EPR Study of Mixed VO_2^+ Chelate Complexes

R. LUNDQVIST,* A. PANFILOV, N. KALINICHENKO and I. MAROV

V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, USSR Academy of Sciences, Moscow B-334, USSR

The stepwise exchange reactions for VO^{2+} chelate complexes $\text{VOL}_2 + \text{HB} \rightleftharpoons \text{VOLB} + \text{HL}$ and $\text{VOLB} + \text{HB} \rightleftharpoons \text{VOB}_2 + \text{HL}$, where HL and HB are the chelating agents acetylacetone (HAA), thenoyltrifluoroacetone (HTTA), salicylaldoxime (HSAO), and 8-hydroxyquinoline (HOX) were investigated in toluene solutions using EPR. Stability constants were derived and it was found that the reactions had negligible ΔH and ΔS values (5–60 °C). It was also concluded that mixed complexes of the type $\text{VO}(\text{SAO})(\beta\text{-diketone})$ were remarkably unstable compared to unmixed VO chelate. The mechanism of the exchange processes was studied by kinetic measurements. Reaction rate constants and activation energies were calculated.

Previously the chelate complexing chemistry of tetravalent metalyl ions PaO^{2+} and HfO^{2+} was studied^{1–2} using solvent extraction. In order to extend the investigations with another metal and to complement the liquid-liquid distribution studies with an independent method, electron paramagnetic resonance EPR studies of VO^{2+} was carried out. EPR studies of ligand substitution of VO^{2+} have been reported for nonchelate complexing^{3,4} (Cl^- , SCN^-) and recently of chelating agents⁵ (thio-oxine and 1-phenyl-3-methyl-4-benzoylpyrazolone-5 in $\text{CHCl}_3 + 0.66 \text{ M CH}_3\text{COOH}$).

EXPERIMENTAL

Chemicals. Benzoylacetone (HBA, Merck *p.a.*), thenoyltrifluoroacetone (HTTA, Merck *p.a.*), and toluene (Reakhim, *p.a.*) were of highest purity whereas the other chemicals

were of ordinary quality. The chelate complexes of VOL_2 , where $\text{L} = \text{HBA}$, HTTA, 8-hydroxyquinoline (HOX), acetylacetone (HAA), or salicylaldoxime (HSAO), were prepared by mixing a water-alcohol solution of $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$ with an alcoholic solution of HL.⁶ The recovered VOL_2 was dried and stored in a cold place (especially important for $\text{VO}(\text{SAO})_2$ and $\text{VO}(\text{OX})_2$). The $\text{VO}(\text{OX})_2$ was poorly recovered and was very unstable [oxidation of $\text{V}(\text{IV})$ to $\text{V}(\text{V})$].

Apparatus. The EPR studies were carried out in the X-band microwave region with a Varian V4502 equipped with a variable temperature controller V4540, and the spectra were recorded with an X-Y-recorder PDP 4-002.

Procedure. The solution of the VO^{2+} chelates were mostly freshly prepared (one day in advance) because it was observed that precipitates of destroyed VO^{2+} complex were formed, after some days or weeks. Concentrations of $\text{V}(\text{IV})$ down to 10^{-5} M were used in order to optimize the reaction rates, although a very weak EPR signal was obtained. The kinetic measurements were made by first recording two solutions representing the initial and final state and then the spectra of the mixture. The solutions were thermostated ($\pm 3^\circ\text{C}$) and spectra were recorded repeatedly after mixing, using a syringe technique (1.3 ml, $\pm 1-2\%$).

Resolving the EPR spectra. The mixed spectrum was regarded as the sum of some pure EPR spectra j with individual parameters ΔH , g etc. A maximum of three components j were found for the investigated systems and the contribution of each spectra were numerically calculated by matrix solution using a small computer allowing an accuracy of about $\pm 5\%$.

EQUILIBRIA OF MIXED COMPLEXES

The stepwise exchange reactions of chelate ligands between a vanadyl(IV) chelate complex VOL_2 and a free undissociated chelating acid

* Permanent address: Department of Nuclear Chemistry, Chalmers University and Technology, S-402 20 Göteborg 5, Sweden.

Table 1. Stability constants for the stepwise ligand exchange of VO³⁺ chelates, VOL₃ + HB ⇌ VOLB + HL and VOLB + HB ⇌ VOB + HL. Experimental data for toluene solutions at different temperatures are given.

System	Temp. °C	[VOL ₃] _{init} × 10 ³	[VOB] ₃ _{init} × 10 ³	[HL] _{init} × 10 ³	[HB] _{init} × 10 ³	VOLB ₃ %	VOLB %	VOB ₃ %	K ₁	K ₂	β ₂
HL=acetyl- acetone	21	0.937	—	—	2.54	7.0	8.8	84.2	2.4	18.1	43.0
HB=salicyl- aldoxime	30	0.910	—	—	2.85	4.0	10.5	85.5	3.6	11.2	40.4
	60	—	0.718	3.80	—	21.5	15.0	61.5	2.5	38.4	95.0
	30	—	0.393	11.7	—	78.9	12.1	9.0	2.5	12.3	30.8
	30	0.538	—	21.6	4.72	44.3	7.1	48.7	0.9	36.7	31.4
	60	0.538	—	21.6	4.72	43.1	12.3	44.5	1.5	19.2	29.2
	100	0.538	—	21.6	4.72	45.1	12.2	42.7	1.4	18.5	26.5
								Mean ± σ	2.0 ± 0.8	22 ± 10	42 ± 22
HL=thenoyl- trifluoro- acetone	21	—	0.788	1.49	—	33	—	67	—	—	7.1
HB=salicyl- aldoxime	22	—	0.767	2.22	—	53	—	47	—	—	2.6
	21	—	0.757	6.69	—	85	—	15	—	—	3.1
	22	0.837	—	—	2.03	31	—	69	—	—	3.9
	3	0.522	—	9.12	4.62	68	—	32	—	—	2.3
	90	0.522	—	9.12	4.62	63	—	37	—	—	3.0
								Mean ± σ			3.7 ± 1.6
HL=acetyl- acetone	30	0.921	—	—	2.04	3.6	11.5	84.9	14.4	33.3	480
HB-oxine	30	0.804	—	—	0.937	30.9	33.5	35.6	9.6	9.4	89
	30	0.615	—	—	1.87	≤ 2.7	8.1	89.2	≥ 4.7	17.4	≥ 82
								Mean ± σ	9.6 ± 4.0	20.0 ± 10	(2.2 ± 1.9)10 ²

HB, $\text{VOL}_2 + \text{HB} \rightleftharpoons \text{VOLB} + \text{HL}$ and $\text{VOLB} + \text{HB} \rightleftharpoons \text{VOB}_2 + \text{HL}$, were studied. The reactions were investigated, starting with mixing $\text{VOL}_2 + \text{HB}$ as well as $\text{VOB}_2 + \text{HL}$. As can be seen from Table 1, where the initial conditions and the final percentages of the different VO²⁺ chelates are listed together with calculated stability constants, true equilibria were reached.

In the case of the reaction between oxine and acetylacetone it must be noted that the equilibria could only be studied from one direction, $\text{VO}(\text{AA})_2 + \text{HOX}$, because pure $\text{VO}(\text{OX})_2$ was found to be unstable under the conditions used. Even the mixtures of $\text{VO}(\text{AA})_2 + \text{HOX}$ were destroyed during a day, but the relative percentages of $\text{VO}(\text{AA})_2$, $\text{VO}(\text{OX})_2$, and $\text{VO}(\text{OX})(\text{AA})$ were appreciably constant in the time interval from about 10 min to 15 h after mixing.

During the exchange between ligands of β -diketones and salicylaldoxime the mixed VO²⁺ complex was formed in remarkably small concentration. However, under certain conditions (high reagent concentrations), the formation of mixed complexes could be followed kinetically soon after mixing. At equilibrium no $\text{VO}(\text{SAO})(\text{TTA})$ could be registered and only a small fraction of $\text{VO}(\text{SAO})(\text{AA})$ could be determined by refined calculation.

The temperature dependency of the equilibria was investigated by taking the EPR spectra at different temperatures of a mixture of $\text{VOB}_2 + \text{VOL}_2 + \text{HL} + \text{HB}$, in which the concentrations of VOL_2 and VOB_2 were set much lower than the concentrations of HL and HB, in order to obtain maximum change in the ratio $[\text{VOB}_2]/[\text{VOL}_2]$ and to increase the accuracy. It was found that the temperature dependency for the ligand exchange was too small, see Table 1, to be detected. It was also concluded that there was no dimerization of VOL_2 for at least up to 10^{-3} M.

KINETICS AND MECHANISMS OF LIGAND SUBSTITUTION

The unexpected low relative stability of the mixed complexes in equilibrated VO²⁺ solutions of β -diketones and salicylaldoxime raised the question of how the ligand exchange occurred. Therefore an investigation of the reaction mechanisms was undertaken. The following

Fig. 1. Kinetics of mixing toluene solutions of $\text{VO}(\text{AA})_2 + \text{HSAO}$ at 60°C . The EPR spectra of peak group 8 at chronologically increased times shows contribution from the mixed complex $\text{VO}(\text{AA})(\text{SAO})$ which has its maximal concentration soon after mixing. 1. Spectra of pure $\text{VO}(\text{AA})_2$. 2–14. Spectra within 1–7 min. $[\text{VO}(\text{AA})_2]_{\text{init}} = 0.281 \times 10^{-3} \text{ M}$, $[\text{HSAO}]_{\text{init}} = 0.412 \times 10^{-3} \text{ M}$. 15. Spectra of pure $\text{VO}(\text{SAO})_2$.

systems were analyzed: $\text{VO}(\text{SAO})_2 + \text{HAA}$, $\text{VO}(\text{AA})_2 + \text{HSAO}$, $\text{VO}(\text{SAO})_2 + \text{HTTA}$, and $\text{VO}(\text{TTA})_2 + \text{HSAO}$. Thus the reaction leading to equilibria was studied from both sides, (a) $\text{VOL}_2 + \text{HB}$ and (b) $\text{VOB}_2 + \text{HL}$.

a. The reaction $\text{VO}(\text{SAO})_2 + \beta$ -diketone was followed and from spectra analysis it was found that no mixed complex was formed. The rate with which the initial concentration of $\text{VO}(\text{SAO})_2$ decreased, was found to be proportional to the concentration of the initial concentrations of β -diketone and $\text{VO}(\text{SAO})_2$. This suggests that one molecule $\text{VO}(\text{SAO})_2$ reacts with one molecule β -diketone. The kinetic constant for the reaction k_1 is obtained from the relation

$$-\lim_{t \rightarrow 0} \frac{\partial [\text{VO}(\text{SAO})_2]}{\partial t} = k_1 [\text{VO}(\text{SAO})_2]_{\text{init}} [\beta\text{-diketone}]_{\text{init}}$$

Table 2. Kinetic constants k_1 and k_2 and activation energy values E_{A1} and E_{A2} for the reactions $\text{VOL}_2 + \text{HB} \rightarrow$ and $\text{VOLB} + \text{HB} \rightarrow$, respectively. Experimental conditions for toluene solutions are given.

System	Temp. °C	$[\text{VOL}_2]^{\text{init}}$ $\text{M} \times 10^3$	$[\text{HB}]^{\text{init}}$ $\text{M} \times 10^3$	$-\partial \% \text{VOL}_2 / \partial t$ $t \rightarrow 0, \text{min}^{-1}$	$\partial \% \text{VOB}_2 / \partial t$ $t \rightarrow 0, \text{min}^{-1}$	k_1 $\text{s}^{-1} \text{mol}^{-1}$	k_2 $\text{s}^{-1} \text{mol}^{-1}$
HL=acetyl- acetone	5	0.128	0.423	50	3.1	20	1.2
	5	0.281	0.412	36	1.7	14	0.7
	5	0.076	0.423	48	3.2	19	1.3
HB=salicyl- aldoxime	30	0.283	0.412	59	3.8	24	1.5
	30	0.0847	0.424	67	6.4	26	2.5
	60	0.281	0.412	77	6.2	31	2.5
	60	0.0847	0.424	71	21	28	8.3
$E_{A1} = 7.5 \pm 1.6 \text{ kJ mol}^{-1}; E_{A2} = 20.6 \pm 5.4 \text{ kJ mol}^{-1} \text{ K}^{-1}$							
HL=salicyl- aldoxime	5	0.393	11.66	17	—	0.25	—
	30	0.718	34.44	67	—	0.33	—
	30	0.718	11.66	29	—	0.42	—
HB=acetyl- acetone	60	0.718	3.80	12	—	0.53	—
	60	0.393	11.66	36	—	0.51	—
$E_{A1} = 10.1 \pm 1.5 \text{ kJ mol}^{-1}$							
HL=thenoyl trifluoro- acetone	5	0.620	4.12	42	17	1.7	0.67
	5	0.155	5.09	50	21	1.7	0.70
	5	0.375	5.12	45	23	1.5	0.76
	21	0.837	2.03	31	13	2.6	1.0
HB=salicyl- aldoxime	30	0.155	5.09	77	50	2.5	1.6
	30	0.176	2.88	63	33	3.6	1.9
$E_{A1} = 17.4 \pm 3.5 \text{ kJ mol}^{-1}; E_{A2} = 24.0 \pm 3.4 \text{ kJ mol}^{-1} \text{ K}^{-1}$							
HL=salicyl aldoxime	5	0.393	9.00	6.4	—	0.12	—
	21	0.852	3.97	5.2	—	0.22	—
HB=thenoyl trifluoro- acetone	21	0.757	6.69	10	—	0.25	—
	60	0.393	9.00	42	—	0.78	—
$E_{A1} = 26.0 \pm 1.2 \text{ kJ mol}^{-1}$							

The reaction product could not be recorded, as it instantly reacts further to the final product $\text{VO}(\beta\text{-diketone})_2$.

b. The second case, $\text{VOB}_2 + \text{HL}$, was consequently studied with the systems $\text{VO}(\beta\text{-diketone})_2 + \text{HSAO}$. The EPR spectra (Fig. 1) of such mixtures showed a contribution from a third transition complex which was quickly built up to its maximum concentration (within a minute) and then decreased to near zero. The position of this transition complex lay between that of $\text{VO}(\beta\text{-diketone})_2$ and $\text{VO}(\text{SAO})_2$, which suggested that the composition was $\text{VO}(\beta\text{-diketone})(\text{SAO})$. The initial step leading to the production of $\text{VO}(\beta\text{-diketone})(\text{SAO})$ was determined to be $\text{VO}(\beta\text{-diketone})_2 + \text{HSAO} \rightarrow \text{VO}(\beta\text{-diketone})(\text{SAO})$, in analogy with the case (a) above. The consecutive reaction $\text{VO}(\beta\text{-diketone})(\text{SAO}) + \text{HSAO} \rightarrow$, with the rate constant k_2 , was studied by its product $\text{VO}(\text{SAO})_2$. If the consecutive reactions $\text{VO}(\beta\text{-diketone})_2 \rightarrow \text{VO}(\beta\text{-diketone})(\text{SAO}) \rightarrow \text{VO}(\text{SAO})_2$

can be regarded as initially irreversible then k_2 can be obtained from the relation $\partial \% [\text{VO}(\text{SAO})_2/100]/\partial t = k_2[\text{HSAO}]^{\text{init}}$. The reaction constants k_1 and k_2 for different temperatures are collected in Table 2.

In order to derive the Arrhenius activation energies, the kinetic constants for the rate-determining steps were determined at various temperatures between ± 0 and 60°C (Table 2).

DISCUSSION

The direct measurements of the relative complexing power toward VO^{2+} of the chelating agents, made it possible to arrange them in the following order of increasing complexing ability: HAA, HTTA, HSAO, and HOX. This order may also be expected from the stability constants.⁷ For bivalent ions like Mn^{2+} , Zn^{2+} , and Ni^{2+} the same order of

complexing ability is reported for complexing reactions in aqueous media. No direct measurements in organic media seem to have been reported.

From the stability constants obtained (Table 1) it is possible to calculate the stability constant for the reaction $\text{VO}(\text{AA})_2 + 2\text{HTTA} \rightleftharpoons \text{VO}(\text{TТА})_2 + 2\text{HAA}$ explicitly to $\log \beta_2 = 1.1 \pm 0.4$. This reaction could only roughly be studied directly by the method used, because of the too small differences in EPR spectra of the two similar chelates, giving an estimate of the overall stability constant of $\log \beta_2 = 1.2 \pm 0.1$.

The negligible temperature influence on the equilibrium between different VO²⁺ chelates in the toluene solution is expected as the number of molecules is constant, *i.e.*, the ΔS term is small. The ΔH term is probably also small as the bonding energies of the different chelates

are of comparable strength and as no interaction with the solvent molecules is expected (especially for HSAO-HTTA).

The stability of the mixed VO²⁺ complexes of β -diketones and salicylaldoxime was significantly lower than is expected on statistical grounds and it was also low compared with that of acetylacetone and oxine and of thio-oxine and 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5.⁵ The reason for this may be explained by assuming some sterical hindrance in the formation of the mixed complex. Such hindrance could be the result if the oxygen on the donor nitrogen of salicylaldoxime also participated (through H-bonding) in the bonding of VO²⁺.

The reaction rates for the substitution reactions studied might be related to the ratio of complexing power of the free and bound chelating agent. The exchange of HAA in $\text{VO}(\text{AA})_2$ with HSAO is faster than the corresponding exchange of HTTA in $\text{VO}(\text{TТА})_2$ with HSAO, *i.e.* $k_1[\text{VO}(\text{AA})_2 + \text{HSAO}] > k_1[\text{VO}(\text{TТА})_2 + \text{HSAO}]$. However, by similar comparison of $k_1[\text{VO}(\text{SAO})_2 + \text{HTTA}]$ and $k_1[\text{VO}(\text{SAO})_2 + \text{HAA}]$ it is suggested that HAA gives weaker complexes than HTTA with VO²⁺ only at higher temperatures than 30 °C. It was not possible to compare HSAO and HAA, *i.e.* $k_2[\text{VO}(\text{AA})_2 + \text{HSAO}]$ against $k_2[\text{VO}(\text{SAO})_2 + \text{HAA}]$ and $k_2[\text{VO}(\text{TТА})_2 + \text{HSAO}]$ against $k_2[\text{VO}(\text{SAO})_2 + \text{HTTA}]$, as the reaction constants $k_2[\text{VO}(\text{SAO})_2 + \beta\text{-diketone}]$ could not be measured. It is also possible to check some of the obtained rate constants by calculating already obtained stability constants. Thus for the reaction $\text{VO}(\text{AA})(\text{SAO}) + \text{HSAO} \rightleftharpoons \text{VO}(\text{SAO})_2 + \text{HAA}$, the ratio between the forward and backward rate reactions obtained at 30 °C (see Table 2 and Fig. 2) is $10^{0.32 \pm 0.08} 10^{-0.44 \pm 0.02} = 10^{0.76 \pm 0.10}$ which is of the same order as the previously calculated value of the stability constant $k_2 = 10^{1.3 \pm 0.4}$. It should, however, be emphasized that the value of the forward reaction is more uncertain than is reflected by the standard deviation only (experimental difficulties). For the analogous reaction $\text{VO}(\text{TТА})(\text{SAO}) + \text{HSAO} \rightleftharpoons \text{VO}(\text{SAO})_2 + \text{HAA}$ the ratio between the rate constants is $10^{0.21 \pm 0.04} / 10^{-0.44 \pm 0.02} = 10^{0.65 \pm 0.06}$. Here the stability constant k_2 is not known but might be estimated from the observed overall stability constant $\beta_2 = 10^{0.8}$. Because of the very small

Fig. 2. The rate constants k_1 and k_2 for the reactions $\text{VO}(\text{AA})_2 + \text{HB} \rightarrow$ and $\text{VO}(\text{TTA})_2 + \text{HB} \rightarrow$ as a function of the temperature.

System	Rate constant
■ $\text{VO}(\text{SAO})_2 + \text{HAA}$	k_1
△ $\text{VO}(\text{SAO})_2 + \text{HTTA}$	k_1
□ $\text{VO}(\text{TТА})_2 + \text{HSAO}$	k_1
○ $\text{VO}(\text{TТА})_2 + \text{HSAO}$	k_2
▲ $\text{VO}(\text{AA})_2 + \text{HSAO}$	k_1
● $\text{VO}(\text{AA})_2 + \text{HSAO}$	k_2

stability of the mixed complex it should follow that $k_2 \leq \beta_1$.

The intermediate complexes formed during the reactions of mixing $\text{VO}(\text{SAO})_2$ with β -diketones, are not observed as they rapidly undergo further reactions to final products. The reaction rate k_2 for the system $\text{VO}(\text{SAO})_2 + \beta$ -diketone could therefore not be directly determined but can be estimated as it should be comparable to (or somewhat less than) k_1 for $\text{VO}(\beta\text{-diketone})_2 + \text{HSAO}$. Such an estimation makes it probable that $k_2 \geq k_1$ for the reaction $\text{VO}(\text{SAO})_2 + \beta$ -diketone and hence no mixed complex will be built up.

The measured activation energy for the reactions may be tested against each other by deriving ΔH for the two equilibrium reactions above. Thus ΔH for the forward and backward reactions of $\text{VO}(\text{TTA})(\text{SAO}) + \text{HSAO} \rightleftharpoons \text{VO}(\text{SAO})_2 + \text{HTTA}$ is $24.0 \pm 3.4 - 26.0 \pm 1.2 = -2 \pm 4.6 \text{ kJ mol}^{-1} \text{ degree}^{-1}$. Such a small ΔH value is expected from the observed negligible temperature influence of similar reactions measured directly. In the same way ΔH for $\text{VO}(\text{AA})(\text{SAO}) + \text{HSAO} \rightleftharpoons \text{VO}(\text{SAO})_2 + \text{HAA}$ is $20.6 \pm 5.4 - 10.1 \pm 1.5 = 10.5 \pm 6.9 \text{ kJ mol}^{-1} \text{ degree}^{-1}$. This ΔH value is, however, too large to be in accordance with the negligible temperature influence, but as was stated above the value of $k_1[\text{VO}(\text{AA})_2 + \text{HSAO}]$ was very uncertain. If the upper point in Fig. 2 is excluded then E_{A_2} is 13.5 ± 4.9 which solves the dilemma.

Finally, as the present investigation of ligand exchange reactions was made using the EPR method only, another independent method should be used in order to make more detailed and definite conclusions. In particular the insensitivity of the EPR signal of VO^{2+} chelates of similar chelating agents is a drawback. The method of liquid-liquid distribution seems to have certain advantages in this respect and studies of various metals, including VO^{2+} , is planned.

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