Kinetics and Mechanism of Replacement of Glycinate in Bis(glycinato)oxovanadium(IV) by Oxalate

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The kinetics of formation of bis(oxalato)oxovanadate(IV) $[VO(ox)_2(H_2O)]^{2-}$ (hereafter water molecule will be omitted) from the reaction of bis(glycinato)oxovanadium(IV) $[VO(gly)_2]$ with oxalate has been studied by the stopped-flow method. The reaction was found to consist of two consecutive steps, a relatively slow step (k_1) and a fast one (k_2). The values of rate constants k_1 and k_2 were independent of the concentration of free oxalate and of the pH of solution ranging from 4.2 to 6.5. Similar behavior was also observed in the acid decomposition of $[VO(gly)_2]$. A mechanism passing through an intermediate, $[VO(ox)(gly)]^-$, was proposed.

The kinetics of ligand-substitution reactions for a variety of oxovanadium(IV) complexes has been studied extensively.[1-12] The study of ^{17}O NMR in $[VO(H_2O)_5]^{2+}$[2,3] revealed that the rate of water exchange at the axial position was extremely fast, but relatively slow at the basal positions, in which the rate constant was determined by the conventional NMR line-broadening method. Since then, much interest has been centered in the kinetic study of ligand substitutions in oxovanadium(IV) complexes to compare the rate constants of various ligand substitutions with those of water exchange.

The kinetic behavior of oxovanadium(IV) complexes appears to be quite interesting, for the rates of ligand substitutions differ as much as some hundreds according to substituting ligands and structures of complexes. In the case of formation of chelate complex, $[VO(gly)]^+$, from $[VO\text{-}gly]^+$, glycinate of which coordinates as a unidentate ligand, the rate constant was about 1/10 of that of water exchange at the basal positions.[6] Much slower rate was reported for the anation reaction in [VO(pmida)](pmida=*N*-(2-pyridylmethyl)iminodiacetate) by NCS^- and N_3^-.[9]

In this paper we report the kinetics of the replacement of glycinate in $[VO(gly)_2]$ by oxalate

$$[VO(gly)_2] + 2ox^{2-} \longrightarrow [VO(ox)_2]^{2-} + 2gly^- \quad (1)$$

for a further understanding of substitution mechanisms in oxovanadium(IV) complexes.

Experimental

The preparation and analysis of the oxovanadium(IV) stock solution were described in a previous paper.[4] Analytical grade (Wako Pure Chemical Ind., Ltd.) perchloric acid, sodium oxalate and sodium perchlorate which was recrystallized twice from aqueous solution were used. The ionic strength was adjusted at 1.0 M (1 M=1 mol dm^{-3}) by using sodium perchlorate. A Union Giken RA-401 stopped-flow spectrophotometer was used for accumulated stopped-flow measurements, where accumulations were carried out at least ten times. Absorption spectra were measured by using a Shimadzu UV-365 spectrophotometer with 20 mm quartz cells.

Results and Discussion

The absorption spectra of $[VO(gly)_2]$ and $[VO(ox)_2]^{2-}$, whose assignment was reported in the earlier papers,[7,14] are shown in Fig. 1. It was found that the spectra of final products of the reaction between $[VO(gly)_2]$ and oxalate were consistent with that of $[VO(ox)_2]^{2-}$ indicating that the stoichiometry can be written by Eq. 1 under the conditions studied. The rate of the reaction was measured from the change in absorbance at 555 nm. A typical stopped-flow trace is shown in Fig. 2 together with a pseudo-first-order plot ($\log(A_t - A_f)$ vs. time), where A_t and A_f refer to the relative absorbances at times t and infinity, respectively. As is seen in Fig. 2, the pseudo-first-order plot deviates from a straight line in spite of excess sodium oxalate suggesting that the reaction consists of two consecutive steps. The results lead to the following reaction mechanism passing through an intermediate complex, (Int),

$$[VO(gly)_2] \xrightarrow{k_1} (Int) \xrightarrow{k_2} [VO(ox)_2]^{2-}, \quad (2)$$

where k_1 and k_2 represent the first-order rate constants for each step. Based on the above reaction mechanism, the stopped-flow traces were analyzed by means of the nonlinear-least-squares method using k_1, k_2, and ε_{Int} (molar extinction coefficient of (Int)) as unknown parameters. The calculated values of absorbance with time agree remarkably with the observed data (Fig. 2), where ε_{Int} is taken to be 9.9 M^{-1}cm^{-1} at 555 nm. Since the consecutive first-order reaction similar to the present reaction admits of two mathematical solutions which are a set of alternative parameters, it is necessary to determine which is the correct set of parameters.[15] The alternative molar extinction coefficient, ε'_{Int}, is give by

$$\varepsilon'_{Int} = \varepsilon_{VO(gly)_2} + \frac{k_1(\varepsilon_{Int} - \varepsilon_{VO(gly)_2})}{k_2} \quad (3)$$

and the value of ε'_{Int} is calculated at 13.2 M^{-1}cm^{-1} by using the values of $\varepsilon_{VO(gly)_2}$=16.0 M^{-1}cm^{-1} and ε_{Int}=

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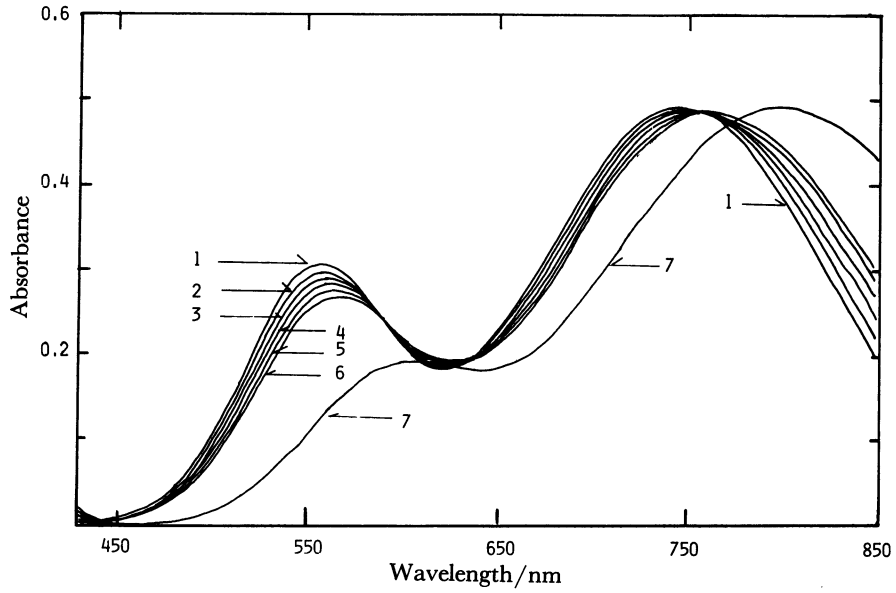


Fig. 1. Absorption spectra of $[VO(gly)_2]$ (1) and $[VO(ox)_2]^{2-}$ (7). Spectra (2—6) were obtained by the addition of small amounts of Na_2ox to the $[VO(gly)_2]$ solution. The conditions are as follow: $[VO(IV)]=9.38\times10^{-3}$ M, [glycine]= 2.00 M, pH=6.5 at 20 °C. $[Na_2ox]=0$ (1), 1.24×10^{-3} (2), 2.49×10^{-3} (3), 4.98×10^{-3} (4), 7.46×10^{-3} (5), 9.95×10^{-3} M (6), and excess Na_2ox (7).

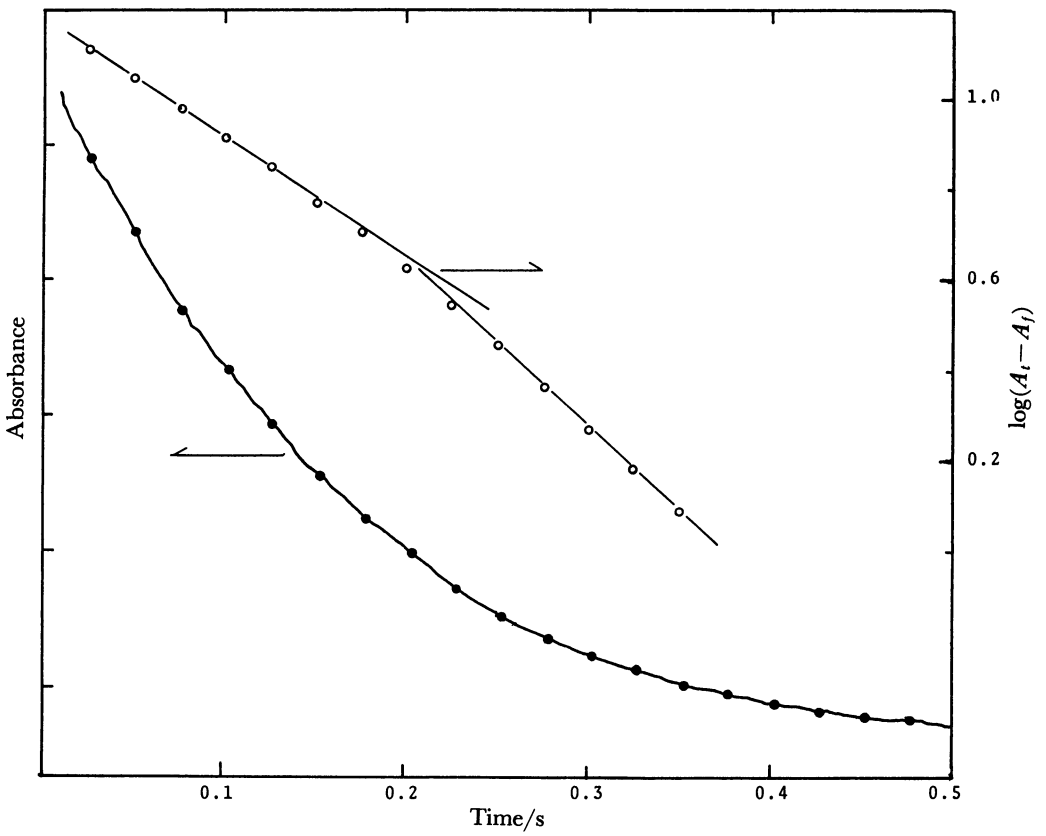


Fig. 2. Typical stopped-flow trace. $[VO(gly)_2]_o=0.0116$ M, $[Na_2ox]_o=0.125$ M, ionic strength= 1.0 M, pH=4.64 at 20 °C.
○: Pseudo-first-order plot, ●: nonlinear-least-squares fits based on reaction mechansim (2).

Table 1. Values of k_1 and k_2 at 20 °C under Various Conditions

pH	[Na$_2$ox] / M		k_1 / s^{-1}	k_2 / s^{-1}
4.64	0.125		6.95	17.5
4.93	0.100		7.76	14.8
5.74	0.075		7.96	16.1
6.57	0.050		8.81	17.8
4.67	0.075		7.45	14.5
4.23	0.050		7.07	19.3
		Average	7.67	16.7

9.9 $M^{-1}cm^{-1}$ at 555 nm, k_1=7.67 s^{-1} and k_2=16.7 $M^{-1}cm^{-1}$ at 20 °C in Table 1. Additional experiments were carried out to estimate the approximate value of molar extinction coefficient of (Int) and to choose between ε_{Int} and ε'_{Int}. A small amount of sodium oxalate was weighed and added to an aqueous solution at pH=6.5 containing [VO(gly)$_2$] (9.38×10^{-3} M) and glycine (2.0 M), where a volume change due to the addition of Na$_2$ox was negligible. In Fig. 1, the absorbance at 555 nm decreases as the concentration of Na$_2$ox increases and the spectra have three isosbestic points at 585, 635, and 735 nm. Addition of excess Na$_2$ox gives the spectrum of $[VO(ox)_2]^{2-}$, which passes through neither of the above isosbestic points. It is clear that the addition of small amounts of Na$_2$ox results in the formation of an intermediate complex and it seems most likely that the intermediate is a mixed-ligand complex, $[VO(ox)(gly)]^-$. The value of ε_{Int} at 555 nm was determined to be 10.4 $M^{-1}cm^{-1}$ assuming that the absorbance change in Fig. 1 is based on the following equilibrium.

$$[VO(gly)_2] + ox^{2-} = [VO(ox)(gly)]^- + gly^- \quad (4)$$

In conclusion, these results support the former solution for k_1 and k_2 with ε_{Int}=9.9 $M^{-1}cm^{-1}$.

It can be seen in Table 1 that both k_1 and k_2 are independent of the initial concentrations of sodium oxalate and pH's within experimental errors. These results are particularly surprising in view of the fact that the substitution rates in oxovanadium(IV) complexes are usually affected by the species of substituting ligands and their concentrations.[4,5,9]

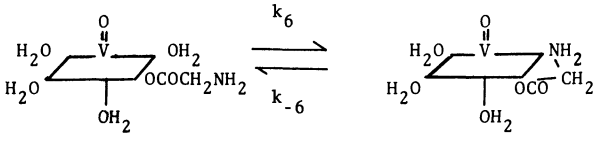
The rate of dissociation of glycinate from [VO(gly)$_2$] by the addition of perchloric acid has been also measured by the stopped-flow method. Since the pH of the solution after mixing [VO(gly)$_2$] and perchloric acid solutions was 3.0 and the major species in such a pH region of oxovanadium(IV)-glycine system was known to be $[VO(H_2O)_5]^{2+}$ and $[VO(Hgly)]^{2+}$ where glycine coordinated as a unidentate ligand,[14] the reaction can be written by

$$[VO(gly)_2] \xrightarrow{+H^+} [VO(H_2O)_5]^{2+} + [VO(Hgly)]^{2+}. \quad (5)$$

The stopped-flow trace was very similar to that in Fig. 2 and showed again two components. Rate constants $k_{d(1)}$ and $k_{d(2)}$ for the initial and latter steps respectively were also determined by the nonlinear-least-squares method. The values of $k_{d(1)}$ and $k_{d(2)}$ in Table 2 were determined with the molar extinction coefficient of an intermediate, $\varepsilon_{d(Int)}$=8.8 $M^{-1}cm^{-1}$, which was about the mean of those of [VO(gly)$_2$] and $[VO(H_2O)_5]^{2+}$ at 555 nm, 16.0 and 2.2 $M^{-1}cm^{-1}$, respectively. In analogy with reaction (1), some uncertainty remains as to the reasonable sets of values of $k_{d(1)}$ and $k_{d(2)}$ in reaction (5). Since the molar extinction coefficient of $[VO(Hgly)]^{2+}$ has not been determined accurately, it is even more difficult to evaluate the molar extinction coefficient of the intermediate in reaction (5) than in reaction (1). Although the complete solution was not obtained at present, the fact that the reaction (5) proceeds via two steps might suggest a similarlity of mechanisms in both reactions. As the difference in rate constants $k_{d(1)}$ and $k_{d(2)}$ is not significant, the above suggestion as to the mechanistic similarity seems to be acceptable even when $k_{d(1)}$ and $k_{d(2)}$ are interchanged.

Considering the results in Tables 1 and 2, we propose a mechanism, in which the ring opening, i.e. the rupture of V-N bonds in [VO(gly)$_2$], is the initiation step of the reaction as shown in Fig. 3. The bond rupture results in the formation of complex II, where one glycinate coordinates as a unidentate ligand. Complex II is attacked by ox^{2-} (Hox^-) and forms complex III, and then more stable complex IV. Complex IV corresponds to the (Int) in Eq. 2. If the initial ring opening is assumed to be rate determining, the oxalate specics, ox^{2-} and Hox^-, and their concentrations give no effect on the substitution rate, and k_1 should be the rate constant of the ring opening in [VO(gly)$_2$]. Similarly the k_2 step corresponds to the over-all process from IV to VI and k_2 refers to the rate constant of the ring opening in complex IV. Similar mechanism passing through an intermediate unis(glycinato)complex, $[VO(gly)]^+$, is proposed for the acid decomposition of [VO(gly)$_2$]. In the earlier study[7] dealing with the formation of $[VO(ox)_2]^{2-}$ from the aqua complex, the rate was dependent on the concentrations of ox^{2-} and Hox^-, and the second-order rate constants were determined to be 1.29×10^4 and 7.0×10^2 $M^{-1}s^{-1}$ at 15 °C for ox^{2-} and Hox^-, respectively. These results clearly indicate that the rate of the over-all process from II to IV in Fig. 3 is at least hundred times faster than that of the initial ring opening under the present conditions.

It is interesting to compare the present reactions with the following reaction in unis(glycinato)oxovanadium(IV).[6]



(6)

Table 2. Rate Constants and Activation Parameters in Ligand-Substitution Reactions in Oxovanadium(IV) Glycine Complexes

Reaction	Rate constant/s^{-1}		ΔH^*	ΔS^*
	20 °C	25 °C	kJ mol^{-1}	JK^{-1} mol^{-1}
$[VO(gly)_2]+ox^2 \longrightarrow [VO(ox)_2]^{2-}$				
k_1	7.67	11.3	51.2	−55
k_2	16.7	29.7	—	—
Acid decomposition of $[VO(gly)_2]$				
$k_{d(1)}$	7.47	—	—	—
$k_{d(2)}$	14.3	—	—	—
Ring closure of $[VO\text{-}gly]^+$	—	35	57.1	−24
Ring opening of $[VO(gly)]^+$	—	19	—	—

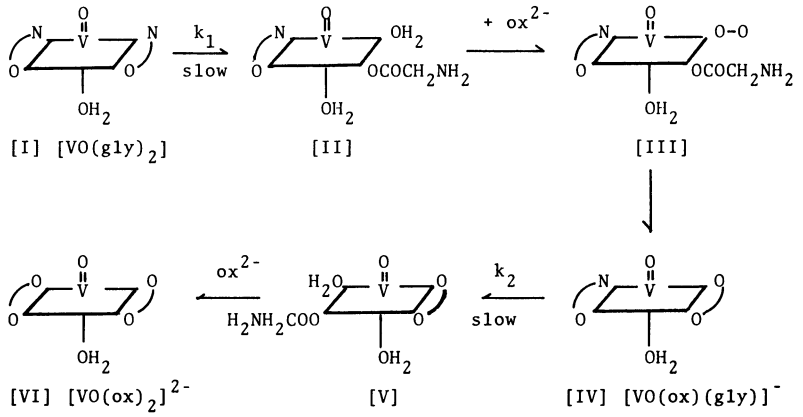


Fig. 3. Proposed reaction mechanism.

The values of rate constants k_6 and k_{-6} for the closing and opening of glycinate chelate ring, respectively, are listed with those of activation parameters in Table 2. The fact that the k_{-6} value (19 s^{-1} at 25 °C) is comparable to k_1 and k_2 values may support the proposed mechanism in Fig. 3.

In Table 1, the values of k_2 are nearly double the k_1 values under various conditions indicating that the amino group of glycine is more labile in $[VO(gly)(ox)]^-$ than in $[VO(gly)_2]$. This result can be accounted for by assuming that the oxalate at the basal positions in $[VO(gly)(ox)]^-$ has much stronger affinity for VO^{2+} than does glycinate and contributes to weakening the V-gly bond on the opposite side.

A mechanism in which the reaction is initiated by the rupture of V-N bonds at the basal positions can be ruled out because only $[VO\text{-}OCOCH_2NH_2]^+$ and $[VO\text{-}OCOCH_2NH_3]^{2+}$ complex ions have been known to be stable when glycine coordinates to the oxovanadium(IV) ion as a unidentate ligand.[13,14]

It may be concluded that there is little doubt of the mechanism in Fig. 3. However, it should be noted that this conclusion does not necessarily mean the dissociative mechanism. In oxovanadium(IV) ions water is a good ligand and said to be quite labile at the basal positions. The rate constant of water exchange was, in fact, reported to be 500 s^{-1} in $[VO(H_2O)_5]^{2+}$,[1,2] which is ten times larger in comparison with the time scale of the present study, and accordingly a water molecule might assist to initiate the ring opening.

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