

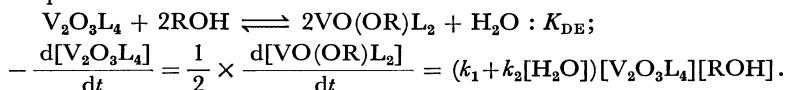
## Kinetic and Equilibrium Studies on the Esterification of Monomeric and $\mu$ -Oxo Dimeric Vanadium(V) Complexes with Butyl Alcohols in Chlorobenzene

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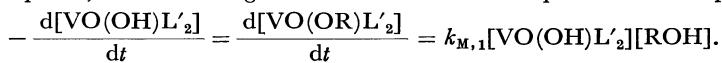
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Kinetic and equilibrium studies were made on the esterification of the  $\mu$ -oxo dimeric vanadium(V) complexes with monoanionic bidentate ligands(HL) such as 8-quinolinol, 5-chloro-8-quinolinol, 5,7-dibromo-8-quinolinol, and 4-isopropyltropolone by butyl alcohols (ROH) in chlorobenzene. The stoichiometry and the rate equation are expressed as follows:



The more basic the bound ligand  $\text{L}^-$ , the lower the water-independent rate constant  $k_1$  is. For less sterically crowded alcohols,  $k_1$  is higher, giving the reactivity order:  $n > i > s > t$ . Water, presumably hydrogen bonded to the terminal oxo group of the complexes, accelerates the esterification( $k_2$  path). The equilibrium constant  $K_{\text{DE}}$  is linearly correlated with the rate constant  $k_1$ . The esterification kinetics of the monomeric complex with 2-methyl-8-quinolinol(HL'), which corresponds to the proposed reactive intermediate in the esterification of the  $\mu$ -oxo dimeric complexes, is also investigated and found the rate equation to be expressed as



$k_{\text{M},1}$  is 5 times higher than the estimated for the corresponding dimeric complex. Large negative values of  $\Delta S_{\text{M},1}^*$  and  $\Delta S_{\text{M},1}^{**}$  point to an associative nucleophilic attack of alcohol to the vanadium center of both dimeric and monomeric complexes. The difference of the reactivity of complexes and alcohols and the detailed mechanism will be discussed.

With 8-quinolinol(HQ) vanadium(V) forms a *black* water-insoluble complex in weakly acidic media.<sup>1-3</sup> The black solution of this complex dissolved in organic solvents gives rise to a *red* coloration in the presence of alcohols(ROH). This reaction, first ascribed to *cis-trans* isomerization of the complex,<sup>4</sup> was found to be the esterification of the complex with alcohols to give their esters,  $\text{VO}(\text{OR})\text{Q}_2$ ,<sup>5,6</sup> and has been utilized for the detection and photometric determination of alcohols.<sup>7-14</sup> On the other hand extensive studies on the black complex have given an erroneous composition of  $\text{VO}(\text{OH})\text{Q}_2$ .<sup>15-18</sup> Alcohols have been believed to react with this monomeric complex according to the following reaction:  $\text{VO}(\text{OH})\text{Q}_2 + \text{ROH} \rightleftharpoons \text{VO}(\text{OR})\text{Q}_2 + \text{H}_2\text{O}$ .<sup>6,19-22</sup>

Recently we have revealed this black complex to be the oxo-bridged dimer,  $\text{VOQ}_2-\text{O}-\text{VOQ}_2$ .<sup>23-25</sup> The crystal structure of the ester has been established by X-ray crystallographic study.<sup>26</sup> Thus the reaction of this dimeric complex with alcohols comes to the stage to be reexamined. In the present paper the esterification of the oxo-bridged dimeric vanadium(V) complexes with 8-quinolinol, 5-chloro-8-quinolinol(H5-Cl-Q), 5,7-dibromo-8-quinolinol (H5,7-Br<sub>2</sub>-Q), and 4-isopropyltropolone(H4-Pr-T) by butyl alcohols is investigated from the kinetic and the thermodynamic points of view. The results are compared with the esterification of the *yellow* monomeric complex with 2-methyl-8-quinolinol(H2-Me-Q),  $\text{VO}(\text{OH})(2\text{-Me-Q})_2$ .

### Experimental

**Materials.** All the butyl alcohols were refluxed over freshly ignited calcium oxide, and then with magnesium turnings, and finally distilled. 5-Chloro-8-quinolinol and

5,7-dibromo-8-quinolinol were recrystallized twice from ethanol and acetone, respectively. Chlorobenzene, 8-quinolinol, 4-isopropyltropolone, 2-methyl-8-quinolinol, and ammonium metavanadate were purified as described previously.<sup>23-25</sup>

Vanadium(V) complexes with 8-quinolinol,  $\text{V}_2\text{O}_3\text{Q}_4$ ,<sup>5,6</sup> with 4-isopropyltropolone,  $\text{V}_2\text{O}_3(4\text{-Pr-T})_4$ ,<sup>25</sup> and with 2-methyl-8-quinolinol,  $\text{VO}(\text{OH})(2\text{-Me-Q})_2 \cdot 2\text{H}_2\text{O}$ <sup>15</sup> were prepared as described elsewhere. Other complexes with 5-chloro-8-quinolinol,  $\text{V}_2\text{O}_3(5\text{-Cl-Q})_4$ , and with 5,7-dibromo-8-quinolinol,  $\text{V}_2\text{O}_3(5,7\text{-Br}_2\text{-Q})_4$  were prepared by mixing dioxovanadium(V) perchlorate solution with the corresponding ligand dissolved in perchloric acid solution and adjusting pH to 4 with ammonia. Found: C, 31.8; H, 1.1; N, 4.2%. Calcd for  $\text{V}_2\text{C}_{36}\text{H}_{16}\text{N}_4\text{O}_7\text{Br}_8$ : C, 31.85; H, 1.19; N, 4.13%. Found: C, 49.6; H, 2.4; N, 7.3%. Calcd for  $\text{V}_2\text{C}_{36}\text{H}_{20}$ :

TABLE 1. SUMMARY OF THE PROPERTIES OF VANADIUM(V) COMPLEXES

| Complex   | $\lambda_{\text{max}}^{\text{a)}$<br>nm | $\nu(\text{V=O})^{\text{b)}$<br>cm <sup>-1</sup> | $\nu(\text{V}-\text{O}-\text{V})^{\text{c)}$<br>cm <sup>-1</sup> |
|---|---|--|--|
| $\text{V}_2\text{O}_3\text{Q}_4$                                  | 550                                     | 950  | 715  |
| $\text{V}_2\text{O}_3(5\text{-Cl-Q})_4$                           | 580                                     | 959<br>(971) <sup>d)</sup>                       | 715  |
| $\text{V}_2\text{O}_3(5,7\text{-Br}_2\text{-Q})_4$                | 570                                     | 970<br>(945) <sup>d)</sup>                       | 720  |
| $\text{V}_2\text{O}_3(4\text{-Pr-T})_4$                           | 530                                     | 950  | 715  |
| $\text{VO}(\text{OH})(2\text{-Me-Q})_2 \cdot 2\text{H}_2\text{O}$ | 340                                     | 925  | —  |

a)  $\lambda_{\text{max}}$  is the wavelength of the absorption maximum in the ultraviolet and visible spectrum. b,c)  $\nu(\text{V=O})$  and  $\nu(\text{V}-\text{O}-\text{V})$  are the wavenumbers of infrared absorption of  $\text{V=O}$  and  $\text{V}-\text{O}-\text{V}$  measured by potassium bromide disc technique, respectively. d) These absorptions are weak and not assignable.

$\text{Na}_4\text{O}_7\text{Cl}_4$ : C, 50.03; H, 2.33; N, 6.48%.

Infrared, visible, and ultraviolet spectral data for these complexes are summarized in Table 1. The presence of  $\nu(\text{V}-\text{O}-\text{V})$  at near  $715\text{ cm}^{-1}$  and absorption near  $550\text{ nm}$  indicates the  $\mu$ -oxo dimeric structure of these complexes. The complex with 2-methyl-8-quinolinol is monomeric because of steric hindrance of methyl group as described previously.<sup>24</sup>

**Measurement.** All the experiments were performed in a room thermostated at  $25 \pm 0.5\text{ }^\circ\text{C}$ . All the measurements were done using the circulating bath thermostated at each temperature within  $\pm 0.1\text{ }^\circ\text{C}$ . The volume change of the solvent due to the temperature change was taken into consideration.<sup>27</sup>

Ultraviolet and visible spectra were recorded on a UNION High Sens Spectrophotometer SM-401. A JASCO infrared spectrophotometer A-3 was used for the IR spectral study by potassium bromide disc technique.

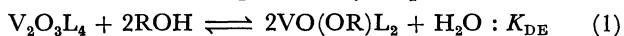
Equilibrium study was performed by measuring the absorbance at  $480\text{ nm}$  with Zeiss spectrophotometer model 1 PMQ II, after the complete equilibration of the reaction mixtures in stoppered tubes. The reaction was followed spectrophotometrically at  $600\text{ nm}$  after the conventional mixing of the reactants.

The water concentration was varied by mixing the dehydrated chlorobenzene ( $C_{\text{H}_2\text{O}} = 4 \times 10^{-3}\text{ mol dm}^{-3}$ ) and the chlorobenzene saturated with water ( $C_{\text{H}_2\text{O}} = 2 \times 10^{-2}\text{ mol dm}^{-3}$ ) at different ratio. The water concentration was checked by the Karl-Fischer method with the coulometric generation of iodine.

## Results

**Equilibrium.** Just dissolved in wet chlorobenzene, vanadium(V) complexes are partially hydrolyzed and give rise to lower species,  $\text{VO}_2\text{L}$ .<sup>25</sup> In the presence of alcohols, furthermore, substitution of the bound ligand by alcohols is also anticipated to yield vanadium(V) alkoxides.<sup>28-30</sup> Actually in the absence of excess ligand, the addition of alcohol causes the color change from black *via* red to yellow, which is characteristic of trialkoxoxovanadium(V),  $\text{VO}(\text{OR})_3$ . To avoid these side reactions an excess amount of ligand ( $\approx 0.01\text{ mol dm}^{-3}$ ) was added in all experiments. The addition of excess ligand (up to  $0.05\text{ mol dm}^{-3}$ ) was confirmed to exert no effect on the esterification.

Visible spectra were recorded for complex solutions with different concentrations of alcohols. The time necessary for equilibration at  $25\text{ }^\circ\text{C}$  is as follows:  $\text{V}_2\text{O}_3(4\text{-Pr-T})_4$  takes 12 h for *n*- and *i*-, 24 h for *s*-, and 48 h for *t*-BuOH;  $\text{V}_2\text{O}_3(5\text{-Cl-Q})_4$  takes 96 h for *n*-BuOH;  $\text{V}_2\text{O}_3\text{Q}_4$  takes 120 h for *n*-BuOH. Two distinct isosbestic points near 430 and 530 nm observed for all systems point to the presence of only one equilibrium, which is expressed by Eq. 1.



As the water concentration is large excess and may be regarded as constant, the conditional esterification constant  $K_{\text{DE}'}$  is given by Eq. 2.

$$K_{\text{DE}'} = K_{\text{DE}}[\text{H}_2\text{O}]^{-1} = \frac{[\text{VO}(\text{OR})\text{L}_2]^2}{[\text{V}_2\text{O}_3\text{L}_4][\text{ROH}]^2} \quad (2)$$

The apparent molar absorption coefficient,  $\bar{\epsilon} = \frac{A}{C_{\text{V}}}$ , is related with  $K_{\text{DE}'}$  by Eq. 3.

$$\frac{(2\bar{\epsilon} - \epsilon_{\text{D}})^2}{\epsilon_{\text{E}} - \bar{\epsilon}} \times \frac{C_{\text{V}}}{2\epsilon_{\text{E}} - \epsilon_{\text{D}}} = K_{\text{DE}'}[\text{ROH}]^2, \quad (3)$$

where  $[\text{ROH}]$  is given by

$$[\text{ROH}] = C_{\text{ROH}} - \frac{2\bar{\epsilon} - \epsilon_{\text{D}}}{2\epsilon_{\text{E}} - \epsilon_{\text{D}}} \times C_{\text{V}},$$

and  $\epsilon_{\text{D}}$  and  $\epsilon_{\text{E}}$  are the molar absorption coefficients of the dimeric vanadium(V) complex and its ester, respectively, and  $C_{\text{ROH}}$  and  $C_{\text{V}}$  are the total concentrations of alcohol and vanadium(V) as a monomeric species, respectively. The logarithm of the left hand side of Eq. 3 being plotted against  $\log[\text{ROH}]$ , the straight line with a slope of two and an intercept of  $\log K_{\text{DE}'}$  should be obtained.

In Fig. 1 are shown the results on the systems of  $\text{V}_2\text{O}_3(4\text{-Pr-T})_4$  and  $\text{V}_2\text{O}_3\text{Q}_4$  at a fixed water concentration. At different water concentrations the plots gave different straight lines with a slope of two. From

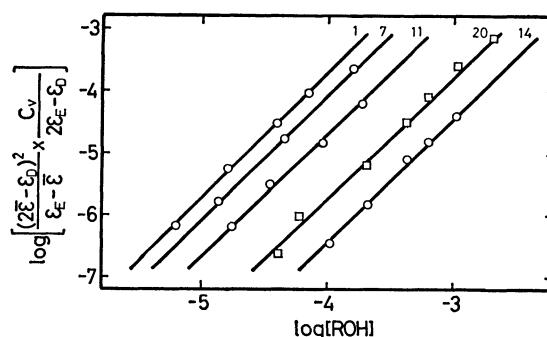


Fig. 1. Determination of the conditional equilibrium constant for the esterification of  $\mu$ -oxo dimeric vanadium(V) complexes with butyl alcohols. Reaction system:  $\text{V}_2\text{O}_3(4\text{-Pr-T})_4$  (○) with *n*-BuOH(1); *i*-BuOH(7); *s*-BuOH(11); *t*-BuOH(14);  $\text{V}_2\text{O}_3\text{Q}_4$  (□) with *n*-BuOH(20). For experimental conditions the same number of Table 2 should be referred.

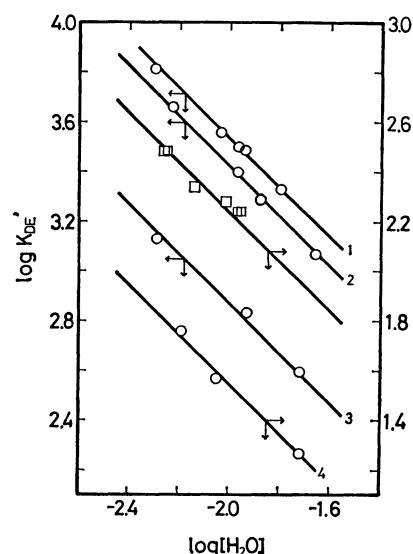


Fig. 2. Determination of the equilibrium constant for the esterification of  $\mu$ -oxo dimeric vanadium(V) complexes with butyl alcohols. Reaction system:  $\text{V}_2\text{O}_3(4\text{-Pr-T})_4$  (○) with *n*-BuOH (1); *i*-BuOH (2); *s*-BuOH (3); *t*-BuOH (4);  $\text{V}_2\text{O}_3\text{Q}_4$  (□) with *n*-BuOH.

TABLE 2. CONDITIONAL EQUILIBRIUM CONSTANTS FOR THE ESTERIFICATION OF THE  $\mu$ -OXO DIMERIC COMPLEXES WITH BUTYL ALCOHOLS OBTAINED AT VARIOUS WATER CONCENTRATIONS AT 25 °C

| No. | Reaction system                         | $C_V$ <sup>a)</sup><br>mol dm <sup>-3</sup> | $C_{HL}$ <sup>b)</sup><br>mol dm <sup>-3</sup> | $\log [H_2O]$ | $\log K_{DE'}$ |
|-----|---|---|--|---------------|----------------|
| 1   | $V_2O_3(4\text{-Pr-T})_4-n\text{-BuOH}$ | $7.17 \times 10^{-5}$                       | $9.80 \times 10^{-3}$                          | -2.30         | 4.27           |
| 2   |   | $6.64 \times 10^{-5}$                       | $9.87 \times 10^{-3}$                          | -2.04         | 4.06           |
| 3   |   | $4.73 \times 10^{-5}$                       | $2.83 \times 10^{-3}$                          | -1.97         | 4.00           |
| 4   |   | $6.51 \times 10^{-5}$                       | $9.80 \times 10^{-3}$                          | -1.94         | 3.99           |
| 5   |   | $6.23 \times 10^{-5}$                       | $9.95 \times 10^{-3}$                          | -1.80         | 3.83           |
| 6   | $V_2O_3(4\text{-Pr-T})_4-i\text{-BuOH}$ | $7.06 \times 10^{-5}$                       | $9.94 \times 10^{-3}$                          | -2.23         | 4.16           |
| 7   |   | $8.48 \times 10^{-5}$                       | $1.01 \times 10^{-2}$                          | -1.97         | 3.90           |
| 8   |   | $6.13 \times 10^{-5}$                       | $1.00 \times 10^{-2}$                          | -1.88         | 3.79           |
| 9   |   | $6.32 \times 10^{-5}$                       | $9.99 \times 10^{-3}$                          | -1.66         | 3.67           |
| 10  | $V_2O_3(4\text{-Pr-T})_4-s\text{-BuOH}$ | $6.28 \times 10^{-5}$                       | $1.00 \times 10^{-2}$                          | -2.29         | 3.63           |
| 11  |   | $6.74 \times 10^{-5}$                       | $9.98 \times 10^{-3}$                          | -1.93         | 3.33           |
| 12  |   | $6.15 \times 10^{-5}$                       | $9.88 \times 10^{-3}$                          | -1.72         | 3.09           |
| 13  | $V_2O_3(4\text{-Pr-T})_4-t\text{-BuOH}$ | $6.63 \times 10^{-5}$                       | $9.83 \times 10^{-3}$                          | -2.19         | 1.76           |
| 14  |   | $6.55 \times 10^{-5}$                       | $9.83 \times 10^{-3}$                          | -2.05         | 1.57           |
| 15  |   | $5.99 \times 10^{-5}$                       | $9.88 \times 10^{-3}$                          | -1.72         | 1.27           |
| 16  | $V_2O_3Q_4-n\text{-BuOH}$               | $5.30 \times 10^{-5}$                       | $8.00 \times 10^{-3}$                          | -2.26         | 2.48           |
| 17  |   | $4.82 \times 10^{-5}$                       | $8.00 \times 10^{-3}$                          | -2.25         | 2.48           |
| 18  |   | $5.93 \times 10^{-5}$                       | $8.00 \times 10^{-3}$                          | -2.14         | 2.34           |
| 19  |   | $5.60 \times 10^{-5}$                       | $8.00 \times 10^{-3}$                          | -2.01         | 2.28           |
| 20  |   | $5.09 \times 10^{-5}$                       | $8.00 \times 10^{-3}$                          | -1.97         | 2.24           |
| 21  |   | $5.41 \times 10^{-5}$                       | $8.00 \times 10^{-3}$                          | -1.96         | 2.24           |
| 22  | $V_2O_3(5\text{-Cl-Q})_4-n\text{-BuOH}$ | $4.82 \times 10^{-5}$                       | $9.99 \times 10^{-3}$                          | -2.31         | 2.69           |

a) Total concentration of vanadium(V) as a monomeric species. b) Total concentration of an excess ligand.

TABLE 3. EQUILIBRIUM AND RATE CONSTANTS, AND ACTIVATION PARAMETERS FOR THE ESTERIFICATION OF  $V_2O_3(4\text{-Pr-T})_4$  WITH BUTYL ALCOHOLS

| Alcohol  | <i>n</i> -BuOH   | <i>i</i> -BuOH  | <i>s</i> -BuOH  | <i>t</i> -BuOH  |
|--|--|---|---|---|
| $\log K_{DE}$ <sup>a)</sup>  | $2.03 \pm 0.02$  | $1.92 \pm 0.02$   | $1.37 \pm 0.03$   | $-0.45 \pm 0.03$  |
| $k_1$ <sup>b)</sup><br>$\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ | $\begin{cases} 25^\circ\text{C} \\ 30^\circ\text{C} \\ 35^\circ\text{C} \end{cases} \begin{cases} 5.76 \times 10^{-2} \\ 8.38 \times 10^{-2} \\ 1.22 \times 10^{-1} \end{cases}$ | $\begin{cases} 3.96 \times 10^{-2} \\ 5.87 \times 10^{-2} \\ 8.64 \times 10^{-2} \end{cases}$ | $\begin{cases} 2.95 \times 10^{-2} \\ 4.43 \times 10^{-2} \\ 6.61 \times 10^{-2} \end{cases}$ | $\begin{cases} 2.91 \times 10^{-3} \\ 4.56 \times 10^{-3} \\ 6.89 \times 10^{-3} \end{cases}$ |
| $\Delta H_1^*$<br>$\text{kJ mol}^{-1}$                             | $56 \pm 1$   | $57 \pm 2$  | $58 \pm 2$  | $63 \pm 2$  |
| $\Delta S_1^*$<br>$\text{J mol}^{-1} \text{K}^{-1}$                | $-80 \pm 3$  | $-81 \pm 5$   | $-79 \pm 5$   | $-81 \pm 5$   |

a) At 25 °C. b) All the values have errors of  $\pm 1\text{--}3\%$ .

these plots we obtained the conditional equilibrium constants summarized in Table 2. The resulted  $\log K_{DE'}$  value is plotted against  $\log[H_2O]$  in Fig. 2. The plots fall along a straight line with a slope of -1 (Eq. 2). This confirms the validity of Eq. 1. The equilibrium constants for the esterification at 25 °C obtained from the intercepts of these plots are summarized in Tables 3 and 4.

*Kinetics of the Esterification of the Dimeric Complexes.* Kinetics of the esterification was studied with large excess alcohol, so that the back reaction can be neglected. The first-order plot gave a good straight line over 95% conversion.

The rate equation for the dimeric complexes is expressed by Eq. 4,

$$-\frac{d[V_2O_3L_4]}{dt} = \frac{1}{2} \times \frac{d[VO(OR)L_2]}{dt}$$

$$= k_0(\text{ROH, HL, H}_2\text{O})[\text{V}_2\text{O}_3\text{L}_4], \quad (4)$$

where  $k_0(\text{ROH, HL, H}_2\text{O})$  is the conditional esterification rate constant involving the concentrations of alcohol, excess ligand, and water. This rate constant was determined from the slope of the first-order plot.

The conditional rate constant was plotted against the alcohol concentration. The results for  $V_2O_3(4\text{-Pr-T})_4$  are given in Fig. 3. The plots show the first-order alcohol dependence of  $k_0(\text{ROH, HL, H}_2\text{O})$ :

$$k_0(\text{ROH, HL, H}_2\text{O}) = k_0(\text{HL, H}_2\text{O})[\text{ROH}].$$

In each system the ligand was added in a sufficient excess to prevent the formation of the lower complex<sup>25)</sup> or alkoxide<sup>28-30)</sup> in equilibrium. Addition of the excess ligand was found to exert no effect on the rate. Then,

$$k_0(\text{ROH, HL, H}_2\text{O}) = k_0(\text{H}_2\text{O})[\text{ROH}].$$

TABLE 4. EQUILIBRIUM AND RATE CONSTANTS, AND ACTIVATION PARAMETERS FOR THE ESTERIFICATION OF THE  $\mu$ -OXO DIMERIC VANADIUM(V) COMPLEXES WITH *n*-BuOH

| Complex  | $V_2O_3Q_4$           | $V_2O_3(5\text{-Cl-Q})_4$ | $V_2O_3(5,7\text{-Br}_2\text{-Q})_4$ |
|--|-----------------------|---------------------------|--------------------------------------|
| $\log K_{DE}^a$  | $0.25 \pm 0.04$       | $0.38 \pm 0.04$           | —                                    |
| $k_1^b$ (25 °C)<br>mol <sup>-1</sup> dm <sup>3</sup> s <sup>-1</sup> | $5.90 \times 10^{-3}$ | $0.92 \times 10^{-2}$     | $2.94 \times 10^{-3}$                |
| 30 °C  | $8.42 \times 10^{-3}$ | $1.37 \times 10^{-2}$     | $4.72 \times 10^{-3}$                |
| 35 °C  | $1.19 \times 10^{-2}$ | $2.05 \times 10^{-2}$     | $7.50 \times 10^{-3}$                |
| $\frac{\Delta H_1^*}{\text{kJ mol}^{-1}}$                            | $52 \pm 2$            | $59 \pm 1$                | $69 \pm 1$                           |
| $\frac{\Delta S_1^*}{\text{J mol}^{-1} \text{K}^{-1}}$               | $-115 \pm 4$          | $-86 \pm 3$               | $-63 \pm 3$                          |
| $k_2^c$ (25 °C)<br>mol <sup>-2</sup> dm <sup>6</sup> s <sup>-1</sup> | $1.24 \times 10^{-1}$ | $0.90 \times 10^{-1}$     | $1.2 \times 10^{-2}$                 |
| 30 °C  | $1.54 \times 10^{-1}$ | $1.05 \times 10^{-1}$     | $2.0 \times 10^{-2}$                 |
| 35 °C  | $1.78 \times 10^{-1}$ | $1.28 \times 10^{-1}$     | $3.3 \times 10^{-2}$                 |
| $\frac{\Delta H_2^*}{\text{kJ mol}^{-1}}$                            | $24 \pm 2$            | $25 \pm 2$                | $73 \pm 4$                           |
| $\frac{\Delta S_2^*}{\text{J mol}^{-1} \text{K}^{-1}}$               | $-181 \pm 8$          | $-181 \pm 8$              | $-30 \pm 15$                         |

a) At 25 °C. b), c) All the values have errors of  $\pm 1\text{--}3$  and  $\pm 3\text{--}8\%$ , respectively.

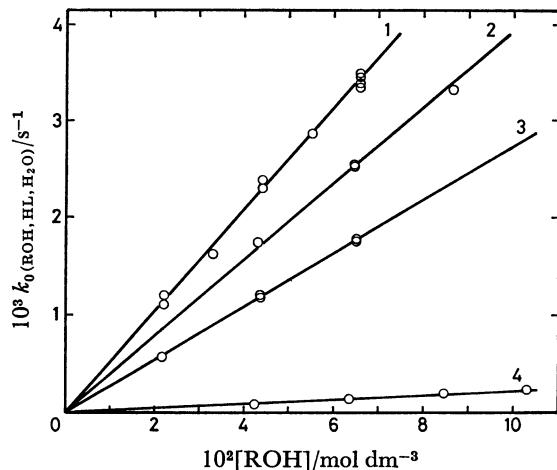


Fig. 3. Plot of  $k_0(ROH, HL, H_2O)$  for  $V_2O_3(4\text{-Pr-T})_4$  vs. [ROH].  $C_v = 6.73 \times 10^{-5}$  mol dm<sup>-3</sup>;  $C_{HL} = 9.83 \times 10^{-3}$  mol dm<sup>-3</sup>;  $C_{H_2O} = 0.007\text{--}0.020$  mol dm<sup>-3</sup>. ROH: *n*-BuOH(1); *i*-BuOH(2); *s*-BuOH(3); *t*-BuOH(4).

In the absence of the excess ligand enough to prevent the formation of lower species, the esterification proceeds faster. This is attributable to the faster reaction of monomeric  $VO_2L$  with alcohol.

Finally  $k_0(H_2O)$  was plotted against  $[H_2O]$ . The results are shown for  $V_2O_3Q_4$  with *n*-BuOH in Fig. 4. According to this Figure,  $k_0(H_2O)$  is rewritten as

$$k_{0(H_2O)} = k_1 + k_2[H_2O].$$

$V_2O_3(5\text{-Cl-Q})_4$  and  $V_2O_3(5,7\text{-Br}_2\text{-Q})_4$  showed the similar behavior, whereas  $V_2O_3(4\text{-Pr-T})_4$  had negligibly small  $k_2[H_2O]$  term as compared to  $k_1$ .

Thus  $k_0(ROH, HL, H_2O)$  is expressed by Eq. 5.

$$k_0(ROH, HL, H_2O) = (k_1 + k_2[H_2O])[ROH] \quad (5)$$

Rate constants at 25, 30, and 35 °C, and activation parameters are summarized in Tables 3 and 4.

*Kinetics of the Esterification of the Monomeric Complex.* The rate equation for the monomeric 2-methyl-8-quinolinolate complex is expressed by Eq. 6.

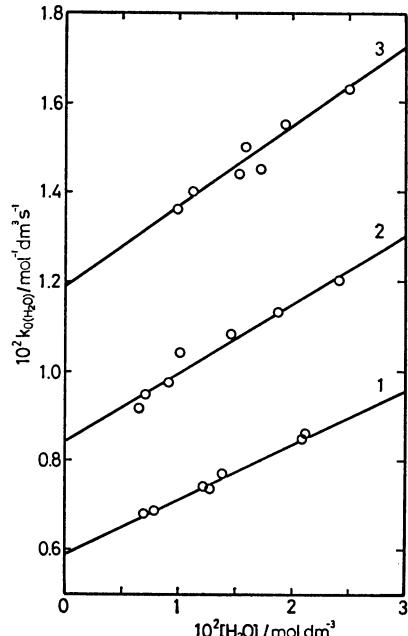


Fig. 4. Plot of  $k_0(H_2O)$  for  $V_2O_3Q_4$  with *n*-BuOH vs.  $[H_2O]$ .  $C_v = 5.67 \times 10^{-5}$  mol dm<sup>-3</sup>;  $C_{HL} = 8.00 \times 10^{-3}$  mol dm<sup>-3</sup>. At 25 °C(1); 30 °C(2); 35 °C(3).

$$\frac{d[VO(OH)(2\text{-Me-Q})_2]}{dt} = \frac{d[VO(OR)(2\text{-Me-Q})_2]}{dt} \\ = k_{M,0}(ROH, HL, H_2O)[VO(OH)(2\text{-Me-Q})_2] \quad (6)$$

The kinetic data were analyzed by the treatment similar to that in the case of the dimeric complexes. Despite a very small contribution from the water-dependent path (1–2% acceleration in chlorobenzene saturated with water), the conditional rate constant  $k_{M,0}(ROH, HL, H_2O)$  is reasonably expressed by Eq. 7 for *n*- and *i*-BuOH.

$$k_{M,0}(ROH, HL, H_2O) = k_{M,1}[ROH] \quad (7)$$

For *s*- and *t*-BuOH the esterification can not be successfully analyzed because of the concurrent ligand

TABLE 5. RATE CONSTANTS AND ACTIVATION PARAMETERS  
FOR THE ESTERIFICATION OF  $\text{VO(OH)}(2\text{-Me-Q})_2$   
WITH BUTYL ALCOHOLS

| Alcohol   | <i>n</i> -BuOH   | <i>i</i> -BuOH  |
|---|--|---|
| $k_{M,1}^a)$<br>$\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ | $(25^\circ\text{C}) 2.29 \times 10^{-2}$<br>$(30^\circ\text{C}) 3.13 \times 10^{-2}$<br>$(35^\circ\text{C}) 4.23 \times 10^{-2}$ | $3.13 \times 10^{-2}$<br>$4.29 \times 10^{-2}$<br>$5.65 \times 10^{-2}$ |
| $\Delta H_{M,1}^*$<br>$\text{kJ mol}^{-1}$                  | $44 \pm 1$   | $42 \pm 1$  |
| $\Delta S_{M,1}^*$<br>$\text{J mol}^{-1} \text{K}^{-1}$     | $-128 \pm 4$   | $-133 \pm 4$  |

a) All the values have errors of  $\pm 1\text{--}3\%$ .

dissociation reaction in the presence of these alcohols. Rate constants at 25, 30, and 35 °C, and activation parameters are summarized in Table 5.

### Discussion

All but 2-methyl-8-quinolinolate complexes have the  $\mu$ -oxo dimeric structure. No X-ray structural analysis being reported for the  $\mu$ -oxo dimeric vanadium(V) complex, it was reasonably supposed to have the terminal oxo *cis* to the bridging oxo group from the analogy of many molybdenum(V) complexes<sup>31)</sup> and the mixed valence vanadium(IV,V) complex.<sup>32)</sup> The strong absorption near 550 nm, which is ascribed to a delocalized three-center pi bond, is characteristic of this configuration.<sup>31)</sup> The two oxo groups attached to each vanadium atom in dimeric complexes have a possibility to be *cis* or *trans* to each other. Whereas according to the X-ray structural analysis the ester has the terminal oxo *cis* to the alkoxo group, and these groups are *trans* to the nitrogen atoms of quinoline rings.<sup>26)</sup> Thus it will be pertinent to conclude that the rupture of the bridging bond must occur during the esterification of the dimeric complexes and that the *cis* configuration of oxo groups is retained. Since the 2-methyl-8-quinolinolate complex is monomeric because of the steric hindrance of methyl group,<sup>24)</sup> the esterification of this complex is the simple nucleophilic substitution reaction of hydroxide by alkoxide group.

**Reaction Mechanism.** The esterification of the  $\mu$ -oxo dimeric vanadium(V) complexes is first-order in the alcohol concentration. The reaction involves the water-independent path ( $k_1$  path) and the other path first-order in the water concentration ( $k_2$  path). Since in  $k_1$  path, only one molecule of alcohol is involved in the rate equation, the reactive species  $\text{VO(OH)}_2$  must be formed in addition to the final product  $\text{VO(OR)}_2$  (Eq. 8).  $\text{VO(OH)}_2$  must react rapidly with one more alcohol to yield  $\text{VO(OR)}_2$  (Eq. 9).



To estimate the bound ligand effect on the reaction rate,  $\log k_1$  value is plotted against  $\Sigma pK_a$ , which is the sum of the logarithmic protonation constants of the two ligands coordinated to vanadium and is a measure of electron donation from the ligands to

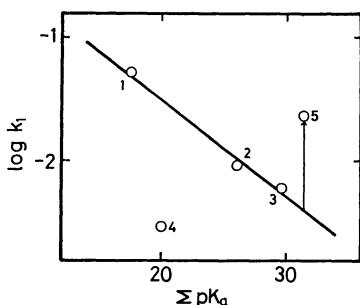


Fig. 5. Correlation of the rate constant for the esterification of vanadium(V) complexes by *n*-BuOH with  $\Sigma pK_a$  of the bound ligand. Complex: 1,  $\text{V}_2\text{O}_3(4\text{-Pr-T})_4$  (Ref. 33); 2,  $\text{V}_2\text{O}_3(5\text{-Cl-Q})_4$  (Ref. 34); 3,  $\text{V}_2\text{O}_3\text{Q}_4$  (Ref. 34); 4,  $\text{V}_2\text{O}_3(5,7\text{-Br}_2\text{-Q})_4$  (Ref. 35); 5,  $\text{VO(OH)}(2\text{-Me-Q})_2$  (Ref. 34). The  $pK_a$  values are taken from the references cited in parentheses. The starting point of an arrow denotes the rate constant for the hypothetical dimeric vanadium(V) complex with 2-methyl-8-quinolinol.

vanadium(V) (Fig. 5). Except the sterically crowded ligand (5,7-dibromo-8-quinolinol), fairly good linear relationship is observed. This implies that the more the coordinated ligand donates, the lower the positive charge on vanadium(V) becomes, resulting in slower esterification. Thus the reaction may be regarded as a nucleophilic attack of alcohol at the vanadium center. However for a given complex (see Table 3) the reactivity of four butyl alcohols does not parallel to nucleophilicity (*t*->*s*->*i*->*n*-), but to sterical freedom (*n*->*i*->*s*->*t*-). Accordingly the difference in reactivity of alcohols mainly stems from the steric factor.

The reactivity of the dimeric complexes is then compared with that of the 2-methyl-8-quinolinolate complex. This complex may be regarded as the proposed reactive intermediate in the esterification of the dimeric complexes (Eq. 8). Although the corresponding dimeric complex with 2-methyl-8-quinolinol has also been synthesized, it is not stable and dissociates to the monomeric complex in wet chlorobenzene.<sup>24)</sup> Accordingly the rate constant for the esterification of this unstable dimeric complex is not directly obtained, but it is reasonably estimated by reading the  $\log k_1$  value for the  $\Sigma pK_a$  of this ligand (the origin of an arrow in Fig. 5). The experimental rate constant of the monomeric complex ( $2.29 \times 10^{-2} \text{ mol}^{-1} \text{dm}^3 \text{s}^{-1}$  at  $25^\circ\text{C}$ ) is at least 5 times as large as this expected value for the dimeric complex ( $4 \times 10^{-8} \text{ mol}^{-1} \text{dm}^3 \text{s}^{-1}$  at  $25^\circ\text{C}$ ). Thus  $\text{VO(OH)}_2$  type complex should be more reactive than the corresponding dimeric complex (Eq. 9). In contrast to the dimeric complexes, the reactivity of alcohols towards the monomeric complex parallels to nucleophilicity (*n*->*i*-).

Exceptionally large negative values of  $\Delta S^*$  point to an associative mode of activation ( $S_N2$ ) in both monomeric and dimeric complexes. In the dimeric complexes,  $\Delta H^*$  is larger with increasing bulkiness of both attacking alcohol and bound ligand, and larger  $\Delta H^*$  values are always associated with smaller negative  $\Delta S^*$  values. These findings, taken together

with the reactivity order with alcohols, suggest that steric factor plays an important role in these systems. For the monomeric complex, the smallest  $\Delta H^*$  values are associated with the negatively largest  $\Delta S^*$  values.

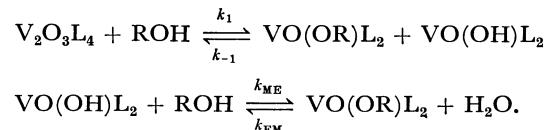
In the dimeric complexes, due to the other vanadium half-unit linked with the bridging oxo group, the nucleophilic attack of alcohol to vanadium center is sterically hindered and the extra bond-weakening energy is necessary to make alcohol close to vanadium center. The mechanism is explained by a concerted bimolecular reaction, in which a molecule of alcohol attacks associatively the vanadium center and at the same time the bond between vanadium and bridging oxo ligand is weakened. This makes  $\Delta H^*$  value considerably larger for more sterically crowded system. For a given complex,  $\Delta H^*$  value increases in the order  $n < i < s < t$  and for a given alcohol  $V_2O_3Q_4 < V_2O_3(5\text{-Cl-Q})_4 < V_2O_3(5,7\text{-Br}_2\text{-Q})_4$ . The small negative  $\Delta S^*$  value associated with large positive  $\Delta H^*$  value suggests that the bond-weakening contribution to the overall activation is more significant as compared to the bond-making, thus the reaction between crowded alcohol and complex becomes less associative. On the other hand in the monomeric complex, alcohol can easily approach to vanadium center without being suffered significant steric hindrance. This makes the reaction more associative. Furthermore since no extra bond-weakening energy is necessary for the activated state, the reactivity order is mainly governed by electronic factor.

*Water-dependent Path.* The water-dependent rate constant in the esterification of the dimeric complexes,  $k_2$  was constant even in changing the concentration of the excess ligand. Accordingly water must not substitute the bound ligand of the dimeric complexes to yield a reactive lower complex, but it interacts with any site in the complexes such as terminal or bridging oxo group to yield a reactive intermediate. Since a small but definite water-dependent path is observed also in the case of the monomeric complex, the interaction with basic terminal oxo group seems plausible. Moreover, this postulation is supported by the fact that the esterification was much more accelerated in the presence of more acidic substance such as phenol.<sup>36</sup>

As can be seen from the relative changes in  $k_2$  and  $\Delta H_2^*$  in the presence of water, the acceleration by water becomes higher with increasing  $\sum pK_a$  of the bound ligand. That is, the interaction of water is stronger with more basic oxo group in complexes having more basic ligand. The acceleration relative to  $k_1$  ( $\log k_2/k_1$ : 1.32 for  $V_2O_3Q_4$ ; 0.99 for  $V_2O_3(5\text{-Cl-Q})_4$ ; 0.61 for  $V_2O_3(5,7\text{-Br}_2\text{-Q})_4$ ) is linearly correlated with  $\sum pK_a$ . Judging from the extrapolated  $k_2(0.4)$  for  $V_2O_3(4\text{-Pr-T})_4$ , the negligibly small contribution of water-dependent path in the reaction with  $n\text{-BuOH}$  as compared to the  $k_1$  is anticipated and this agrees with our results. In the monomeric complex the same type of acceleration will be anticipated. However the intramolecular hydrogen bonding between terminal oxo and hydroxo groups prevents the formation of a reactive intermediate and the reaction will not be accelerated so much as expected from the

estimated  $k_2$  ( $5.8 \times 10^{-1} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ ). The  $k_2$  path reaction has an energy of activation ( $\Delta H_2^*$ ) less than for the corresponding reaction not involving such an intermediate ( $\Delta H_1^*$ ) by about the heat of formation of the hydrogen bond. Larger negative  $\Delta S_2^*$  value as compared to  $\Delta S_1^*$  is also attributable to this pre-equilibrium.

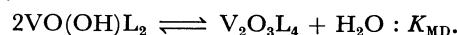
*Relationship between  $K_{DE}$  and  $k_1$ .* The detailed reaction scheme is expressed as



Then the overall esterification equilibrium constant is equated to

$$K_{DE} = \frac{k_1}{k_{-1}} K_{ME},$$

where  $K_{ME} = k_{ME}/k_{EM}$ . Using the dimerization constant given by



$k_1$  is expressed by

$$k_1 = k_{-1}(K_{DE}/K_{MD})^{1/2}.$$

$k_{-1}$  corresponds to the rate constant of the nucleophilic attack of the oxo group in the monomeric complex to the vanadium center of the ester. In this reaction, alcohol accommodated as alkoxide in the ester will not largely affect the rate  $k_{-1}$  both electronically and sterically for the complexes with the same bound ligand. Furthermore  $K_{MD}$  being constant for the complex with the same ligand, in the reaction system of  $V_2O_3(4\text{-Pr-T})_4$  with butyl alcohols  $\log k_1$  should be linearly correlated with  $\log K_{DE}$  with a slope of  $1/2$  as in Fig. 6. On the other hand, the results obtained in the systems of  $V_2O_3Q_4$  and  $V_2O_3(5\text{-Cl-Q})_4$  with  $n\text{-BuOH}$  are also well accommodated in the correlation given in Fig. 6. It appears unlikely that  $k_{-1}$  and  $K_{MD}$  are both constant irrespective of the bound ligand. Thus the linear correlation of  $\log k_1$  with  $\log K_{DE}$  may be resulted from the adequate compensation of  $k_{-1}$  and  $K_{MD}$  making  $(\log k_{-1} - 1/2 \log$

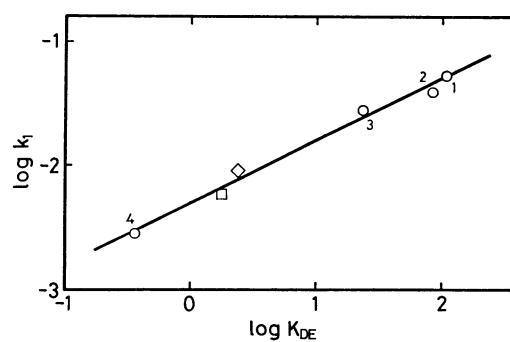


Fig. 6. Correlation of the rate constant for the esterification of the  $\mu$ -oxo dimeric vanadium(V) complex with its equilibrium constant. Reaction system:  $V_2O_3(4\text{-Pr-T})_4$  (○) with  $n\text{-BuOH}$ (1);  $i\text{-BuOH}$ (2);  $s\text{-BuOH}$ (3);  $t\text{-BuOH}$ (4);  $V_2O_3Q_4$  (□) with  $n\text{-BuOH}$ ;  $V_2O_3(5\text{-Cl-Q})_4$  (◇) with  $n\text{-BuOH}$ . The solid line is the straight line with a slope of  $1/2$ .

$K_{MD}$ ) constant. In any event, the lower the activation energy for the esterification, the stabler the resulted ester is.

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