these data is that the complexes are molecular crystals in the solid state, though our evidence is not strong and we cannot eliminate the possibility that the structure is phase dependent.

A marked decrease in the highest Te–X absorption frequency occurs in the tmtu complexes relative to the parent organotellurium trihalides. For example in solid CH_3TeCl_3 the highest Te–Cl frequencies (338, 315 cm^{-1}) are most likely associated with a terminal cis $TeCl_2$ group.[1a] In contrast the highest Te–Cl frequency in solid CH_3TeCl_3tmtu is found at 251 cm^{-1} which is quite close to the highest frequency in $(CH_3)_2TeCl_2$ (277 cm^{-1}).[19] It is therefore suggested that the 251-cm^{-1} absorption in CH_3TeCl_3tmtu is primarily due to trans Cl–Te–Cl stretching. This argument might be questioned as there are cis $TeCl_2$ groups in the suggested structure. Sulfur in thioureas appears to have a stronger trans bond lengthening effect in organotellurium(II) halide adducts than does halogen.[17,18] We suggest a similar lengthening may occur in the above organotellurium(IV) halide complexes to such a degree that only the trans chlorines are involved in the highest Te–Cl frequency. Analogous ir data were obtained on other $RTeX_3$tmtu complexes in the respective Te–X stretching regions allowing similar conclusions. These spectral interpretations must of course be regarded as tentative until detailed information is available concerning crystal structures.

In methyl- and ethyltriiodo(tetramethylthiourea)tellurium(IV) Te–S absorptions are clearly seen at 210 and 215 cm^{-1}, respectively. These frequencies compare favorably with the 200-cm^{-1} Te–S frequency reported for $TeX_4(tmtu)_2$ complexes.[14] In $RTeBr_3$tmtu complexes the Tt–S absorption is obscured by Te–Br modes, while in $RTeCl_3$tmtu complexes the situation is uncertain. Peaks at 210 (solid) and 204 cm^{-1} (solution) for $C_2H_5TeCl_3$tmtu and at 205 cm^{-1} (solution) for p-$CH_3OC_6H_4TeCl_3$tmtu may be due to Te–S stretching, but these peaks might also arise from Te–Cl modes.

Examples of five-coordination are becoming more common in group VIa. Thus $SeOCl_2 \cdot 2py$,[20] $SeOCl_4^{2-}$,[21] $CH_3TeI_4^-$,[13] TeF_5^-,[22,23] $TeF_4(s)$,[24] and $ClCH_2CH_2TeCl_3$[12] all have been shown to contain pentacoordinate chalcogen atoms. Methyltrihalogeno(tetramethylthiourea)tellurium(IV) compounds appear to be a new class of monomeric neutral molecules in which a group VIa element is pentacoordinate.

Acknowledgment.—The author thanks the National Science Foundation for generous support of this research through Grant GP 9486. The author also thanks the Canadian Copper Refiners Ltd. for a gift of tellurium through the Selenium–Tellurium Development Association.

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Ligand Substitution Processes of Complex Oxovanadium(IV) Species in Aqueous Hydrochloric Acid Solutions. Nuclear Magnetic Resonances of Oxygen-17 and Chlorine-35[1]

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Received February 10, 1971

Wide-line nuclear magnetic resonance spectra of oxygen-17 and chlorine-35 were obtained for complex oxovanadium(IV) species in hydrochloric acid solutions over a wide range of concentrations and temperatures. Line broadening attributable to paramagnetic species was interpreted in terms of equilibria among $VO(H_2O)_4^{2+}$, $VO(H_2O)_3Cl^+$, and $VO(H_2O)_2Cl_2$, in which only equatorial ligands are specified. Rate constants and activation energies were determined for $H_2{}^{17}O$ and $^{35}Cl^-$ exchange between the complexes and bulk solvent. In each case the exchange process is best represented as H_2O dependent and rate equations incorporate the activity of water, referred to unity at infinite dilution. For H_2O exchange the rate constants at 300°K were found to be 5.9×10^2, 2.3×10^4, and 8.5×10^5 sec^{-1} for $VO(H_2O)_4^{2+}$, $VO(H_2O)_3Cl^+$, and $VO(H_2O)_2Cl_2$, respectively; for Cl^- exchange, the calculated values are 2.0×10^3 and 2.2×10^5 sec^{-1} for the last two species. Formation constants for the two chloro complexes are 1.2×10^{-2} and 1.0×10^{-3}, with enthalpies of 7.5 and 2.6 kcal/mol. These results were found to be compatible with the electron paramagnetic resonance observations of Kon and Sharpless.

I. Introduction

Ligand-exchange processes and magnetic interactions occurring in oxovanadium(IV) aqueous solutions have recently received a great deal of attention.[3-9]

[1] Work done under the auspices of the U. S. Atomic Energy Commission. Presented in part at the Second International Symposium on Nuclear Magnetic Resonance, São Paulo, Brazil, July 8–11, 1968, and at the Southwest Regional Meeting of the American Chemical Society, Austin, Texas, Dec 4–6, 1968.

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Those investigations have been primarily concerned with the nature of ligand coordination with relation to the microcrystalline structure of the cationic complex and have utilized proton and oxygen-17 nuclear magnetic resonance techniques, together with electron paramagnetic resonance in some instances. In this work we have observed the oxygen-17 and chlorine-35 resonances in hydrochloric acid solutions of oxovanadium(IV) in order to obtain information about the possible chloro complexes formed in the solutions. Similar work with iron(III)[10] and cobalt(II)[11,12] has proved to be quite successful in elaborating species distributions as functions of solution composition and in determination of exchange-rate parameters for individual complex species. In this instance, analysis is complicated by the small chemical shifts observed for both chlorine-35 and oxygen-17, which have made it necessary to rely primarily on line width measurements to delineate the systems.

A single resonance was obtained for either chlorine-35 or oxygen-17 in all solutions studied. Signals attributable to nuclei found in the paramagnetic complexes are too weak and too broad to be seen directly. Thus, the observed resonances are those of unbound chloride or water in the bulk solution, as modified by exchange with bound ligands. If exchange is sufficiently slow, a direct measurement of the mean residence time of the ligand in the complex coordination sphere may be obtained, and if it is fast, relaxation rates of nuclei in the coordinated ligands are determined. A third alternative, that rapid switching of nuclear environments produces observable line broadening, is not applicable here because of the small chemical shifts produced by oxovanadium(IV).

The most satisfactory model of aquated oxovanadium(IV) cation is one in which four equivalent water molecules occupy planar equatorial positions about the vanadium atom and a fifth water molecule is in an axial position opposite an oxo group.[13–15] The axial water molecule is apparently held quite weakly and exchanges rapidly with bulk water, while equatorial water molecules exchange more slowly and give measurable exchange rates over the available temperature range.[5,7,9]

The single unpaired electron in oxovanadium(IV) is in an essentially nonbonding orbital of b_2 symmetry,[14] distributed in the equatorial plane between the $V-OH_2$ bonds. Electron spin is presumably transferred to the equatorial ligands *via* π bonding and the small observed contact shift at elevated temperatures is upfield relative to unbound $H_2{}^{17}O$.[9] Under conditions in which exchange of the equatorial water molecules does not lead to an observed effect on the bulk water, a small downfield shift is found. Reuben and Fiat[5,9] attributed the latter shift to the axial water molecule or to others in a second coordination sphere. In either event, the contribution to relaxation of oxygen-17 is very small and can be observed only at low temperatures.

Exchange of the oxo group has been assumed to be too slow on the nmr time scale to contribute to observed effects in the resonance experiment.[6] However, it is also possible that exchange is relatively rapid and that spin transfer does not occur to an appreciable extent. Recent experiments in this laboratory,[16] utilizing an isotope dilution technique with highly enriched oxygen-18, suggest that the exchange half-time is less than 5 sec at 25.6°. (It is possible that the process is catalyzed by trace amounts of $VO_2{}^+$, which exchanges vanadium rapidly with VO^{2+} and must simultaneously exchange oxygen.) If the oxo-exchange half-time is between 10^{-3} and 5 sec, both criteria can be met.

On the basis of spectroscopic evidence, it has been suggested[17] that all five water molecules in the aquooxovanadium(IV) cation are replaced simultaneously to produce $VOCl_5{}^{3-}$ in concentrated HCl solutions. The principal evidence leading to that conclusion is the absence of bands in the visible spectrum resulting from species of lower symmetry. In a similar vein, Kon and Sharpless[18] compared the electron paramagnetic resonance (epr) spectra of tetramethylammonium tetrachlorooxovanadium(IV) in glacial acetic acid with those of concentrated HCl (12 *N*) solutions containing oxovanadium(IV) and concluded that the *g* tensor and hyperfine coupling constants were sufficiently similar to suggest that the species in HCl solution was probably $VOCl_4{}^{2-}$. They found no evidence for intermediate species. There is very little reason to doubt the authenticity of highly substituted chloro species in solutions with exceedingly low water activity,[18,19] but the cumulative evidence for their existence in predominantly aqueous media is tenuous.

The only reported formation constant for a monochlorooxovanadium species appears to be that of Ahrland and Noren,[20] who estimated a value for β_1 of the order of unity. In their experiments competition between chloride and fluoride for positions in the complex was evaluated using the quinhydrone electrode to determine $[H^+]$. In all probability, the constant they obtained for chloride represents occupancy of the axial position of the oxovanadium(IV) ion, opposite to the oxo group.

In the following sections the various complex species are denoted by specification of the four equatorial ligands only. It is assumed that occupancy of the axial position is essentially indeterminate by the method used here.

II. Experimental Section

Preparation of Solutions.—Oxovanadium(IV) chloride solutions were prepared by dissolving vanadium pentoxide in concentrated HCl. Sulfur dioxide was passed into solution to reduce any $VO_2{}^+$ present. The solutions were boiled and excess SO_2 purged by bubbling CO_2 through the solution. Sulfate ion was removed by adding an equivalent amount of $BaCl_2$ solution and filtering. Solutions were standardized by titration with $KMnO_4$. The solutions were shown to be free of V^{3+} by reducing the titrated solution with SO_2, purging with CO_2, and titrating again. The titer should be reduced in the amount of V^{3+} present and increased in the amount of $VO_2{}^+$ present. Acid was determined by stirring an aliquot of solution with Dowex 50 ion-

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exchange resin. After filtering off the resin, the supernate and washings were titrated with standardized NaOH. The titer represents the total cation equivalents of $H_3O^+ + VO^{2+}$. After subtracting the oxovanadium(IV) titer, one obtains the acid content of the solution.

Oxovanadium(IV) perchlorate solution was prepared by dissolving equimolar amounts of V_2O_5 and V_2O_3 in perchloric acid. The V_2O_3 was made by reducing V_2O_5 with H_2.[21]

Hydrochloric acid solutions were prepared by absorbing "dried" HCl (Matheson) gas in 2.0% $H_2{}^{17}O$, whose preparation has been described elsewhere.[10]

Nmr Measurements.—Measurements were made using a Varian wide-line magnetic resonance spectrometer. Resonances were observed in the absorption mode with 40-Hz modulation frequency. When the lines were sufficiently narrow, measurements were obtained by the side-band technique using a modulation of 400 Hz.

Chlorine-35 measurements were made at 5.000 MHz and ^{17}O measurements at 8.000 MHz. Measurements at constant temperature were made using spherical bulbs. Variable-temperature measurements were made in cylindrical vacuum-jacketed vessels. There was no significant difference in measurements in cylindrical or spherical vessels at the same temperature. The temperature was varied by passing heated or cooled nitrogen gas through a glass coil immersed in the oxovanadium(IV) chloride solution. The blank correction is a serious problem in determining line broadening by the paramagnetic oxovanadium(IV) ion. Concentrated oxovanadium(IV) ion contributes substantially to the viscosity of the solutions and in turn to the line broadening of the unbound $H_2{}^{17}O$ and $^{35}Cl^-$. In order to assign the proper corrections it was necessary to determine the viscosity over a wide range of temperatures and concentrations of oxovanadium(IV) chloride in hydrochloric acid. It was assumed that the proper ^{17}O or ^{35}Cl correction for an oxovanadium(IV) ion solution was the width measured in an HCl solution of the same viscosity and temperature. This method seemed to be the best compromise and was internally consistent over a wide range of oxovanadium(IV) ion concentrations at a given HCl concentration. Wüthrich and Connick made similar corrections on analysis of ^{17}O line widths in oxovanadium(IV) perchlorate solutions.[6]

The error which results from assuming that the proper blank is well approximated by a solution of HCl of the same viscosity and temperature is estimated to be no greater than 10% of the relaxation rate in the blank. The importance of this error decreases with increased temperature. The viscosity of solutions and, therefore, the blank decrease with temperature while the rates of relaxation due to vanadyl ion increase rapidly. The error could affect calculated activation energies measured for $^{35}Cl^-$ exchange but probably does not because widely varied concentrations of oxovanadium chloride at constant HCl concentration yield the same relaxation rates and activation energies. The increasing importance of errors in blanks makes it unwise to attach great significance to broadening results in solutions much below room temperature.

In estimating blank corrections for an nmr solution experiment several contributing effects are usually combined in a linear fashion. Soundness of the assumption that synergistic effects are not so large as to vitiate such treatment is supported by the consistency of final results obtained over a wide range of experimental variables.

III. Analysis and Interpretation

The observed increase in chlorine-35 relaxation rate with increasing chloride activity reflects a dependence intermediate between first and second power. The dependence becomes approximately linear at the highest HCl concentrations. Those observations are most readily interpreted through consideration of two chloro species whose formation depends upon the ratio $a_\pm/a_1$, in which $a_\pm$ is the HCl mean ion activity and a_1 the activity of water (referred to unity at infinite dilution). The complexes are assumed to be formed sequentially as in

$$VO(H_2O)_4{}^{2+} + Cl^- \rightleftarrows VO(H_2O)_3Cl^+ + H_2O \qquad (1)$$

$$VO(H_2O)_3Cl^+ + Cl^- \rightleftarrows VO(H_2O)_2Cl_2 + H_2O \qquad (2)$$

Chemical shift measurements of oxygen-17 and chlorine-35 in the experimental solutions indicate that broadening attributable to exchange of nuclei between differing environments, shift broadening, is negligible in any of the oxovanadium(IV) solution species. Thus, it is expected that each complex exerts an influence on transverse relaxation of noncomplexed nuclei which can be expressed by

$$T_{2\mathrm{P}i}{}^{-1} = p'\alpha_i n_i/(T_{2\mathrm{M}i} + \tau_{\mathrm{M}i}) \qquad (3)$$

and the observed overall transverse relaxation rate, by

$$(p'T_{2\mathrm{P}})^{-1} = \sum_i \alpha_i n_i/(T_{2\mathrm{M}i} + \tau_{\mathrm{M}i}) \qquad (4)$$

In these equations α_i is the fraction of oxovanadium(IV) species in complex i, n_i is the number of resonant nuclei in exchanging ligands in complex i, $T_{2\mathrm{M}i}$ is the transverse relaxation time for nuclei coordinated in complex i, and $\tau_{\mathrm{M}i}$ is the mean residence time for nuclei in complex i. Equation 3 represents a limiting case (small chemical shift) of the more general equation given by Swift and Connick[22] but may also be derived directly from the Bloch equations[23,24] by neglecting the contribution of chemical shift. Equivalent expressions may be separately written for chlorine-35 and oxygen-17. The two sets are then related through the α_i's which are common to both.

In this work, fractional concentrations of complex species are represented by

$$\alpha_i = K_i\alpha_{i-1}a_\pm/a_1 \qquad (5)$$

and

$$\alpha_0 = 1 - \sum_i \alpha_i \qquad (6)$$

where i = 0, 1, and 2 denotes $VO(H_2O)_4{}^{2+}$, $VO(H_2O)_3Cl^+$, and $VO(H_2O)_2Cl_2$, respectively. Concentration quotients α_i/α_{i-1} should, in principle, be multiplied by the activity coefficient ratios γ_i/γ_{i-1} as they appear in expressions for the equilibrium constants. If appropriate information were available for chlorides of the several charge types in concentrated HCl solutions, it would probably be best to evaluate the γ_i/γ_{i-1} for model systems. That is not possible in this case, and none of the widely used analytical expressions for $\gamma_\pm$ is usable over the concentration range employed here. Having accounted for the activities of water and HCl as completely as possible in the equilibrium expressions, we find that the assumption that the various γ_i/γ_{i-1} are independent of solution composition under the conditions of these experiments is sufficient to rationalize the data over a broad range of conditions and has the virtue of simplicity. That assumption has been made in previous work[10-12,25] and provides consistent analyses of experimental results. Recently, Matwiyoff and Wageman[26] have observed that the assumption is compatible with the distribution of aluminum fluoride complex species in nitrate solutions over a wide range of ionic strengths, regardless of ionic charge differences. It should be pointed out that species concentrations are effectively determined over relatively narrow ranges of conditions.

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Relationships among the relaxation parameters and relative concentrations are such that the contribution from each species is important in the overall observed effect only over a restricted HCl concentration range. Thus, the demands of constancy on γ_i/γ_{i-1} are less severe than would be necessary for the entire range of conditions. With that assumption, the activity coefficient ratios are incorporated into the equilibrium constants, K_i, which are then semithermodynamic and must be treated as such.

Specific ligand-exchange rate constants, k_i, are related to the mean ligand residence times, τ_{Mi}, by

$$k_i a_1 = 1/\tau_{Mi} \qquad (7)$$

if the rate is pseudounimolecular and dependent on water activity. That suggests a true bimolecular mechanism in which the activated complex is formed by incorporation of H_2O in the coordination sphere of the parent complex. However, the change in a_1 over the range of solution composition, within which the contribution of a given complex is important, is relatively small.

Temperature dependences of the several parameters in eq 4 and 5 were assumed to be exponential, as in

$$K_i = K_i^0 \exp(\Delta H_i/RT) \qquad (8)$$

$$k_i = k_i^0 \exp(E_i/RT) \qquad (9)$$

$$T_{2Mi}^{-1} = c \exp(V_i/RT) \qquad (10)$$

Because of the semithermodynamic character of the equilibrium constants and reservations concerning the reference states for the rate and relaxation processes, we have refrained from evaluating entropy or activation entropy values from these treatments of the data.

At constant temperature, the overall equation for oxygen-17 broadening is

$$\frac{1}{p'_{^{17}O}T_{2P}} = \frac{4\alpha_0}{T_{2M0} + \tau_{M0}} + \frac{3\alpha_1}{T_{2M1} + \tau_{M1}} + \frac{2\alpha_2}{T_{2M2} + \tau_{M2}} \qquad (11)$$

and for chlorine-35 is

$$\frac{1}{p'_{^{35}Cl}T_{2P}} = \frac{\alpha_1}{T_{2M1} + \tau_{M1}} + \frac{2\alpha_2}{T_{2M2} + \tau_{M2}} \qquad (12)$$

In each instance T_{2P}, T_{2Mi}, and τ_{Mi} refer to the specific nucleus in question.

A nonlinear least-squares program[27] was adapted to analysis of the broadening data at all temperatures and concentrations, using eq 5–12. Because of the large number of variable parameters and high correlations of a number of them, the program could not be run with all parameters free. Therefore, K_1 and the several activation energies and enthalpies were estimated from the broadening behavior at both limits of temperature and HCl concentration. The remaining parameters were then calculated. An extensive series of such approximations and calculations was done to reduce the variance to a minimum value. Approximate values of K_1 and K_2 were used to calculate fractions of each complex species. The approximate ionic strength was then obtained by the relation

$$\mu = m_{HCl} + m_{VOCl_2}(3\alpha_0 + \alpha_1) \qquad (13)$$

with

$$c/\mu = 0.9972 - 0.01817m_{HCl} - 0.092m_{VOCl_2}$$

Values of $\gamma_\pm$(HCl) were calculated[28] for solutions up to 4 m in HCl. For higher concentrations, those values were taken from the data of Akerlöf and Teare.[29] In each instance, the activity of water, a_1, was obtained by integration of the Gibbs–Duhem equation over the appropriate range of $\gamma_\pm$. The activity values were then used to determine best estimates of K_1 and K_2 by least-squares fit of the broadening data for both oxygen-17 and chlorine-35. Calculations were then repeated to refine the activity coefficients. Free chloride ion concentrations were obtained from

$$[Cl^-] = m_{HCl} + m_{VOCl_2}(2\alpha_0 + \alpha_1) \qquad (14)$$

and

$$\alpha_\pm = \gamma_\pm[Cl^-] \qquad (15)$$

Final results, using the parameters listed in Table I, are shown as solid lines in Figures 1–3 and Tables

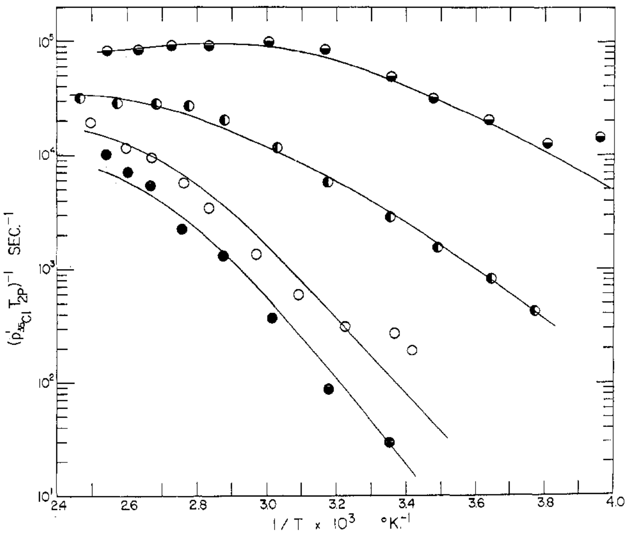

Figure 1.—Temperature dependence of relaxation rate of ^{35}Cl in HCl solutions of oxovanadium(IV) chloride: ●, 0.525 m HCl–0.416 m $VOCl_2$; ○, 2.06 m HCl–0.386 m $VOCl_2$; ◐, 5.35 m HCl–0.793 m $VOCl_2$; ◒, 12.89 m HCl–0.569 m $VOCl_2$.

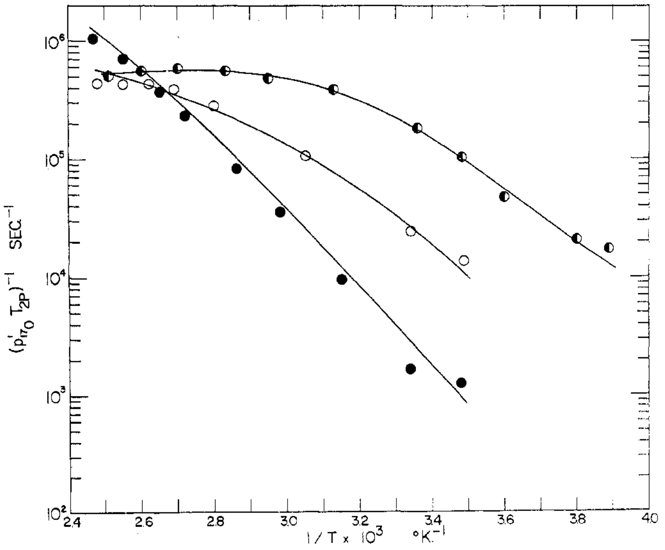

Figure 2.—Temperature dependence of relaxation rate of ^{17}O in HCl solutions of oxovanadium(IV) chloride: ●, 0.525 m HCl–0.416 m $VOCl_2$; ○, 5.35 m HCl–0.793 m $VOCl_2$; ◐, 12.89 m HCl–0.569 m $VOCl_2$.

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TABLE I

EQUILIBRIUM AND RELAXATION PARAMETERS AT 27 ± 1°

	Complex		
	$VO(H_2O)_4^{2+}$	$VO(H_2O)_3Cl^+$	$VO(H_2O)_2Cl_2$
	$H_2{}^{17}O$ ligand		
Specific ligand reaction rate constant, sec^{-1}	$(5.9 \pm 0.2) \times 10^2$	$(2.3 \pm 0.6) \times 10^4$	$(8.5 \pm 0.3) \times 10^5$
Activation energy, kcal/mol	15 ± 1	11 ± 1	10 ± 1
Contact relaxation rate, sec^{-1}	1.9×10^6 [a]	$(2.9 \pm 0.4) \times 10^5$	$(9.4 \pm 1.2) + 10^5$
Activation energy, kcal/mol	0	-1.5[b]	-1.5[b]
	$^{35}Cl^-$ Ligand		
Specific ligand reaction rate constant, sec^{-1}		$(2.0 \pm 1.6) \times 10^3$	$(2.3 \pm 0.2) \times 10^5$
Activation energy, kcal/mol		12 ± 2	7 ± 1
Contact relaxation rate, sec^{-1}		$(8.2 \pm 3.5) \times 10^4$	$(2.2 \pm 0.5) \times 10^5$
Activation energy, kcal/mol		-1.5[b]	-1.5[b]
	Equilibrium Data		
Constant		$(1.2 \pm 0.3) \times 10^{-2}$	$(1.0 \pm 0.2) \times 10^{-3}$
Enthalpy, kcal/mol		7.5 ± 1.0	2.6 ± 0.5

[a] Estimated from data given in ref 9. The contribution to overall broadening is negligible under conditions employed in these experiments. [b] Estimated from high-temperature data at high HCl concentrations. The value was assumed to be constant in all calculations. Temperature dependence of T_{1e} for oxovanadium(IV) species is expected to be very nearly zero.[7]

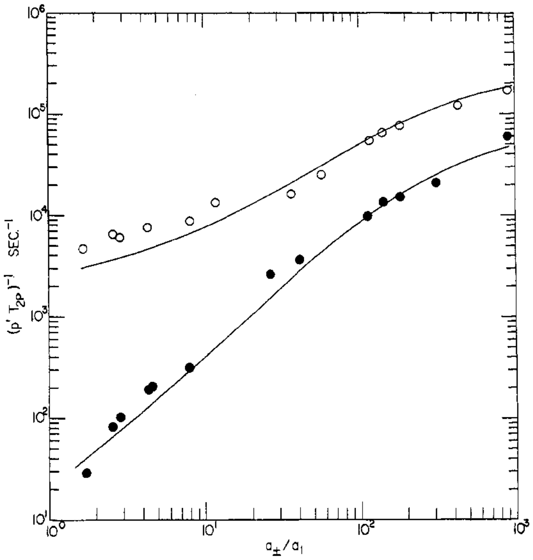

Figure 3.—Relaxation rate at 27° in HCl solutions of oxovanadium(IV) chloride as a function of the ratio $a_\pm/a_1$: ●, $(p'_{^{35}Cl}T_{2P})^{-1}$; ○, $(p'_{^{17}O}T_{2P})^{-1}$.

TABLE II

VARIATION OF ^{35}Cl RELAXATION RATE WITH HCl CONCENTRATION AT 27 ± 1°

Molality							$10^{-2}(p'_{^{35}Cl}T_{2P})^{-1}$, sec^{-1}	
HCl	$VOCl_2$	$a_\pm$	a_1	α_0	α_1	α_2	Exptl	Calcd
0.195	0.636	1.47	0.896	0.981	0.019	...	0.28	0.41
0.497	0.722	2.21	0.863	0.970	0.030	...	0.81	0.66
0.762	0.664	2.43	0.857	0.967	0.033	...	1.04	0.75
1.31	0.669	3.53	0.822	0.951	0.049	...	1.90	1.23
2.14	0.720	6.33	0.794	0.912	0.087	0.001	3.21	2.78
4.15	0.786	17.9	0.664	0.751	0.242	0.007	26.5	15.2
5.00	0.790	25.2	0.616	0.662	0.324	0.014	37.0	27.4
7.34	0.717	56.6	0.499	0.398	0.539	0.063	98.4	99.8
7.69	0.826	67.0	0.474	0.340	0.576	0.084	137	127
8.26	0.863	82.0	0.444	0.276	0.608	0.116	153	166
9.39	0.963	119	0.389	0.172	0.629	0.199	210	257
12.16	0.963	258	0.284	0.045	0.493	0.462	611	465
12.89	0.569	296	0.266	0.034	0.450	0.516	700	494

II and III. It should be recognized that the constraints placed on the calculation by the requirement that all data be fitted simultaneously are quite stringent. Error limits given in Table I are standard deviations obtained in the computer calculations.

TABLE III

VARIATION OF ^{17}O RELAXATION RATE WITH HCl CONCENTRATION AT 27 ± 1°

Molality							$10^{-3}(p'_{^{17}O}T_{2P})^{-1}$, sec^{-1}	
HCl	$VOCl_2$	$a_\pm$	a_1	α_0	α_1	α_2	Exptl	Calcd
0.195	0.636	1.46	0.896	0.981	0.019	...	4.72	3.19
0.497	0.722	2.20	0.863	0.970	0.030	...	6.54	3.68
0.762	0.664	2.43	0.857	0.967	0.033	...	6.05	3.84
1.31	0.669	3.53	0.822	0.951	0.049	...	7.66	4.60
2.14	0.720	6.33	0.794	0.912	0.087	0.001	8.84	6.74
3.33	0.587	10.0	0.744	0.860	0.138	0.002	13.7	9.66
5.08	0.622	22.9	0.633	0.691	0.298	0.011	16.3	21.0
6.22	0.506	32.8	0.582	0.584	0.394	0.023	25.8	30.7
7.30	0.793	58	0.495	0.389	0.545	0.066	54.6	56.5
7.69	0.826	67	0.474	0.340	0.576	0.084	65.7	65.8
8.262	0.863	82	0.444	0.276	0.608	0.116	77.2	80.5
10.39	0.811	153	0.354	0.118	0.610	0.272	120	138
12.16	0.963	258	0.284	0.045	0.493	0.462	190	186

The nuclear transverse relaxation time, T_{2M}, for oxygen-17 coordinated in oxovanadium(IV) complexes is probably determined by the nuclear–electron spin exchange process,[6-9] and that for chlorine-35, by a corresponding mechanism. In the latter case, quadrupolar relaxation may also be important because of the large quadrupole coupling constant observed for chlorine-35. However, by comparison with the measured quadrupolar relaxation in cobalt(II)–chloro species[12] it is estimated that the effect here is several orders of magnitude smaller than the spin-exchange contribution and cannot explain the results.

As the electronic spin–lattice (longitudinal) relaxation time for oxovanadium(IV) is generally thought to be of the order of 10^{-8}–10^{-9} sec,[6-9,30] the appropriate expression for T_{2M} is[31]

$$T_{2M}^{-1} = (1/3)S(S + 1)(A/\hbar)^2\tau_e \tag{16}$$

in which

$$\tau_e^{-1} = T_{1e}^{-1} + \tau_M^{-1} \tag{17}$$

With $\tau_M \gg T_{1e}$, τ_e may be equated with T_{1e} for these systems.

Given accurate measured values for the coupling constant, $A/\hbar$, correlation times, τ_e, may be estimated. In oxovanadium(IV) solutions the chemical shifts are quite small relative to broadening, and exchange rates are sufficiently slow at all but the highest temperatures and most concentrated HCl solutions that they cannot be relied upon for quantitative treatment. We have calculated the quantity $(A/\hbar^2)\tau_e$ for each species from

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(31) N. Bloembergen, *J. Chem. Phys.*, **27**, 572, 595 (1957).

TABLE IV

SPIN-EXCHANGE RELAXATION PARAMETERS

	$(A/\hbar)^2\tau_e$, radians²/sec	
	^{17}O	^{35}Cl
$VO(H_2O)_4^{2+}$	7.6×10^6 [a]	
$VO(H_2O)_3Cl^+$	1.2×10^6	3.3×10^5
$VO(H_2O)_2Cl_2$	3.8×10^6	8.8×10^5

[a] Taken from ref 9; $A/\hbar = (4.4 \pm 1.5) \times 10^6$ Hz; $\tau_e \leqq 10^{-8}$ sec.

values of T_{2M} and listed them in Table IV. There it is apparent that either $A/\hbar$ or τ_e varies from species to species or that both do.

IV. Discussion

A number of different interpretations of the data were attempted before settling on the one given in the preceding section. Those included consideration of additional complexes, cis and trans isomers of $VO(H_2O)_2Cl_2$ with different rate constants, and additional terms in the exchange rate laws. In the majority of trials additional parameters did nothing to improve the fit of experimental data, as compared to the model chosen, or made it worse. However, in one instance the fit was as good with an equal number of parameters. In that model it was assumed that a single, monochloro complex is formed and that exchange of both H_2O and Cl^- is subject to a two-term rate law, one involving association of H_2O with the complex to form the activated complex; the other, Cl^-. This model is really not a great deal different from the two-complex one-term model, except that the rate of the process

$$VO(H_2O)_2Cl_2 + H_2O \longrightarrow VO(H_2O)_3Cl^+ + Cl^-$$

is large enough to prevent build-up of the dichloro species. Thus, the essential difference between the two models lies in the relative rates of processes participating in the complex equilibria. Mathematically, the two models are very nearly equivalent and a choice is difficult on the basis of parametric analysis alone.

The two-complex model yields H_2O-exchange rate constants which are consistent with previous results in other metal ion systems[10-12] and with the results of Wüthrich and Connick[7] for chelate complexes of oxovanadium(IV). Substitution of water by another basic ligand tends to increase the pseudounimolecular H_2O-exchange rate constant in a progressive manner. The value $k_2 = 8.5 \times 10^5$ sec^{-1} for $VO(H_2O)_2Cl_2$ may be compared with those obtained[7] for $VO(H_2O)_2(SSA)^-$ (SSA = 5-sulfosalicylic acid), 1.5×10^5 sec^{-1}, and $VO(H_2O)_2(Tiron)^{2-}$ (Tiron = 1,2-dihydroxybenzene-3,5-disulfonic acid), 5.3×10^5 sec^{-1}. The small differences among the values are probably attributable to the varying abilities of the ligands to reduce the effective charge of the V^{4+} central ion. Overall charge on the complex species does not appear to play a major role in determination of the H_2O-exchange rate constant.

In each instance, the Cl^--exchange rate constant is less than that for H_2O. (Note that the constants refer to specific H_2O molecules or Cl^- ions, rather than to the entire complex.) That is especially true for $VO(H_2O)_3Cl^+$, in which H_2O exchange is *ca.* 12 times faster than that of Cl^-.

Examination of the equilibrium expressions 1 and 2 reveals that the reactions

$$VO(H_2O)_4^{2+} + Cl^- \xrightarrow{k_3} VO(H_2O)_3Cl^+ + H_2O \qquad (18)$$

and

$$VO(H_2O)_3Cl^+ + Cl^- \xrightarrow{k_4} VO(H_2O)_2Cl_2 + H_2O \qquad (19)$$

could limit the residence times for H_2O in the parent complexes. As the reverse reaction rates and equilibrium constants have been determined in each case, k_3 and k_4 may be estimated to be 16 and 284 l. mol^{-1} sec^{-1}. The contributions to τ_{M1} and τ_{M2} are given by

$$\tau_M^{-1} = ka_\pm$$

and the relative importance of Cl^--dependent mechanisms can be approximated. On that basis, we find that reaction 19 could contribute about 20% of the broadening in 13 *m* HCl solution at 300°K and 12% in 5.3 *m* HCl solution. Elsewhere, the effect is essentially negligible (<2%). Thus, the process is not expected to affect the mathematical analysis significantly and would be indeterminate in terms of variable parameters included in the data-reduction process.

Species abundances shown in Figure 4 are compatible with the epr results of Kon and Sharpless[18] for 3 *M* HCl in that the dominant species at low temperatures is $VO(H_2O)_4^{2+}$. We must conclude that the two epr spectra they observed in low-temperature glassy solutions at 12 *M* HCl are those of $VO(H_2O)_3Cl^+$ and $VO(H_2O)_2Cl_2$, giving *g*- and *A*-tensor components similar to those of $VO(H_2O)_4^{2+}$ for the former and to those of $VOCl_4^{2-}$ for the latter. A single spectrum was obtained in liquid solution at room temperature whose $\langle g \rangle$ and $\langle A \rangle$ corresponded to the second species ($VO(H_2O)_2Cl_2$ in our interpretation). Such an effect could be observed if T_{2e} for $VO(H_2O)_3Cl^+$ is significantly shorter than that of $VO(H_2O)_2Cl_2$ at room temperature. There is some justification for that in the values for $A/\hbar^2\tau_e$ given in Table IV, where the ratios of values for oxygen-17 in the two chloro complexes and for chlorine-35 in the two are both *ca.* 3. That suggests that the lower values found for $VO(H_2O)_3Cl^+$ are attributable to shorter τ_e, which should be the same for both nuclei if $\tau_e = T_{1e}$.

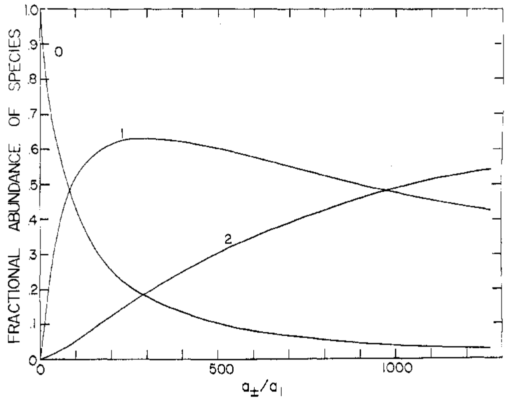

Figure 4.—Fractional abundance of complex ion species in HCl solutions of oxovanadium(IV) chloride as a function of the ratio $a_\pm/a_1$: 0, $VO(H_2O)_4^{2+}$; 1, $VO(H_2O)Cl^+$; 2, $VO(H_2O)_2Cl_2$.

Then, assuming that the difference is also reflected in T_{2e}, much broader epr lines are expected for the monochloro species, which would be difficult to detect in the presence of the sharper spectrum of $VO(H_2O)_2Cl_2$.

The liquid solution epr spectra for a number of HCl concentrations were also observed in this laboratory. The intensity of the spectrum attributed to $VO(H_2O)_4^{2+}$ appeared to follow qualitatively the relative concentrations indicated in Tables II and III and Figure 4. However, no attempt was made to do an absolute spin count. In 12 *M* HCl solution the $\langle g \rangle$ and $\langle A \rangle$ values obtained corresponded well with those reported by Kon and Sharpless and the observed line widths were somewhat broader than those of the $VO(H_2O)_4^{2+}$ spectrum. That observation is compatible with a decreased τ_e relative to that of the aquo complex, but a much more detailed investigation of the relaxation processes would be necessary for quantitative comparison.

Acknowledgments.—We are indebted to Dr. W. Burton Lewis and others for helpful comments during discussions of the work reported here. We also wish to thank Dr. B. B. McInteer and Mr. R. M. Potter of the Los Alamos Scientific Laboratory for supplying the enriched $N^{17}O$.

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Tungstovanadate Heteropoly Complexes. II. Products of Acidification of $V_2W_4O_{19}^{4-}$ [1]

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Received April 30, 1971

Acidification of solutions of $V_2W_4O_{19}^{4-}$ is an efficient means of preparing the red complex $V_4W_9O_{40}^{6-}$, isolated as K, NH_4, Na, $N(CH_3)_4$, $C(NH_2)_3$, and $C_2H_4(NH_3)_2$ salts. This complex is the same as that previously formulated as $V_3W_7O_{31}^{5-}$. This complex is most stable at pH near 3. At pH 5 it is converted to $V_2W_4O_{19}^{4-}$ and isopolytungstate. On acidification it does not give an oxide precipitate; the free acid can be extracted with ether. Infrared data, elemental analyses, chemical behavior, and comparisons with metatungstate lead to proposal of a Keggin structure $V(W_9V_3)O_{40}^{6-}$ for the complex. At least three other complexes are formed on acidification of $V_2W_4O_{19}^{4-}$; one of these has been isolated as orange-red $K_6V_3W_{10}O_{40}\cdot 20H_2O$. It appears to have a Keggin structure $V(W_{10}V_2)O_{40}^{6-}$.

Introduction

As part of our investigations on tungstovanadate heteropoly complexes,[2] we have obtained at least four products on acidification of salts of $V_2W_4O_{19}^{4-}$ in the pH range 0–3. One of these products has been isolated as potassium, ammonium, sodium, and organic cation salts; their analyses all agree with the composition $M'_6V_4W_9O_{40}\cdot nH_2O$. These salts evidently contain the same anion as some prepared, *e.g.*, by Rosenheim and Pieck[3] which, however, they formulated as (modern notation) $M'_5V_3W_7O_{31}\cdot nH_2O$. Our characterization of these compounds, presented here, leads to a structure proposal based on a 12-tungstometalate (Keggin) constitution. Only one of the other products has been successfully purified. It has been isolated as $K_6V_3W_{10}O_{40}\cdot 20H_2O$ and appears also to possess a Keggin structure.

Experimental Section

Ammonium paratungstate was prepared by reaction of $WO_3\cdot H_2O$ with excess NH_4OH in aqueous solution. After all the solid had reacted and dissolved, the solution was evaporated at 80–90°. Ammonium hydroxide was added at intervals to keep the pH in the range 5–7. The white slightly soluble product which separated was collected on a Büchner funnel, washed with small portions of hot water, and air dried. *Anal.* Calcd for $(NH_4)_{10}(H_2W_{12}O_{42})\cdot 4H_2O$: NH_4, 5.76; W, 70.43. Found: NH_4, 5.72, 5.74; W (by ignition to 600°), 70.67, 70.74.

Sodium metatungstate was prepared by Pope and Varga[4] according to Freedman's method.[5]

The preparation of other reagents not obtained commercially has been described.[2]

Guanidinium Metatungstate.—A solution of 0.5 mmol of sodium metatungstate in 20 ml of hot water was treated with a solution of 3 mmol of guanidinium chloride in 3 ml of water. The mixture was reheated and allowed to cool. A nearly white powder separated on cooling. It was filtered off, washed with water followed by 95% ethanol, and air dried. *Anal.* Calcd for $(CN_3H_6)_6(H_2W_{12}O_{40})\cdot 3H_2O$: C, 2.08; H, 1.28. Found: C, 2.30; H, 1.40.

Tetramethylammonium Metatungstate.—A solution of 0.5 mmol of the sodium salt in 5 ml of water was treated with a solution of 6 mmol (0.7 g) of tetramethylammonium chloride in 3 ml of water. The resulting white precipitate was isolated and recrystallized from water containing 1 mmol of tetramethylammonium chloride by room-temperature evaporation. Colorless (very pale yellow in bulk) six-sided tablets or blocks (parallel extinction, optically biaxial) were obtained. They were isolated by washing with water–ethanol and 95% ethanol and air drying. The crystals were stored over sodium sulfate decahydrate, since they are efflorescent in a dry atmosphere. *Anal.* Calcd for $[N(CH_3)_4]_6[H_2W_{12}O_{40}]\cdot 10H_2O$: C, 8.30; H, 2.73; W, 63.4. Found: C, 8.41; H, 2.70; W (by ignition to 600°), 63.4.

Salts of the 9-Tungsto-4-vanadate(V) Anion, $M'_6V_4W_9O_{40}\cdot nH_2O$ (M' = Univalent Cation). (a) **Potassium Salt.**—A solution of 50 mmol of $K_4V_2W_4O_{19}$ was prepared from stoichiometric quantities of K_2CO_3, V_2O_5, and $WO_3\cdot H_2O$.[2] The solution was diluted to about 200 ml and treated with a solution of 70 mmol (9.5 g) of $KHSO_4$ in 50 ml of water. There was little or no immediate visible change. The mixture was heated and stirred at about 80° for 4 hr, during which time it became red and

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[1] Presented as part of Paper IN-10 at the Sixth Middle Atlantic Regional Meeting of the American Chemical Society, Baltimore, Md., Feb 3–5, 1971.

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