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Kinetics of Ligand Substitution Reactions in Trimalonatovanadium(III)

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(Received April 22, 1981)

The kinetics of ligand substitution reactions in trimalonatovanadium(III), $V(mal)_3{}^{3-}$, with various multidentate ligands, malonate (MAL), ethylenediaminetetraacetate (EDTA), and nitrilotriacetate (NTA) have been studied. The rate constant of the malonate exchange in $V(mal)_3{}^{3-}$ was obtained from the NMR line-broadening method to be $k_{ex}=50\ s^{-1}$ at 70 °C. The rate of EDTA substitution depends on the entering EDTA species. The values of second order rate constants are $k_{21}=0.04\ M^{-1}\ s^{-1}$ ($1\ M=1\ mol\ dm^{-3}$) for H_2edta as an entering ligand and $k_{22}=0.25\ M^{-1}\ s^{-1}$ for H_3edta at 25 °C. The NTA substitution is reversible under the experimental conditions studied. The apparent rate constants of the forward and backward reactions are $k_3=1.3\times10^{-2}\ M^{-1}\ s^{-1}$ and $k_{-3}=2.0\times10^{-3}\ M^{-1}\ s^{-1}$ at pH 3.5 and 25 °C, respectively. The univalent H_2nta is found to be the only entering ligand.

In spite of numerous investigations on the kinetics of ligand substitutions of various transition metal complexes, sufficient data are not available on vanadium(III) complexes.[1–7)] Among vanadium species, ligand substitution reactions have been most extensively studied for oxovanadium(IV)[8–16)] and it has been found that the rates depend largely on the properties of entering ligands. Similar substitution processes can be expected for V(III) complexes by considering the electronic configurations of these complexes.

In the present paper, a detailed analysis of the kinetics of ligand substitution reactions for V(III) complexes will be presented for the following reactions.[17)]

$$V(mal)_3{}^{3-} + MAL \rightleftarrows V(mal)_3{}^{3-} + MAL \quad (1)$$

$$V(mal)_3{}^{3-} + EDTA \longrightarrow V(edta)^{-} + 3MAL \quad (2)$$

$$V(mal)_3{}^{3-} + NTA \rightleftarrows V(nta)(mal)^{2-} + 2MAL \quad (3)$$

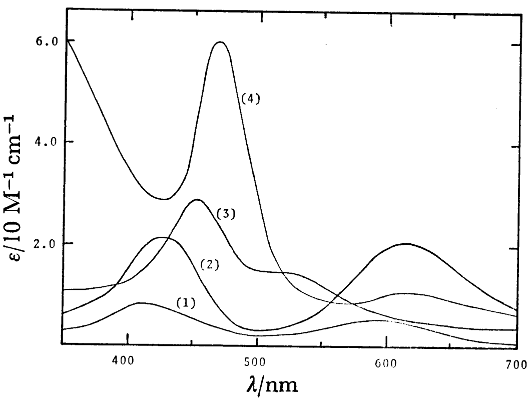


Fig. 1. Absorption spectra of various vanadium(III) complexes: (1): $V(H_2O)_6{}^{3+}$, (2): $V(mal)_3{}^{3-}$, (3): $V(edta)^{-}$, (4): $V(nta)(mal)^{2-}$.

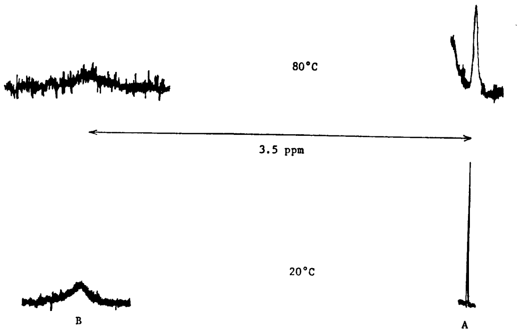


Fig. 2. NMR spectra of the malonate methylene protons in the presence of V(III) ions at 20 and 80 °C: A and B correspond to the methylene protons of bulk malonate and coordinated malonate, respectively.

Experimental

Vanadium(III) perchlorate solutions were prepared by electrolytic reduction of VO^{2+} in 1.0 M $HClO_4$ at a mercury cathode under an atmosphere of nitrogen. The preparation of VO^{2+} perchlorate was described elsewhere,[11)] The concentration of V(III) solutions was determined by titration with standard permanganate. Since V(III) perchlorate is very easily oxidized to VO^{2+}, the preparation of V(III) was carried out just before kinetic experiments. Reagent grade malonic acid (Wako Pure Chemical Ind. Ltd.) was recrystallized twice from distilled water and dried under reduced pressure. Sodium perchlerate was prepared as described earlier.[11)] Analytical grade EDTA and NTA were used without further purification. The NMR measurements were carried out on a JEOL JNM-4H-100 spectrometer. The spectrophotometric and kinetic measurements for the EDTA and NTA substitution reactions were made by using a Shimadzu MPS-50 spectrophotometer. The pH was obtained by measurement with a Hitachi-Horiba Model F-7SS pH meter. The ionic strength was kept at 2.5 by the addition of $NaClO_4$ throughout the kinetic experiments.

Results and Discussion

Absorption Spectra of V(III) Complexes. The absorption spectra of various V(III) complexes, $V(H_2O)_6{}^{3+}$, $V(mal)_3{}^{3-}$, $V(nta)(mal)^{2-}$, and $V(edta)^{-}$, are shown in Fig. 1. The main absorption bands, which appear at about 420 and 590 nm for $V(H_2O)_6{}^{3+}$, are slightly shifted in $V(mal)_3{}^{3-}$. However, $V(mal)_3{}^{3-}$ has much larger extinction coefficients than $V(H_2O)_6{}^{3+}$ in both bands, so that the assignment of the bands to the aqua or malonato complexes can be made from the spectra. The spectra of $V(edta)^{-}$ and $V(nta)(mal)^{2-}$ are much different from those of $V(H_2O)_6{}^{3+}$ and $V(mal)_3{}^{3-}$. Therefore, the rates of ligand substitution between these complex species can be determined from the changes in absorbance.

NMR Measurements in $V(mal)_3{}^{3-}$ Solutions. The NMR measurements of the methylene protons of malonic acid were made in the presence of V(III) ions and two peaks of the malonate methylene protons were observed as shown in Fig. 2. The downfield and upfield signals are assigned to the coordinated malonate

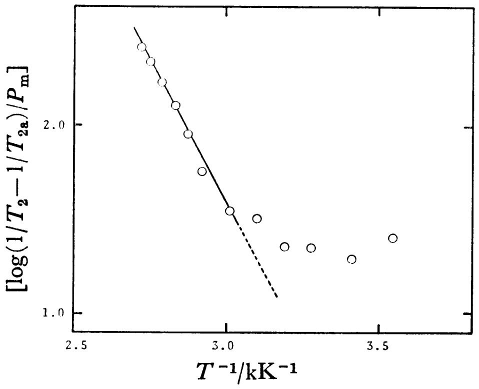


Fig. 3. A plot of log((1/T_2−1/T_{2a})/P_m) *vs.* 1/*T* for methylene protons of malonic acid in V(III) solution. [V(III)]=0.075 M, $[MAL]_T$=1.0 M, and pH=3.75.

and bulk malonate, respectively. The earlier work on ^{17}O NMR measurements of H_2O in the presence of $V(H_2O)_6^{3+}$ observed a similar splitting of the H_2O signal.[1]

The signal of the coordinated malonate protons is broad at room temperature because of the direct interaction with the paramagnetic V(III) ion, while that of bulk malonate is very sharp. Figure 2 shows that these malonate signals become broad as the temperature increases above 80 °C. This suggests that the line widths are affected by a chemical exchange between bulk malonate and the coordinated malonate. In order to examine the line broadening in detail, the expression log (1/T_2−1/T_{2a}), where T_2 is the transverse relaxation time of the bulk malonate protons in the presence of V(III) ion and T_{2a} is the transverse relaxation time in the absence of V(III) ion, was plotted against the reciprocal temperature as shown in Fig. 3. The plot gives a straight line with a negative slope. The deviation from the straight line in the region below 50 °C corresponds to the so-called region I.[18,19] Therefore, it may be concluded that the relaxation process is controlled by a chemical exchange[18] and the mean life-time of a ligand in the first coordination sphere of V(III) ion, τ_m, is expressed by the equation

$$1/T_2 - 1/T_{2a} = P_m/\tau_m, \quad (4)$$

where P_m is approximated by the Eq. 5 in a dilute solution.

$$P_m = n[\text{complex}]/[\text{total ligand}], \quad (5)$$

where *n* is the number of coordinated ligands and assumed to be 3 in the present case. The first order rate constants of the malonate exchange in $V(mal)_3^{3-}$, k_{ex}= 1/τ_m, are listed in Table 1 for a variety of pH values. Since the NMR measurements were carried out at high temperatures above 70 °C, it was very hard to maintain the V(III) solution and the instrument at constant condition. Consequently, the errors in k_{ex} values are estimated at approximately 20% and it is concluded that k_{ex} does not depend on pH within experimental errors. In the EDTA and NTA substitution reactions, which will be mentioned later, the rates were found to be first order with respect to entering ligands. Although the dependence of the exchange rate on malonate concentrations was not tested, it may be also expected for the malonate exchange that the rate is first order to entering malonate ion, which exists principally in the Hmal or mal form in solution. However, the concentration of Hmal is much larger than that of mal over the pH range studied so that Hmal should play an important role as an entering ligand. In addition, Hmal appears to be more reactive as an entering ligand compared with mal because it is favorable for coming close to the negatively charged complex ion, $V(mal)_3^{3-}$. The values of second order rate constant calculated from the expression, $k_1=k_{ex}/[Hmal]$, are listed in Table 1, which shows that k_1 changes only slightly with pH values. The activation parameters for the malonate exchange obtained from Fig. 3, are summarized in Table 6.

Substitution by EDTA. The substitution of the coordinated malonate by EDTA can be written by Eq. 2. The rate law which consists with the experimental results is expressed by the equation:

$$-d[V(mal)_3^{3-}]/dt = k_2[V(mal)_3^{3-}][EDTA]_T, \quad (6)$$

where $[EDTA]_T$ indicates the total concentartion of EDTA at *t*=0. The rate constant, k_2, was calculated by a least squares method. The values of k_2 obtained at various EDTA concentrations were constant within the experimental errors (Table 2). The pH dependence of k_2 is shown in Table 3 together with the apparent first order rate constant, k_{2f} defined by $k_{2f}=k_2[EDTA]_T$. Since H_3edta and H_2edta are major species in the pH region studied, two substitution processes by H_2edta (k_{21} path) and H_3edta (k_{22} path) are considered leading to the following rate equation:

$$R_2 = k_{21}[V(mal)_3^{3-}][H_2edta] + k_{22}[V(mal)_3^{3-}][H_3edta]. \quad (7)$$

Hence k_{2f} can be given by Eq. 8.

Table 1. Rate constants of the malonate exchange in $V(mal)_3^{3-}$ at 70 °C

pH	k_{ex} / s^{-1}	k_1 / $M^{-1} s^{-1}$
2.89	44	81
2.95	44	77
2.99	40	67
3.40	57	72
3.75	50	56
3.99	50	54

The concentrations of the MAL species were calculated by using the following p*K* values; pK_1=5.78 and pK_2= 2.82.[22]

Table 2. Values of second order rate constants of the EDTA substitution reaction at various EDTA concentrations

pH	$[EDTA]_T$ / M	k_2 / $M^{-1} s^{-1}$
3.66	0.049	0.083
3.65	0.075	0.082
3.67	0.100	0.073
3.67	0.125	0.078
3.68	0.150	0.079
		Average 0.079±0.003

[V(III)]=0.0127 M, $[MAL]_T$=1.0 M and 26 °C.

TABLE 3. pH DEPENDENCE ON THE RATE OF THE EDTA SUBSTITUTION REACTION

pH	$\frac{k_2}{\mathrm{M^{-1}\,s^{-1}}}$	$\frac{k_{2f}}{10^{-3}\,\mathrm{s^{-1}}}$
2.62	0.142	3.98
2.86	0.109	3.05
3.25	0.078	2.18
3.59	0.066	1.85
4.00	0.053	1.48
4.80	0.042	1.18

[V(III)]=0.0127 M, $[\mathrm{EDTA}]_T=2.8\times10^{-2}$ M, $[\mathrm{MAL}]_T=1.0$ M at 25 °C. The concentrations of EDTA species were calculated by using the following pK values, pK_1=10.26, pK_2=6.16, pK_3=2.67, pK_4=1.99.[23]

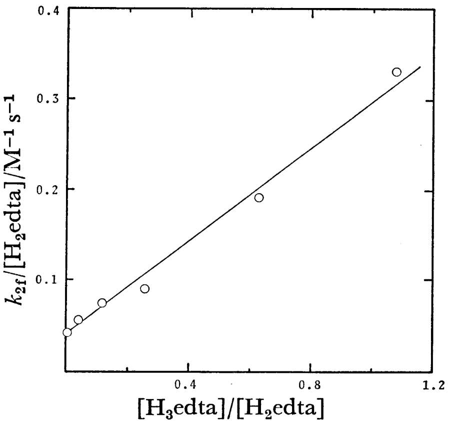


Fig. 4. A plot of $k_{2f}/[\mathrm{H_2edta}]$ *vs.* $[\mathrm{H_3edta}]/[\mathrm{H_2edta}]$ in the substitution reaction of the coordinated malonate by EDTA.

$$k_{2f} = k_{21}[\mathrm{H_2edta}] + k_{22}[\mathrm{H_3edta}] \qquad (8)$$

As shown in Fig. 4, the plot of $k_{2f}/[\mathrm{H_2edta}]$ *vs.* $[\mathrm{H_3edta}]/[\mathrm{H_2edta}]$ is linear and it proves Eq. 8 to be valid. The intercept and the slope of the straight line yield $k_{21}=0.04\ \mathrm{M^{-1}\,s^{-1}}$ and $k_{22}=0.25\ \mathrm{M^{-1}\,s^{-1}}$, respectively. The activation parameters obtained from the measurements at temperatures ranging from 20 to 40 °C were summarized in Table 6.

Substitution by NTA. The substitution of the coordinated malonate by NTA can be described by Eq. 3. The $\mathrm{V(nta)(mal)^{2-}}$ complex, though its structure is not known, seems to have an octahedral structure. The following explanation will give the stoichiometric evidence for Reaction 3.

Under the experimental conditions studied, Reaction 3 was reversible and the rate equation is

$$-\mathrm{d}[\mathrm{V(mal)_3}^{3-}]/\mathrm{d}t = k_3[\mathrm{V(mal)_3}^{3-}][\mathrm{NTA}]_T - k_{-3}[\mathrm{V(nta)(mal)^{2-}}][\mathrm{MAL}]_T. \qquad (9)$$

The values of the forward and backward rate constants, k_3 and k_{-3}, were calculated by the least squares method. A typical least squares fit to experimental data is shown in Fig. 5. The results are listed in Table 4 for a variety of $[\mathrm{NTA}]_T$ and $[\mathrm{MAL}]_T$ values. The pH dependence of the substitution rates is shown in Table 5.

At infinite time, $-\mathrm{d}[\mathrm{V(mal)_3}^{3-}]/\mathrm{d}t=0$, which leads to

$$[\mathrm{V(nta)(mal)^{2-}}][\mathrm{MAL}]_T/([\mathrm{V(mal)_3}^{3-}][\mathrm{NTA}]_T) = k_3/k_{-3}. \qquad (10)$$

On the other hand, the equilibrium constant, K, of the Eq. 3 is

$$[\mathrm{V(nta)(mal)^{2-}}][\mathrm{mal}]^2/([\mathrm{V(mal)_3}^{3-}][\mathrm{nta}]) = K. \qquad (11)$$

From Eqs. 10 and 11

$$k_3/k_{-3} = K[\mathrm{MAL}]_T[\mathrm{nta}]/([\mathrm{NTA}]_T[\mathrm{mal}]^2). \qquad (12)$$

If the stoichiometry in Eq. 3 is correct, a plot of k_3/k_{-3} *vs.* $[\mathrm{nta}]/[\mathrm{mal}]^2$ should be linear. The equilibrium constant

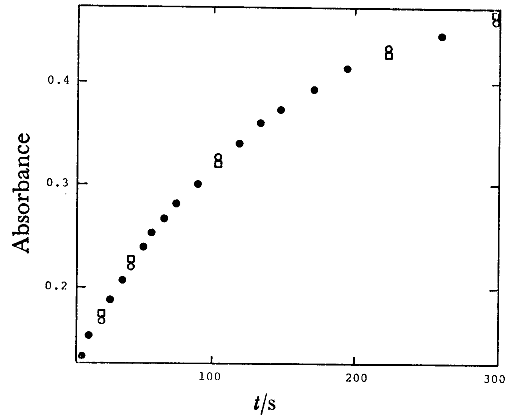


Fig. 5. The variation of absorbance with time in the substitution reaction of the coordinated malonate by NTA.

□: Experimental, ○: calculated. Closed circles indicate the points where the values of □ in accord with those of ○.

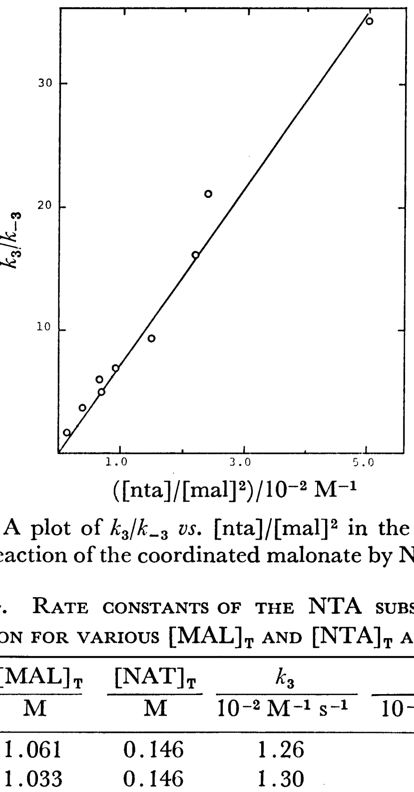


Fig. 6. A plot of k_3/k_{-3} *vs.* $[\mathrm{nta}]/[\mathrm{mal}]^2$ in the substitution reaction of the coordinated malonate by NTA.

TABLE 4. RATE CONSTANTS OF THE NTA SUBSTITUTION REACTION FOR VARIOUS $[\mathrm{MAL}]_T$ AND $[\mathrm{NTA}]_T$ AT 25 °C

pH	$\frac{[\mathrm{MAL}]_T}{\mathrm{M}}$	$\frac{[\mathrm{NAT}]_T}{\mathrm{M}}$	$\frac{k_3}{10^{-2}\,\mathrm{M^{-1}\,s^{-1}}}$	$\frac{k_{-3}}{10^{-3}\,\mathrm{M^{-1}\,s^{-1}}}$
3.53	1.061	0.146	1.26	2.3
3.50	1.033	0.146	1.30	2.0
3.59	0.884	0.146	1.06	2.4
3.47	0.778	0.146	1.36	2.2
3.47	0.707	0.146	1.72	2.5
3.40	1.167	0.0732	1.31	2.8
3.40	1.167	0.110	1.36	2.5
3.44	1.167	0.146	1.43	2.5

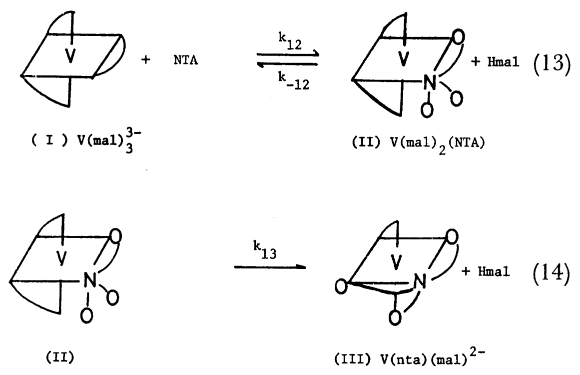
Table 5. pH dependence on the rate of the NTA substitution reaction

pH	$\frac{k_3}{10^{-2}\,M^{-1}\,s^{-1}}$	$\frac{k_{-3}}{10^{-3}\,M^{-1}\,s^{-1}}$	$\frac{k_{3f}}{10^{-3}\,s^{-1}}$
2.95	7.08	2.0	10.3
3.15	4.19	2.0	6.12
3.18	4.38	2.7	6.39
3.31	2.62	2.8	3.83
3.47	1.72	2.5	2.51
3.57	1.01	1.7	1.47
3.77	0.64	1.7	0.93
4.18	0.32	1.9	0.47

[V(III)]=0.00429 M, $[MAL]_T$=0.707 M, $[NTA]_T$=0.146 M, at 25 °C. The concentrations of the NTA species were calculated by using the following pK values; pK_1=9.73, pK_2=2.49, pK_3=1.89.[23]

is obtained from the slope in Fig. 6 to be 1.5×10^2 M. Hence it is confirmed that V(nta)(mal)$^{2-}$ is the most reasonable species for the product of the substitution of the coordinated malonate by NTA.

In comparison with the EDTA substitution reaction, the mechanism seems to be more complicated for the NTA substitution. A plot of k_{3f}/[Hnta] *vs.* [H$_2$nta]/[Hnta], where k_{3f} is the first order rate constant for Reaction 3, does not give a straight line, while the corresponding plot for the EDTA substitution was linear as shown in Fig. 4. Considering these results, we estimate the following substitution scheme for the NTA substitution. The initial step is a reversible substitution process between V(mal)$_3$$^{3-}$ (I) and the intermediate complex V(mal)$_2$(NTA) (II), whose charge can not be determined, followed by the chelation of NTA.



where NTA is supposed to be Hnta or H$_2$nta. In the intermediate complex (II), NTA, which is primarily a quadridentate ligand, coordinates to V(III) as a bidentate. Such a complex is presumed to be unstable compared with the complexes (I) and (III). On the basis of the above assumption, a steady state approximation for the complex (II) leads to the following rate law:

$$R_3 = k_{12}k_{13}[V(mal)_3{}^{3-}][NTA]/(k_{-12}[Hmal]+k_{13}). \quad (15)$$

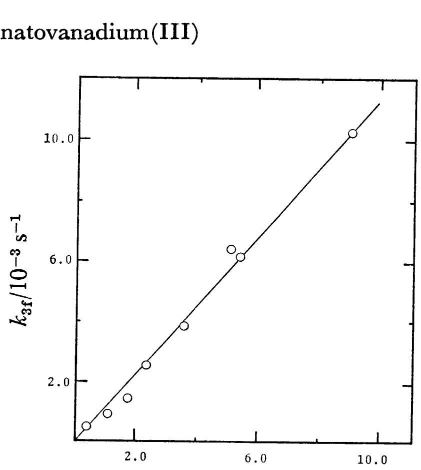


Fig. 7. A plot of k_{3f} *vs.* [H$_2$nta]/[Hmal] in the substitution reaction of the coordinated malonate by NTA.

Table 6. Activation parameters for the substitution reactions in V(mal)$_3$$^{3-}$

Reaction	$\frac{\Delta H^{\ddagger}}{kJ\,mol^{-1}}$	$\frac{\Delta S^{\ddagger}}{J\,mol^{-1}\,K^{-1}}$
Malonate exchange (Reaction 1)	54.8$^{a)}$	−50.2$^{a)}$
EDTA substitution (Reaction 2)	42.3±1.7	−119±5
NTA substitution (k_3 path in Reaction 3)	67.4±3.8	−44±13

a) The errors in these values are estimated at approximately 20%.

The backward rate of Reaction 13 (k_{-12} path) is supposed to be as fast as that of Reaction 1, because both processes are the substitution of bidentate ligands by Hmal. Since the rate constant of the malonate exchange (1) is 3.5 s^{-1} at 25 °C, which is about hundred times greater than that of the NTA substitution (3), it may be assumed that k_{-12}[Hmal] is relatively larger than k_{13}. If $k_{-12}[Hmal]\gg k_{13}$ is assumed, Eq. 15 becomes

$$R_3 = k_{12}k_{13}[V(mal)_3{}^{3-}][NTA]/k_{-12}[Hmal], \quad (16)$$

or

$$k_{3f} = k_{12}k_{13}[NTA]/k_{-12}[Hmal]. \quad (17)$$

The plot of k_{3f} as a function of [H$_2$nta]/[Hmal] is linear (Fig. 7) and this fact supports that the reaction mechanism described above is reasonable. It is also found that only H$_2$nta of NTA species acts as an entering ligand because the intercept in Fig. 7 is approximately zero. Recently, Tanaka *et al.* reported the existence and reactivity of the protonated species, H$_4$nta.[20] However, H$_4$nta will not play the important role, since the concentration of H$_4$nta (10^{-5}—10^{-7} M) is much lower than those of H$_2$nta and Hnta in the pH region studied.

The activation parameters were obtained from the measurements at temperatures ranging from 20 to 40 °C. The results were summarized in Table 6.

Conclusion

We conclude that the ligand substitution reactions in V(mal)$_3$$^{3-}$ proceed *via* an A mechanism.[21] These results are consistent with those of earlier studies.[2,3] Larger negative values of activation entropies as shown in Table 6 may support the A mechanism.

It is of particular interest that univalent anions are markedly reactive as the entering ligand in substitution reactions compared with other multivalent ions. This is quite reasonable because a mutual repulsion between the univalent anion and trivalent complex anion, $V(mal)_3^{3-}$, is supposed to be much smaller than that between $V(mal)_3^{3-}$ and multivalent anions.

In the earlier study dealing with the malonate exchange in $VO(mal)_2^{2-}$, it was suggested that the reaction would proceed *via* acid catalysis,[12] where the second order rate constants for $VO(mal)_2^{2-}$ and $Hmal^-$ increased more than fivefold when pH changed from 2.30 to 4.05. From the present study, however, we conclude that the acid effect is very small or nearly negligible. In the case of the EDTA substitution reaction, it can not be determined whether the pH dependence of the rate constant is due to the acid catalysis or the concentration dependence of the entering ligand, if only H_2edta is assumed to be active as an entering ligand. However, such an assumption seems unlikely, because H_2edta should be more inactive than H_3edta to $V(mal)_3^{3-}$ owing to the electric repulsion. In fact, the linear relationship between the substitution rate and the hydrogen ion concentration was not obtained in the NTA substitution reaction. As shown in Table 1, the second order rate constant of the malonate exchange in $V(mal)_3^{3-}$ increases slightly with increasing hydrogen ion concentrations. However, it may be hard to conclude whether the exchange rate is slightly accelerated by acid or not, because unlike the malonate exchange reaction in $VO(mal)_2^{2-}$ the pH dependence of the rate constant is too small by considering large experimental errors in NMR measurements.

The authors wish to thank Professor Gilbert Gordon of Miami University for his helpful discussions.

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17) For the convenience, malonate and bimalonate ions will be expressed as mal and Hmal, respectively. Corresponding species of ethylenediaminetetraacetic acid will be expressed as edta, Hedta, H_2edta, and H_3edta. Similarly, nitrilotriacetic acid species will be abbreviated as nta, Hnta, and H_2nta. The charge on these species will be omitted. Abbreviations, MAL, EDTA, and NTA, will be used for the system including all nonprotonated and protonated species of malonic acid, ethylenediaminetetraacetic acid, and nitrilotriacetic acid, respectively.

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