departure from ideal stoichiometry.

One further point of interest in $VSbO_4$ is the presence of magnetic ordering at 4 K. Figure 1 shows the effect on the spectrum of lowering the temperature from 77 to 4 K. This broadening can only be due to magnetic hyperfine splitting, which must arise from an ordering of the V^{3+} spins and be transferred to the antimony sites through the oxygen linkages in the structure. The magnetic data of Schüer and Klemm[3] also indicate that "$VSbO_4$" becomes magnetically ordered below 90 K.

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Registry No. $VSbO_4$, 58151-20-5; ^{121}Sb, 14265-72-6.

References and Notes

(1) L. W. Vernon and W. O. Milligan, *Tex. J. Sci.*, **3**, 82 (1951).
(2) R. S. Roth and J. L. Waring, *Am. Mineral.*, **48**, 1348 (1963).
(3) H. Schüer and W. Klemm, *Z. Anorg. Allg. Chem.*, **395**, 287 (1973).
(4) T. Birchall, R. J. Bouchard, and R. D. Shannon, *Can. J. Chem.*, **51**, 2077 (1973).
(5) G. M. Bancroft, W. K. Cling, A. F. Maddock, R. K. Prime, and A. J. Stone, *J. Chem. Soc. A*, 1966 (1967).
(6) T. Birchall and B. Della Valle, *Can. J. Chem.*, **49**, 2808 (1971).
(7) G. G. Long, J. G. Stevens, and L. H. Bowen, *Inorg. Nucl. Chem. Lett.*, **5**, 799 (1969).
(8) T. Birchall and B. Della Valle, *Chem. Commun.*, 675, (1970).
(9) J. B. Wooten, G. G. Long, and L. H. Bowen, *J. Inorg. Nucl. Chem.*, **36**, 2177 (1974).
(10) R. S. Roth and L. W. Coughernour, *J. Res. Natl. Bur. Stand.*, **55**, 211 (1955).
(11) J. L. Waring and R. S Roth, *J. Res. Natl. Bur. Stand., Sect. A*, **72**, 177 (1968).

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Ring Closure in the Reaction of Metal Chelates. Formation of the Bidentate Oxovanadium(IV)–Glycine Complex

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The details of the rate of ring closure for the monodentate glycinatooxovanadium(IV) species have been studied by both stopped-flow and temperature-jump techniques. The rate corresponds to 35 s^{-1} at 25 °C and the values of the activation parameters are 13.6 kcal/mol for $\Delta H^{\ddagger}$ and −5.8 eu for $\Delta S^{\ddagger}$. Various potential mechanisms are discussed and the direct interaction between the nitrogen of the monodentate glycine and the trigonal face of the oxovanadium(IV) complex is presented as the most reasonable alternative. Appropriate rate constants are calculated in terms of this mechanism.

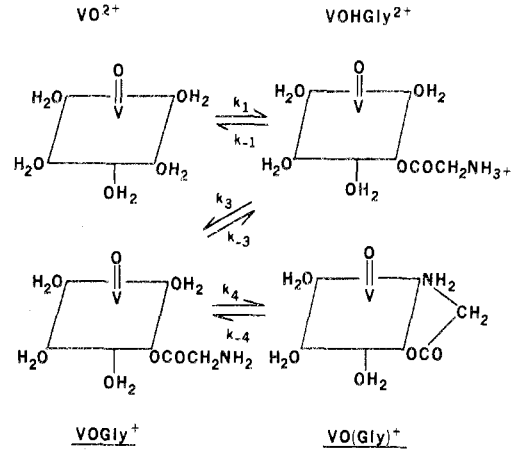
Introduction

The reactions between metal ions and various bidentate ligands are of considerable interest.[1-11] The rates and mechanisms of processes involving bidentate ligands have received particular attention.[8-11] Oxovanadium(IV) appears to be quite interesting in this context in that it has a d^1 electronic configuration and is readily amenable to studies of both oxidation–reduction[12,13] and substitution processes.[8-10] In this paper, we present a detailed study of the rate of ring closure for monodentate glycinatovanadium(IV) in which the final product is the bidentate complex. The system is characterized by equilibria 1–11 at 25 °C.

$VO^{2+} + HGly \rightleftarrows VOHGly^{2+}$	$K_1 = 2.88$	(1)
$VO^{2+} + Gly^- \rightleftarrows VO(Gly)^+$	$K_2 = 1.1 \times 10^6$	(2)
$VOHGly^{2+} \rightleftarrows VOGly^+ + H^+$	$K_3 = 5.3_0 \times 10^{-5}$	(3)
$VOGly^+ \rightleftarrows VO(Gly)^+$	$K_4 = 1.8_1$	(4)
$VO(Gly)^+ + Gly^- \rightleftarrows VO(Gly)_2$	$K_5 = 5.4 \times 10^4$	(5)
$VO^{2+} + Gly^- \rightleftarrows VOGly^+$	$K_6 = 6 \times 10^5$	(6)
$VOHGly^{2+} \rightleftarrows VO(Gly)^+ + H^+$	$K_7 = 9.6 \times 10^{-5}$	(7)
$H^+ + HGly \rightleftarrows H_2Gly^+$	$K_8 = 2.18 \times 10^2$	(8)[15]
$H^+ + Gly^- \rightleftarrows HGly$	$K_9 = 3.98 \times 10^9$	(9)[15]
$VO^{2+} + H_2O \rightleftarrows VOOH^+ + H^+$	$K_{M_1} = 1.0 \times 10^{-6}$	(10)[14]
$2VO^{2+} + 2H_2O \rightleftarrows (VO)_2(OH)_2^{2+} + 2H^+$	$K_{M_2} = 1.3_2 \times 10^{-7}$	(11)[14]

For the purpose of convenience, the oxotetraaquovanadium(IV) ion will be written as VO^{2+} or oxovanadium(IV) and glycine will be abbreviated as HGly. When glycine is coordinated as a monodentate ligand, the complex is written as $VOHGly^{2+}$. The formula $VOGly^+$ represents the deprotonated form of $VOHGly^{2+}$. For glycine functioning as a bidentate ligand, the complex is specified as $VO(Gly)^+$. The structures and equilibrium[1,10] relationships between oxovanadium(IV) and the various monoglycinato complexes are shown diagrammatically in Scheme I.

Scheme I



The rate of water exchange in the equatorial position for oxovanadium(IV) has been reported[14,15] as 5.2×10^2 s^{-1} and the rate of $VOHGly^{2+}$ formation[10] from oxovanadium(IV) and HGly is 1.3×10^3 M^{-1} s^{-1}. The corresponding rate of dissociation is 4.6×10^2 s^{-1}.

Experimental Section

The stock solution of oxovanadium(IV) was prepared by electrolytically reducing a slurry of vanadium pentoxide in perchloric acid as has been described previously.[10,16] The stock solution gave negative tests[17] for both vanadium(III) and vanadium(V). The oxovanadium(IV) solutions were analyzed by titration with standard $KMnO_4$. The total acid concentration was determined by passing aliquots of the stock solution through a Dowex 50-X8 cation-exchange column and by titrating the eluent with standard NaOH to the phenolphthalein end point. The acid concentration was obtained by making corrections

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for the hydrogen ions released by the oxovanadium(IV). Glycine was purified and analyzed as described previously. Other chemicals were used as available commercially.

The pH of each solution was measured with a Radiometer Model 26 pH meter or with a Hitachi-Horiba F-7s pH meter. The pH meters were calibrated in the region of interest with standard Radiometer buffers. Stopped-flow measurements were made at 15.5, 20.0, and 25.0 °C and a wavelength of 580 nm by an instrument which was manufactured by the Union Scientific Engineering Co. Ltd. Japan Electron Optics Lab and by means of a Durrum stopped-flow spectrophotometer. Measurements were taken by following the photomultiplier output with a storage type oxcilloscope and photographing the traces. A Jeol JNM-4H-100 NMR instrument was used for the proton resonance measurements. The peak of the water proton was observed in 90% D_2O solutions at a scanning rate of 1.5 Hz.

Temperature-jump measurements were made at 25 °C and a wavelength of 580 nm which corresponds to a maximum for the species $VO(Gly)^+$ by means of an apparatus similar to that described by Hurwitz and Kustin[18] and with a Durrum T-jump apparatus. Only one relaxation is observed under the range of conditions used: $3.37 \leq pH \leq 3.88$, $0.4 \leq [Gly] \leq 1.0$ M, $[VO^{2+}] = 0.02$ M. The method of recording the data was the same as in the stopped-flow apparatus.

Distilled water was prepared from a Barnstead still followed by passage through Barnstead inorganic and organic exchange columns. The resulting water was passed through an 18-in. column of glass wool and was stored in the dark.

Results

In our previous paper[10] the kinetics of formation of $VOHGly^{2+}$ was reported at pH <3.0 in which region the major oxovanadium(IV) species in H_2O is either VO^{2+} or $VOHGly^{2+}$. The stopped-flow measurements were made at 10 °C at a wavelength of 760 nm which corresponds to the maximum absorbance for $VOHGly^{2+}$. From the observed oscilloscope traces, the second-order rate constant was calculated to be 421 M^{-1} s^{-1} at 10 °C.

In the present study, both stopped-flow and temperature-jump measurements were made in the range $3.0 < pH < 4.0$. Under these conditions, the concentrations of both $VOGly^+$ and $VO(Gly)^+$ are described by eq 1, 2, and 4.

For the stopped-flow measurements, the VO^{2+} and glycine solutions were mixed in the instrument and the oscillograms were obtained on a time scale of 20 ms/cm at 25 °C. These traces are considerably slower than the earlier traces[10] which corresponded to the direct formation of $VOHGly^{2+}$ and are readily distinguishable.

Reaction 3 is a deprotonation process and can be assumed to be very fast. Thus, the traces observed in these stopped flow measurements can be assigned to the chelation process represented by eq 4. The rate for this process is given by

$$d[VO(Gly)^+]/dt = k_4[VOGly^+] - k_{-4}[VO(Gly)^+] \quad (12)$$

Since reactions 1 and 2 are rapid as compared to reaction 4 (vide infra), direct integration results in

$$\ln \frac{B}{B - [VO(Gly)^+]} = k_4(A + K_4^{-1})t \quad (13)$$

where

$$A = \left[1 + \frac{[H^+]}{K_2} + \frac{[H^+]}{K_1K_2[HGly]}\right]^{-1} \quad (14a)$$

$$B = [V(IV)]_{tot}/(1 + 1/AK_4) \quad (14b)$$

On the basis of these assumptions, it was possible to plot $\ln (B/(B - [VO(Gly)^+]))$ as a function of time in order to obtain the rate constant k_4. The plots were rigorously linear under all conditions studied and a typical example is shown in Figure 1. The results of various experiments at 25, 20, and 15.5 °C are shown in Table I. The average rate constant at 25 °C is 34.8 ± 3.1 s^{-1}.

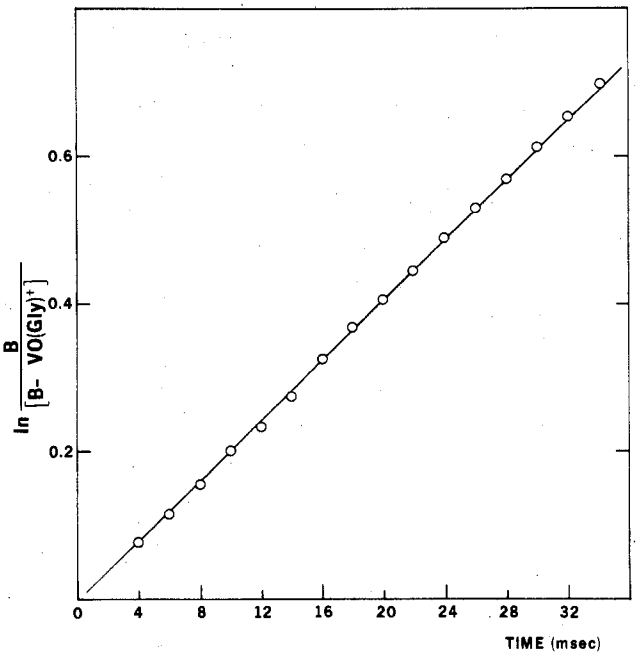


Figure 1. Second-order plot for the formation of $Vo(Gly)^+$ from stopped-flow data at 25 °C.

Table I. Rate Constants for the Chelation of $VOGly^+$ by Stopped-Flow Measurements at 25 °C with 0.0185 M Oxovanadium(IV)

[Glycine], M	pH	k_4, s^{-1}	[Glycine], M	pH	k_4, s^{-1}
0.5	3.70	30.6	1.0	3.79	32.0
0.5	3.35	35.2	1.0	3.95	35.1
0.5	3.45	36.6	1.0	3.95[a]	22
0.5	3.54	39.3	1.0	3.95[b]	16

[a] 20.0 °C. [b] 15.5 °C.

In addition to the stopped-flow experiments, temperature-jump experiments were made on the same system. At 25 °C and under the conditions $3.37 \leq pH \leq 3.88$, $0.4 \leq [HGly] \leq 1.0$ M, and $[VO^{2+}] = 0.02$ M, only one temperature-jump relaxation is observed at 580 nm which corresponds to a maximum in the visible absorption spectrum for $VO(Gly)^+$. A single relaxation time of about 35 ms is observed. In view of the stopped-flow results, it can be shown that this 35-ms process is also associated with the chelation reaction as is shown in eq 4.

This can be demonstrated by the following considerations. The rate of change of the concentration of $VO(Gly)^+$ may be expressed as in eq 12. If the perturbation results in only a small displacement from equilibrium, the variation of concentration from the equilibrium values may be given by

$$d(\delta[VO(Gly)^+])/dt = k_4\delta[VOGly^+] - k_{-4}\delta[VO(Gly)^+] \quad (15)$$

The relaxation time is defined as

$$-d(\delta[VO(Gly)^+])/dt = (1/\tau)\delta[VO(Gly)^+] \quad (16)$$

Hence

$$1/\tau = -k_4(A - 1/K_4) \quad (17)$$

where

$$A = \delta[VOGly^+]/\delta[VO(Gly)^+] \quad (18)$$

Thus, if A is known and since τ is determined from an exponential fit of the temperature-jump trace, k_4 may be calculated directly.

A is specified by means of a series of differential equations which arise from considerations of mass conservation and the

Table II. Relaxation Times and Rate Constants for the Chelation of $VOGly^+$ at 25 °C

Total [oxovanadium(IV)], M	Total [Glycine], M	pH	$10^3[VO^{2+}]$, M	$10^3[VOHGly^{2+}]$, M	$10^3[VOGly^+]$, M	$10^3[VO(Gly)^+]$, M	τ, ms	k_4, s^{-1}
0.02039	0.3900	3.598	7.73	7.96	1.67	3.03	42.6 ± 2.3	32.6
0.02039	0.3900	3.879	6.30	6.63	2.68	4.81	33.3 ± 2.1	34.5
0.02039	0.5949	3.368	6.66	10.19	1.26	2.28	43.6 ± 1.4	35.5
0.02039	0.5949	3.408	6.52	10.05	1.36	2.47	43.7 ± 1.2	34.8
0.02039	0.5949	3.458	6.33	9.85	1.50	2.71	37.8 ± 1.2	39.5
0.02039	0.5949	3.542	6.02	9.46	1.75	3.16	35.8 ± 0.6	40.0
0.02039	0.5949	3.642	5.62	8.94	2.08	3.76	36.0 ± 1.2	37.7
0.02039	0.6817	3.515	5.54	9.98	1.73	3.13	41.9 ± 1.7	34.7
0.02039	0.7800	3.512	5.02	10.36	1.78	3.23	38.7 ± 2.8	37.5
0.02039	1.019	3.528	4.02	10.90	1.95	3.53	33.6 ± 0.8	42.8
0.02410	0.5949	3.509	7.28	11.36	1.94	3.52	36.5 ± 2.0	39.5
								Av 37.2 ± 2.9

Table III. Rates and Activation Parameters for Oxovanadium(IV) Substitution Reactions

Reaction	k(25 °C), s^{-1}	Method	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
H_2O exchange	5.2×10^2	NMR[a]	13.7	−0.6
HGly formation[b]	1.3×10^3	Stopped flow[c]	12.0	−4.0
HGly dissociation	4.6×10^2	Calcd[c] (equil data)	13.1	−2.4
$VOGly^+$ chelation	37.2	T jump[d]		
	34.8	Stopped flow	13.6	−5.8
$VOPro^+$ chelation	5.5	Stopped flow[e]	13.9	−8.6
$VOOx^+$ chelation	$>2 \times 10^2$	Stopped flow[e]		
$VOMal^+$ chelation	Unmeasurable	Stopped flow[e]		
HGly exchange with $VOHGly^{2+}$	$<2.5 \times 10^3$	NMR[c]	12	−2.7
HAla formation	$>10^3$	Stopped flow[e]	13	−2
HGly exchange with $VO(Gly)_2$	3.6×10^2	NMR[c]	8.0	−20.0
HMal exchange with $VO(Mal)_2^{2-}$	7.9×10^2	NMR[f]	8.6	−16.2

[a] K. Wuthrich and R. E. Connick, *Inorg. Chem.*, 7, 1377 (1968). [b] Second-order rate constant with units of M^{-1} s^{-1}. [c] H. Tomiyasu, H. Dreyer, and G. Gordon, *Inorg. Chem.*, **11**, 2409 (1972). [d] This work. [e] H. Tomiyasu, *Bull. Chem. Soc. Jpn.*, in press. [f] H. Tomiyasu, S. Ito, and S. Tagami, *ibid.*, 47, 2843 (1974).

equilibrium conditions for the eight species which are perturbed. See eq 19, where the bars over species represent the equilibrium conditions.

$$\delta[VO^{2+}] + \delta[VOHGly^{2+}] + \delta[VOGly^+] + \delta[VO(Gly)^+] = 0$$

$$\delta[HGly] + \delta[Gly^-] + \delta[H_2Gly^+] + \delta[VOHGly^{2+}] + \delta[VOGly^+] + \delta[VO(Gly)^+] = 0$$

$$\delta[H^+] + \delta[VOHGly^{2+}] + \delta[HGly] + 2\delta[H_2Gly^+] = 0$$

$$\overline{[VOGly^+]}(\delta[H^+]) + \overline{[H^+]}(\delta[VOGly^+]) - K_3(\delta[VOHGly^{2+}]) = 0 \quad (19)$$

$$K_8\{\overline{[H^+]}(\delta[HGly]) + \overline{[HGly]}(\delta[H^+])\} - \delta[H_2Gly^+] = 0$$

$$K_9\{\overline{[H^+]}(\delta[Gly^-]) + \overline{[Gly^-]}(\delta[H^+])\} - \delta[HGly] = 0$$

$$K_1\{\overline{[VO^{2+}]}(\delta[HGly]) + \overline{[HGly]}(\delta[VO^{2+}])\} - \delta[VOHGly^{2+}] = 0$$

These equations were solved by the Gaussian elimination method for A. This permitted a direct calculation of k_4. The concentrations of the various species and the values of τ and k_4 are listed in Table II. In view of the range of concentrations reported, we conclude that the value of $k_4 = 37.2 \pm 2.9$ s^{-1} corresponds to the first-order rate constant for chelation of the $VOGly^+$ species as is shown in eq 4. This is in excellent agreement with the value of 34.8 ± 3.1 s^{-1} obtained from the stopped-flow measurements.

A series of stopped flow measurements was also made at 15.5 and 20 °C. Since the equilibrium data for the oxovanadium(IV)–glycine system were reported[1] at 25 °C, it was assumed that the 25 °C equilibrium data could be used in the calculation of the rate constants at the lower temperatures. In the measurement of the absorption spectra for oxovanadium(IV)–glycine solutions, where $VO(Gly)^+$ exists to the extent of about 20% of the total oxovanadium(IV) species, the peak maximum for $VO(Gly)^+$ at 580 nm decreases slightly with decreasing temperature. The absorbances measured at 10 °C were smaller by about 10% than those measured for the same solutions at 25 °C. This is about the magnitude expected for the deprotonation reactions for HGly. On this basis, the errors associated with the rate constants at 15.5 and 20 °C should be less than 10%. These results are summarized in Table I.

A compilation of the rates[8,10,14] of substitution, chelation, and exchange reactions at 25 °C for various closely related oxovanadium(IV)–bidentate ligand reactions and the associated activation parameters is given in Table III. The rate of water exchange (oxygen-17) for the aquo complex is reported[14] to be about 500 s^{-1}. Oxygen-17 data are unavailable for monodentate oxovanadium(IV) complexes of interest here. In a series of proton NMR experiments, the line widths of protons from solvent water were measured for a variety of oxovanadium(IV)–glycine mixtures in 90% D_2O at 25 °C. These results, along with the principal species in solution, are presented at various pH values from 1.0 to 3.0 in Table IV. For all practical purposes (and within the experimental error), the line width was invariant with pH. Thus, it is suggested that the water-exchange rates for species such as $VOHGly^{2+}$ and perhaps $VOGly^+$ do not vary appreciably from that reported for the aquo complex.

Discussion

The mechanism for ligand formation reactions has been formulated by Eigen and Tamm[19] (eq 20, 21). In their

$$M_{aq}^{n+} + L_{aq}^{-} \overset{K_{os}}{\rightleftharpoons} [M_{aq}\cdots L]^{(n-1)+} \quad (20)$$

$$[M_{aq}\cdots L]^{(n-1)+} \xrightarrow{k_{ex}} ML_{aq}^{(n-1)+} + H_2O \quad (21)$$

Table IV. Proton NMR Line Widths for H_2O in 90% D_2O Solutions Containing 0.01 M V(IV) and 1.0 M Glycine at 25 °C[a]

pH	3.0	2.5	2.0	1.5	1.0
$[VO^{2+}]$, M	2.8×10^{-3}	3.7×10^{-3}	5.4×10^{-3}	7.3×10^{-3}	8.8×10^{-3}
$[VOHGly^{2+}]$, M	6.5×10^{-3}	6.1×10^{-3}	4.6×10^{-3}	2.7×10^{-3}	1.2×10^{-3}
$[VO(Gly)^+]$, M	4.2×10^{-4}	1.3×10^{-4}	2.9×10^{-5}		
Line width at the half-height, Hz	9.9 ± 0.4	10.3 ± 0.4	11.3 ± 0.4	9.8 ± 0.4	9.9 ± 0.4

[a] Major species concentration listed based on equilibrium data.

general proposal $[M_{aq}\cdots L]^{(n-1)+}$ represents an ion pair or an outer-sphere association complex with an equilibrium constant K_{os}. The formation of this complex is usually considered to be rapid when compared with the rate of water exchange of the species M_{aq}^{n+}. Under these conditions, k_{ex} becomes rate determining, and in the simplest case, the second-order rate constant is related to these processes by the expression

$$k_{obsd} = K_{os}k_{ex} \quad (22)$$

The formation of the chelated glycine complex might be envisioned as occurring stepwise as in eq 23–25. Since the

$$VO^{2+} + HGly \overset{K_{os}}{\rightleftharpoons} [VO\cdots HGly]^{2+} \quad (23)$$

$$[VO\cdots HGly]^{2+} \xrightarrow{k_{H_2O}} VOHGly^{2+} + H_2O \quad (24)$$

$$VOHGly^{2+} \xrightarrow{k_{H_2O}} VO(Gly)^{+} + H_3O^{+} \quad (25)$$

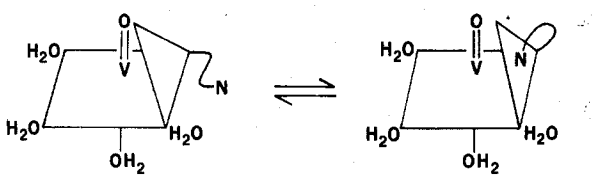
rate of interchange between $VOHGly^{2+}$ and $VO(Gly)^{+}$ can be observed directly,[10] it should be expected that the rate of chelate formation should be very nearly that of water exchange. The value for k_{H_2O} is 5×10^2 s^{-1} for $VO(OH_2)_4^{2+}$, and since the proton NMR line width appears to be unaffected by formation of the monodentate glycine complex, we would assume that the value of 5×10^2 is still a good approximation for the rate of water exchange.[14] Clearly, the value of 35 s^{-1} we observe both by temperature-jump and by independent stopped-flow measurements for chelate closure is inconsistent with the mechanism proposed in reactions 23–25.

We would also rule out the possibility of axial coordination in that Wüthrich and Connick[14,20] have shown that the rate of axial water exchange must exceed 5×10^7 s^{-1}. On this basis, the closing of the chelate ring would be expected to take place at a similar rate. If instead, however, the process is envisioned to occur by initial axial coordination followed by a water-exchange process in which the axial ligand becomes equatorial, this mechanism is still inadequate to explain the very slow rate of chelation.

In many ligand replacement reactions, the effect of specific interactions cannot be entirely neglected. Watts[21] has shown clearly that hydrogen bonding of incoming ligands plays a very important role in the formation of many substituted cobalt(III) complexes. Also, in the Eigen mechanism,[19] the distance of closest approach between the cation and the substituting ligand is usually considered to be about 5–7 Å for most substitution reactions.

One important possible difference between oxovanadium(IV) and nickel(II), cobalt(III), or other similarly related cations might be the electron density in the trigonal face of the coordination octahedron surrounding the metal ion. In the electron-rich transition metal ions, the electron density in this trigonal face is considerably higher than that expected for the oxovanadium(IV) ion which is a d^1 ion.

On this basis, we propose that the mechanism of formation of the chelated monoglycine complex from the corresponding monodentate complex requires a direct interaction between nitrogen of the monodentate glycine and the trigonal face of the oxovanadium(IV) complex as is shown by



TRIGONAL FACE INTERACTION

The formation of this pseudo-ion-pair or this pseudo-inner-sphere type interaction can be represented by an apparent equilibrium constant K_p. Formation of the equatorially chelated complex from the intermediate would proceed at the rate of water exchange and the observed rate would be

$$k_{obsd} = K_p k_{H_2O}$$

and K_p would be a direct measure of the trigonal-face interaction. In other words, K_p (i.e., k_{obsd}/k_{H_2O}) would be a direct measure of the effective probability of forming the chelate from the monodentate complex during the actual water-exchange process. Under these conditions, our experimental value of ~0.07 for K_p is not at all surprising.

The comparison of glycine with proline is particularly interesting in that proline has pK values similar to those of glycine (pK_1 = 10.52 and pK_2 = 2.02) and the rate of chelation is more than 6 times slower but the activation enthalpies are almost identical. In terms of this model, the value of K_p for proline would be ~0.01 which can be interpreted as a result of the less favorable geometry of the proline–trigonal face intermediate as compared to that for glycine.

Additional support for this type of pseudo-inner-sphere process also comes from a comparison between charged and uncharged ligands under very similar conditions. The experiment in which we observe that the monodentate oxovanadium(IV)–oxalic acid complex forms the chelated complex at a rate *at least* 6–8 times faster than the corresponding monodentate glycine complex is very encouraging. In the case of the monodentate oxalate coordinated to oxovanadium(IV) and in terms of this model, K_p would be expected to be 6–8 times greater than that for glycine. Certainly, the interaction at the trigonal face should be much greater for a negative end of a molecule (i.e., a carboxylate ion) than it should for a neutral species (i.e., an amino group) and the negative species should dissociate less readily than should the neutral species. In other words, the oxalate complex should have a higher probability of interacting in the appropriate position when water exchange occurs, and the relative rates of chelate formation should be $k_{chelate}$(oxalate) > $k_{chelate}$(glycine). This is what is observed experimentally.

Additional emphasis for this argument comes from a consideration of the activation parameters for the water-exchange reaction and the glycine chelation reaction. In both cases, the values of $\Delta H^{\ddagger}$ are indistinguishable (13.7 ± 0.3 and 13.6 ± 0.2 kcal/mol, respectively) and the difference in rate is solely due to difference in entropy (−0.6 and −5.6 eu, respectively).

The mechanism of formation of the $VOHGly^{2+}$ complex from VO^{2+} and HGly should also be given some additional consideration in that two discrete (but frequently experimentally indistinguishable) processes have been proposed.[10] These are as follows

process I

M + HLL ⇌ MLLH	(rate determining)
MLLH ⇌ MLL + H$^+$	(fast)
MLL ⇌ M(LL)	(fast)

process II

HLL ⇌ LL + H$^+$	(fast)
M + LL ⇌ MLL	(rate determining)
MLL ⇌ M(LL)	(fast)

Both processes result in the overall chelate formation reaction

$$M + HLL \rightleftharpoons M(LL) + H^+$$

In the reactions of most metal ions such as iron(II), cobalt(II), and nickel(II), the intermediate species cannot be identified and only the rate of product formation and/or reactant disappearance is observed. Thus, in these cases, a meaningful distinction between process I and process II cannot be made. Only infrequently have exceptions been reported.[2e,f]

In the case of oxovanadium(IV) complexes, the intermediate species are relatively stable and their properties can be observed directly. Furthermore, the differences in lability between axially[14,20] and equatorially coordinated species have been measured and k_{H_2O}(axial) and k_{H_2O}(equatorial) differ by at least a factor of 10^6. Clearly, this rules out mechanisms of the type

$$HGly \overset{1/K_g}{\rightleftharpoons} H^+ + Gly^- \qquad \text{(fast)}$$

$$Gly^- + VO^{2+} \overset{K_{os}}{\rightleftharpoons} [VO\cdots Gly]^+ \qquad \text{(fast)}$$

$$[VO\cdots Gly]^+ \overset{k_{H_2O}}{\rightleftharpoons} VOGly^+ \qquad \text{(axial rate determining)}$$

$$VOGly^+ + H^+ \overset{K_3}{\rightleftharpoons} VOHGly^{2+} \qquad \text{(fast)}$$

in that the formation processes are independent of acid and the stable species in the pH region of concern is $VOHGly^{2+}$.

An additional mechanism recently proposed by Margerum[22] also involves formation of the chelated product. This mechanism, in the case of the glycine complex, would not involve initial coordination of the carboxyl group, even though it is the more stable species thermodynamically, but initial coordination of the amino group followed by rapid chelation of the carboxyl group.

If this mechanism were valid for reactions with oxovanadium(IV), the chelation step for oxalic acid should not be observable and no difference should be observed between malonic acid and oxalic acid. Clearly this is not the case, and in each reaction, the major difference is reflected in changes in ΔS^* and not ΔH^*.

In conclusion, we have shown that the oxovanadium(IV) species is a particularly useful probe in attempting to understand the microscopic details of chelate reactions in that the monodentate oxovanadium(IV) intermediates can be observed directly because of marked differences in lability between coordination in the axial and equatorial positions.

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Registry No. $VOHGly^{2+}$, 58281-22-4; $VO(Gly)^+$, 58281-23-5.

References and Notes

(1) H. Tomiyasu and G. Gordon, *J. Coord. Chem.*, **3**, 47 (1973).
(2) (a) W. B. Makinen, A. F. Pearlmutter, and J. E. Stuehr, *J. Am. Chem. Soc.*, **91**, 4083 (1969); (b) A. Kowalak, K. Kustin, R. F. Pasternack, and S. Petrucci, *ibid.*, **89**, 3126 (1967); (c) O. Farooq, A. U. Malik, N. Ahmad, and S. M. F. Rahman, *J. Electroanal. Chem.*, **24**, 464 (1970); (d) K. Kustin and R. Pizer, *Inorg. Chem.*, **9**, 1537 (1970); (e) H. Hoffmann, *Ber. Bunsenges. Phys. Chem.*, **73**, 432 (1969); (f) H. Hoffmann and U. Nickel, *Z. Naturforsch.*, **26**, 299 (1971).
(3) (a) R. P. Dodge, D. N. Templeton, and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961); (b) J. G. Forest and C. K. Prout, *J. Chem. Soc. A*, 1312 (1967); (c) J. Selbin, *Chem. Rev.*, **65**, 153 (1965), and references therein; (d) N. S. Angerman and R. E. Jordan, *Inorg. Chem.*, **8**, 65 (1969); (e) R. E. Tapscott and R. L. Belford, *ibid.*, **6**, 735 (1967).
(4) (a) V. S. Sharma and D. L. Leussing, *Inorg. Chem.*, **11**, 138, 1955 (1972); (b) P. Moore and D. M. W. Buck, *J. Chem. Soc., Dalton Trans.*, 1602 (1973).
(5) R. F. Pasternack, E. Gibbs, and J. C. Cassatt, *J. Phys. Chem.*, **73**, 3814 (1969).
(6) R. G. Wilkins, *Acc. Chem. Res.*, **3**, 408 (1970).
(7) (a) H. P. Bennetto and E. F. Caldin, *J. Chem. Soc. A*, 2191, 2198, 2207, 2211 (1971); (b) J. Feeney and S. M. Walker, *ibid.*, 1148 (1966); (c) F. Franks and D. J. G. Ives, *Q. Rev., Chem. Soc.*, **22**, 2 (1966).
(8) H. Tomiyasu, S. Ito, and S. Tagami, *Bull. Chem. Soc. Jpn.*, **47**, 2843 (1974).
(9) F. P. Cavasino, *Ric. Sci., Parte 2: Sez. A.*, **8**, 1120 (1965).
(10) H. Tomiyasu, K. Dreyer, and G. Gordon, *Inorg. Chem.*, **11**, 2409 (1972).
(11) J. C. Cassatt and R. Wilkins, *J. Am. Chem. Soc.*, **90**, 6045 (1968).
(12) K. Dreyer and G. Gordon, *Inorg. Chem.*, **11**, 1174 (1972).
(13) W. Melvin and G. Gordon, *Inorg. Chem.*, **11**, 1912 (1972).
(14) (a) K. Wüthrich and R. E. Connick, *Inorg. Chem.*, **7**, 1377 (1968); (b) J. Reuben and D. Fiat, *ibid.*, **6**, 579 (1967); **8**, 1821 (1969).
(15) (a) D. L. Leussing and K. S. Bai, *Anal. Chem.*, **40**, 575 (1968); (b) D. L. Leussing and E. M. Hanna, *J. Am. Chem. Soc.*, **88**, 693 (1966).
(16) S. C. Furman and C. S. Garner, *J. Am. Chem. Soc.*, **72**, 1785 (1950).
(17) K. V. Krishnamurty and A. C. Wahl, *J. Am. Chem. Soc.*, **80**, 5921 (1958).
(18) P. Hurwitz and K. Kustin, *Inorg. Chem.*, **3**, 823 (1964).
(19) M. Eigen and K. Tamm, *Z. Elektrochem.*, **64**, 115 (1960).
(20) K. Wüthrich and R. E. Connick, *Inorg. Chem.*, **6**, 583 (1967).
(21) B. A. Mathews and D. W. Watts, *Inorg. Chim. Acta*, **11**, 127 (1974), and references quoted therein.
(22) W. H. Woodruff, D. W. Margerum, M. J. Milano, H. L. Pardue, and R. E. Santini, *Inorg. Chem.*, **12**, 1490 (1973).

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Synthesis and Fluxional Behavior of (η^5-Cycloheptatrienyl)tricarbonylmanganese. Rearrangement by 1,2 Shifts

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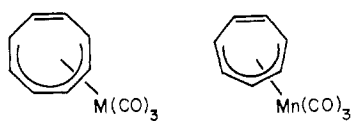
The synthesis of the π-excessive fluxional molecule (η^5-cycloheptatrienyl)tricarbonylmanganese by low-temperature photochemical decarbonylation of (7-cycloheptatrienylacyl)pentacarbonylmanganese is described. Low-temperature NMR studies confirm the structure as the expected η^5 species. Characterization of the mechanism of the fluxional rearrangement by ^{13}C NMR clearly demonstrates a 1,2 shift mechanism. The random or 1,3 shift process observed for (η^6-cyclooctatetraene)tricarbonylmolybdenum is thus unique among characterized mononuclear ring whizzers. The existence of only a single uncomplexed bond is not sufficient to guarantee such a mechanism.

Introduction

Over the last several years a substantial number of organometallic species have been shown to display fluxional behavior involving the sequential occupation by a metal fragment of several equivalent locations around the periphery of a continuously conjugated cyclic polyolefin. Such molecules, known as "ring whizzers", have been the subject of intensive study,[1] particularly by Cotton and co-workers,[2] who have in several cases characterized the detailed nature of the fluxional process by NMR line shape analysis. By far the most commonly observed mechanism involves the occupation of *adjacent* sites by the metal atom; i.e., the rearrangement occurs via 1,2 shifts. Recently, Cotton, Hunter, and Lahuerta[3] described a study of $COTM(CO)_3$ (M = Cr, Mo, W), **1**. In



1 **2**

these cases, line shape analysis shows that either a 1,3 shift or a random process (indistinguishable in the eight-membered