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Electron Spin Resonance and pH Studies of Vanadyl Complex Formation with α-Hydroxy and α-Mercapto Carboxylic Acids

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Received July 28, 1970

The esr spectrum of vanadyl ion in the presence of lactic or glycolic acids (H_2A) indicates the existence of at least six different species over the pH range 1–7. By studying the behavior of the esr intensities in the vanadyl–lactic acid system as a function of pH and ligand-to-metal ratio, the observed species are identified as (1) the aquovanadyl ion and the 1:1 complex $VO(HA)^+$, which give virtually indistinguishable esr spectra, $a = 116$ G, $g = 1.965$; (2) the 2:1 complex $VO(HA)_2$, $a = 108$ G; (3) the chelates with one hydroxyl proton ionized, VO(A) and $VO(A)(HA)^-$, which give indistinguishable spectra, $a = 102$ G, $g = 1.968$; and (4) the cis and trans chelates with both hydroxyl protons ionized, $VO(A)_2{}^{2-}$, $a = 90, 87$ G, $g = 1.972$; although two isomers can be disinguished, they cannot be uniquely identified. An additional species, present in very low concentration at neutral pH, is probably a dimer containing two equivalent vanadium nuclei, $a = 33$ G. Complex formation equilibrium constants are estimated from the room-temperature data and acid dissociation constants measured for the hydroxyl protons in the complexes. The pK_a's for the first and second dissociations of the lactic and glycolic acid complexes are, respectively, 3.5 and 5.0 and 3.5 and 5.7. Similar experiments with the mercapto analogs thiolactic and thioglycolic acids give somewhat analogous results, except that the formation constants are much smaller and the mercapto protons much more acidic. Thus with thiolactic acid, only five species were observed: the aquo ion; the 1:1 complex with the mercapto protons ionized, VOA, $a = 102$ G, $g = 1.970$; the cis and trans isomers of the 2:1 complex with both mercapto protons ionized, $VOA_2{}^{2-}$, $a = 88, 85$ G, $g = 1.978$; and the low-intensity dimer observed with the hydroxy acids. No esr evidence could be obtained for stable complexes above pH 4 for the following ligands: methoxyacetic acid, β-hydroxypropionic acid, β-mercaptopropionic acid, glycine, *N*-acetylglycine, *N*-acetyl-L-cysteine, α-aminobutyric acid, β-aminobutyric acid, γ-aminobutyric acid, ethylene glycol, and acetoin. It is argued that the high acidity of the hydroxyl and mercapto protons in vanadyl complexes is due to delocalization of the unshared pair of electrons on oxygen or sulfur in a molecular orbital containing appreciable metal character and that the corresponding decrease in the vanadium nuclear hyperfine splittings and the increase in the *g* values is due to decreased vanadium character in the molecular orbital containing the odd electron.

Introduction

There has been considerable interest in the recent literature in the structure and spectra of complexes of the oxovanadium(IV) or vanadyl ion with α-hydroxy carboxylic acids.[1–11] Much of the recent work has dealt with tartrate complexes, where a dimeric 1:1 vanadyl tartrate complex has been found in crystals and in aqueous solutions at neutral pH.[4–11] Under these conditions, the tartrate ion is tetradentate, and both hydroxyl protons are ionized. Evidence for other complexes at lower pH has been presented. The complexation of vanadyl ion with simpler α-hydroxy acids such as glycolic acid and lactic acid has been studied in a preliminary fashion,[2,3,9] but no complete study of the various equilibria has been presented. In particular, there seems to be no unique proof that hydroxyl protons ionize in vanadyl complexes with the simple aliphatic hydroxy acids; indeed, there is no hint in the literature on exactly what species are present in aqueous solutions of vanadyl ion and α-hydroxy carboxylates. Furthermore, there has been no work on the related α-mercapto acids or on hydroxy acids with the hydroxyl group situated in the β or γ position. In this paper, we will present the results of a study of vanadyl ion with glycolic and lactic acids, with the mercapto analogs thioglycolic and thiolactic acids, and with a variety of other aliphatic ligands.

Solution equilibria involving the vanadyl ion can be followed very conveniently using esr spectroscopy. Wüthrich[12] has shown that a well-resolved esr spectrum is obtained for vanadyl ion in a wide variety of complexes with oxygen donors and that the vanadium nuclear hyperfine splitting is sensitive to the nature of the bonding. For example, the hyperfine splitting of the aquo ion is 116 G, whereas that of the 1:1 complex of the vanadyl ion with 1,2-dihydroxybenzene-3,5-disulfonic acid (Tiron) is 102 G and that of the 1:2 complex is 86 G.[12] Since the shift in the position of the low-field hyperfine line is approximately $^7/_2$ times the shift in the splitting constant and the low-field line is typically on the order of 20 G wide (width between second-derivative minima), species having splitting constant differences on the order of 5 G should be easily resolved. In the present work, we have employed second-derivative presentation in order to improve the resolution; we can easily detect two species having a splitting constant difference as small as 6 G when they are present with a concentration ratio of 20/1 or more.

Although solution color changes do take place on complex formation of vanadyl ion with hydroxy acids, some preliminary study indicated that the band shifts were relatively small and that deducing the nature of the species present would be difficult at best from the optical spectrum. Resolution of the esr spectra was very much better. Thus in the present work, we have relied entirely on pH measurements and esr spectroscopy in unraveling the various equilibria involved in such solutions.

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Experimental Section

Reagents.—Vanadyl perchlorate solutions were prepared by a procedure similar to that of Jones and Larsen.[3] The vanadyl concentration was determined by titration with standard permanganate solution at 70°. The excess acid in the vanadyl stock solutions was determined by first removing the vanadyl ion from an aliquot by passage through a column containing the acid form of Amberlite IR-120 ion-exchange resin. The resulting solution was titrated with standard sodium hydroxide, and the titer was corrected for the known amount of acid added by the ion-exchange resin.

Glycolic and lactic acids were obtained from Fisher, thiolactic acid was from Aldrich, and thioglycolic acid was from chemical stock. The thioglycolic acid was purified by distillation before use. Stock solutions of the acids were prepared containing 0.47 *M* sodium perchlorate; acid concentrations were determined by acid–base titration with standard sodium hydroxide.

Other potential ligands which were used without further purification included β-hydroxypropionic acid, β-mercaptopropionic acid, α-aminobutyric acid, β-aminobutyric acid, γ-aminobutyric acid, glycine, *N*-acetylglycine, and *N*-acetyl-L-cysteine from Aldrich, ethylene glycol from Baker, methoxyacetic acid from K & K, and acetoin from chemical stock.

pH Titrations.—pH titrations were carried out on solutions of the ligands as well as on solutions containing various ligand-to-metal ratios. All titration solutions were approximately 0.47 *M* in sodium perchlorate. Solutions were titrated with 4 *M* sodium hydroxide standard solution to minimize dilution effects and were thermostated at 25.0 ± 0.1°. The pH was measured with a Coleman Model 39 pH meter using a Coleman 3-625 combination electrode, calibrated with Fisher BuffAR standards. The sodium hydroxide solution was added using a Hamilton PB600 repeating dispenser which delivered 0.099 ml/increment. All solutions were magnetically stirred and were protected from air oxidation by nitrogen.

Esr Spectra.—First-derivative esr spectra were recorded using an X-band superheterodyne spectrometer with 1000-Hz field modulation. Simultaneous proton resonance field calibration was employed to obtain accurate splitting constants and *g* values for the α-hydroxy carboxylic acid complexes. Splitting constants were computed from the experimentally observed hyperfine line separations using a fourth-order expansion of the Breit–Rabi equation.

In order to interpret the equilibria, second-derivative spectra were employed; these were obtained using a Varian V-4502 spectrometer with 100-kHz and 400-Hz field modulation. The splitting constants for the α-mercapto carboxylic acid complexes were obtained relying on the calibration of the Varian Fieldial unit; this calibration was checked several times over the course of the work. Many of the spectra were recorded for samples thermostated at 25 ± 2° with a modified Varian variable-temperature accessory.[13] No appreciable temperature effect was observed on the position of the various equilibria (with one exception discussed below), so that data obtained both at 25° and at room temperature were used in obtaining estimates of the equilibrium constants.

Samples for esr spectra were prepared by pH titration in a thermostated pH titration vessel as in the ordinary pH titration experiments. Solutions were transferred to the spectrometer cavity by a flow system under nitrogen pressure. After spectra were recorded, the samples were returned to the titration vessel where another aliquot of base was added, the pH was measured, and the sample was returned to the cavity for another recording.

Results

pH Titrations.—pH titrations of the four ligands—glycolic acid, lactic acid, thioglycolic acid, and thiolactic acid—in the absence of vanadyl ion gave the values of pK_a listed in Table I. In the presence of vanadyl ion, a sharp break in the pH titration curve was always observed and always when 2 mol of base/mol of vanadyl ion had been added beyond that required to titrate all the carboxyl protons of the ligands. Thus, as shown in Table I, the equivalence point of a solution containing 0.01 *M* $VO(ClO_4)_2$ and 0.04 *M* α-hydroxy or α-mercapto carboxylic acid occurred when 6 equiv of base, referred to the vanadyl concentration, had been added. When the ligand-to-metal mole ratio was 10, 12 equiv of base was required; when the ratio was 2, 4 equiv of base was required.

Table I

Results of pH Titrations

Ligand	pK_a[a]	Equiv point[b]	Ligand	pK_a[a]	Equiv point[b]
Glycolic acid	3.44	6.00	Thioglycolic acid	3.59	5.93
Lactic acid	3.50	6.02	Thiolactic acid	3.51	5.94

[a] Measured for a solution 0.47 *M* in $NaClO_4$ at 25°. [b] Measured in equivalents of NaOH for solutions of vanadyl ion and ligand having a ligand-to-metal mole ratio of 4.

Esr of Lactic Acid Solutions.—Esr spectra of solutions containing vanadyl ion and lactic acid indicated the presence of at least six different vanadium-containing species in the pH range 1–7. A solution with a ligand-to-metal mole ratio of 4 provides a good example of the behavior observed. The low-field hyperfine line is shown as a function of pH in Figure 1. In the pH range 1–2, the solution exhibited a single eight-line spectrum (I) indistinguishable from that obtained in the absence of ligand. At pH 3, two superimposed spectra were observed having comparable intensity. The new set of lines (II) had a smaller hyperfine splitting constant than I (see Table II). At pH 3.2, a third set of lines (III) appeared, and at pH 3.5 the intensities of the three superimposed spectra were nearly equal. Spectrum III had a smaller hyperfine splitting constant than II. At pH 4, spectra I and II had almost disappeared, III was predominant, and

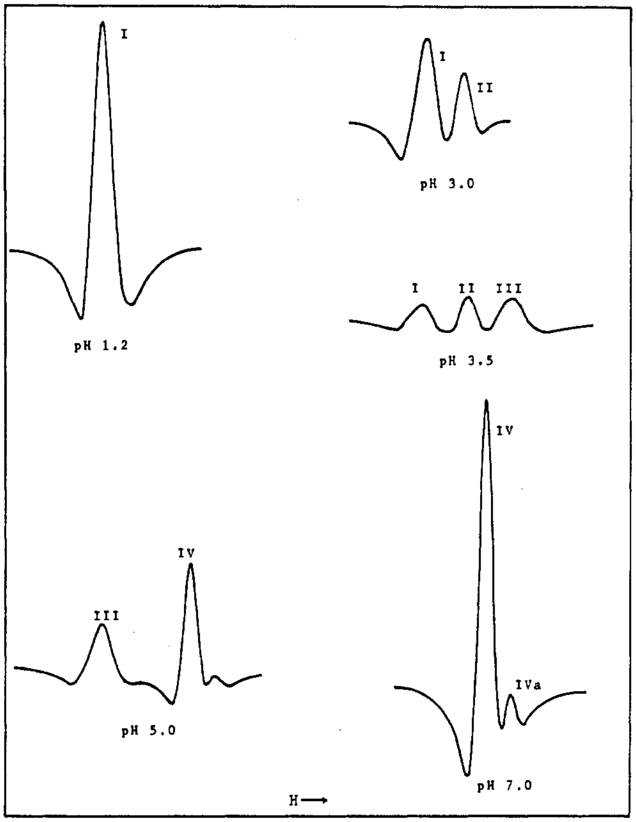

Figure 1.—Second-derivative esr spectra ($M_I = -{}^7/_2$ components) of vanadyl–lactic acid solutions with a ligand-to-metal mole ratio of 4 at 25° as a function of pH.

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[13] R. L. James and W. C. Neikam, *J. Sci. Instrum.*, **43**, 272 (1966).

TABLE II

ESR PARAMETERS

Ligand	*a*, G	*g*	Ligand	*a*, G	*g*
Lactic acid			Thiolactic acid		
I (pH 1.3)	115.7	1.965	I	116	1.965
II	108		III	102	1.970
III (pH 4.7)	101.8	1.968	IV	87.6	1.978
IV (pH 7.0)	89.8	1.972	IVa	85.0	1.978
IVa (pH 7.0)	86.9	1.972			
Glycolic acid			Thioglycolic acid		
I (pH 1.2)	115.6	1.965	I	116	1.965
III (pH 4.3)	102.8	1.968	III	101	1.970
IV (pH 7.0)	91.2	1.972	IV	88.2	1.977
IVa (pH 7.0)	88.7	1.972	IVa	85.8	1.977

two additional sets of lines (IV and IVa) had begun to emerge. Spectrum IV had a hyperfine splitting smaller than that of III, and that of IVa was slightly smaller still. Spectrum IVa was always at lower intensity than IV (see below). The lines of both IV and IVa were noticeably narrower than those of the other three spectra. At pH 7, spectrum III had disappeared, spectra IV and IVa were the dominant species, but 8 new low-intensity lines could be seen. Examination of these lines indicated the presence of at least 12 nearly equally spaced lines with a splitting of approximately 33 G. These are due to a dimeric species and are discussed in further detail below.

There are potentially six different vanadyl species present in solutions of vanadyl ion with lactic acid in the pH range under consideration if we neglect possible hydroxo complexes and polymeric species. These are the aquovanadyl ion, the simple 1:1 and 1:2 vanadyl–lactate complexes with the hydroxyl protons intact, the 1:1 complex with the hydroxyl proton ionized, and the 1:2 complex with one or both hydroxyl protons ionized. In addition to the acid dissociation constant of lactic acid, five independent equilibrium constants are required to describe the system in general

$$\mathrm{VO^{2+} + HA^- \rightleftarrows VO(HA)^+} \qquad K_1 = \frac{[\mathrm{VO(HA)^+}]}{[\mathrm{VO^{2+}}][\mathrm{HA^-}]}$$

$$\mathrm{VO(HA)^+ + HA^- \rightleftarrows VO(HA)_2} \qquad K_2 = \frac{[\mathrm{VO(HA)_2}]}{[\mathrm{VO(HA)^+}][\mathrm{HA^-}]}$$

$$\mathrm{VO(HA)^+ \rightleftarrows VO(A) + H^+} \qquad K'_{\mathrm{a1}} = \frac{[\mathrm{VO(A)}][\mathrm{H^+}]}{[\mathrm{VO(HA)^+}]}$$

$$\mathrm{VO(HA)_2 \rightleftarrows VO(A)(HA)^- + H^+} \qquad K_{\mathrm{a1}} = \frac{[\mathrm{VO(A)(HA)^-}][\mathrm{H^+}]}{[\mathrm{VO(HA)_2}]}$$

$$\mathrm{VO(A)(HA)^- \rightleftarrows VO(A)_2{}^{2-} + H^+} \qquad K_{\mathrm{a2}} = \frac{[\mathrm{VO(A)_2{}^{2-}}][\mathrm{H^+}]}{[\mathrm{VO(A)(HA)^-}]}$$

In attempting to deduce the identity of the various observed species, quantitative estimates of the spectral intensities were made, assuming Lorentzian second-derivative lines with the intensity proportional to the second-derivative amplitude multiplied by the cube of the line width. This procedure is subject to considerable uncertainty, particularly in those cases where there is evidence that a set of lines results from the superposition of two slightly different spectra. Nevertheless, the results are internally consistent as will be seen below, though there may remain a significant systematic error.

Starting with the high-pH species, we assume from the stoichiometry of the pH titrations that spectrum IV is due to the 2:1 lactate–vanadyl complex with both hydroxyl protons ionized, $\mathrm{VO(A)_2{}^{2-}}$. Since the logarithm of the III/IV ratio is very nearly linear in pH and virtually identical with that for ligand-to-metal mole ratios of 4 and 10, spectrum III is assigned to $\mathrm{VO(A)(HA)^-}$, and pK_{a2} is found to be 5.0 ± 0.1. Solutions with a mole ratio of 1 gave qualitatively similar results, although some precipitation occurred on the appearance of spectrum IV, and the intensities of spectra III and IV were equal at pH 5.5. This is explicable if spectrum III for such solutions is due to VO(A), with the III to IV conversion corresponsing to the equilibrium

$$\mathrm{2VO(A) + 2H_2O \rightleftarrows VO(A)_2{}^{2-} + VO(OH)_2\!\downarrow + 2H^+}$$

Spectrum II was only barely detectable with the solutions having a mole ratio of 1 but was very prominent when the mole ratio was 10. This spectrum therefore is most likely due to the 2:1 complex $\mathrm{VO(HA)_2}$. The II–III equilibrium then would correspond to hydroxyl proton ionization. A quantitative treatment of the II/III spectral intensity ratio is more difficult than for the III/IV ratio primarily because of the difficulty in measuring accurately the intensity of spectrum II in the presence of spectra I and III. Nonetheless, examination of the II/III ratio as a function of pH gave an apparent pK_{a1} of 3.5 ± 0.5.

If spectrum I is the aquovanadyl ion, one would expect a logarithmic plot of the II/I intensity ratio *vs.* the lactate ion concentration, computed using the lactic acid ionization constant, to give a straight line with a slope of 2. Actual plots give slopes of around 1.3 and perhaps exhibit some curvature. This can be explained if spectrum I is the superposition of the spectra of the aquovanadyl ion and the 1:1 complex with the hydroxyl proton intact, $\mathrm{VO(HA)^+}$. This interpretation receives some support from an observed slight broadening of the esr lines in spectrum I when the pH is increased from ~1. If it is assumed that spectrum I is due primarily to $\mathrm{VO(HA)^+}$ when the pH is 3 or above, the above analysis results in a value of K_2 of 40 ± 20 l./mol.

Assuming that for a mole ratio of 1, spectrum I is due to $\mathrm{VO(HA)^+}$ above pH 3 and III is due to VO(A), a log plot of the I/III ratio *vs.* pH gives an estimate of pK'_{a1}, approximately 4.25.

In summary, the assignments are as follows: spectrum I is a superposition of lines due to $\mathrm{VO^{2+}}$ and $\mathrm{VO(HA)^+}$; spectrum II is due to $\mathrm{VO(HA)_2}$; spectrum III is due to VO(A) and $\mathrm{VO(A)(HA)^-}$; and spectrum IV is due to $\mathrm{VO(A)_2{}^{2-}}$. The assignment of spectrum IVa is discussed in connection with the results on the glycolic acid system below.

Calculations of the pH titration curve and the concentrations of the various species were carried out using a wide variety of values of the various equilibrium constants covering ranges of approximately an order of magnitude larger and smaller than those estimated above. It was found that the results were relatively insensitive to K_1, and a rather arbitrarily chosen value of K_1 = 300 l./mol was chosen to investigate the effects of the other constants. This procedure resulted in verification of the values found above as the best set to fit the esr intensity measurements.

The results of a calculation using K_1 = 300 l./mol, K_2 = 40 l./mol, pK'_{a1} = 4.25, pK_{a1} = 3.5, and pK_{a2} = 5.0 are shown in Figures 2 and 3, respectively. The fit of the relative concentrations is moderately good with

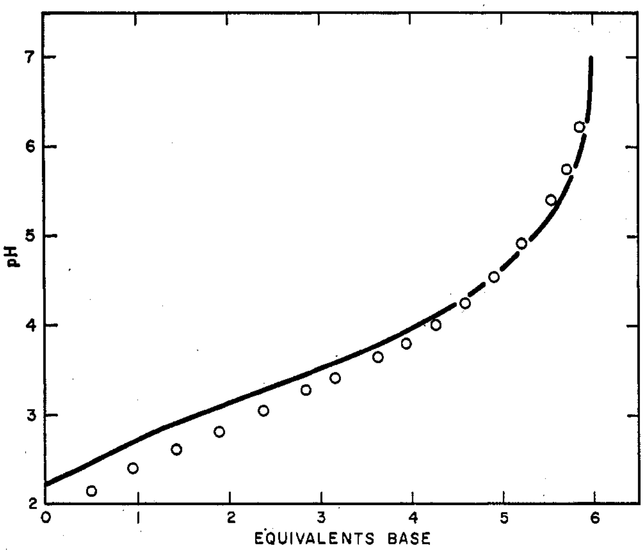

Figure 2.—Experimental (solid line) and calculated (circles) pH titration curves for a vanadyl–lactic acid solution with a ligand-to-metal mole ratio of 4.

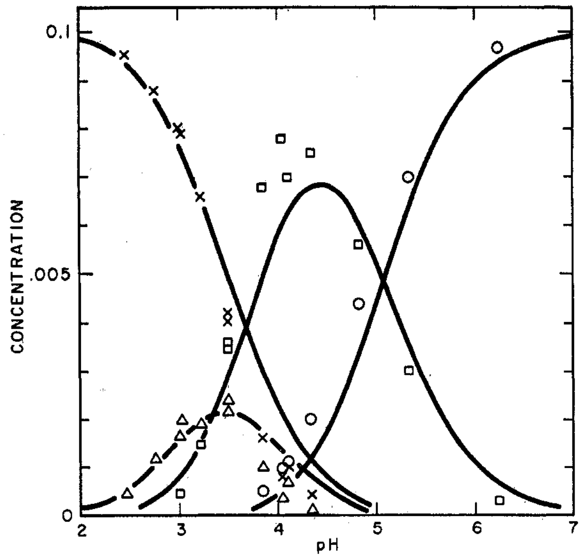

Figure 3.—Experimental (symbols) and calculated (solid lines) concentrations of various species in a vanadyl–lactic acid solution with a ligand-to-metal mole ratio of 4 as a function of pH. The spectral intensities designated by the symbols are as follows: ×, I; △, II; □, III; ○, IV.

the exception of the region around pH 4 where the calculated concentrations of VO(A) and $VO(A)(HA)^-$ are less than those obtained from spectrum III. This is probably a result of uncertainties in the spectral intensity measurements. Spectrum III is particularly uncertain since it is presumably the superposition of lines from two species. The experimental lines are somewhat asymmetric and a little broader than might have been expected. The assumption of a Lorentzian line shape is therefore probably most suspect in this case. Furthermore, in this region the concentrations of $VO(HA)^+$ and $VO(HA)_2$ are predicted to be small but significant in normalizing the concentration of VO(A)-$(HA)^-$. The experimental uncertainties in the estimates of the intensities of spectra I and II above pH 4 are very large, as much as 100–200%, so that the normalized intensity of spectrum III may be too large by as much as 10% in this region.

The pH titration curve is more disappointing, however. The calculated curve falls approximately 0.3 pH unit higher than the experimental points in the low-pH region of the curve. This discrepancy could be reduced slightly be using a larger value for K_1 but could not be removed entirely. The problem is probably either that the acid dissociation constant is larger than that listed in Table I or that the pH measurements themselves are in error. Although the pH titration curves could be reproduced within approximately 0.05 pH unit, the pH values measured could still be in error since the pH meter was routinely calibrated at pH 4 and 7 only.

Equilibrium constants for complex formation in the vanadyl–lactic acid system have been measured by Jones and Larsen[3] using the method of corresponding solutions with absorbance and circular dichroism measurements. Their results, obtained at 20° in a medium of unit ionic strength at pH 3.32, should be consistent with those reported here. In terms of the equilibrium constants defined above, their β_1 should be equivalent to our $K_1(1 + K'_{a1}/[H^+])$, while their β_2 should be equivalent to our $K_1K_2(1 + K_{a1}/[H^+] + K_{a1}K_{a2}/[H^+]^2)$. Taking the values of the K_a's estimated above, and the values of β_1 and β_2 of 4.77×10^2 and 6.73×10^4 given by Jones and Larsen, we can compute values of K_1 and K_2: 425 and 95 l./mol, respectively. We have no reliable way to estimate K_1 from the present data, but this value is consistent with our results. The value of K_2 is about twice our estimate, but the difference in temperature between our work and that of Jones and Larsen, together with the uncertainties in our value of K_2, probably accounts for the difference.

The eight low-intensity lines observed in the spectra of the high-pH solutions result from a spectrum of at least 12 equally spaced lines. The lines increase in intensity toward the center and thus could arise from a species containing two or possibly three equivalent vanadium nuclei. Hyperfine interaction with two equivalent vanadium nuclei should result in 15 lines with intensity ratios 1:2:3:4:5:6:7:8:7:6:5:4:3:2:1. Examination of the spectrum in detail convinces us that the missing 7 lines could be obscured by the much higher intensity lines of the monomeric $VO(A)_2^{2-}$. A trimer with three equivalent vanadium atoms should give 22 lines with intensity ratios 1:3:6:10:15:21:28:36:42:46:48:48:46:42:36:28:21:15:10:6:3:1. Some of the missing lines can be accounted for by their predicted positions under high intensity monomer lines, but others should have been observable. Several attempts to observe the lines predicted for a trimer were unsuccessful, so we ascribe the lines to a dimer with two equivalent vanadiums. The intensity of these lines was always less than 1% of that of the monomer and did not appear to be sensitive to pH or to the concentrations of vanadyl ion or ligand. They were observed not only in the case of lactic acid but also with glycolic, thiolactic, and thioglycolic acids. Very little can be said about the species responsible since we were unsuccessful in finding conditions where the apparent dimer was the dominant species.

Esr of Glycolic Acid Solutions.—The esr spectra of solutions containing vanadyl ion and glycolic acid were similar to those observed with lactic acid. Spectra with approximately the same hyperfine coupling constants as those labeled I, II, III, IV, and IVa for the

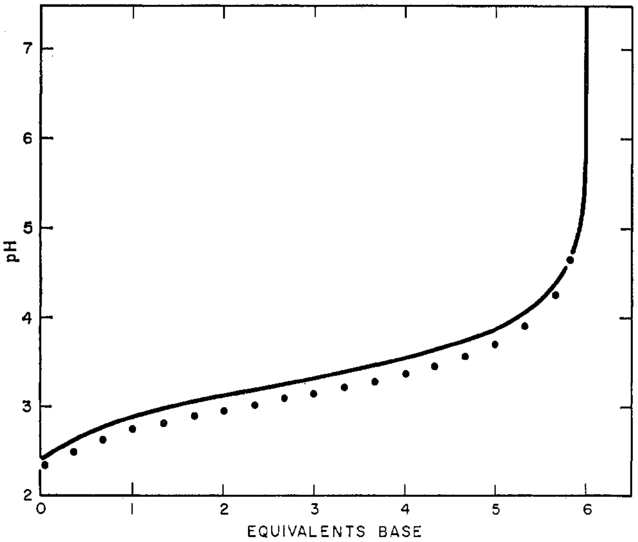

Figure 4.—Experimental (solid line) and calculated (circles) pH titration curves for a vanadyl–thiolactic acid solution with a ligand-to-metal mole ratio of 4.

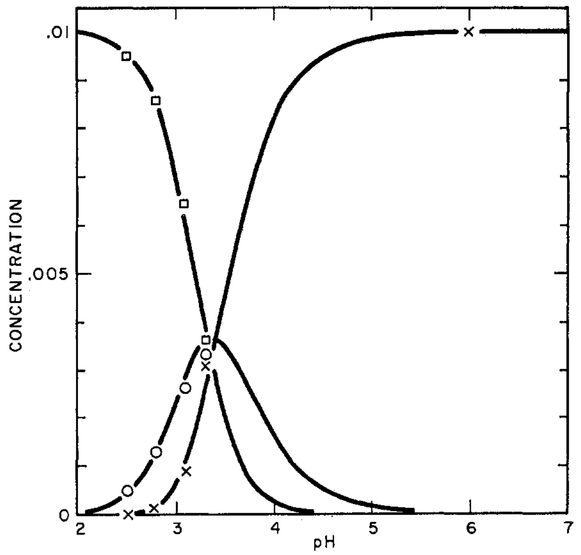

Figure 5.—Experimental (symbols) and calculated (solid lines) concentrations of various species in a vanadyl–thiolactic acid solution with a ligand-to-metal mole ratio of 4 as a function of pH. The species designated by the symbols are as follows: □, VO^{2+}; ○, VO(A); ×, VO(A)$_2^{2-}$.

lactic acid solutions were observed and are labeled in the same manner. The behavior of the spectral intensity ratios as functions of pH and the ligand-to-metal mole ratio was qualitatively the same for solutions with glycolic acid as it was in the case of lactic acid except that (1) spectrum II was only barely detectable in the vicinity of pH 3 for a ligand-to-metal mole ratio of 4 and (2) spectrum IV (and IVa) appeared at somewhat higher pH. The acid dissociation constants of the hydroxyl groups in the complexes were $pK_{a1} = 3.5 \pm 0.5$ and $pK_{a2} = 5.8 \pm 0.3$. Since spectrum II was not seen in sufficiently great intensity, no estimate can be made of K_2; it must of course be somewhat smaller than in the case of lactic acid.

Since resolution of the esr spectra IV and IVa was best in the case of glycolic acid, several experiments were performed in an attempt to determine their relationship. Spectrum IVa was always seen in conjunction with IV for all four ligand systems studied and in about the same intensity ratio.

The measured IV/IVa intensity ratios when corrected for overlap were found to be independent of pH and of ligand and vanadyl concentrations. The ratio was, however, found to be temperature dependent, with values of 0.14, 0.23, and 0.38 at 5, 25, and 60°, respectively. An Arrhenius plot of these numbers gives a moderately good straight line with apparent thermodynamic parameters $\Delta H° = +3$ kcal/mol and $\Delta S° = +8$ eu for the conversion of compound IV to IVa. Since the two spectra are very similar, both in line widths and hyperfine splitting constant, we are led to postulate, despite the anomalously large entropy difference, that compounds IV and IVa are geometrical isomers, probably trans and cis, respectively.

Esr of Thioglycolic and Thiolactic Acid Solutions.—The esr spectra of vanadyl solutions with thioglycolic or thiolactic acids contained four sets of lines in the pH range 1–10. The behavior of the solutions and the appearance of the esr spectra were qualitatively similar to the results on the lactic and glycolic acid systems. The principal differences in solutions containing the α-mercapto acids were the appearance of spectra III, IV, and IVa at lower pH and the failure to detect any trace of spectrum II under any conditions. Thus, at pH 3.1, spectra I, III, and IV (and IVa) could be observed with I predominant, but at pH 3.3, the three sets of lines were of nearly the same intensity. The intensity ratios of spectra I to III and of spectra III to IV were nearly identical over the pH range where the three could be observed simultaneously (2.8–3.6), and log plots of the intensity ratios *vs.* pH gave approximate straight lines but with slopes around 2. The equilibria then are apparently not simple proton-transfer reactions but probably involve addition of ligand as well. In other words, at sufficiently high pH that enough free anionic ligand is present in solution to form a complex, the mercapto protons are ionized. Assuming that only three species are thus involved—VO^{2+}, VO(A), and VO(A)$_2^{2-}$—it is possible to compute the products of equilibrium constants $K_1K'_{a1}$ and K_2K_{a2}. These are, respectively, 0.04 ± 0.01 and 0.03 ± 0.01 for both ligands. Examination of the equilibrium expression convinces one that the complex formation constants K_1 and K_2 must be rather small for the α-mercapto acids and that the mercapto protons are in turn strongly acidic in the vanadyl complexes.

The pH titration curve and the concentrations of the various species, calculated using the above equilibrium constants and assuming that only the above three species are present, are shown in Figures 4 and 5, respectively. The agreement between calculated and experimental concentrations is excellent, but, just as in the case of lactic acid, the calculated pH titration curve falls approximately 0.15 pH unit higher then the experimental curve. This discrepancy could be removed by using larger equilibrium constants but only at the cost of destroying the agreement shown in Figure 4.

Esr of Solutions of Other Ligands.—A variety of other ligands was tested which failed to complex vanadyl ion sufficiently to prevent precipitation from weakly acidic solutions. In the cases of glycine, α-aminobutyric acid, β-aminobutyric acid, γ-aminobutyric acid, *N*-acetylglycine, *N*-acetyl-L-cysteine, β-mercaptopropionic acid, ethylene glycol, and acetoin, solutions containing the ligand and vanadyl ion exhibited a single eight-line esr spectrum with a splitting constant of approximately 116 G. No change in splitting constant or line widths was detectable in the pH range 1–4. The esr intensity decreased as the pH approached 4, and above pH 4, a precipitate formed, and the spectrum disappeared entirely.

Solutions containing methoxyacetic acid and vanadyl ion behaved in a manner very similar to the above unsuccessful ligands: a precipitate formed above pH 4, and the esr spectrum disappeared. However, in the pH range 1–4, there was a noticeable shift in the line positions and increase in the line widths. For example at pH 3.75, the vanadium hyperfine splitting was about 114 G, and the second-derivative width of the $+^7/_2$ line was 31 G (21 G at pH 1). This effect is most probably due to the unresolved spectrum of a second species with a somewhat smaller splitting than constant that of aquo ion. Thus, in this case, there is evidence for complexation, although the stability of the complex does not compete effectively with base hydrolysis of vanadyl ion and precipitation occurs.

Solutions of β-hydroxypropionic acid and vanadyl ion with a ligand-to-metal mole ratio of 4 yielded a single esr spectrum, the intensity of which decreased with increasing pH until a precipitate formed above pH 4. Increasing the mole ratio to 100 gave esr results similar to those with methoxyacetic acid. A single spectrum was observed with a hyperfine splitting of 116 G which decreased to about 115 G after 40 equiv of base had been added. As the pH was increased, the width of the $+^5/_2$ line increased from an initial 22 to 28 G, and the spectrum amplitude decreased markedly. No precipitation was observed, however, and when more base was added to bring the total to 60 equiv, the solution was dark amber and clear. Little further change was observed on addition of up to 160 equiv of base (pH 13). An eight-line esr spectrum was still observable in basic solution with a hyperfine splitting of 111 G. As with methoxyacetic acid, the spectra indicate some degree of complexation, but there is no evidence for ionization of the hydroxyl protons. It is likely that a similar result could be obtained with any carboxylic acid in sufficiently large excess.

Discussion

π Bonding in Vanadyl Complexes.—The very high acidity of protons in hydroxyl or mercapto groups coordinated to vanadyl ion can easily be understood if the pair of electrons remaining after proton ionization is delocalized in a molecular orbital extending onto the metal. Equatorial π bonding has been suggested to explain electronic absorption spectra in vanadyl complexes,[2,14] and evidence for such bonding has been found in the electron–proton hyperfine interaction in the vanadyl–aquo complex.[15] A recent molecular orbital calculation on the $VOCl_4^{2-}$ ion has included chlorine–vanadium π bonding.[16] If π bonding is excluded, the unpaired electron is predicted to reside in a nonbonding vanadium d_{xy} orbital with b_2 symmetry.[17] With the inclusion of equatorial ligand orbitals of the appropriate symmetry, Drake, *et al.*,[16] obtained a b_2 bonding orbital, which is primarily ligand in character, and a $b_2{}^*$ antibonding orbital, which is primarily metal in character and which contains the odd electron. In general, one would expect that the greater the degree of π bonding, the greater the participation of the metal atomic orbital in the bonding b_2 orbital and the greater ligand character in the antibonding orbital which contains the odd electron.

Vanadium nuclear hyperfine splitting in vanadyl complexes is thought to arise from polarization of filled metal s orbitals by spin density in the d_{xy} orbital.[18] McGarvey[18] has suggested that the vanadium 4s orbital may be mixed into the ground state in complexes of low symmetry and that this effect may account for the observed variations in the hyperfine splitting constant among the various vanadyl complexes. In the present group of complexes, however, we feel that the variations in the hyperfine splitting may be more easily understood as arising from delocalization of spin density onto the ligand atoms through π bonding. A similar suggestion has been made by Bozis and McCormick[19] to account for the hyperfine splittings and g values of vanadyl–monothio-β-diketone complexes which were, respectively, smaller and larger than those of the corresponding vanadyl–β-diketone complexes.

The average g value differs from the free-electron value because of spin–orbit coupling, which, generally speaking, increases with the size of the atom. Thus, if the odd electron is delocalized onto lighter atoms, one would expect that the g value should approach the free-electron value; the observed increase in g from 1.965 in the aquo ion to 1.972 to 1.977 in the hydroxy or mercapto acid complexes thus corresponds to a 20–30% decrease in the deviation from the free-electron value. This decrease, which parallels almost exactly the decrease in the hyperfine splitting, lends further weight to the overall interpretation of our results.

Metal–ligand π bonding seems to be much more important in the interaction of vanadium with hydroxyl or mercapto groups than with carboxyl groups. The effect on the a and g values of formation of the 1:1 or 1:2 complexes without the hydroxyl protons ionized is very small. This is consistent with the relatively small shifts in a and g observed by Wüthrich for the oxalic, malonic, and phthalic acid complexes of vanadyl ion: 106 G, 1.964; 102 G, 1.967; 109 G, 1.963.[12] For comparison, Wüthrich found a and g values very similar to ours for the Tiron and sulfosalicylic acid complexes: 86 G, 1.972; 96.5 G, 1.966.[12]

Discussion of Negative Results.—The failure to observe the formation of stable complexes involving β-hydroxyl or β-mercapto carboxylic acids is at first somewhat surprising. Since the presence of an sp^3 carbon atom in the five-membered ring of the chelates involving the α-hydroxy or α-mercapto acids would seem to preclude the formation of a delocalized π-electron system, the additional sp^3 carbon in the β-substituted acids would not be expected to have an important electronic effect. The six-membered rings which would be formed by chelation involving β-substituted acids would be slightly more strained than the five-membered rings, and this effect may be significant. Since none of the formation constants is large, a rela-

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tively small change in the enthalpy of formation because of strain energy could have a major effect on the equilibrium constants. Probably more important, however, is the greater loss in configuration entropy on formation of the six-membered ring. Ellison, *et al.*,[20] have measured thermodynamic parameters for the formation of diol complexes of the tellurate ion and found entropies of formation 4–11 eu more negative for the 1,3-diols than for the 1,2-diols but almost no difference in the enthalpies. Such a difference in the present case would decrease K_1 and K_2 sufficiently that virtually no complex would form under the conditions normally employed, *i.e.*, ligand-to-metal mole ratios ≤ 10.

The failure to observe complex formation in the case of α-amino or α-amido carboxylic acids is particularly interesting. Copper(II) has been shown to form stable complexes with peptides in which the amide proton is removed with the formation of a strong copper–nitrogen bond.[21] The absence of such complexes of vanadyl ion is further evidence for the importance of π bonding involving partial donation of a second unshared pair of electrons from oxygen or sulfur to vanadium. Such bonding is not possible with amino or amido groups.

The failure to observe stable complexes in solutions of vanadyl ion containing ethylene glycol or acetoin suggests the importance of an anionic ligand for the initial formation of a complex with vanadyl ion.

The failure to observe a stable complex of vanadyl ion with methoxyacetic acid above pH 4 is not surprising in light of the interpretation given for the equilibria involving α-hydroxy carboxylic acids. This result does, however, supply further evidence for the conclusions drawn, particularly since there is evidence in the esr spectra for the formation of a 1:1 and possibly a 1:2 complex. The equilibrium constant for the formation of the 1:1 complex with this ligand is apparently smaller than those for the α-hydroxy acids however. A combination of the steric effect introduced by the methyl group and the electronic effect involved in replacement of a proton by a methyl group probably accounts for the reduction in this equilibrium constant.

Esr Line Widths.—The esr line widths observed in spectra IV and IVa, $VO(A)_2^{2-}$, were substantially less than were observed in the spectra of the other species. There are two factors which are responsible for this effect. In the first place, the line widths in the spectrum of the aquovanadyl ion contain a contribution from an unresolved proton hyperfine interaction with the equatorial water molecules;[22] this splitting is approximately 1.1 G,[15] giving a 4–5-G contribution to the esr line widths. A similar splitting would no doubt arise from the hydroxyl protons in the various complexes and from remaining equatorial water molecules. Only in the cases of $VO(A)_2^{2-}$ are such protons missing from the complexes, so that this contribution is absent in the spectra of these species. The second factor which is important in accounting for the narrower observed lines is that the anisotropies of the a and g tensors are probably somewhat smaller. These factors are harder to assess since the tensor components are not known. In any case, accurate line width measurements are extremely difficult to make for these spectra because of the partial resolution of spectra IV and IVa, so that a detailed accounting of the line widths is not presently possible.

Acknowledgments.—Helpful discussions with Professors J. O. Edwards and R. G. Lawler are gratefully acknowledged. This work was supported in part by the National Science Foundation under Grants GP-7811 and GP-8536.

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Redetermination of the Crystal Structure of Potassium Lead Hexanitrocuprate(II), $K_2PbCu(NO_2)_6$

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Received August 1, 1969

The structure of potassium lead hexanitrocuprate(II), $K_2PbCu(NO_2)_6$, has been redetermined using three-dimensional X-ray data and anisotropic thermal parameters. The space group is $Fm3$, with $a_0 = 10.672\ (1)$ Å. The calculated density for four formula units in the unit cell is 3.42 g/cm^3; 1366 reflections, of which 464 are independent, were collected with an automated four-circle diffractometer. The structure was refined by full-matrix least-squares techniques to a conventional R factor of 0.028. The hexanitrocuprate ion has T_h symmetry in apparent violation of the Jahn–Teller theorem, but the thermal parameters of the nitrogen atom are in accord with the assumption of a dynamic Jahn–Teller effect. The Cu–N bond length is 2.111 (4) Å, the N–O bond length is 1.260 (4) Å, and the O–N–O angle is 117.9 (4)°. $K_2SrCu(NO_2)_6$ has also been prepared and it is not isomorphous with $K_2PbCu(NO_2)_6$ but with $K_2BaCu(NO_2)_6$.

Introduction

In their well-known theorem, Jahn and Teller[1] have predicted that a molecule possessing a symmetry-induced electronic degeneracy of either orbital or spin nature must distort in order to remove as much degeneracy as possible. The classic example of an ion which exhibits this effect is Cu(II), a d^9 system. In virtually all six-coordinate complexes of this ion, the coordination octahedron is distorted, usually with two bonds longer than the other four. However three X-ray determina-

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