

## KINETICS AND MECHANISM OF LIGAND SUBSTITUTION IN TRIGLYCINATOVANADIUM(III) BY EDTA AND NTA IN AQUEOUS SOLUTIONS

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Received February 11, 1993

Accepted July 15, 1993

The kinetics of ligand substitution reactions in triglycinatovanadium(III) by EDTA and NTA as multidentate ligands were investigated at a constant ionic strength of 2.5 mol dm<sup>-3</sup> spectrophotometrically. The substitutions were second-order reactions, first order in both reactants. Their rate could be expressed in the form  $r = k [\text{V}(\text{gly})_3] [\text{EDTA}(\text{NTA})]$  where  $k = 2.62 \cdot 10^{-2}$  and  $6.96 \cdot 10^{-2}$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup> at 25 °C for EDTA and NTA, respectively. The results obtained at different pH indicated that [H<sub>2</sub>edta]<sup>2-</sup> and [Hnta]<sup>2-</sup> ions were the most reactive species in the substitution. Kinetic parameters have been evaluated and a tentative mechanism of the reaction has been proposed.

Although much work was done on the kinetics of substitution reactions of vanadium(III) complexes<sup>1-8</sup>, no attention has been paid to the ligand substitution in triglycinatovanadium(III), V(gly)<sub>3</sub>, by ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA). The likely reason was the recognized complexity of the reaction resulting from the protonation, deprotonation, and hydrolysis of the reactants in aqueous solutions of different pH. Therefore, to minimize these effects, the lower hydrogen ion concentrations were used in general in such studies.

A previous kinetic study<sup>9</sup> of the substitution in trimalonatovanadium(III), V(mal)<sub>3</sub>, by EDTA and NTA showed that the rate of the substitution depends strongly on the charge of EDTA and NTA substituting ligands. The univalent anionic species derived from EDTA and NTA were regarded as the most reactive ions in the substitution. This

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finding was ascribed to a small electrostatic repulsion between these ions and the vanadium(III) complex compared to that with multicharged ions.

Therefore, it was of particular interest to examine EDTA and NTA as substituting ligands for the reactions of analogous vanadium(III) complexes as well as to elucidate mechanism of the substitution process. The results obtained are discussed in the present work.

## EXPERIMENTAL

**Chemicals.** Vanadium(III) perchlorate solutions were prepared as described earlier<sup>9</sup>. V(III) ion concentrations were determined spectrophotometrically at the corresponding absorption maxima (400 and 580 nm) where molar extinction coefficients were 8.5 and 5.6 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>, respectively<sup>10</sup>. Glycine (Wako Pure Chemicals) was recrystallized from water-methanol solution, and the product was dried in an electric oven at 110 °C for 48 h. V(gly)<sub>3</sub> complex was obtained by mixing the V(III) perchlorate solution with 0.8 M HClO<sub>4</sub> containing excess of glycine, pH of which was adjusted to 2 – 3 by NaOH under nitrogen<sup>9,11</sup>. Analytical grade EDTA and NTA (Wako Pure Chemicals) were used as obtained. Sodium perchlorate used to adjust ionic strength was prepared as described elsewhere<sup>11</sup>.

**Kinetic measurements.** As the rates of the studied substitutions were found to change with reactant concentrations, kinetic measurements were carried out under pseudo-first order conditions, using EDTA and NTA in large excess with respect to V(gly)<sub>3</sub> and a constant ionic strength (2.5 mol dm<sup>-3</sup>). All the measurements were performed under nitrogen on Jasco Unidec-505 spectrophotometer equipped with a thermostated cell compartment, using 1 cm cells. pH values were measured with a Corning digital pH-meter. The ionic strength of the reaction mixtures was maintained constant at 2.5 mol dm<sup>-3</sup> by sodium perchlorate as a non-complexing agent.

## RESULTS

### *Absorption Spectra*

Preliminary experiments made at different glycine concentrations ranging from 0.54 to 1.8 mol dm<sup>-3</sup> pointed to the presence of only one vanadium complex, namely V(gly)<sub>3</sub>, similarly to the situation observed previously<sup>9</sup> for V(mal)<sub>3</sub>. The absorption spectra of the starting complex and of the complexes formed after addition of excess EDTA and NTA are shown in Fig. 1.

### *Dependence of the Reaction Rate on Reactants Concentration*

Pseudo-first-order plots were linear over three half-lives for both substitution reactions studied. This demonstrates that the reactions are first order in V(gly)<sub>3</sub>. The slopes of these plots were used to calculate pseudo-first-order rate constants,  $k_{\text{obs}}$ . These when plotted against [EDTA] or [NTA] gave good straight lines passing through origin (Fig. 2), indicating that the substitution is also first-order in the substituting ligand.

Therefore, the rate could be expressed by Eq. (1) for the ligands in excess and by Eq. (2) in general,

$$r = k_{\text{obs}} [\text{V}(\text{gly})_3] \quad (1)$$

$$r = k [\text{V}(\text{gly})_3] [\text{EDTA}(\text{NTA})], \quad (2)$$

where  $k_{\text{obs}}$  and  $k$  are the observed first-order and the second-order rate constants, respectively. Their values were obtained from experimental data by the least-squares method and are presented in Table I.

### Dependence of the Reaction Rate on pH

This dependence could not be tested over a wide range of pH values because of the already mentioned complexity resulting from hydrolysis at the lower and protonation at the higher hydrogen ion concentrations. An increase of pH value of the reaction mixture was found to accelerate both substitution reactions. Again, in the pH region used, the second-order rate constants,  $k$ , vs  $[\text{H}^+]^{-1}$  and/or  $[\text{H}^+]^{-2}$  plots gave curved lines passing through origin. A typical plot is shown in Fig. 3. The results are summarized in Table II.

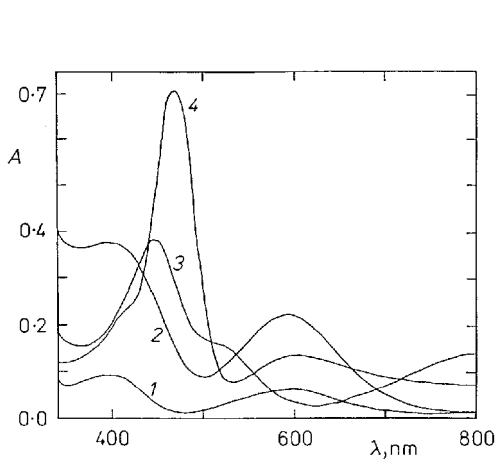


FIG. 1  
Absorption spectra of various vanadium(III) complexes. 1  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$  ( $0.011 \text{ mol dm}^{-3}$ ), 2  $[\text{V}(\text{gly})_3]$  ( $0.016 \text{ mol dm}^{-3}$ ), 3  $[\text{V}(\text{edta})]^{2-}$ , and 4  $[\text{V}(\text{nta})]^{2-}$

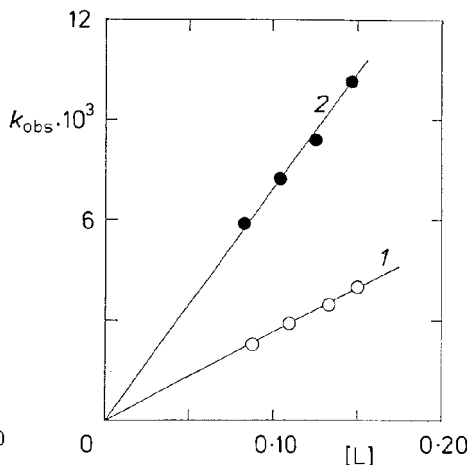


FIG. 2  
Dependence of experimental pseudo-first-order rate constants  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) of  $\text{V}(\text{gly})_3$  substitution on EDTA (1) and NTA (2) concentrations ( $L$  in  $\text{mol dm}^{-3}$ ) at  $20^\circ\text{C}$

## DISCUSSION

A question of fundamental interest in connection with these substitution reactions is whether univalent or polyvalent anions of EDTA and NTA are the more reactive species in the substitution of vanadium(III) complexes. Under our experimental conditions  $V(\text{gly})_3$  is the only one present of possible vanadium(III) complexes, and the uncharged EDTA and NTA could be expected to be the more reactive species in the substitution. These conclusions are based on the similarity of the absorption spectra of  $V(\text{gly})_3$  and  $[V(\text{mal})_3]^{2-}$  and further on the observed rate vs pH dependence<sup>12</sup>.

Furthermore, at pH values chosen in the present study, the concentration of a non-deprotonated species is negligibly small<sup>13</sup>.

TABLE I

Pseudo-first-order ( $k_{\text{obs}}$  in  $\text{s}^{-1}$ ) and second-order ( $k$  in  $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ ) rate constants for substitution of  $V(\text{gly})_3$  by EDTA and NTA ( $V(\text{III})$  concentration =  $0.013 \text{ mol dm}^{-3}$ , pH 2.37 for EDTA and  $V(\text{III})$  concentration =  $0.015 \text{ mol dm}^{-3}$ , pH 1.1 for NTA) at  $25^\circ \text{C}$

[EDTA]	$k_{\text{obs}} \cdot 10^3$	$k \cdot 10^2{}^a$	[NTA]	$k_{\text{obs}} \cdot 10^3$	$k \cdot 10^2{}^a$
0.09	$2.33 \pm 0.08$	2.59	0.08	$5.66 \pm 0.17$	7.07
0.11	$2.89 \pm 0.09$	2.63	0.10	$6.94 \pm 0.24$	6.94
0.13	$3.38 \pm 0.12$	2.59	0.13	$8.75 \pm 0.26$	6.73
0.15	$4.01 \pm 0.16$	2.67	0.15	$10.38 \pm 0.42$	6.92

<sup>a</sup> Experimental error  $\pm 3 - 4\%$ .

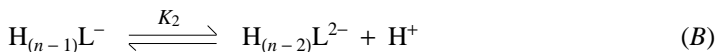
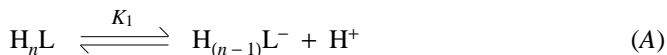
TABLE II

Dependence of the rate constants  $k_{\text{obs}}$  and  $k$  on pH (temperature  $20^\circ \text{C}$ ;  $[V(\text{gly})_3] = 0.015 \text{ mol dm}^{-3}$  and  $[\text{EDTA}] = 0.11 \text{ mol dm}^{-3}$  or  $[V(\text{gly})_3] = 0.013 \text{ mol dm}^{-3}$  and  $[\text{NTA}] = 0.10 \text{ mol dm}^{-3}$ )

EDTA <sup>a</sup>			NTA <sup>a</sup>		
pH	$k_{\text{obs}} \cdot 10^3$	$k \cdot 10^2{}^b$	pH	$k_{\text{obs}} \cdot 10^3$	$k \cdot 10^2{}^b$
2.54	$1.11 \pm 0.04$	1.00	1.92	$3.94 \pm 0.12$	3.79
2.66	$1.43 \pm 0.04$	1.29	2.11	$7.17 \pm 0.29$	6.89
2.76	$1.67 \pm 0.06$	1.50	2.23	$9.34 \pm 0.32$	8.98
2.85	$1.89 \pm 0.08$	1.70	2.28	$10.10 \pm 0.40$	9.71
2.94	$2.04 \pm 0.08$	1.84	2.42	$11.80 \pm 0.41$	11.30

<sup>a</sup> For dimensions of the constants see Table I; <sup>b</sup> see note<sup>a</sup> in Table I.

Hence, the most likely reaction mechanism is that involving deprotonation of the substituting ligand L (Eq. (A) for NTA and Eq. (B) for EDTA, where  $n$  is the number of hydrogen atoms associated with the ligand<sup>13</sup>).



This deprotonation is then followed by the competitive reactions (C) and (D), respectively.

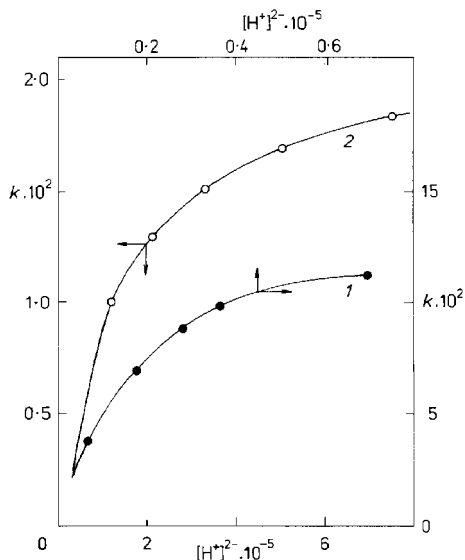
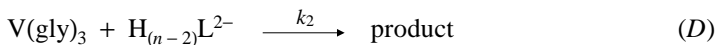
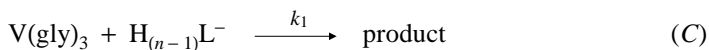


FIG. 3

Dependence of second-order rate constants  $k$  ( $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ ) of  $\text{V}(\text{gly})_3$  substitution on the squared reciprocal  $\text{H}^+$  ion concentration (in  $\text{mol}^{-2} \text{dm}^6$ ) at 20 °C. 1  $[\text{V}(\text{gly})_3] = 0.015 \text{ mol dm}^{-3}$ ,  $[\text{EDTA}] = 0.11 \text{ mol dm}^{-3}$ ; 2  $[\text{V}(\text{gly})_3] = 0.013 \text{ mol dm}^{-3}$ ,  $[\text{NTA}] = 0.10 \text{ mol dm}^{-3}$

TABLE III

Kinetic parameters for ligand substitution reactions in vanadium(III) complexes at 25 °C

Reaction	Solution	$k_f^a$	$k_b^b$	$\Delta H^{*c}$	$\Delta S^{*c}$	Ref.
$[\text{V}(\text{H}_2\text{O})_6]^{3+} + \text{H}_2\text{O}$	$\text{H}_2\text{O}$ ( $\mu = 1.0$ )					4
$[\text{V}(\text{H}_2\text{O})_6]^{3+} + \text{H}_2\text{O}$	$\text{H}_2\text{O}$			49.4	-28	18
$[\text{V}(\text{H}_2\text{O})_6]^{3+} + \text{SCN}^-$	$\text{H}_2\text{O}$ ( $\mu = 0.15$ )	10		33.5	-100	15
	pH 1 – 1.6		0.03	46.0	-96.2	
$[\text{V}(\text{H}_2\text{O})_6]^{3+} + \text{N}_3^-$	$\text{H}_2\text{O}$ ( $\mu = 1.0$ )	900				16
	pH 0.4 – 1.3		3.9	64.4	-17.8	
$[\text{V}(\text{H}_2\text{O})_6]^{3+} + \text{HC}_2\text{O}_4^-$	$\text{H}_2\text{O}$ ( $\mu = 0.5$ )	1 300				3
	pH 0.3 – 1					
$[\text{V}(\text{H}_2\text{O})_6]^{3+} + \text{MAL}$	$\text{H}_2\text{O}$ ( $\mu = 1.2$ )	3 800		31.7	-69.4	8
	pH 0.4 – 1		18	68.1	-3.2	
$[\text{V}(\text{H}_2\text{O})_6]^{3+} + \text{SAL}$	$\text{H}_2\text{O}$ ( $\mu = 1.0$ )	1 400 ( $\text{Hsal}^-$ )		57.7	9.2	5
	pH 0.09 – 1.82	4.9 ( $\text{H}_2\text{sal}$ )		69.8	0.4	
$[\text{V}(\text{H}_2\text{O})_6]^{3+} + \text{ASAL}$	$\text{H}_2\text{O}$ ( $\mu = 1.0$ )	7 000 ( $\text{Hasal}^-$ )				6
	pH 0.15 – 1.52	1 600 – 7 000 ( $\text{H}_2\text{asal}^{\pm}$ ) <sup>d</sup> 3.3 – 25 ( $\text{H}_2\text{asal}$ ) 3.3 ( $\text{H}_3\text{asal}^+$ )				
$[\text{V}(\text{dmsO})_6]^{3+} + \text{SCN}^-$	$\text{DMSO}^e$ ( $\mu = 0.15$ )	210	1.5			2
$[\text{V}(\text{dmsO})_6]^{3+} + \text{bpy}^f$	$\text{DMSO}$ ( $\mu = 0.15$ )	0.11	0.0036	48.9	-105	2
$[\text{V}(\text{dmsO})_6]^{3+} + \text{SSA}^g$	$\text{DMSO}$ ( $\mu = 0.15$ )	0.21	0.0017			2
$\text{V}(\text{acac})_3 + \text{Hacac}^h$	$\text{Hacac}$			75.3	-92.0	7
$[\text{V}(\text{mal})_3]^{3-} + \text{MAL}$	$\text{H}_2\text{O}$ ( $\mu = 2.5$ )			54.8	-50.2	9
	pH 2.9 – 4.0					
$[\text{V}(\text{mal})_3]^{3-} + \text{EDTA}$	$\text{H}_2\text{O}$ ( $\mu = 2.5$ )	0.25 ( $\text{H}_3\text{edta}^-$ )		42.3	-119	9
	pH 2.6 – 4.8	0.04 ( $\text{H}_2\text{edta}^{2-}$ )				
$[\text{V}(\text{mal})_3]^{3-} + \text{NTA}$	$\text{H}_2\text{O}$ ( $\mu = 2.5$ )	0.014 ( $\text{H}_2\text{nta}^-$ )		67.4	-44	9
	pH 3.0 – 4.2					
$\text{V}(\text{gly})_3 + \text{EDTA}$	$\text{H}_2\text{O}$ ( $\mu = 2.5$ )	0.026 ( $\text{H}_2\text{edta}^{2-}$ )		75.7	-22.9	<sup>i</sup>
	pH 2.5 – 2.9					
$\text{V}(\text{gly})_3 + \text{NTA}$	$\text{H}_2\text{O}$ ( $\mu = 2.5$ )	0.079 ( $\text{Hnta}^{2-}$ )		49.6	-101	<sup>i</sup>
	pH 1.9 – 2.4					

<sup>a</sup> Forward rate constant ( $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ ); <sup>b</sup> backward rate constant ( $\text{s}^{-1}$ ); <sup>c</sup>  $\Delta H^\#$  in  $\text{kJ mol}^{-1}$  and  $\Delta S^\#$  in  $\text{J K}^{-1} \text{ mol}^{-1}$ ; <sup>d</sup>  $\text{H}_2\text{asal}^\pm$  denotes  $4\text{-H}_3\text{N}^+, 2\text{-HOC}_6\text{H}_3\text{COO}^-$ ; <sup>e</sup> dimethyl sulfoxide; <sup>f</sup> 2,2'-bipyridyl; <sup>g</sup> sulfosalicylic acid; <sup>h</sup> 2,4-pentanedione; <sup>i</sup> this work.

Taking the reactions (C) and (D) as the rate determining steps, the change of the reaction rate  $r$  with pH could be expressed by Eq. (3), where  $[L]_T$  is the total ligand concentration.

$$r = \frac{(k_1 K_1 [H^+]^{-1} + k_2 K_1 K_2 [H^+]^{-2}) [(Vgly)_3] [L]_T}{1 + K_1 [H^+]^{-1} + K_1 K_2 [H^+]^{-2}} \quad (3)$$

Comparing Eqs (2) and (3) and assuming that  $K_1 [H^+]^{-1}$  and  $K_1 K_2 [H^+]^{-2} \gg 1$ , one obtains Eq. (4).

$$k = \frac{k_1 K_1 [H^+]^{-1} + k_2 K_1 K_2 [H^+]^{-2}}{K_1 [H^+]^{-1} + K_1 K_2 [H^+]^{-2}} \quad (4)$$

According to this relation, the  $k$  vs  $[H^+]^{-1}$  and/or  $k$  vs  $[H^+]^{-2}$  plots should be linear with a positive intercept on the  $k$  axis. However, under our conditions, the results did not obey Eq. (4), yielding the curved dependences passing through origin (Fig. 3). This shows that the first term of Eq. (4) corresponding to the equilibrium (C) is relatively small, and can be thus neglected. The reaction (D) thus becomes the sole reaction path for which the rate equation takes the following form:

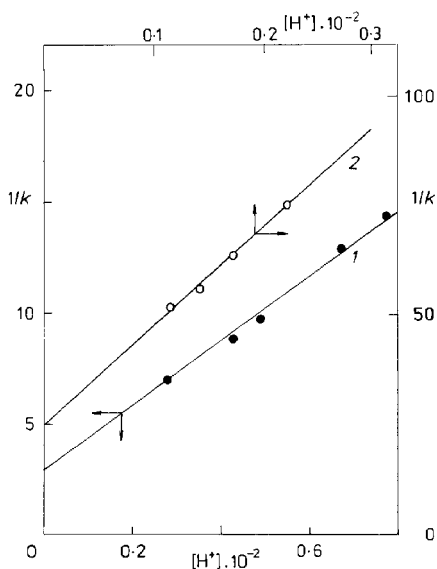


FIG. 4  
Plot of  $1/k$  vs  $[H^+]$  (for experimental conditions see Fig. 3)

$$1/k = ([H^+])/(k_2 K_2) + 1/k_2. \quad (5)$$

Equation (5) predicts that  $k^{-1}$  vs  $[H^+]$  plots should be linear, as experimentally found (Fig. 4). The  $K_2$  values at 20 °C calculated from such plots were  $1.2 \pm 0.2 \cdot 10^{-3}$  for EDTA and  $2.3 \pm 0.2 \cdot 10^{-2}$  for NTA, respectively, in a good agreement with the values reported elsewhere<sup>13</sup>.

The thermodynamic parameters determined from the Eyring equation are summarized in Table III, along with kinetic data for other substitution reactions of V(III) complexes. The results document a wide range of the rates of such reactions. Perlumutter-Hayman and Tapuhi<sup>5,6</sup> have pointed out that the basicity of the substituting ligand is the main factor determining the reactivity of the entering species and thus also the magnitude of the rate constant.

Ikeda and coworkers<sup>9</sup> reported that the univalent anions  $[H_3\text{edta}]^-$  and  $[H_2\text{nta}]^-$ , in spite of their lower basicity<sup>13</sup>, were the more reactive species in the substitution of  $[V(\text{mal})_3]^{3-}$  by EDTA and NTA. This finding was explained in terms of electrostatic repulsion, this being weaker between the above trivalent complex anion and the monovalent  $[H_3\text{edta}]^-$  or  $[H_2\text{nta}]^-$  species<sup>14</sup> compared to the multicharged ions ( $[H_2\text{edta}]^{2-}$  or  $[H\text{nta}]^{2-}$ ).

Contrary to the above discussed situation, the results of the present study show that in the case of  $V(\text{gly})_3$  complex, it is the multicharged  $[H_2\text{edta}]^{2-}$  and  $[H\text{nta}]^{2-}$  which are more reactive. This provides the evidence that the charge on the vanadium(III) complex plays a very important role in determining the reactivity of the substituting ligand, which depends on the electrostatic attraction between V(III) complex and the ligand species during formation of the activated complex.

In view of these facts, it seems likely that substitution reactions in V(III) complexes proceed via an associative mechanism<sup>15</sup>. The large negative entropy of the activation observed in our case supports this assumption. The strong ligand dependence of the rates of the substitutions presented in Table III allows to conclude that substitution reactions in V(III) complexes proceed in general via the associative process. This is further supported by the large negative entropies for most of these reactions, and also by the fact that the activation volume in the water exchange reaction of  $[V(\text{H}_2\text{O})_6]^{3+}$  has a negative value<sup>18</sup> ( $-8.9 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$ ).

*The author (M. M. A.-F.) wishes to express his gratitude to the Ministry of Education, Japan, for the fellowship.*



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Translation revised by J. Hetflejš.