)][U(III)]$. The value of k_1 was determined as $(1.12 \pm 0.1) \times 10^6\ M^{-1}\ sec^{-1}$ at 20°C and ionic strength of 2.00 and was found to be independent of acid concentration at constant ionic strength. The temperature dependence of the reaction was studied in the range 11–31°C and the values of $\Delta H^‡$ and $\Delta S^‡$ were determined as 2.00 ± 0.25 kcal mol^{-1} and -25.6 ± 0.8 cal deg^{-1} mol^{-1}, respectively. In common with many other reactions of Co(III), the rate constant of this reaction is much lower than expected from the very high $\Delta G°$ value and plausible reasons for this observation are discussed.

Introduction

The chemical properties[1] and the kinetics and mechanisms of the oxidation–reduction reactions[2,3] of hexaaquocobalt(III) have been the subject of recent and comprehensive reviews. These have confirmed the earlier observation[4] that, although the experimental free energy change of activation ($\Delta G^‡$) for a series of Co(III) reactions at first decreases as predicted by the Marcus expression as the free energy change ($\Delta G°$) for the reaction becomes more negative, the values of $\Delta G^‡$ become essentially constant at 10 kcal mol^{-1} in reactions whose $\Delta G°$ value exceeds -40 kcal mol^{-1}. This behavior suggests some rate-limiting factor which is not normally included in the Marcus expression and which for reactions of Co(III) ions has often been identified as spin multiplicity restrictions involving the $Co^{III}(t_{2g}^6)$–$Co^{III}(t_{2g}^5e_g^1)$ equilibrium.[5]

As noted elsewhere,[5b] the determination of the activation parameters for other Co(III) reactions of high $\Delta G°$ values would be of interest and might provide further experimental verification of the above observation. Since preliminary experiments showed that the Co(III)–U(III) reaction with a $\Delta G°$ value of -55.7 kcal mol^{-1} [6] could be followed by stopped-flow techniques, this reaction was studied in perchloric acid solution.

Experimental Section

Reagents. Solutions of $UO_2(ClO_4)_2$, $NaClO_4$, and $HClO_4$ were prepared as reported elsewhere,[7] and the method of preparation and handling of the U(III) solutions was identical with that described previously.[8] A Co(II) stock solution was prepared from $Co(ClO_4)_2$