cause of the uncertainty involved in choosing the correction factors. (5) The values of the activation parameters for the steps 3 and 6, which represent a cyclization reaction forming the ionic carbenoid complexes from the neutral haloacyl complexes, are similar to the values observed for similar SN2 reactions.[40] (6) The rates of the geometrical isomerizations of the cis isomer of the cyclopentylidene complexes to the trans isomers, k_5, decrease in the order $Cl^- > Br^- > {}^-BPh_4$ by an overall factor of at least 26. This effect appears to arise mainly from the enthalpy of activation term, although the cause of the relatively large negative value for the entropy of activation of the chloride salt is unknown. This kinetic effect of the anion on k_5 was unexpected and may reflect different changes in the degree of ion pairing between the reactant and the activated complex for the different cases. The values of the activation parameters for the steps (5) correlate well with those values reported for the cis and trans geometrical isomerization of the complexes, $(h^5\text{-}C_5H_5)Mo(CO)_2(Me)(L)$.[41]

L	$\Delta H^{\ddagger}$ kcal/mol	$\Delta S^{\ddagger}$, eu
PPh_3	20.9 ± 0.2	−0.2 ± 0.6
$P(OMe)_3$	19.6 ± 0.4	−0.9 ± 1.3
$P(OPh)_3$	17.7 ± 0.3	−4.7 ± 0.7

The reactions involving the 3-chloro-*n*-propyl and 4-iodo-*n*-butyl complexes have particular importance since the "internal" rate constants, k_3 and k_4, were measured. Since the model (reaction 27) correctly explains the kinetic behavior of these complex reactions and since the rate constants k_3 and k_4 are influenced by the nature of the haloalkyl ligand, it is felt that there is satisfactory evidence for the existence of a cis haloacyl intermediate in all cases.

[40] See ref 12, p 138 and ref 13, p 418.

[41] J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, **92**, 5852 (1970).

Kinetics of Complexation of Vanadate Anions by Ethylenediaminetetraacetic Acid and 1,2-Dihydroxyanthraquinone

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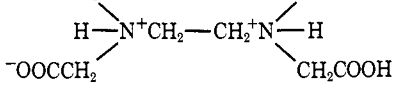
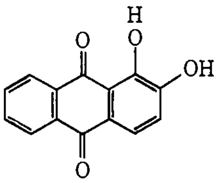
Abstract: The stopped-flow technique has been utilized in kinetics studies of the formation of 1:1 complexes between vanadium(V) anions and EDTA (H_4Y) as well as 1,2-dihydroxyanthraquinone (H_2A). These studies have been conducted at 25° in weakly alkaline media at an ionic strength of 0.5 *M* (NH_4Cl). Reaction schemes for formation of the 1:1 complexes which account for the observed hydrogen ion dependences of the forward rate constants are presented. The rate constants for complex formation are essentially independent of the identity of the complexing ligands used in this study and agree with the previously determined rate constant for vanadate dimerization. The experimentally determined rate constants for complexation of $VO_2(OH)_2^-$ and $VO_2(OH)_3^{2-}$ by H_2Y^{2-} are $(2.34 \pm 0.05) \times 10^4$ and $(2.4 \pm 0.1) \times 10^3\ M^{-1}\ sec^{-1}$, respectively. For complexation of $VO_2(OH)_2^-$ and $VO_2(OH)_3^{2-}$ by HA^-, rate constants of $(2.28 \pm 0.08) \times 10^4$ and $(1.2 \pm 0.3) \times 10^3\ M^{-1}\ sec^{-1}$, respectively, were determined. The value of the stability constant for the $HA^-\text{–}VO_2(OH)_2^-$ complex was found to be $(1.0 \pm 0.2) \times 10^4\ M$.

Few studies of the kinetics of complexation of vanadium(V) ions have been undertaken. This is due, in part, to the number and complexity of vanadate species present in aqueous media, where monomeric cationic and anionic as well as dimeric, trimeric, and decameric species can be found as the acidity of the media and concentration of V(V) are varied.[1] Furthermore, the complexation and polymerization[2] reactions of vanadate ions occur too rapidly to be studied by conventional kinetics methods. During the course of our investigations into the *in vivo* complexation of V(V) by specific marine urochordates (*e.g.*, *Ascidia*), we have utilized the stopped-flow technique to study the kinetics of complexation of monomeric vanadate ions by EDTA and alizarin (1,2-dihydroxyanthraquinone).



H_4Y



H_2A

Experimental Section

A stock solution of V(V) was prepared by dissolution of sodium vanadate hydrate in distilled water. Hydrochloric acid was used to adjust the pH to an approximate value of 9 whereupon the solution assumed an intense yellow color. The solution was then allowed to stand until the bright color of decavanadate had entirely faded.[2] Total vanadium in the solution was determined spectrophotometrically as the $V(V)\text{–}H_2O_2$ complex.[3] The concentration of

[1] F. J. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **10**, 957 (1956).

[2] M. D. Whittaker, J. Asay, and E. M. Eyring, *J. Phys. Chem.*, **70**, 1005 (1966).

[3] R. Guenther and R. G. Linck, *J. Amer. Chem. Soc.*, **91**, 3769 (1969).

Table I. Kinetics Data for the Complexation of V(V) by EDTA[d]

pH	10^3[EDTA],[a] M	k_{obsd},[b] sec^{-1}	k_{obsd}/[EDTA],[a] M^{-1} sec^{-1}
8.13	3.98	0.73 ± 0.04	183
8.13	7.96	1.40 ± 0.06	176
8.13	11.9	2.11 ± 0.09	177
8.13	15.9	2.62 ± 0.07	165
8.13[c]	19.9	3.57 ± 0.20	179
8.21	3.98	0.522 ± 0.012	131
8.21	7.96	1.01 ± 0.01	127
8.21	11.9	1.58 ± 0.02	133
8.21	15.9	2.06 ± 0.04	130
8.21[c]	19.9	2.64 ± 0.09	133
8.42	3.98	0.283 ± 0.008	71.1
8.42	7.96	0.544 ± 0.007	68.3
8.42	11.9	0.840 ± 0.036	70.6
8.42	15.9	1.10 ± 0.03	69.2
8.42	19.9	1.33 ± 0.02	66.8
8.76	3.98	0.097 ± 0.007	24.4
8.76	7.96	0.158 ± 0.002	19.8
8.76	11.9	0.224 ± 0.010	18.8
8.76	15.9	0.315 ± 0.015	19.8
8.76	19.9	0.408 ± 0.024	20.5

[a] [EDTA] is the total initial concentration of all forms of the ligand. [b] The reported values of k_{obsd} are the average values of at least three individual kinetics runs. Errors are standard deviations. [c] A few of these runs were conducted at [V(V)] = 6.44×10^{-4} M. No significant effect on k_{obsd} was detected, indicating that dimeric or other polymeric vanadate species do not appear in the rate law. [d] 25.0°, ionic strength = 0.5 M (NH_4Cl), [V(V)] = 3.22×10^{-4} M.

V(V) was determined titrimetrically[4] with Fe(II) in 5 M H_2SO_4 and agreed with total vanadium within 1%. Stock solutions of EDTA were obtained by dissolution of weighed amounts of the disodium salt. Alizarin solutions were prepared from material recrystallized from MeOH-H_2O mixtures. All studies were carried out in buffered media consisting of 0.50 M NH_4Cl and sufficient ammonia to give the desired pH. Measurements of pH were conducted with a Corning Model 12 pH meter equipped with a Sargent miniature glass electrode. No evidence of V(V) oxidation of either EDTA or alizarin was detected for periods of time in great excess of the times required for completion of these studies. Distilled water used in all experiments was obtained in polyethylene containers from Belmont Springs Co., Belmont, Mass.

In all kinetic studies one of the reactants was present in sufficient excess to ensure that reactions were pseudo first order, and that only 1:1 complexes would be formed. EDTA and V(V) were the reagents in excess in the V(V)-EDTA and V(V)-alizarin systems, respectively. The stopped-flow spectrophotometer, equipped with transient recorder and output interface as well as the computer programs used for data treatment have been described previously.[5] Formation of the V(V)-EDTA complex was followed at 320 nm,[6] whereas the V(V)-alizarin reaction was studied at 520 nm.

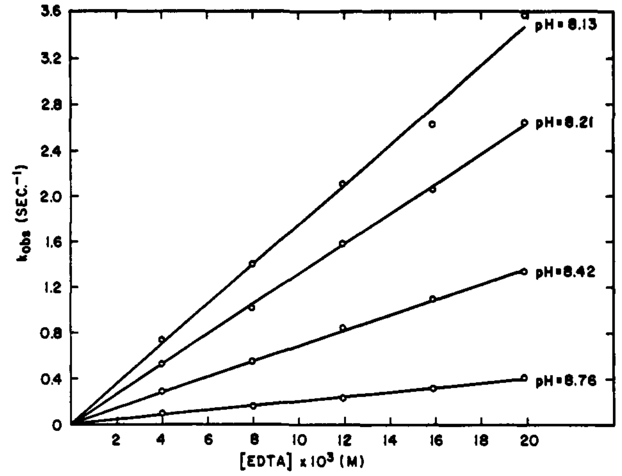


Figure 1. Plots of k_{obsd} *vs.* total [EDTA] (25.0°, ionic strength = 0.50 M).

Table II. Values of k_f for the Complexation of V(V) by EDTA[d]

$10^9[H^+]$,[a] M	k_f, M^{-1} sec^{-1}	$10^4k_fQ_{(obsd)}$[b]	$10^4k_fQ_{(calcd)}$[b,c]
10.64	173 ± 9	2.72	2.73
8.81	133 ± 2	2.30	2.30
5.47	66.5 ± 1.6	1.52	1.51
2.47	19.5 ± 1.1	0.81	0.81

[a] $[H^+]$ calculated using $\gamma_{H^+} = 0.7$. [b] Q is defined as $(K_m + [H^+])(K_2(K_1 + [H^+]) + [H^+]^2)[H^+]^{-2}$, see text. [c] Calculated by least-squares analysis of k_fQ *vs.* $[H^+]$. [d] 25.0°, ionic strength = 0.50 M (NH_4Cl).

Results

Complexation of V(V) by EDTA. The values of k_{obsd}, the pseudo-first-order rate constants for complexation of V(V) by EDTA, are presented in Table I. Each kinetics experiment was first order in [V(V)]. To a close approximation the rate constant for approach to equilibrium for a system of this type can be expressed as $k_{obsd} = k_f([M] + [L]) + k_r$, where k_f, k_r, [M] and [L] represent the bimolecular rate constant for complex formation, the unimolecular rate constant for complex dissociation, and the equilibrium concentrations of the metal-containing ion and ligand, respectively. Under the pseudo-first-order conditions in the present study [M] + [L] can be approximated as the initial concentration of EDTA. Values of k_f, the apparent rate constant for complex formation, were obtained by linear least-squares analysis of k_{obsd} *vs.* [EDTA] at each pH, Figure 1.

The absence of any significant intercept terms in Figure 1 indicates that there is no detectable contribution to the rate of complex formation from the dissociation path. (The relatively constant value of k_{obsd}/[EDTA], Table I, also demonstrates the absence of any k_r contribution to the complexation rate as well as the first-order dependence of the rate of complexation on [EDTA].) The values of k_f so obtained are presented in Table II.

Under the conditions of this study both the vanadate and EDTA ions exist in various protonated forms. The stability constants of the species present in basic vanadate solutions have been reported by Brito, Ingri, and Sillén.[7-9] At 25° and an ionic strength of 0.5 M, the monomeric vanadate anions exist in a hydrogen ion concentration dependent equilibrium which can be expressed as[10]

$$H_2O + VO_2(OH)_2^- \rightleftharpoons VO_2(OH)_3^{2-} + H^+;\ K_m = 10^{-8.0}\ M$$

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(4) I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. III, Interscience, New York, N. Y., 1957, p 607.

(5) K. Kustin and D. L. Toppen, *Inorg. Chem.*, in press.

(6) A. Ringbom, S. Siitonen, and B. Skrifvars, *Acta Chem. Scand.*, 11, 551 (1957).

(7) N. Ingri and F. Brito, *ibid.*, 13, 1971 (1959).

(8) F. Brito, N. Ingri, and L. G. Sillén, *ibid.*, 18, 1557 (1964).

(9) The conditions of this study were chosen to minimize the concentration of dimeric and trimeric V(V) species, ref 7 and 8. Using the thermodynamic data from ref 7, we calculate that under the most adverse conditions, pH 8.13, the concentration of condensed vanadate species is less than 10% of the total vanadium(V) present.

(10) The formulas $VO_2(OH)_2^-$ and $VO_2(OH)_3^{2-}$ are to be interpreted as representations of the degree of protonation of the various anions and do not necessarily reflect the composition of the primary coordination sphere of the metal ion; F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1966, pp 821-823.

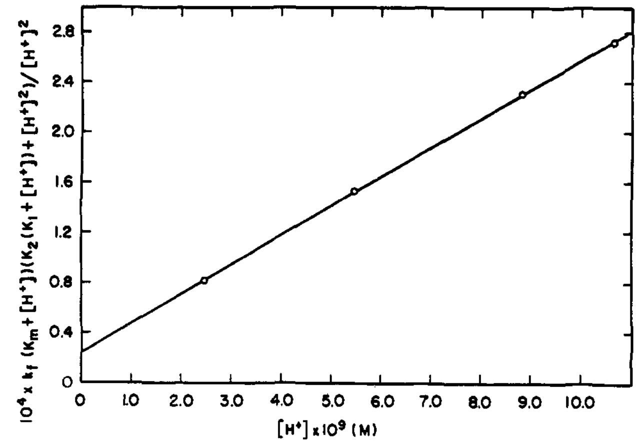


Figure 2. Plot of $k_f(K_m + [H^+])(K_2(K_1 + [H^+]) + [H^+]^2)\,[H^+]^{-2}$ *vs.* $[H^+]$ for V(V)–EDTA.

The pertinent protolytic equilibrium constants of EDTA are[11]

$$HY^{3-} \rightleftharpoons Y^{4-} + H^+;\ K_1 = 10^{-10.11}\ M$$

$$H_2Y^{2-} \rightleftharpoons HY^{3-} + H^+;\ K_2 = 10^{-6.1}\ M$$

Consideration of the values of K_1 and K_2 indicates that >95% of the EDTA species are present as the singly protonated HY^{3-} ion under the conditions of these experiments. If HY^{3-} is the sole EDTA reactant and both vanadate anions in the above equilibrium are reactive, then the rate equation for complex formation may be written as

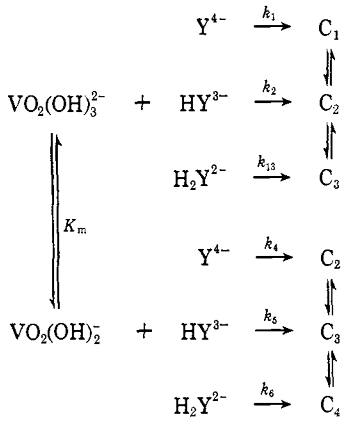
$$-d[V(V)]/dt = (k_2[VO_2(OH)_3{}^{2-}] + k_5[VO_2(OH)_2{}^-])[HY^{3-}] \quad (1)$$

for which

$$k_f = (k_2K_m + k_5[H^+])/(K_m + [H^+]) \quad (2)$$

A plot of $k_f(K_m + [H^+])$ *vs.* $[H^+]$ is expected to be linear, with slope k_5 and intercept k_2K_m. Such a plot is nonlinear, however, suggesting that HY^{3-} is not the only EDTA species participating in the complexation of V(V). Therefore, the reactions in Scheme I were considered.[12] In Scheme I proton transfer reactions of EDTA and V(V) are represented by vertical steps and are assumed to occur rapidly compared with complexation reactions. Products C_1 and C_4 represent V(V)–EDTA complexes differing only in the degree of protonation and are also assumed to exist in rapid protolytic equilibria with one another.[13]

Scheme I



For a scheme of this type the expression for the rate of complex formation is

$$-d[V(V)]/dt = k_f[M][L] \quad (3)$$

where $[M] = [VO_2(OH)_3{}^{2-}] + [VO_2(OH)_2{}^-]$ and $[L] = [Y^{4-}] + [HY^{3-}] + [H_2Y^{2-}]$ and for which k_f, the apparent forward rate constant, can be expressed as

$$k_f = \frac{k_1K_mK_1K_2 + (k_2K_mK_2 + k_4K_1K_2)[H^+] + (k_3K_m + k_5K_2)[H^+]^2 + k_6[H^+]^3}{(K_m + [H^+])(K_2(K_1 + [H^+]) + [H^+]^2)} \quad (4)$$

Rearrangement of eq 4 gives

$$\{k_f(K_m + [H^+])(K_2(K_1 + [H^+]) + [H^+]^2)\}[H^+]^{-2} = k_1K_mK_1K_2[H^+]^{-2} + (k_2K_mK_2 + k_4K_1K_2)[H^+]^{-1} + (k_3K_m + k_5K_2) + k_6[H^+] \quad (5)$$

A plot of $k_f(K_m + [H^+])(K_2(K_1 + [H^+]) + [H^+]^2)/[H^+]^2$ *vs.* $[H^+]$, using the data of Table II, is presented in Figure 2. The linearity of this plot indicates that the k_1, k_2, and k_4 pathways do not measurably contribute to the rate of complex formation under these conditions. Least-squares analysis of the data in Table II gives unambiguously $k_6 = (2.34 \pm 0.05) \times 10^4\ M^{-1}\ sec^{-1}$. The value of $k_3K_m + k_5K_2$, the intercept of Figure 2, is found to be $(2.36 \pm 0.10) \times 10^{-5}\ sec^{-1}$. If $k_3K_m \gg k_5K_2$ the value of k_3 is $(2.4 \pm 0.1) \times 10^3\ M^{-1}\ sec^{-1}$. In the alternate limiting case, where $k_5K_2 \gg k_3K_m$, the value of k_5 is $29.7 \pm 0.2\ M^{-1}\ sec^{-1}$.

Complexation of V(V) by Alizarin. The values of k_{obsd}, the pseudo-first-order rate constants for complexation of V(V) by alizarin, are presented in Table III. A first-order dependence on [alizarin] was observed in each experiment. Plots of k_{obsd} *vs.* [V(V)] at each

Table III. Kinetics Data for Complexation of V(V) by Alizarin[c]

pH	10^3[V(V)],[a] M	k_{obsd},[b] sec^{-1}
8.33	0.515	8.34 ± 0.71
8.33	1.03	13.5 ± 0.6
8.33	2.06	23.6 ± 0.6
8.63	0.258	4.38 ± 0.19
8.63	0.515	6.27 ± 0.49
8.63	1.03	10.1 ± 0.6
8.63	1.55	12.3 ± 0.4
8.63	2.06	16.9 ± 0.6
8.95	0.515	4.68 ± 0.49
8.95	1.03	6.60 ± 0.33
8.95	2.06	10.2 ± 0.2
8.95	3.09	14.6 ± 1.2
8.95	4.12	18.3 ± 0.5
9.23	1.03	6.52 ± 0.27
9.23	3.09	13.2 ± 0.3
9.23	4.12	16.3 ± 0.7

[a] [V(V)] is the total initial concentration of all forms of the metal ion. [b] The reported k_{obsd} values are the average of at least three individual determinations. Errors are standard deviations. [c] 25.0°, ionic strength = 0.50 M (NH_4Cl), [alizarin] = 1.98×10^{-5} M.

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(11) G. Schwarzenbach, quoted in "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964, p 635.

(12) P. F. Knowles and H. Diebler, *Trans. Faraday Soc.*, **64**, 977 (1968).

(13) The spectrophotometric study of Ringbom, *et al.*, ref 6, suggests that only one V(V)–EDTA complex is thermodynamically stable in the pH range of 6–9.

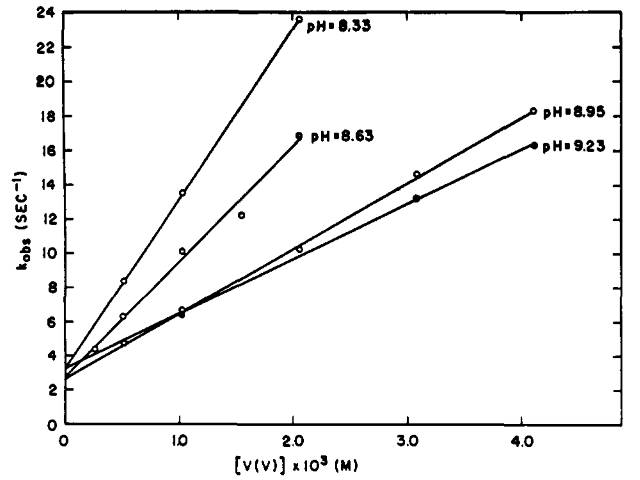

Figure 3. Plots of k_{obsd} *vs.* total [V(V)] (25.0°, ionic strength = 0.05 *M*) for V(V)–alizarin.

pH are shown in Figure 3. Unlike the EDTA system, there is a detectable contribution to k_{obsd} from k_r', the apparent rate constant for alizarin complex dissociation. This contribution is reflected in the small but statistically significant intercepts seen in Figure 3. Least-squares analysis of the data in Table III gives values of k_f' and k_r' at each pH which are presented in Table IV.

The protolytic equilibrium constants for alizarin are[14]

$$HA^- \rightleftharpoons A^{2-} + H^+;\ K_1' = 10^{-11.1}\ M$$

$$H_2A \rightleftharpoons HA^- + H^+;\ K_2' = 10^{-6.1}\ M$$

The predominant alizarin species, under the experimental conditions, is HA^-. Assuming that this is the only kinetically significant alizarin species, the reactions in Scheme II were considered. Here again,

Scheme II

$$\begin{tikzcd}
VO_2(OH)_3^{2-} + HA^- \arrow[r, shift left, "k'_2"] \arrow[d, shift left] & C_1 \arrow[l, shift left, "k'_{-2}"] \arrow[d, shift left] \\
VO_2(OH)_2^- + HA^- \arrow[r, shift left, "k'_5"] \arrow[u, shift left, "K_m"'] & C_2 \arrow[l, shift left, "k'_{-5}"] \arrow[u, shift left, "K_c"']
\end{tikzcd}$$

C_1 and C_2 represent products differing only in the degree of protonation, and vertical steps are assumed to occur rapidly. The protolytic complex ion equilibrium is expressed as $C_2 \rightleftharpoons C_1 + H^+$; $K_c = [C_1][H^+]/[C_2]$. For a scheme of this type, k_f', the apparent forward rate constant is given by

$$k_f' = (k_2'K_m + k_5'[H^+])/(K_m + [H^+]) \quad (6)$$

The apparent dissociation rate constant, k_r', is given by

$$k_r' = (k_{-2}K_c + k_{-5}[H^+])/(K_c + [H^+]) \quad (7)$$

A plot of $k_f'(K_m + [H^+])$ *vs.* $[H^+]$, from the data of Table IV, is presented in Figure 4. Least-squares analysis gives unambiguous values of (2.28 ± 0.08) × 10^4 M^{-1} sec^{-1} for k_5' and (1.2 ± 0.3) × 10^3 M^{-1} sec^{-1} for k_2'. The apparent rate constant for complex dissociation, k_r', was found to have the value 3.0 ± 0.4 sec^{-1} and to be independent of $[H^+]$, within experimental error. In the absence of information regarding the magnitude of K_c, no attempt has been made to establish limits on the individual magnitudes of k_{-2}' and k_{-5}'.

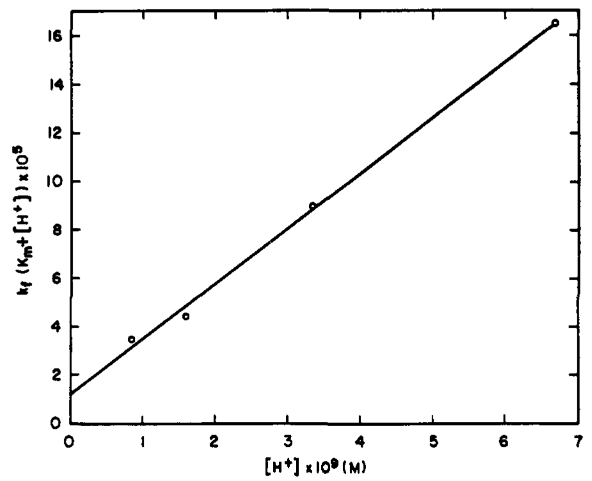

Figure 4. Plot of $k_f'(K_m + [H^+])$ *vs.* $[H^+]$ for V(V)–alizarin.

Table IV. Values of k_f' and k_r' for the Complexation of V(V) by Alizarin[d]

$10^9[H^+]$,[a] *M*	$10^3k_f'$,[b] M^{-1} sec^{-1}	k_r',[b] sec^{-1}	$10^5k_f'_{(\text{obsd})} \cdot (K_m + [H^+])$, sec^{-1}	$10^5k_f'_{(\text{calcd})} \cdot (K_m + [H^+])$,[c] sec^{-1}
6.68	9.86 ± 0.24	3.3 ± 0.3	16.4	16.4
3.35	6.72 ± 0.23	2.7 ± 0.3	8.96	8.85
1.60	3.80 ± 0.09	2.7 ± 0.3	4.41	4.86
0.84	3.18 ± 0.11	3.3 ± 0.1	3.44	3.12

[a] $[H^+]$ calculated using $\gamma_{H^+} = 0.7$. [b] Calculated by least-squares analysis of the data in Table III. [c] Calculated by least-squares analysis of $k_f'(K_m + [H^+])$ *vs.* $[H^+]$, see text. [d] 25.0°, ionic strength = 0.5 *M* (NH_4Cl).

The determination of both k_f' and k_r' as a function of $[H^+]$ allows the evaluation of K_{eq}, the equilibrium constant for formation of the V(V)–alizarin complex. If the equilibrium expression for complex formation is written as $K_{eq} = [C_2]/[VO_2(OH)_2^-][HA^-]$, the value of K_{eq} obtained from kinetics measurements can be expressed as

$$K_{eq} = (k_f'/k_r')([H^+] + K_m)([H^+] + K_c)^{-1} \quad (8)$$

where

$$k_f'/k_r' = K_{app} = ([C_1] + [C_2])/([VO_2(OH)_3^{2-}] + [VO_2(OH)_2^-])[HA^-]$$

Upon assuming that $[H^+] \gg K_c$ (not an unreasonable assumption in light of the $[H^+]$ independence of k_r') the value of K_{eq}, using the data of Table IV, is found to be (1.0 ± 0.2) × 10^4 *M*.

Discussion

Through the application of the rapid mixing technique, it has been possible to determine the rate constants for two vanadate complex formation reactions. No other data for the kinetics of complex formation of anionic V(V) exist, although the rate of dimerization of anionic V(V) has been measured by temperature-jump.[2] Therefore, the value of approximately 2 × 10^4 M^{-1} sec^{-1} found for H_2Y^{2-} and HA^- may not

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(14) M. Bartusek and J. Zelinku, *Collect. Czech. Chem. Commun.*, 32, 992 (1967).

reflect a characteristic substitution rate constant for $VO_2(OH)_2^-$, as is the case for divalent first-row transition metal ions. However, a comparison of the complexation of V(V) by ligands as diverse in character as EDTA and alizarin, coupled with information regarding the rate of dimerization of anionic V(V) species, leads to a picture of the mechanism of complexation of vanadate which is, at least, self-consistent.

The value of k_6, the rate constant for complexation of $VO_2(OH)_2^-$ by H_2Y^{2-}, is $(2.34 \pm 0.05) \times 10^4\ M^{-1}\ sec^{-1}$. This value is to be compared to the value of $(2.28 \pm 0.08) \times 10^4\ M^{-1}\ sec^{-1}$ obtained for k_5', the rate constant for $VO_2(OH)_2^-$ by HA^-. Under similar experimental conditions, k_D, the rate constant for association of $VO_2(OH)_2^-$ and $VO_2(OH)_3^{2-}$ to form the dimeric vanadate anion has been reported[2] to be $3.1 \times 10^4\ M^{-1}\ sec^{-1}$. The most striking feature of the present study is the similarity of the magnitudes of these rate constants.

A value of $(1.2 \pm 0.3) \times 10^3\ M^{-1}\ sec^{-1}$ was obtained for k_2', corresponding to the complexation of $VO_2(OH)_3^{2-}$ by HA^-. The values of k_3 and k_5, corresponding to the kinetically indistinguishable $VO_2(OH)_3^{2-} + H_2Y^{2-}$ and $VO_2(OH)_2^- + HY^{3-}$ pathways in the EDTA system, were found to be $(2.4 \pm 0.1) \times 10^3\ M^{-1}$ and $29.7 \pm 0.2\ M^{-1}\ sec^{-1}$, respectively. On the grounds of the similarity between the values of k_2' and k_3, we suggest that between k_3 and k_5 the k_3 pathway is the most probable route for EDTA complex formation. This suggestion is further supported by the observation that it leads to a similar mechanism for complex formation in both the EDTA and alizarin systems. That is, there is only one kinetically significant form of the ligand, H_2Y^{2-} and HA^-, respectively, which can bind either $VO_2(OH)_2^-$ or $VO_2(OH)_3^{2-}$. Furthermore, the reactivity of the anionic V(V) species toward complexing ligands decreases with the loss of a dissociable proton. Hence, the same behavior is displayed by both oxo anion and ligand; namely, increased protonation increases reactivity with respect to complex formation. This kinetics behavior is also shown by chromate[15] and molybdate.[12,16]

Studies of the kinetics of complexation of oxo anions are not numerous, and few specific comparisons between the rates of complexation of vanadate and other species can be made at this time.

Despite the obvious differences (*e.g.*, K_m for molybdate is $10^{-4}\ M$ rather than $10^{-8}\ M$), some meaningful conclusions can be drawn from comparisons with complexation reactions of the isoelectronic molybdate anion. Kinetics data for the complexation of molybdate by catechol (H_2Cat)[16] and 8-hydroxyquinoline (Hox)[12] indicate the same ligand independent rate constants which have been observed in the present work. That is, for the reactions

$$MoO_4^{2-} + L \xrightarrow{k_a} \text{complex}$$

for which L represents H_2Cat or Hox, respective values for k_a of 2.90×10^2 and $4.1 \times 10^2\ M^{-1}\ sec^{-1}$ have been determined. For the alternative, indistinguishable, reactions

$$MoO_3(OH)^- + L^- \xrightarrow{k_b} \text{complex}$$

L^- representing $HCat^-$ or ox^-, respective values for k_b of 1.9×10^8 and $1.5 \times 10^8\ M^{-1}\ sec^{-1}$ were found.

It has been suggested that oxo anion polymerizations, and therefore oxo anion complexations as well, might be considered as addition reactions;[17] that is, complexation of a tetrahedral anion by a bicoordinate ligand results in an octahedral complex. For such a reaction the ligand independent rate constants observed might be rationalized on the basis of a rate determining expansion of the coordination sphere of the metal ion. However, contrary to the expectation based on this type of mechanism, the rate constant for complexation of the monocatechol–molybdate complex by a second catechol molecule is roughly the same as the rate constant for monocomplex formation.[16] Moreover, as previously mentioned, the rate constants for complex formation increase with increasing degree of protonation. This evidence suggests that both polymerization and complexation may be condensation reactions.

It has also been proposed[18] that addition of a proton to the tetrahedral VO_4^{3-}, MoO_4^{2-}, and WO_4^{2-} ions results in the formation of an octahedral hydrated species. Ultrasonic attenuation studies on molybdate provide some support for this hypothesis.[19] Such species could exist in the weakly alkaline media employed in the molybdate studies cited above as well as in the present work. The absence of a ligand dependence of the rate constants could in many cases reflect a rate determining process of loss of coordinated hydroxo and aquo ligands, the former probably as water molecules, from such six-coordinate species. However, the development of a clearer picture of the mechanism of complexation of oxo anions awaits the results of further study in this area.

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