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Study of the Mechanism of Decomplexation of Some Vanadium(V), Molybdenum(VI), and Tungsten(VI) Aminocarboxylate Complexes

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The kinetics of the decomplexation by hydroxyl ions of some pervanadyl, molybdate, and tungstate aminocarboxylate complexes have been studied spectrophotometrically by means of a stopped-flow technique. The chelate groups used were iminodiacetic acid (IDA), ethylenediamine-*N,N'*-diacetic acid (EDDA), nitrilotriacetic acid (NTA), and ethylenediamine-*N,N,N',N'*-tetraacetic acid (EDTA). The chelates were 1:1 complexes except for the V(V)–IDA chelate which was 1:2. The rate law for decomplexation can be expressed by $-\mathrm{d}[\text{complex}]/\mathrm{d}t = (k_1 + k_2K_0[\mathrm{OH^-}]^n)[\text{complex}]/(1 + K_0[\mathrm{OH^-}]^n)$ ($n = 2$ for the V(V) chelates and $n = 1$ for the Mo(VI) and W(VI) chelates). K_0 is the stability constant of an outer-sphere complex preequilibrium between the chelate and hydroxyl ions, k_1 is the rate constant of the direct decomplexation by water, and k_2 is that by $\mathrm{OH^-}$. The slow step of the reaction should be an interchange between $\mathrm{OH^-}$ (or H_2O) and the chelate group in the outer-sphere complex. The differences in the reactivities of the complexes are discussed. The most important effect observed on k_1 and k_2 is that, for a given metal, the rate constants diminish by a factor of 100–1000 when a ligand which has vacant chelating sites replaces a ligand in which all of the chelating sites are occupied. This is interpreted as an inductive effect by the acetate group, which is not bonded to the metal, on the nitrogen–metal bond.

Introduction

Few studies of the kinetics and mechanism of the formation and decomplexation of vanadium(V), molybdenum(VI), and tungsten(VI) aminocarboxylate complexes have been undertaken. Only the complexation of pervanadyl ions with ethylenediamine-*N,N,N',N'*-tetraacetic acid (EDTA),[1-3] nitrilotriacetic acid (NTA),[3,4] ethylenediamine-*N,N'*-diacetic acid (EDDA), and *N*-methyliminodiacetic acid (MIDA)[3] and the decomplexation of molybdenum(VI) and tungsten(VI) nitrilotriacetate complexes[5] have been reported.

The present paper describes the kinetics of decomplexation by hydroxyl ions of the vanadium(V), molybdenum(VI), and tungsten(VI) complexes of IDA (iminodiacetic acid), NTA, EDDA, and EDTA. This study of the hydrolysis allows us to propose a general mechanism for the decomposition of oxometal–aminocarboxylate complexes.

All of these kinetic studies were carried out using the stopped-flow technique at 25 °C with 3 M sodium perchlorate as an ionic medium. The stability of the complexes was determined at 25 °C in the same ionic medium as previously described.[6,7] In our kinetic investigations we chose experimental conditions such that only the 1:1 complexes were entirely formed except for the vanadium(V)–IDA chelate which was a 1:2 complex. In the presence of an excess of hydroxyl ions we can write the reactions as eq 1–4 (where L^{n-} is the fully dissociated ligand anion).

$$\mathrm{VO_2L^{(n-1)-} + 4OH^- \rightarrow VO_4^{3-} + L^{n-} + 2H_2O} \quad \text{(NTA, EDDA, EDTA)} \tag{1}$$

$$\mathrm{VO_2L_2^{3-} + 4OH^- \rightarrow VO_4^{3-} + 2L^{2-} + 2H_2O} \quad \text{(IDA)} \tag{2}$$

$$\mathrm{MoO_3L^{n-} + 2OH^- \rightarrow MoO_4^{2-} + L^{n-} + H_2O} \quad \text{(IDA, NTA, EDDA, EDTA)} \tag{3}$$

$$\mathrm{WO_3L^{n-} + 2OH^- \rightarrow WO_4^{2-} + L^{n-} + H_2O} \quad \text{(IDA, NTA, EDDA, EDTA)} \tag{4}$$

Experimental Section

Sodium perchlorate, sodium monovanadate, sodium molybdate, sodium tungstate, sodium hydroxide, EDTA, and NTA were obtained from Merck; the chemicals were analytical reagent grade and were used without any purification.

IDA and EDDA purchased from Fluka were recrystallized twice from distilled water. Their concentrations were checked by pH titration.

Perchloric acid solutions were standardized against $KHCO_3$.

A sodium hydroxide solution free from carbonate was prepared: a 50% solution was prepared from the commercial p.a. material filtered through a G4 Jena glass filter and stored in a polyethylene bottle. The dilute solutions were prepared with boiled distilled water from the 50% stock solution under a stream of purified nitrogen; they were standardized against $HClO_4$.

Vanadium(V) solutions were standardized titrimetrically against a standard ferrous sulfate solution.[8]

The ionic strength was maintained at 3 M with sodium perchlorate. In all kinetic studies, the solutions of the aminocarboxylate complex contained chelating agent in sufficient excess at a given pH to ensure that only the 1:1 complex was entirely formed (except for V(V)–IDA where the 1:2 complex was formed). The hydroxyl ions were present in the stopped-flow apparatus in sufficient excess to obtain instantaneous neutralization of the free ligand and to ensure that reactions were pseudo first order.

No evidence for oxidation of IDA, EDDA, NTA, or EDTA by V(V), Mo(VI), and W(VI) was detected for periods of time in great excess of the time required for completion of the experiments.

Measurements of pH were conducted with a Tacussel Aries 20000 pH meter equipped with Beckman 39099E-3 glass and Ag–AgCl reference electrodes.

The stopped-flow spectrophotometer, of the type Durrum D131, equipped with a transient recorder, Datalab DL905, was interfaced to an Olivetti P652 microcomputer. This system and the computer programs used for data treatment have been previously described.[4,5]

Results and Discussion

Rate Law and Proposed Mechanism. The values of k_{obsd}, the pseudo-first-order rate constant of reactions 1–4, are presented in Tables I–III. Each value of k_{obsd} is the average of at least three determinations. Each kinetic experiment was first order with respect to the complex. Under our experimental conditions (large excess of $\mathrm{OH^-}$) we can neglect the backward reaction of complex formation. We have also neglected the neutralization of excess ligand which is quasi-instantaneous. The concentration of the free ligand was without effect. The plots of $\ln |A_t - A_\infty|$ vs. t were linear for over 95% of the reaction (A_t and A_∞ are the absorbances of the system at reaction times t and ∞, respectively). The slope of each plot gave k_{obsd} by linear least-squares analysis.

The $k_{\mathrm{obsd}} = \mathrm{f}([\mathrm{OH^-}]_0)$ functions are of the sigmoid type for the vanadium(V) complexes and of the hyperbolic type for the molybdenum(VI) and tungsten(VI) complexes ($[\mathrm{OH^-}]_0$ is the hydroxyl ion concentration after mixing and neutralization of the ligand excess). In each case the rate of the reaction seems to be almost independent of the $\mathrm{OH^-}$ concentration above a certain limit as is observed in the complexation of pervanadyl

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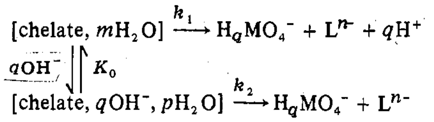
Table I. Observed Rate Constants of the Vanadium(V) Chelates' Decomplexations[a]

$[\mathrm{chelate}]_0$/M	$[\mathrm{OH^-}]_0$/M	$k_{\mathrm{obsd}}(\mathrm{exptl})/\mathrm{s^{-1}}$	$k_{\mathrm{obsd}}(\mathrm{calcd})/\mathrm{s^{-1}}$
	V(V)-IDA		
10^{-4} [b]	0.00117	8.89 ± 0.34	8.63
	0.00140	6.90 ± 0.44	7.52
	0.00371	3.18 ± 0.15	3.17
	0.00836	2.32 ± 0.17	3.14
	0.0177	2.01 ± 0.11	1.92
	0.0270	1.82 ± 0.13	1.88
	0.0363	1.81 ± 0.14	1.86
	0.0456	1.83 ± 0.14	1.86
	V(V)-EDDA		
10^{-4} [b]	0.00294	2.54 ± 0.12	2.81
	0.00758	2.99 ± 0.10	2.91
	0.0169	3.72 ± 0.18	3.34
	0.0262	4.44 ± 0.19	4.03
	0.0355	5.24 ± 0.20	4.90
	0.0448	5.74 ± 0.17	5.86
	0.0681	8.13 ± 0.24	8.21
	0.0914	10.5 ± 0.37	10.14
	V(V)-NTA		
10^{-5} [c]	0.000114	2.45 ± 0.16	2.43
	0.000231	6.11 ± 0.75	7.15
	0.000362	16.0 ± 3.2	14.8
	0.000478	25.2 ± 4.0	22.6
	0.000544	28.6 ± 5.0	26.9
	0.00206	75.0 ± 7.0	73.9
	0.00453	86.6 ± 7.0	82.6
10^{-4} [b]	0.00861	84.0 ± 5.0	84.5
	0.0277	86.4 ± 4.3	85.1
	V(V)-EDTA		
0.5×10^{-5} [d]	0.0000604	0.016 ± 0.002	0.0157
	0.000102	0.022 ± 0.002	0.0213
10^{-5} [c]	0.000111	0.024 ± 0.002	0.0230
	0.000241	0.026 ± 0.003	0.0279
	0.000332	0.027 ± 0.003	0.0289
	0.000423	0.029 ± 0.003	0.0294
	0.000561	0.029 ± 0.003	0.0297
	0.00194	0.030 ± 0.003	0.0302
	0.00425	0.029 ± 0.003	0.0303
10^{-4} [b]	0.0368	0.030 ± 0.001	0.0303

[a] All concentrations are given at the initial time after mixing and neutralization of the ligand excess. The reactions were followed at 270 nm (IDA, EDDA, NTA) and at 320 nm (EDTA). [b] $[\mathrm{ligand}]_0 = 10^{-3}$ M; $[\mathrm{V(V)}]_0 = 10^{-4}$ M. [c] $[\mathrm{ligand}]_0 = 2.5 \times 10^{-4}$ M; $[\mathrm{V(V)}]_0 = 10^{-5}$ M. [d] $[\mathrm{ligand}]_0 = 1.25 \times 10^{-4}$ M; $[\mathrm{V(V)}]_0 = 0.5 \times 10^{-5}$ M; $[\mathrm{ligand}]_0$ and $[\mathrm{V(V)}]_0$ total ligand and metal concentrations in all solution forms.

Scheme I



$$\begin{tikzcd}
{[\text{chelate}, m\mathrm{H_2O}]} \arrow[r, "k_1"] \arrow[d, shift right, "q\mathrm{OH}^-"'] & \mathrm{H}_q\mathrm{MO_4}^- + \mathrm{L}^{n-} + q\mathrm{H}^+ \\
{[\text{chelate}, q\mathrm{OH}^-, p\mathrm{H_2O}]} \arrow[r, "k_2"] \arrow[u, shift right, "K_0"'] & \mathrm{H}_q\mathrm{MO_4}^- + \mathrm{L}^{n-}
\end{tikzcd}$$

Table II. Observed Rate Constants of the Molybdenum(VI) Chelates' Decomplexations[a]

$[\mathrm{chelate}]_0$/M	$[\mathrm{OH^-}]_0$/M	$k_{\mathrm{obsd}}(\mathrm{expt})/\mathrm{s^{-1}}$	$k_{\mathrm{obsd}}(\mathrm{calcd})/\mathrm{s^{-1}}$
	Mo(VI)-IDA		
2.5×10^{-4} [b]	0.00694	109 ± 6	109
	0.0162	147 ± 9	145
	0.0255	176 ± 10	177
	0.0349	203 ± 15	205
	0.0442	232 ± 12	230
	0.0674	283 ± 11	281
	0.0907	319 ± 16	322
	Mo(VI)-EDDA		
2.5×10^{-4} [b]	0.00464	0.925 ± 0.03	0.924
	0.0139	1.12 ± 0.03	1.08
	0.0232	1.20 ± 0.04	1.20
	0.0325	1.23 ± 0.04	1.28
	0.0418	1.33 ± 0.05	1.35
	0.0651	1.48 ± 0.05	1.47
	0.0884	1.57 ± 0.05	1.54
	Mo(VI)-NTA		
5×10^{-4} [c]	0.0218	0.434 ± 0.01	0.435
	0.0335	0.630 ± 0.04	0.625
	0.0452	0.800 ± 0.03	0.799
	0.0685	1.11 ± 0.04	1.10
	0.0918	1.33 ± 0.06	1.36
	0.115	1.60 ± 0.06	1.58
	0.135	1.73 ± 0.05	1.74
	Mo(VI)-EDTA		
5×10^{-4} [c]	0.00896	0.399 ± 0.007	0.400
	0.0206	0.583 ± 0.01	0.566
	0.0322	0.717 ± 0.01	0.715
	0.0438	0.846 ± 0.02	0.849
	0.0671	1.11 ± 0.03	1.09
	0.0903	1.24 ± 0.02	1.28
	0.137	1.59 ± 0.04	1.60
	0.183	1.87 ± 0.04	1.84

[a] All concentrations are given at the initial time after mixing and neutralization of the ligand excess. The reactions were followed at 275 nm (IDA, EDTA), 280 nm (EDDA), and 290 nm (NTA). [b] $[\mathrm{ligand}]_0 = 2.5 \times 10^{-3}$ M; $[\mathrm{Mo(VI)}]_0 = 2.5 \times 10^{-4}$ M. [c] $[\mathrm{ligand}]_0 = 2.5 \times 10^{-2}$ M; $[\mathrm{Mo(VI)}]_0 = 5 \times 10^{-4}$ M. $[\mathrm{ligand}]_0$ and $[\mathrm{Mo(VI)}]_0$ total ligand and metal concentrations in all solution forms.

ion with EDTA or NTA.[1,4] We can explain this observation by proposing that there is a preequilibrium step leading to the formation of an outer-sphere-type complex, the rearrangement of which gives the final products of the reaction.[9] From the stoichiometry of the oxo anion formed, we can postulate that the preequilibrium involves two $\mathrm{OH^-}$ ions for the vanadium(V) chelates and only one $\mathrm{OH^-}$ ion for the molybdenum(VI) and the tungsten(VI) chelates as in Scheme I, where M is V, Mo, or W, L is a chelate group with n carboxylic functions, and $q = 2$ for the V(V) complexes and $q = 1$ for the Mo(VI) and W(VI) complexes. Each of these reactions would be followed by steps in which $\mathrm{H_2VO_4^-}$, $\mathrm{HMoO_4^-}$, or $\mathrm{HWO_4^-}$ is neutralized with the conversion of an octahedral structure to a tetrahedral structure. These reactions are very fast as in the condensation of the isopolyanions of the metals.[10-12]

Thus the rate law is given by

$$v = k_{\mathrm{obsd}}[\mathrm{chelate}]_{\mathrm{tot}} = \frac{k_1 + k_2K_0[\mathrm{OH^-}]^q}{1 + K_0[\mathrm{OH^-}]^q}[\mathrm{chelate}]_{\mathrm{tot}}$$

with $[\mathrm{chelate}]_{\mathrm{tot}} = [\mathrm{chelate}, m\mathrm{H_2O}] + [\mathrm{chelate}, q\mathrm{OH^-}, p\mathrm{H_2O}]$ and $q = 2$ for the vanadium(V) chelates and $q = 1$ for the molybdenum(VI) and tungsten(VI) chelates. We can write the rate law as

$$\frac{1}{k_{\mathrm{obsd}} - k_1} - \frac{1}{k_2 - k_1} = \frac{1}{K_0(k_2 - k_1)}\,\frac{1}{[\mathrm{OH^-}]^q}$$

The analysis of the $k_{\mathrm{obsd}}(\mathrm{exptl}) = \mathrm{f}([\mathrm{OH^-}]_0)$ curves allow us to obtain approximate values of k_1 and k_2 for low and high values of $[\mathrm{OH^-}]_0$, respectively. When we introduce these approximate values of k_1 and k_2 which are varied step by step, the above equation becomes a linear function of $1/K_0$. We can calculate the $1/K_0$ value by a linear least-squares method and also for all experimental points:

$$S = \sum\left(\frac{k_{\mathrm{obsd}}(\mathrm{exptl}) - k_{\mathrm{obsd}}(\mathrm{calcd})}{k_{\mathrm{obsd}}(\mathrm{exptl})}\right)^2$$

The minimum of the function $S = \mathrm{f}(k_1,k_2)$ gives the best set of values of k_1, k_2, and K_0. The values of k_1, k_2, and K_0 are

Table III. Observed Rate Constants of the Tungsten(VI) Chelates' Decomplexations[a]

$[\text{chelate}]_0$/M	$[\text{OH}^-]_0$/M	k_{obsd}(exptl)/s^{-1}	k_{obsd}(calcd)/s^{-1}
	W(VI)-IDA		
2.5×10^{-4} [b]	0.00695	10.7 ± 0.3	10.7
	0.0163	13.7 ± 0.3	13.3
	0.0256	15.1 ± 0.5	15.4
	0.0349	17.3 ± 0.6	17.2
	0.0442	18.8 ± 0.7	18.7
	0.0667	21.7 ± 0.6	21.6
	0.0889	23.6 ± 0.7	23.7
	W(VI)-EDDA		
2.5×10^{-4} [c]	0.00797	0.0373 ± 0.002	0.0368
	0.0172	0.0505 ± 0.003	0.0535
	0.0264	0.0701 ± 0.004	0.0687
	0.0358	0.0848 ± 0.005	0.0829
	0.0451	0.0989 ± 0.006	0.0958
	0.0684	0.125 ± 0.009	0.124
	0.0917	0.142 ± 0.010	0.147
	W(VI)-NTA		
5×10^{-4} [d]	0.0102	0.0343 ± 0.001	0.0343
	0.0219	0.0495 ± 0.002	0.0500
	0.0335	0.0574 ± 0.003	0.0584
	0.0452	0.0656 ± 0.002	0.0638
	0.0685	0.0713 ± 0.002	0.0701
	0.0918	0.0730 ± 0.003	0.0737
	0.115	0.0755 ± 0.003	0.0760
	W(VI)-EDTA		
5×10^{-4} [d]	0.00877	0.0364 ± 0.001	0.0364
	0.0204	0.0491 ± 0.002	0.0486
	0.0320	0.0556 ± 0.002	0.0560
	0.0436	0.0614 ± 0.002	0.0611
	0.0669	0.0670 ± 0.002	0.0675
	0.0901	0.0721 ± 0.002	0.0713
	0.137	0.0753 ± 0.002	0.0758
	0.183	0.0779 ± 0.002	0.0782

[a] All concentrations are given at the initial time after mixing and neutralization of the ligand excess. The reactions were followed at 255 nm (IDA), 260 nm (EDDA), 265 nm (NTA), and 250 nm (EDTA). [b] $[\text{ligand}]_0 = 2.5 \times 10^{-3}$ M; $[\text{W(VI)}]_0 = 2.5 \times 10^{-4}$ M. [c] $[\text{ligand}]_0 = 2.5 \times 10^{-2}$ M; $[\text{W(VI)}]_0 = 2.5 \times 10^{-4}$ M. [d] $[\text{ligand}]_0 = 2.5 \times 10^{-2}$ M; $[\text{W(VI)}]_0 = 5 \times 10^{-4}$ M; $[\text{ligand}]_0$ and $[\text{W(VI)}]_0$ total ligand and metal concentrations in all solution forms.

summarized in Table IV. The pseudo-first-order rate constants calculated from these values are compared with the experimental values (Tables I–III). The calculated and the experimental values of k_{obsd} are in good agreement.

Since the formation of an outer-sphere complex (equilibrium constant K_0) is a very fast reaction (half-life of the reaction $\simeq 10^{-9}$–10^{-10} s), we can conclude that the rate-determining step in the decomplexation by hydroxyl ions is probably a ligand interchange in the outer sphere of the complex. This interchange occurs between hydroxyl ions of the outer sphere and one of the chelating groups bonded to the metal. This step is apparently first order with rate constant k_2, because the reaction occurs in an outer-sphere complex and does not involve direct attack of an external species. The direct decomplexation reaction (rate constant k_1) is similarly an interchange between water molecules of the outer sphere and the chelate group. The outer sphere is formed from the chelate and hydroxyl ions, both negatively charged. We can suppose that the electrical charges of the complex are unequally distributed on the surface giving a dipole moment of sufficient magnitude favoring the association rate between the chelate and OH^-.[17,18] Such an effect of dipole moment is not incuded in the Bjerrum theory, and we cannot estimate K_0 values by calculations. But, the values of K_0 obtained kinetically could be checked directly before reaction to produce H_qMO_4^-.[19] For each kinetic experiment we can calculate the absorbance corresponding to time zero by addition of the absorbances for each of the reactants after mixing and fast neutralization of the excess free ligand. The difference between this calculated value and the experimental absorbance must be due to the formation of the outer-sphere complex with OH^-. No significant differences were observed. The mechanism of these steps cannot be unambiguously determined from our kinetic data because the outer-sphere complexes [chelate, $q\text{OH}^-$, $p\text{H}_2\text{O}$] probably have the same absorbance as [chelate, $m\text{H}_2\text{O}$]. A direct potentiometric determination[20] of the equilibrium constant K_0 is not possible because of the order of magnitude of the stability constants of the outer-sphere complexes and the instability of the chelate in basic medium.

For the decomplexation of IDA and EDDA chelates, a conjugate-base mechanism[21] could be proposed: a preequilibrium in which the hydroxyl ions remove the proton from one amine nitrogen to form the conjugate base. This mechanism is not consistent with the interpretation given in the following paragraph.

Comparison of the Rate Constants Determined for the 1:1 Complexes. No correlation can be seen between k_1 and k_2 and the formation constants of the 1:1 chelates or the last ionization constants of the free ligands because the exchange reactions occur in the outer-sphere complexes.

The reactions with the hydroxyl ions are faster than those with water ($k_2 > k_1$): OH^- is a better nucleophile than H_2O.

The effect of the ligand on the reactivity of the 1:1 chelates may be seen if we consider the different structures of these compounds. Figure 1 shows the structure in solution derived from literature data.[7,13-16] We observe that the Mo(VI) and W(VI) complexes of IDA and EDDA have very different values of k_1 or k_2. But the V(V), Mo(VI), and W(VI) complexes of EDDA and NTA have values of k_1 or k_2 of the same orders of magnitude. Thus, we can conclude that a $\text{S}_\text{N}1$ cB mechanism is not satisfactory. A very large difference in reactivity is observed between the complexes which have a chelating group which is not bonded to the metal and those

Table IV. Kinetic Parameters of the Decomplexation of 1:1 Chelates

chelate		ligand			
		IDA	EDDA	NTA	EDTA
vanadium(V)-chelate	k_1/s^{-1}	14.3[a]	2.80	0.80	0.0060
	k_2/s^{-1}	1.85[a]	160	85.2	0.0303
	K_0/M^{-2}	6.10×10^5 [a]	1.50×10^2	1.52×10^6	1.82×10^8
molybdenum(VI)-chelate	k_1/s^{-1}	79	0.82	0.020	0.26
	k_2/s^{-1}	660	1.90	4.40	3.60
	K_0/M^{-1}	7.93	23.0	4.79	4.90
tungsten(VI)-chelate	k_1/s^{-1}	8.4	0.021	0.0030	0.020
	k_2/s^{-1}	38.0	0.400	0.0870	0.0870
	K_0/M^{-1}	12.1	5.46	57.9	35.9

[a] Decomplexation of the 1:2 chelate.

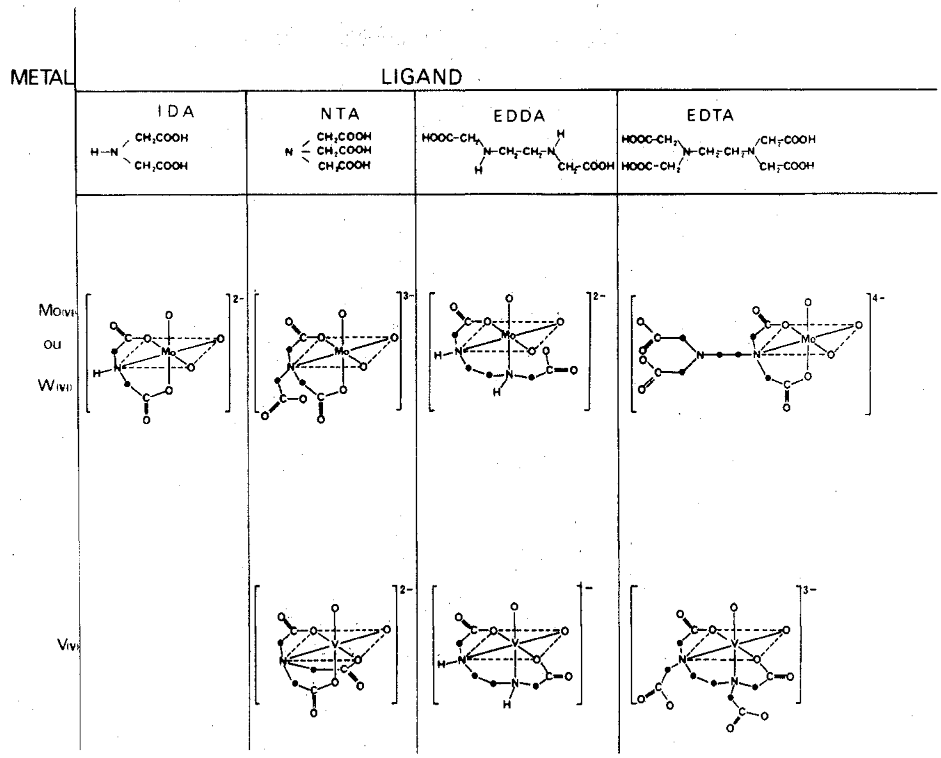


Figure 1. Structures of the 1:1 chelates in solution.

in which all the chelating groups are bonded. The rate constants (k_1 or k_2) are a 100 or a 1000 times lower for the first type of complex than for the second: for complexes of vanadium(V) EDDA $\sim$ NTA $\gg$ EDTA; for complexes of molybdenum(VI) and tungsten(VI) IDA $\gg$ EDDA $\sim$ NTA $\sim$ EDTA.

The lability of the system is greatly diminished by the presence of CH_2COO^- groups not bonded to the metal. These groups have an inductive effect on the nitrogen of the ligand bonded to the metal. The nitrogen–metal bond is thus stabilized and it is more difficult to break. The effect of the free CH_2COO^- groups, not bonded to the metal, on the rate constants could be due to a competition between one of chelating group–metal bond ruptures and new bond formation between the acetate group and the metal, which attends the complete cleavage of the multidentate ligand. This bond re-formation, which could occur between one of the free acetate groups and the metal, is the second reason for greater kinetic stability of the chelates having free acetate groups.

The effect of the metal on the reactivity can be seen by examination of the data for chelates which have the same structure. Thus we can only compare the chelates of molybdenum(VI) and tungsten(VI). We observe that, for a given ligand, k_1 and k_2 are always greater for the molybdenum(VI) than for the tungsten(VI) complexes. This effect has also been observed in the decondensation of molybdenum(VI) and tungsten(VI) polyanions.[11,12]

Decomplexation of the 1:2 Chelate Vanadium(V)–IDA. The order of magnitude of k_1 and k_2 is comparable to those obtained for the 1:1 chelates. The value of k_2 seems rather low, but the important difference found here is that $k_2 < k_1$. We think that the two amine groups are in a trans relationship in this complex. This would have less effect on the attack by H_2O than on the attack by OH^-.

In this work we have attempted to summarize the various factors which can influence the rate of decomplexation of some vanadium(V), molybdenum(VI), and tungsten(VI) aminocarboxylate chelates. It seems that the rate of cleavage of the metal–nitrogen bond is the key process. There is a genuine difficulty in attempting to discriminate between the S_N1 and S_N2 mechanisms. Our results are equally compatible with either unimolecular or bimolecular substitution.

Registry No. $VO_2(IDA)_2^{3-}$, 68890-48-2; VO_2EDDA^-, 38868-05-2; VO_2NTA^{2-}, 59368-60-4; VO_2EDTA^{3-}, 68907-94-8; MoO_3IDA^{2-}, 19709-67-2; MoO_3EDDA^{2-}, 68890-47-1; MoO_3NTA^{3-}, 67316-58-9; MoO_3EDTA^{4-}, 68890-46-0; WO_3IDA^{2-}, 67316-63-6; WO_3EDDA^{2-}, 68890-45-9; WO_3NTA^{3-}, 67316-60-3; WO_3EDTA^{4-}, 21910-18-9.

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