

Nuclear Magnetic Resonance Study of the Kinetics of Ligand Exchange on the Oxovanadium(IV)-malonato Complex

Hiroshi TOMIYASU,* Satoshi ITO,** and Shiro TAGAMI

Department of Chemistry, Faculty of Science, Shinshu University, Asahi, Matsumoto 390

(Received April 26, 1974)

The kinetics of malonate exchange on $\text{VO}(\text{mal})_2^{2-}$ has been studied by the NMR line-broadening method. The reaction was found to be dependent on the Hmal and hydrogen-ion concentrations, and the mechanism producing the intermediate complexes, where malonic acid was coordinated partly as an unidentate ligand, was estimated from the rate law. The activation parameters were determined for the acid-independent and acid-catalyzed paths as: $\Delta H^\ddagger = 8.6$ kcal/mol, $\Delta S^\ddagger = -16.2$ e.u., and $\Delta H^\ddagger = 8.9$ kcal/mol, $\Delta S^\ddagger = -13.5$ e.u.

A number of kinetic studies of the ligand substitution of various oxovanadium(IV) complexes have been reported. These include H_2O exchange by ^{17}O NMR,¹⁻³⁾ CH_3CN , glycine and other ligand exchanges by proton NMR,^{4,5)} the formation of VOHGly^{2+} and $\text{VO}(\text{Tart})_2^{2-}$ by the stopped-flow and Temp.-Jump methods,⁵⁻⁷⁾ and the rapid interaction of axial- or second-sphere water by NMR and ESR.^{3,8,9,14)}

We found in a previous work that, in the formation of the chelate complex, $\text{VO}(\text{Gly})^+$, the rate-determining step was the path from VOGly^+ , which represents the deprotonated form of VOHGly^{2+} , to $\text{VO}(\text{Gly})^+$ instead of the formation of VOHGly^{2+} , where glycine is coordinated on the equatorial position as a unidentate ligand.^{5,7)}

This led to the problem of the unusual reactivity of bidentate ligands which are coordinated on VO^{2+} as unidentate ligands. In this work we wish to report the kinetics of malonate exchange on $\text{VO}(\text{mal})_2^{2-}$ † in order to discuss the problems which arose from the previous work.

Experimental

The preparation and analysis of the VO^{2+} stock solution were described in a previous paper.⁵⁾ Reagent-grade malonic acid (Wako Pure Chemicals, Co. Ltd.) was recrystallized twice from distilled water and dried under reduced pressure. The sodium perchlorate was prepared from stoichiometric amounts of Na_2CO_3 and HClO_4 and was purified by recrystallization from an aqueous solution. A JEOL Co. Ltd. JNM-4H-100 NMR spectrometer was used to record the NMR spectra. The peak observed was that of the methylene protons of malonic acid in the bulk phase. The spectrophotometric measurements were made at 25 °C on a Shimadzu MPS-50L spectrometer. The pH of each solution was measured with a Hitachi-Horiba pH meter F-7ss equipped with a glass electrode, Horiba 1026-05T.

Results and Discussion

Absorption Spectrum of the Oxovanadium(IV)-malonate Complex. The absorption spectrum and the elec-

tronic structure of the VO^{2+} complexes have been studied elsewhere.¹²⁾ The two absorption bands at about 760 and 630 nm which are characteristic of the VO^{2+} ion were observed at slightly shifted wavelengths of 780 and 600 nm in the presence of malonic acid, according to the complex formation. The optical densities of the malonate-complex were much larger than those of the aquo-complex in both bands; therefore, the observed absorbances increased as the concentration of malonic acid or the pH of solution was increased. Under the conditions of malonic acid > 1.0 M and $\text{pH} > 2.8$, the complex formation was saturated and no further increase in absorbance was observed. In such conditions, all the VO^{2+} ions were present as dimalonatooxovanadium(IV) ions, $\text{VO}(\text{mal})_2^{2-}$, which may be analogous to diglycinato-oxovanadium(IV), $\text{VO}(\text{Gly})_2$, which was studied in earlier works.^{5,10)} The $\text{VO}(\text{mal})_2^{2-}$ thus prepared was very stable, and the absorption spectrum did not change for several days at the pH of 4.5.

NMR Measurements. Swift and Connick derived the relaxation time in a paramagnetic solution from a rigorous solution of the Bloch equation.¹¹⁾ If the chemical exchange between the metal ion and the ligand controls the relaxation process, the observed relaxation time T_2 , is related to the life-time of a ligand staying in the environment of the coordination sphere by;

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

where T_{2a} is the relaxation time in the absence of metal ions and where P_m is approximated in a dilute solution as;

$$P_m = n[\text{complex}]/[\text{total ligand}] \quad (2)$$

where n is the number of coordinated ligands. In this work, [ligand] corresponds to the total concentration of malonic acid, and n is assumed to be 2. Thus, the rate constant for the dissociation of a ligand from the coordination sphere is given by;

$$k' = \tau_m^{-1} \quad (3)$$

Whether or not a chemical exchange controls the relaxation process can be tested by plotting $\log(1/T_2 - 1/T_{2a})$ as a function of the reciprocal temperature. Equation (1) is applicable if the graph of $\log(1/T_2 - 1/T_{2a})$ vs. $1/T$ is linear, with a negative slope. The full line-width at the half height of malonate methylene protons is listed in Table 1 for various malonic acid concentrations. The line-width in the absence of VO^{2+}

* To whom correspondence should be addressed.

** Present address: Department of Chemistry, Faculty of Science, Osaka University.

† For the purpose of convenience, the oxovanadium(IV) ion will be written as VO^{2+} and the malonate and bimalonate ions will be abbreviated as "mal" and "Hmal" respectively.

TABLE 1. LINE-WIDTH OF MALONATE METHYLENE PROTONS FOR VARIOUS TEMPERATURES AT IONIC STRENGTH=1.4, $[\text{VO}^{2+}] = 0.00719\text{M}$ and $[\text{Malonic acid}] = 1.5\text{M}$

Temp. (°C)	Line-width (Hz)	$(1/T_2 - 1/T_{2a})/P_m$ ($10^3 \times \text{s}^{-1}$)
0	$5.0_6 \pm 0.7_1$	$1.19 \pm 0.2_3$
5	$4.5_8 \pm 0.4_0$	$1.03 \pm 0.1_3$
10	$4.6_2 \pm 0.5_4$	$1.06 \pm 0.1_8$
15	$3.6_9 \pm 0.1_4$	$0.74 \pm 0.0_5$
20	$4.8_6 \pm 0.4_0$	$1.12 \pm 0.1_3$
25	$6.0_3 \pm 0.6_9$	$1.51 \pm 0.2_3$
29	$6.0_9 \pm 0.6_5$	$1.53 \pm 0.2_1$
35	$9.2_7 \pm 0.7_5$	$2.57 \pm 0.2_5$
38	$10.6_2 \pm 0.4_9$	$3.01 \pm 0.1_6$
45	$13.2_7 \pm 0.4_9$	$3.88 \pm 0.1_6$
50	$17.2_9 \pm 1.1$	$5.20 \pm 0.3_7$
55	$21.6_7 \pm 1.3$	$6.63 \pm 0.4_4$
60	$23.2_1 \pm 1.6$	$7.14 \pm 0.5_2$
65	$28.5_6 \pm 1.0$	$8.89 \pm 0.3_0$
70	$29.2_7 \pm 1.0$	$9.12 \pm 0.3_0$
76	$32.0_7 \pm 1.5$	$10.04 \pm 0.4_9$

TABLE 2. LINE-WIDTH OF MALONATE METHYLENE PROTONS IN THE ABSENCE OF VO^{2+}

[Malonic acid] (M)	Ionic strength	Temp. (°C)	Line-width (Hz)
0.70	1.4	25	$1.4_1 \pm 0.1_8$
1.25	1.4	25	$1.2_2 \pm 0.2_6$
1.50	1.4	25	$1.2_0 \pm 0.2_6$
1.75	1.4	25	$1.1_7 \pm 0.1_2$
1.50	1.4	38	$1.4_3 \pm 0.1_8$
1.50	3.0	25	$1.4_6 \pm 0.0_9$
1.50	3.0	70	$1.2_3 \pm 0.1_4$

was very sharp, and, as is shown in Table 2, no broadening was observed within the limits of experimental error in solutions of high malonic acid concentrations, where a relatively high viscosity would be expected compared with that of pure water. Therefore, the effect of the viscosity on the line-width of the malonate methylene proton may be ignored in the solutions studied. From Tables 1 and 2, $\log(1/T_2 - 1/T_{2a})/P_m$ can be calculated; the plot vs. $1/T$ is shown in Fig. 1. It can be seen in Fig. 1 that a linear relationship is obtained over most of the temperature range studied; hence, Eq. (1) is applicable.

The rate constants, k' , thus obtained in the low pH range are listed in Tables 3 and 4 at 25 °C. In higher pH values (above 4), the reaction is too slow at 25 °C

TABLE 3. RATE CONSTANTS FOR VARIOUS MALONIC ACID CONCENTRATIONS AT 25 °C AND IONIC STRENGTH = 1.4

$[\text{VO}^{2+}]$ ($\text{M} \times 10^3$)	[Malonic acid] (M)	pH	[Hmal] (M)	$k'^{(a)}$ ($\text{s}^{-1} \times 10^{-3}$)	$k(\text{M}^{-1}\text{s}^{-1})$ $\times 10^{-3}$	k_{cal} ($\text{s}^{-1} \times 10^{-3}$)
7.19	0.700	3.73	0.623	0.74	1.2	0.76
7.19	1.00	3.30	0.751	1.2	1.6	1.1 ₂
7.19	1.25	3.40	0.990	1.5	1.5	1.3 ₉
7.19	1.50	3.40	1.19	1.7	1.4	1.6 ₇
7.19	1.75	3.57	1.49	2.1	1.4	1.9 ₂ ^{b)}

a) k' represents the first-order rate constant for VO^{2+} and is related to k by $k' = k[\text{Hmal}]$. b) Because of high malonic acid concentration, an ionic strength was held at 1.6.

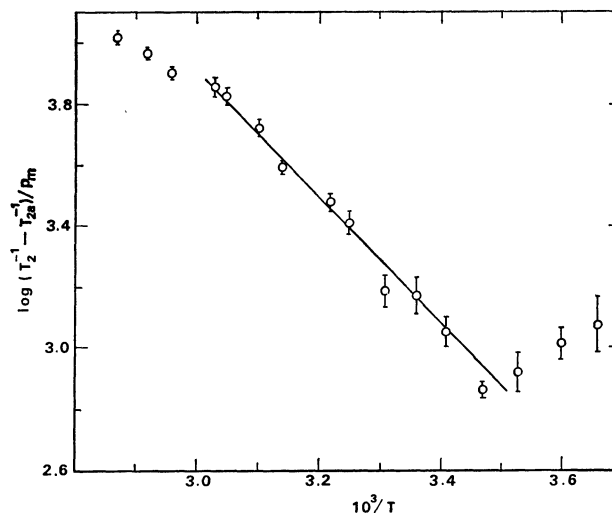


Fig. 1. Plot of line-width of methylene proton of malonic acid as a function of reciprocal temperature.

for us to be able to determine the accurate value of k' from the line-width measurements; therefore, the data listed in Tables 5 and 6 represent the values at 40 °C.

It can be seen in Tables 3 and 4 that k' increases with the concentrations of malonic acid. This suggests that the reaction is first order in relation to both $\text{VO}(\text{mal})_2^{2-}$ and malonic acid. Since H_2mal seems unlikely to react with $\text{VO}(\text{mal})_2^{2-}$, Hmal or mal must be important for the substitution reaction. However, in the high pH region ($\text{pH} > 4.6$), it can be seen in Table 6 that k' becomes smaller as the pH of the solution increases, where [mal] increases, while [Hmal] decreases in this pH region. From these facts, we may

TABLE 4. HYDROGEN ION DEPENDENCE ON THE RATE OF MALONATE EXCHANGE AT 25 °C AND IONIC STRENGTH=1.4 IN LOW pH SOLUTIONS $[\text{VO}^{2+}] = 0.00719\text{M}$, $[\text{Malonic acid}] = 1.50\text{M}$

pH	[Hmal] (M)	k' ($\text{s}^{-1} \times 10^{-3}$)	$k(\text{M}^{-1})$ $\text{s}^{-1} \times 10^{-3}$
2.30	0.348	1.9	5.5
2.37	0.393	1.9	4.8
2.45	0.449	1.9	4.2
2.60	0.564	1.8	3.2
2.77	0.707	1.9	2.7
2.95	0.861	1.6	1.9
3.60	1.29	1.5	1.1 ₇
4.05	1.42	1.5	1.0 ₁ ^{a)}

a) Ionic strength=1.6

TABLE 5. RATE CONSTANTS FOR VARIOUS MALONIC ACID CONCENTRATIONS AT 40 °C AND IONIC STRENGTH=3.0

[VO ²⁺] (M × 10 ³)	[Malonic acid] (M)	pH	[Hmal] (M)	<i>k'</i> (s ⁻¹ × 10 ⁻³)	<i>k</i> (M ⁻¹ s ⁻¹ × 10 ⁻³)
7.23	1.00	4.49	0.952	2.13	2.24
7.23	1.25	4.50	1.19	2.53	2.13
7.23	1.50	4.61	1.40	3.11	2.22
7.23	1.75	4.61	1.64	3.35	2.04
7.23	2.00	4.60	1.88	3.56	1.86
Average=2.10					

TABLE 6. pH DEPENDENCE ON THE RATE OF MALONATE EXCHANGE AT 40 °C AND IONIC STRENGTH=3.0 IN HIGH pH SOLUTIONS
[VO²⁺]=0.00723 M, [Malonic acid]=1.50 M

pH	[Hmal] (M)	<i>k'</i> (s ⁻¹ × 10 ⁻³)	<i>k</i> (M ⁻¹ s ⁻¹ × 10 ⁻³)
4.31	1.45	2.85	1.96
4.56	1.42	3.11	2.19
4.62	1.40	3.11	2.22
4.73	1.38	2.58	1.87
4.91	1.32	2.53	1.92
5.00	1.29	2.50	1.93
5.50	0.962	1.82	1.89
Average=2.00			

conclude that mal is also inactive and that Hmal is the only species which interacts directly with VO(mal)₂²⁻. The second-order rate constant, *k*, where $k = k'/[\text{Hmal}]$, is constant within the limits of experimental error, as is shown in Tables 3, 5, and 6 for various malonic acid concentrations.

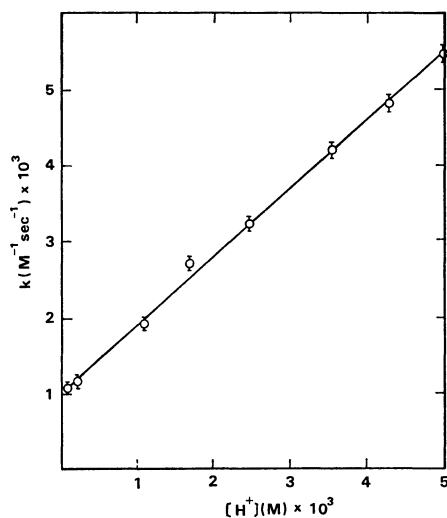


Fig. 2. Plot of rate constant, *k*, vs. hydrogen ion concentration.

The hydrogen-ion dependence for *k* is shown in Table 4. As can be seen in Fig. 2, the plot of *k* vs. [H⁺] is linear; *k* is given by the following equation:

$$k = k_1 + k_2[\text{H}^+] \quad (4)$$

The values of *k*₁ and *k*₂ are obtained from the intercept and the slope of Fig. 2 as 1.1 × 10³ M⁻¹ s⁻¹ and 8.4 × 10⁵ M⁻² s⁻¹ respectively. The first term gives the estimated value for *k* in the high pH region; it agrees very closely with that of 0.91 × 10³ M⁻¹ s⁻¹ which was obtained experimentally from the measurement at pH=5.5 and 25 °C. The second term corresponds the acid-catalyzed path, which is predominant in the low pH region. In Table 3 the values calculated for *k* using Eq. (4), *k*_{cal}, are listed. These values are in satisfactory agreement with the observed values. The activation parameters for both paths were determined from the measurements at pH=5.50 and pH=2.45. They are Δ*H*[‡]=8.6 kcal/mol, Δ*S*[‡]=−16.2 e.u. for the acid-independent path and Δ*H*[‡]=8.9 kcal/mol, Δ*S*[‡]=−13.5 e.u. for the acid-catalyzed path.

From the potentiometric and spectrophotometric studies,¹³⁾ we found that VO²⁺ formed such complexes that bidentate ligands, malonic acid and glycine, are coordinated on the equatorial position as unidentate ligands. Furthermore, in a kinetic study of the formation of the chelate complex, VO(Gly)⁺,⁷⁾ it was found that the rate of chelation from the unidentate complex, VOGly⁺, was surprisingly slow (35 s⁻¹) compared with that of the formation of VOHgly²⁺ (1.3 × 10³ M⁻¹ s⁻¹)⁵⁾ or water exchange on the equatorial positions of the VO²⁺ aquo complex (500 s⁻¹).^{1,2)} This reaction, which we called the "slow chelation process", was estimated to proceed through the intermediate complex, where the −COO⁻ and −NH₂ of the glycinate ion may be coordinated on the equatorial position and the position above the triangular face of the tetragonal pyramid structure.

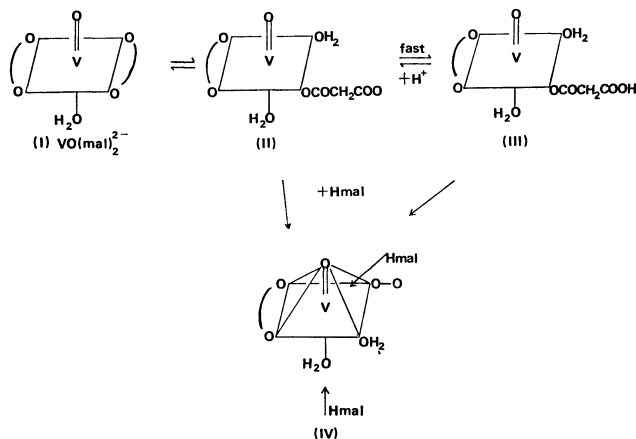


Fig. 3. Reaction scheme of malonate exchange on VO(mal)₂²⁻.

These findings suggest that the first step of malonate exchange on VO(mal)₂²⁻ is the dissociation of one of the chelate rings forming an intermediate complex (II) in Fig. 3, where one of the two malonate ions on equatorial positions is coordinated as a unidentate ligand. In an acidic solution, the (II) complex may be protonated to form a (III) complex. Then, these complexes, (II) and (III), which are analogous in structure to the VOGly⁺ and VOHgly²⁺ respectively,

could accept the attack of Hmal from the axial position or the position above the triangular face of the tetragonal pyramid structure, as is estimated in the chelation process of $\text{VO}(\text{Gly})^+$.

Since the equilibrium between (II) and (III) should be very fast, the rate Eq. (4) can be explained by the following processes: (I) \rightarrow (II) \rightarrow (IV) for the acid-independent path and (I) \rightarrow (II) \rightleftharpoons (III) \rightarrow (IV) for the acid-catalyzed path. The approximately identical values of ΔH^\ddagger for the two paths may support substitution mechanisms similar to those described above.

The authors would like to thank Professor Hiroshi Fukutomi of Tokyo Institute of Technology for his helpful discussions.

References

- 1) K. Wüthrich and R. E. Connick, *Inorg. Chem.*, **6**, 583 (1967).
- 2) J. Reuben and D. Fiat, *ibid.*, **6**, 579 (1967).
- 3) K. Wüthrich and R. E. Connick, *ibid.*, **7**, 1377 (1968).
- 4) N. S. Angerman and R. E. Jordan, a) *ibid.*, **8**, 65 (1969); b) *ibid.*, **8**, 1824 (1969).
- 5) H. Tomiyasu, K. Dreyer, and G. Gordon, *ibid.*, **11**, 2409 (1972).
- 6) K. Kustin and R. Pizer, *ibid.*, **9**, 1536 (1970).
- 7) H. Tomiyasu and G. Gordon, Proceedings of 15th International Conference on Coordination Chemistry, 423 (1973).
- 8) F. A. Walker, R. L. Carlin, and P. H. Rieger, *J. Chem. Phys.*, **45**, 4181 (1966).
- 9) N. S. Angerman and R. E. Jordan, *ibid.*, **54**, 837 (1971).
- 10) H. Tomiyasu and G. Gordon, *J. Coord. Chem.*, **3**, 47 (1973).
- 11) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).
- 12) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).
- 13) S. Ito, H. Tomiyasu, and H. Ohtaki, This Bulletin, **46**, 2238 (1973).
- 14) G. A. Miller and R. E. D. McClung, *Inorg. Chem.*, **12**, 2522 (1973).