Kinetics of 1:1 chelate formation between 2-acetylcyclopentanone and oxovanadium(IV)

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ABSTRACT: The kinetic parameters of the 1:1 chelate complex of 2-acetylcyclopentanone with the oxovanadium(IV) ion in aqueous solution at 25 °C and 0.5 mol dm^{-3} ionic strength are reported. A spectrophotometric study indicates that the species present in solutions of oxovanadium(IV) ion and of 2-acetylcyclopentanone below pH 2 can be formulated as 1:1 complexes of the type $VO(C_7H_9O_2)^+$. The kinetic data are consistent with a scheme in which both the enol form of the ligand and the enolate ion react with the oxovanadium(IV) ion. From a study of the kinetic results over a range of temperatures, subsequent activation parameters for the chelation processes, $\Delta H\ddagger$ and $\Delta S\ddagger$, were determined. Some discussions are provided on the basis of the Eigen–Wilkins theory considering the effect of solvent exchange on the chelation process. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: 2-acetylcylopentanone–oxovanadium(IV) chelate formation; kinetics; solvent exchange

INTRODUCTION

Although the chelation kinetics of metal ions by linear 1,3-dicarbonyl compounds have been extensively studied,[1–4] little work on metal chelate complexes of 2-acetylcycloalkanones has been reported.

2-Acetylcycloalkanones are interesting ligands because they may exist simultaneously in endo- and exocyclic enol forms[5] and in addition intramolecular proton transfer reactions in these ligands are particularly attractive even from a theoretical[6] point of view. Furthermore, 2-acetylcycloalkanones have become useful in current health issues[7] (intermediate in preparation of HIV inhibitors) and other industrial applications.[8]

The uncommon monomeric first-row transition oxometal ions, such as VO^{2+}, are of substantial interest for solvent exchange and ligand substitution studies.[9] Oxovanadium(IV), which forms hundreds of stable species with different ligands,[10] plays a significant role in the genetic information transfer mechanism.[11,12] In particular, vanadyl sulphate, has demonstrated insulin-like effects on glucose metabolism in both animal and human trials.[13,14]

The most satisfactory model of the aquated oxovanadium(IV) cation is one in which four equivalent water molecules occupy planar equatorial positions around the vanadium atom and a fifth water molecule is in an axial position opposite an oxo group.[15] It is well known that the axial vanadium–ligand bond is weaker than the equatorial bonds, since many six-coordinate oxovanadium(IV) complexes release the ligand from the axial position when heated or dissolved in inert solvents.[16,17] Consequently, the rates of chemical exchange of the two types of coordinated sites would be different.

Owing to the lack of chelation studies of oxo-metal ions with 2-acetylcycloalkanones, we now report a kinetic study of the reaction of oxovanadium(IV) with 2-acetylcyclopentanone in aqueous solution.

EXPERIMENTAL

Reagent-grade 2-acetylcyclopentanone (Hacpt) (Aldrich) was freshly distilled under reduced pressure. Stock solutions were standardized by titration with standard sodium hydroxide. End-points were determined by the use of an iterative computer program based on the method of Gran and Johansson.[18]

Solutions of oxovanadium(IV) were prepared from $VOSO_4 \cdot 3H_2O$ (Aldrich, 99.99%). Aliquots of these solutions were analysed by adding an excess of standard ethylenediaminetetraacetate solution and back-titrating the excess with a standard Mg^{2+} solution to an

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Eriochrome Black T end-point. The titration was carried out at pH < 10 in the presence of an aqueous NH_3–NH_4Cl buffer. Since VO^{2+} is air oxidized, the solutions were freshly prepared prior to use. In the acidic solutions used in all experiments, oxidation of prepared oxovanadium(IV) solutions was not noted for at least 1 day.

The source of hydrogen ions was perchloric acid (Merck) and the ionic strength of reactant solutions was 0.5 mol dm^{-3}, adjusted using $NaClO_4 \cdot H_2O$ (Merck).

Unless indicated otherwise, all materials were of analytical-reagent grade and were used without further purification.

A Crison Model 2002 pH meter, previously calibrated by titrating solutions of perchloric acid with standard sodium hydroxide solutions, was used to read hydrogen ion concentration directly. The relative pH accuracy was 0.01 pH unit.

UV–visible spectra were recorded on a Hitachi U-3000 spectrophotometer. A Spectronic 1201 UV–VIS spectrophotometer, which includes a kinetic resident program, was used to follow the kinetic runs. The reported rate constants are the average of at least two determinations.

The rate constant of enolization, k_e, was studied by a bromination procedure.[19] A small volume (100–200 μl) of bromine stock solution was added to 2.5–3.0 ml of a previously standardized ligand solution placed in the thermostated cell compartment of the spectrophotometer. Changes in absorption at 452 nm were recorded at 6 s intervals. Each of the bromine solutions contained 10^{-3} mol dm^{-3} NaBr in order to suppress hydrolysis of bromine.

The ligand dissociation constant, K_{HL}, was evaluated potentiometrically by titrating solutions of the ligand having concentrations in the range 1.0×10^{-3}–1.0×10^{-2} mol dm^{-3} with standard sodium hydroxide solutions in a double-walled titration cell under an atmosphere of nitrogen gas. Data treatment was carried out using the program SUPERQUAD.[20] With this program the dissociation constant of the ligand was determined by minimization of an error-square sum based on measured electrode potentials.

RESULTS AND DISCUSSION

The keto–enol tautomerism exhibited by the ligand is usually represented by

$$HK \underset{k_k}{\overset{k_e}{\rightleftharpoons}} HE \qquad (1)$$

where k_e is the rate constant of enolization, k_k the rate constant of ketonization and HK and HE represent the keto and enol tautomers of the ligand, respectively. Since bromine reacts instantaneously with the enol tautomer, first-order bromination is governed by the rate of enol formation, k_e, which was determined from Eqn. (2)

following the experimental procedure indicated previously.

$$-\ln(A/\varepsilon l + [HL]_0 - [Br_2]_0) = k_e t + C \qquad (2)$$

where the term in parentheses corresponds to the keto tautomer concentration, A is the absorbance due to bromine at any time t at the observation wavelength (452 nm), l is the pathlength, $\varepsilon = 103$ is the absorption coefficient of bromine at 452 nm and $[HL]_0$ and $[Br_2]_0$ are the total concentrations of ligand and bromine, respectively, at time zero. A plot of the left-hand side of Eqn. (2) vs time gives a straight line of slope k_e. Since $k_e/k_k = [HE]/[HK]$ and $[HL] = [HE] + [HK]$, the intercepts were used to determine the enol ratio, $y = [HE]/[HL]$, which allows the determination of ketonization rate constants.

At 25 °C, it was found that $k_e = 3.5 \times 10^{-2}$ s^{-1} and $y = 0.15$, from which the value $k_k = 19.7 \times 10^{-2}$ s^{-1} was determined. Similar experiments carried out at low temperatures show that the enol fraction decreases slightly when the temperature is reduced (e.g. $y(15 °C) = 0.14$, $y(5 °C) = 0.13$).

The equilibrium constant for ligand ionization [Eqn. (3)] was determined potentiometrically and at 25 °C it was found to be $(1.58 \pm 0.05) \times 10^{-8}$ mol dm^{-3}.

$$HL \overset{K_{HL}}{\rightleftharpoons} H^+ + L^- \qquad (3)$$

where HL represents the undissociated ligand and L^- the enolate ion (common product of ionization of either the keto or enol tautomer). This overall dissociation constant K_{HL} can be partitioned between the equilibrium constant K_{HE} and K_{HK}, the dissociation constants of the enol and keto tautomers, respectively:

$$HK \overset{K_{HK}}{\rightleftharpoons} H^+ + K^- \qquad (4)$$

$$HE \overset{K_{HE}}{\rightleftharpoons} H^+ + E^- \qquad (5)$$
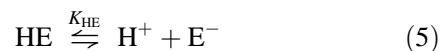
where $K_{HK}/K_{HE} = [HE]/[HK]$ and, taking into account that $1/K_{HL} = 1/K_{HK} + 1/K_{HE}$, we have $K_{HK} = (1.86 \pm 0.05) \times 10^{-8}$ and $K_{HE} = (1.15 \pm 0.05) \times 10^{-7}$.

The composition of the complex that oxovanium(IV) forms with 2-acetylcyclopentanone in aqueous solution was investigated spectrophotometrically using the Job[21] and Yoe and Jones[22] methods. The results obtained indicate a 1:1 stoichiometry.

Monochelated complex formation may be regarded structurally as a coordinated sphere where two molecules of equatorial water are replaced by two carbonyl oxygens from the 2-acetylcyclopentanone, and simultaneously the loss of the proton from the tertiary ring carbon occurs. The monochelated complex may be represented as shown in approximate terms in Fig. 1.
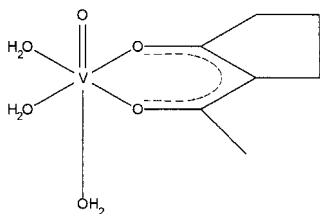
Figure 1. Structure of chelate complex

The equilibrium constant of the monochelated complex, K_{ML}, was evaluated from spectrophotometric measurements:

$$VO^{2+} + HL \overset{K_{ML}}{\rightleftharpoons} VOL^+ + H^+ \qquad (6)$$

The absorbance change at 300 nm, where the complex absorbs strongly, is a function of the equilibrium constant, and the metal, ligand and proton concentrations used:

$$[HL]_0/A = [H^+]/([VO^{2+}]\varepsilon K_{ML}) + 1/\varepsilon \qquad (7)$$

From a plot of the left-hand side of Eqn. (7) against $[H^+]/[VO^{2+}]$, K_{ML} can be readily determined. Several series of solutions were prepared in which the concentration of $[H^+]$ ranged from 2.0×10^{-2} to 0.10 mol dm^{-3}, with $[VO^{2+}] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $[HL]_0 = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$. The value obtained for K_{ML} was 1.3 ± 0.1, which agrees with the results obtained by using Schwarzenbach coefficients.[23] From this value, the stability constant of the monocomplex, $\beta = [VOL^+]/[VO^{2+}][L^-]$, was calculated from the relationship $\beta = K_{ML}/K_{HL}$, giving $(8.20 \pm 0.05) \times 10^7$.

The complex formation reaction was carried out with the metal ion concentration in large excess over the ligand to ensure pseudo-first-order conditions. Kinetic measurements of complex formation were monitored by recording absorbance changes at 300 nm. To avoid the appearance of hydroxovanadyl species, kinetic runs were carried out in solutions $\geq 0.01 \text{ mol dm}^{-3}$ in perchloric acid.

The pseudo-first-order rate constants, k_{obs}, were obtained by fitting values of $\ln(A_\infty - A_t)$ versus time, where A_t and A_∞ are the absorbances of the chelate at t s after starting the reaction and when the reaction is over, respectively. It has also been proved in this study that the k_{obs} values were absolutely independent of the initial concentration of Hacpt. To study the influence of the VO^{2+} concentration on k_{obs}, several series of experiments with constant values of ligand concentration, acidity, ionic strength and temperature were performed (Table 1).

The dependence of k_{obs} on metal ion and hydrogen ion concentrations is consistent with a mechanism which involves a double reversible pathway where both the enol
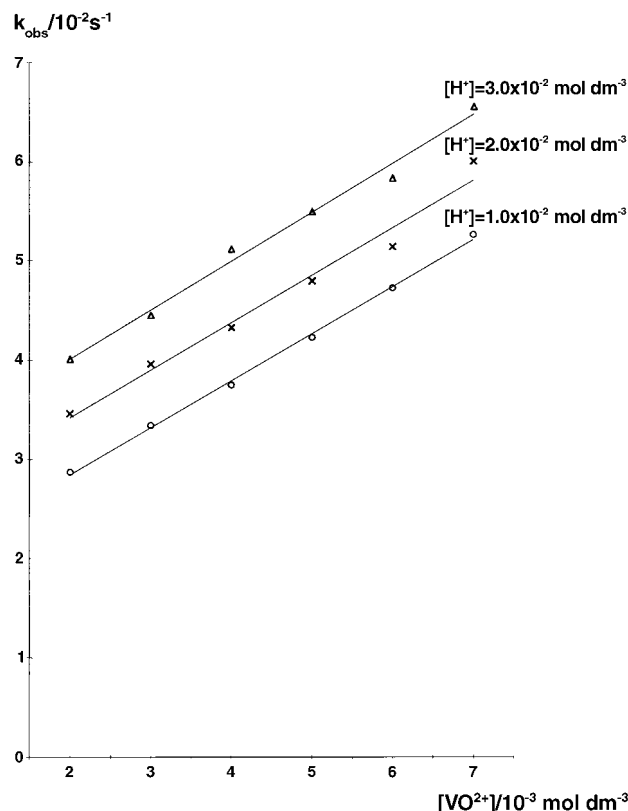

Figure 2. Observed rate constants as a function of the total concentration of oxovanadium(IV) ion at 25 °C and ionic strength 0.5 mol dm^{-3}. [Hacpt] = 2.0×10^{-4} mol dm^{-3}

tautomer and the enolate ion react with the oxometal ion (Scheme 1).

Applying the steady-state approximation to E$^-$ and assuming that VOHE^{2+} and VOE$^+$ are in equilibrium, the rate of complex formation can be expressed as

$$\begin{aligned}
v = &(k_1 k_a [VO^{2+}][HE] - k_{-1} k_{-a} [H^+][VOE^+] \\
&+ k_2 k_{-a} [H^+][VO^{2+}][HE] + k_1 k_2 [VO^{2+}]^2 [HE] \\
&- k_{-a} k_{-2} [H^+][VOHE^{2+}] \\
&- k_1 k_{-2} [VO^{2+}][VOHE^{2+}])/(k_{-a}[H^+] \\
&+ k_1 [VO^{2+}])
\end{aligned} \qquad (8)$$
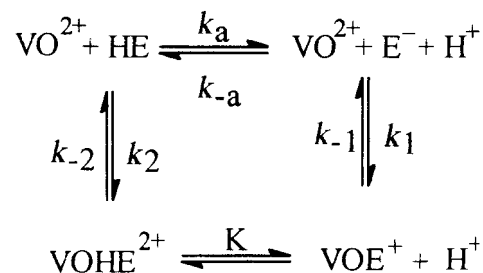
Scheme 1

Table 1. Observed and calculated rate constants for the reaction of VO^{2+} with 2-acetylcyclopentanone in aqueous solution[a]

$[H^+]/10^{-2}$ (mol dm^{-3})	$[VO^{2+}]/10^{-3}$ (mol dm^{-3})	278 K		283 K		288 K		293 K		298 K	
		$k_{obs}/10^{-2}$ (s^{-1})	$k_{cal}/10^{-2}$ (s^{-1})	$k_{obs}/10^{-2}$ (s^{-1})	$k_{cal}/10^{-2}$ (s^{-1})	$k_{obs}/10^{-2}$ (s^{-1})	$k_{cal}/10^{-2}$ (s^{-1})	$k_{obs}/10^{-2}$ (s^{-1})	$k_{cal}/10^{-2}$ (s^{-1})	$k_{obs}/10^{-2}$ (s^{-1})	$k_{cal}/10^{-2}$ (s^{-1})
1.0	2.0	1.11	0.94	1.18	1.23	1.70	1.56	2.52	2.16	2.87	2.47
1.0	3.0	1.31	1.18	1.65	1.53	1.90	1.94	2.80	2.66	3.34	3.05
1.0	4.0	1.50	1.42	1.98	1.83	2.46	2.32	3.31	3.17	3.75	3.63
1.0	5.0	1.73	1.66	2.10	2.13	2.60	2.70	3.80	3.68	4.23	4.22
1.0	6.0	2.00	1.91	2.52	2.43	3.28	3.08	4.15	4.19	4.73	4.80
1.0	7.0	2.20	2.15	2.83	2.73	3.53	3.46	4.70	4.70	5.27	5.38
2.0	2.0	1.14	1.18	1.63	1.54	2.14	1.97	2.78	2.72	3.46	3.11
2.0	3.0	1.20[b]	1.42[b]	1.80	1.84	2.30	2.35	3.41	3.23	3.96	3.69
2.0	4.0	1.66	1.66	2.13	2.14	2.83	2.73	3.76	3.74	4.33	4.27
2.0	5.0	1.85	1.90	2.52	2.44	2.94	3.11	4.11	4.24	4.80	4.86
2.0	6.0	2.20	2.14	2.77	2.74	3.58	3.49	4.70	4.75	5.15	5.44
2.0	7.0	2.30	2.39	3.01	3.04	3.90	3.87	5.25	5.26	6.01	6.02
3.0	2.0	1.33	1.42	1.88	1.86	2.43	2.38	3.42	3.28	4.01	3.75
3.0	3.0	1.58	1.66	2.02	2.16	2.61	2.76	3.76	3.79	4.45	4.33
3.0	4.0	1.85	1.90	2.42	2.46	2.93	3.14	4.26	4.30	5.12	4.91
3.0	5.0	2.10	2.14	2.77	2.76	3.56	3.52	4.60	4.81	5.50	5.50
3.0	6.0	2.20[b]	2.38[b]	2.92	3.06	3.60	3.90	5.20	5.32	5.84	6.08
3.0	7.0	2.61	2.62	3.25	3.35	4.20	4.28	5.80	5.83	6.56	6.66

[a] Ionic strength 0.5 mol dm^{-3}, [Hacpt] = 2.0×10^{-4} mol dm^{-3}. The relative deviation in the observed rate constants, k_{obs}, was always <4%.
[b] Values which were not used in the overall fitting.

Table 2. Equilibrium constants (K_{HL} and β), rate constants (k_1 and k_2) and activation parameters [$\Delta H\ddagger$ ($kJmol^{-1}$) and $\Delta S\ddagger$ (JK^{-1} mol^{-1})] in the formation of the oxovanadium(IV) monochelate of 2-acetylcyclopentanone

T (K)	$K_{HL}/10^{-8}$	$\beta/10^7$	$k_1/10^5$ (mol^{-1} dm^3 s^{-1})	k_2 (mol^{-1} dm^3 s^{-1})	RSS
278.15	1.70	7.75	1.80	2.39	4.09
283.15	1.66	7.90	2.62	2.99	3.34
288.15	1.64	8.00	3.14	3.79	3.99
293.15	1.61	8.08	4.70	5.08	3.19
298.15	1.58	8.20	5.43	5.83	2.69

$\Delta H_1\ddagger = +34 \pm 4$ kJ mol^{-1} $\Delta H_2\ddagger = +30 \pm 1$ kJ mol^{-1}
$\Delta S_1\ddagger = -13 \pm 4$ J K^{-1} mol^{-1} $\Delta S_2\ddagger = -130 \pm 4$ J K^{-1} mol^{-1}

Since $[VOHE^{2+}] = [VOE^+][H^+]/K$, Eqn. (9) is obtained for the observed rate constant:

$$k_{obs} = \frac{\begin{array}{c} k_1 k_a[VO^{2+}] + k_{-1}k_{-a}[H^+] + k_2 k_{-a}[H^+][VO^{2+}] \\ + k_1 k_2[VO^{2+}]^2 + k_{-a}k_{-2}[H^+]^2/K \\ + k_1 k_{-2}[VO^{2+}][H^+]/K \end{array}}{k_{-a}[H^+] + k_1[VO^{2+}]}$$

(9)

Considering that the k_{-a} pathway is diffusion controlled,[24] it is reasonable to assume that $k_{-a}[H^+] \gg k_1[VO^{2+}]$ and that the terms having k_{-a} in the numerator will be large compared with the other terms. Applying these approximations to Eqn. (9), Eqn. (10) is obtained for k_{obs}:

$$k_{obs} = k_2[VO^{2+}] + k_{-1} + \frac{k_{-2}[H^+]}{K}$$

(10)

Taking into account that

$$k_{-1} = \frac{k_1}{\beta}$$

(11)

$$k_{-2} = k_2 \frac{yK}{k_{ML}}$$

(12)

the following equation may be derived:

$$k_{obs} = k_2\left([VO^{2+}] + \frac{y}{\beta K_{HL}}[H^+]\right) + \frac{k_1}{\beta}$$

(13)

Equation (13) illustrates that k_{obs} values are independent of the initial concentration of Hacpt as was found experimentally. The observed rate constant from Eqn. (13) now contains only two unknown parameters, k_1 and k_2. In order to calculate k_1 and k_2, the equilibrium and kinetic data obtained at 25 °C were fitted to the above-mentioned equations. Using a NAG Fortran Library routine, values of k_1 and k_2 were determined at 25 °C (Table 2). The 'goodness of fit' as denoted by the corrected residual sum of squares (RSS), Eqn. (14),

clearly demonstrates that the data are well described by the Scheme 1.

$$RSS = 100\left[\frac{\sum W_t(k_{obs} - k_{calc})^2}{\sum W_t(k_{calc})^2}\right]^{1/2}$$

(14)

The observed linear dependence between k_{obs} and proton concentration shown in Eqn. (13) may be justified from data in Table 1. Accordingly, for a series of kinetic runs where $[H^+]$ is constant, a plot of k_{obs} against $[VO^{2+}]$ should be a straight line. This was verified in all cases with excellent correlation coefficients. The k_1 and k_2 values obtained from the slopes agree fairly well with those obtained from the overall fitting, as was expected.

In order to confirm the proposed mechanism and calculate the activation parameters associated with the k_1 and k_2 pathways, a full kinetic and thermodynamic study was carried out in the range of temperatures shown in Table 2. Consequently, the kinetic and equilibrium data obtained at every temperature were fitted to Eqn. (13).

The rate constants k_1 and k_2 obtained from the NAG fitting, which satisfy the Arrhenius law and Eyring equation, allowed us to determine the $\Delta H\ddagger$ and $\Delta S\ddagger$ corresponding to each process (Table 2).

The general order of reactivity of the various forms of β-diketones appears to be enolate ion > enol tautomer > keto tautomer.[2] In the case of Hacpt the keto tautomer is unreactive, which is probably due to the inability of the metal to stabilize the proposed precursor complex,[25] and complex formation occurs exclusively by reaction between the enol tautomer or enolate ion and the oxo-metal ion.

The rate of the reaction of VO^{2+} with the enol tautomer of Hacpt is considerably lower than might reasonably be expected on the basis of the Eigen–Wilkins mechanism.[26,27] According to this, the rate constant for complex formation would be given by $k_f = \frac{3}{4} k_s K_{os}$, where $\frac{3}{4}$ is a statistical factor representing the probability that a ligand will enter in a particular coordination site vacated by a solvent molecule, $k_s \approx 500$ s^{-1} is the oxovanadium(IV) rate of solvent exchange at an equatorial site[9] and K_{os} is the outer-sphere association

constant. This association constant for reaction of VO^{2+} with an uncharged ligand has been estimated to be $0.3 \, mol^{-1} \, dm^3$.[28] The reduction in rate compared with 'normal' reactions is, however, considerably less than the three orders of magnitude observed for reaction of Ni^{2+} with the enol tautomer of 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione.[29]

It is clear that the reaction rate between enolate and oxovanadium(IV) is considerably more rapid than would be predicted on the basis of the Eigen–Wilkins mechanism. In this case, in view of the fact that the enolate species is a charged ion, the Eigen–Fuoss equation[30,31] was used to calculate K_{os}. A value of 0.9 was used throughout and therefore $k_{E-W} \approx 300$.

Rate constants for solvent exchange at the equatorial site in $[VO(H_2O)_5]^{2+}$ are mostly in the range 10^2–10^3 s^{-1}, whereas axial substitutions proceed at rate constant of approximately[9] $10^9 \, s^{-1}$. This suggests that the larger values required for ligand substitution characterizing oxovanadium(IV)–enolate complexation arise through a rapid migration between axial and equatorial sites. This migration may be characterized by $k_{migration} > 10^3 \, s^{-1}$ for charged ligands. Such a mechanism involving axial to equatorial migration of the charged ligand appears to operate in this case.

A contribution to the mentioned rate enhancement [10^2 for oxovanadium(IV)–enolate complexation] may be attributed to the strong electron-donating capability of the enolate ion. The strong interaction between the ionized ligand and the metal centre will weaken metal–water bonds and favour a very fast water–ligand interchange.

The variation of the activation entropy may give a guide to the mechanism of water–ligand interchange. This activation parameter is commonly regarded as a measure of the 'increases in randomness' occurring on going from the initial state. Thus the negative value of $\Delta S_1\ddagger$, very close to zero (Table 2), suggests an intermediate situation between dissociative and associative interchanges, although under our conditions the presence of ClO_4^- ion and solvation effects may mask, by secondary effects, the meaning of this activation parameter.[32] However, the strongly negative value for the enol pathway ($\Delta S_2\ddagger$) clearly demonstrates an associative transition state, which involves association of the enol tautomer with the five-coordinate oxovanadium(IV) in a

rate-determining step leading to an intermediate of increased coordination number.

REFERENCES

1. Mehrota RC, Bohra R, Gaur DP. *Metal β-Diketonates and Allied Derivatives.* Academic Press: London, 1978.
2. Hynes MJ. *Rev. Inorg. Chem.* 1991; **11**: 21.
3. Blanco CA, Hynes MJ. *Can. J. Chem.* 1992; **70**: 2285.
4. Blanco CA. *New J. Chem.* 1995; **19**: 99.
5. Ebraheem KAK, Hamdi ST, Khalaf MN. *Can. J. Spectrosc.* 1981; **26**: 225.
6. Lee D, Kim CK, Lee BS, Lee I, Lee BC. *J. Comput. Chem.* 1997; **18**: 56.
7. Hoffman JM Jr., Rooney CS, Saari WS, Wai JS, Williams TM, Bamberger DL, Jones JH (Merck). Eur. Pat. Appl. EP 462 800, 1991.
8. German H (Dow Chemical). US Pat. 4 324 676, 1982.
9. Lincoln SF, Merbach AE. *Adv. Inorg. Chem.* 1995; **42**.
10. Vilas Boas L, Costa Pessoa J. In *Comprehensive Coordination Chemistry*, vol. 3, Wilkinson G (ed). Pergamon Press: Oxford, 1987.
11. Orioli P, Cini R. Donati D, Mangani S. *J. Am. Chem. Soc.* 1981; **103**: 4446.
12. Giorgi G, Cini R. *Inorg. Chim. Acta* 1988; **151**: 153.
13. Pederson R. *Diabetes* 1989; **38**: 1390.
14. Goldfine AB. *J. Clin. Endocrinol. Metab.* 1995; **89**: 331.
15. Zeltmann H, Morgan LO. *Inorg. Chem.* 1971; **20**: 2740).
16. Walker FA, Carlin RL, Rieger PH. *J. Chem. Phys.* 1966; **45**: 4181.
17. Carlin RL, Walker FA. *J. Am. Chem. Soc.* 1965; **87**: 2128.
18. Johansson A. *Analyst* 1970; **95**: 535.
19. Blanco CA, Hynes MJ. *J. Chim. Phys.* 1989; **86**: 1989.
20. Gans P, Sabatini A, Vacca A. *J. Chem. Soc., Dalton Trans.* 1985; 1195.
21. Job P. *Ann. Chim.* 1928; **9**: 13; Rose J. *Dynamic Physical Chemistry.* Pitman: London, 1961; 501.
22. Yoe JH, Jones AL. *Ind. Eng. Chem., Anal. Ed.* 1944; **16**: 11.
23. Ringbom A. *Formación de Complejos en Química Analítica.* Alhambra: Madrid, 1979.
24. Eigen M, Maeyer LC. In *Techniques of Organic Chemistry*, vol. VIII, part II, Friess SL, Lewis ES, Weissberger A. (eds). Interscience: New York, 1963.
25. Pearson RG, Anderson OP. *Inorg. Chem.* 1970; **9**: 39.
26. Wilkins RG, Eigen M. *Adv. Chem. Ser.* 1969; **49**: 55.
27. Wilkins RG. *Adv. Chem. Ser.* 1970; **3**: 408.
28. Rorabacher DB. *Inorg. Chem. Ser.* 1966; **5**: 1891.
29. Fay DP, Nichols AR, Sutin N. *Inorg. Chem.*, 1971; **10**: 2096.
30. Eigen M. *Z. Phys. Chem. (Frankfurt am Main)* 1954; **1**: 176.
31. Fuoss RM. *J. Am. Chem. Soc.* 1958; **80**: 5059.
32. Swaddle TW. *Coord. Chem. Rev.* 1974; **14**: 217.