A Kinetic Study of the Ligand Exchange between Bis(acetylacetonato)-oxovanadium(IV) and Acetylacetone[^{14}C] in Organic Solvents

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(Received July 19, 1977)

Square pyramidal [VO(acac)$_2$] (acac, acetylacetonate) undergoes ligand exchange with Hacac[^{14}C] in 1,2-dichloroethane (DCE) without side reactions. The rate is expressed by $R=k_2$[complex][Hacac], where [Hacac] stands for the concentration of free acetylacetone in enol form. The second order rate constant and activation parameters are 0.071 M^{-1} s^{-1} (M=mol dm^{-3}) at −33 °C, $\Delta H^{*}=(46.7\pm1.7)$ kJ mol^{-1} and $\Delta S^{*}=(-61.9\pm8.4)$ J·mol^{-1} K^{-1}. The deuterium isotope effect is $k_H/k_D=1.3\pm0.2$. It appears as if the free Hacac first interacts with the complex as unidentate and the chelation of the unidentate accompanied by proton transfer to the leaving $acac^-$ is the rate determining step. On addition of a donor solvent the exchange rate decreases, and the extent is correlated with Gutmann's donor number. The k_2, ΔH^{*} and ΔS^{*} in 0.06 M dimethyl sulfoxide (DMSO) in DCE are 0.0038 M^{-1} s^{-1} at −33 °C, (71.9±10.0) kJ mol^{-1}, and (−4±40) J mol^{-1} K^{-1}, respectively. The DMSO molecule seems to interact with the intermediate species with a unidentate Hacac and inhibits the associative rate determining step.

Vanadium(IV) gives characteristic square pyramidal complexes with an oxo-anion on the apical position. Interaction of various species including the solvent molecules with the complex has been studied by visible and ultraviolet (UV) absorption spectrometry[1] and correlated with various parameters of the interacting molecule such as donor number.[2] ESR studies in organic solvents disclosed that the interaction at the apical site was a very rapid phenomenon and the rate was mostly diffusion controlled.[3] Reuben and Fiat, and Wüthrich and Connick found two rates for the exchange of water between $[VO(H_2O)_5]^{2+}$ and the solvent by NMR spectroscopy with ^{17}O, and assigned them to the exchanges at the apical ($\approx10^{11}$ s^{-1}) and the basal site (5.2×10^2 s^{-1}).[4] Substitution reactions at the basal site have been studied by absorption and PMR spectrometry by use of bidentate ligands such as glycinate[5] and malonate,[6] and found to be much slower than those at the apical site.

As an extension of our studies of isotopic exchange of various acetylacetonato complexes of main group and transition elements,[7] we have found that the exchange between bis(acetylacetonato)oxovanadium(IV), [VO(acac)$_2$], and acetylacetone[^{14}C] is measurable in 1,2-dichloroethane at a temperature below −20 °C, and the rate decreases on addition of donor solvents. This paper deals with the kinetic studies, and presents a plausible reaction mechanism.

Experimental

Materials. VO(acac)$_2$ was prepared by Rowe and Jones' method[8] and recrystallized from benzene. The purity was examined by elemental analysis of carbon and hydrogen, and visible and ultraviolet absorption spectra. Acetylacetone[^{14}C] was synthesized by the known method.[9]

1,2-Dichloroethane (DCE) was washed with potassium hydroxide solution and water, dried with calcium chloride, fractionally distilled through an effective column, and the distillate dried with Molecular Sieve 4A. Acetonitrile (AN) was dried with calcium chloride and distilled over phosphorus pentoxide. Nitromethane (NM) was distilled, frozen at −40 °C and distilled over Molecular Sieve 4A under a reduced pressure. Dimethyl sulfoxide (DMSO) was dried with activated alumina and distilled under a reduced pressure. *N,N*-Dimethylformamide (DMF) was dried with anhydrous copper(II) sulfate and distilled under a reduced pressure. Methanol was distilled and dried with Molecular Sieve 3A. 1,1,2,2-Tetrachloroethane (TCE) was shaken with several portions of concentrated sulfuric acid until the acid layer remained colorless, washed with water and distilled under a reduced pressure. The purity of the purified solvents was examined by gas chromatography, and the water content determined by Karl-Fischer titration.

Kinetic Runs. The complex solution (≈0.02 M, M=mol dm^{-3}; 5 to 8 cm^3) and acetylacetone (Hacac) labelled with ^{14}C (*ca.* 0.2 μCi) in DCE (10^{-2}—10^{-1} M, 2 to 5 cm^3) were introduced into each of the two bottoms of a co-necked flask with a glass stopper. It was placed in a thermostat, and both solutions were mixed. One cubic centimeter portions were pipetted out at appropriate time intervals, and poured into hexane (10 cm^3) in a test tube chilled at −55 to −58 °C within 8 s. The tubes were shaken and placed in a mixture of dry ice and methanol (−77 °C) to freeze DCE. The curd was filtered with filter paper at room temperature to leave crystalline VO(acac)$_2$, which was washed with hexane and dried *in vacuo*. For kinetic runs at −39.8 °C, 10% TCE (v/v) was added to the DCE solvent to prevent the freezing of DCE. Donor solvents (NM, AN, DMF, and DMSO) were added to DCE prior to the dissolution of the complex. When the reaction mixture contained NM and AN, 10% diethyl ether (v/v) was added to hexane.

The purified DCE contained *ca.* 3×10^{-3} M water, which floated mostly as ice on the surface of the reaction mixture in the thermostat. Hence the water content of the reaction mixture should be much less than 0.03 M but remained unknown.

The separated VO(acac)$_2$ was dissolved in AN (3 cm^3) and the absorption coefficient measured at 394 nm ($\varepsilon_{max}=77$ cm^{-1} M^{-1}). A 1 cm^3 portion was dissolved in toluene containing 0.01% (w/v) 1,4-bis(5-phenyl-2-oxazolyl)benzene (POPOP) and 0.4% (w/v) *p*-terphenyl (14 cm^3) and the counting rate measured by liquid scintillation counting.

Apparatus. The visible and UV absorption spectra were recorded with a Hitachi 323 Spectrometer. The counting rate due to ^{14}C was recorded with a Nuclear Chicago Unilux IIA Counter. A Haake KT 33 Thermostat was used for keeping the temperature the range from −40 to −20 °C (±0.3 °C).

Calculation of the Exchange Rate. The specific counting

rate of the recovered $[VO(acac)_2]$ was known from the recorded counting rate and the weight of $[VO(acac)_2]$, which was calculated from the extinction coefficient of the AN solution. McKay's formula was used to find the rate of exchange.

$$R = -2.3[2ab/(2a+b)][\log(1-F)]/t. \quad (1)$$

Where a and b stand for the concentrations of the complex and the free ligand, respectively. The t is the lapse of time and F is the fraction of reaction expressed by $(x_t-x_0)/(x_\infty-x_0)$. The x's are the specific counting rates at time 0, i, and infinity, respectively. The x_∞ is known by both calculation and experiment. Acetylacetone is in tautomeric equilibrium between keto and enol form, and the interchange rate (*ca.* 10^{-5} s^{-1} at 25 °C[10]) is smaller than the present ligand exchange. The percentages of enol form are 81.4[11] and 80 in itself and in DCE, respectively at 25 °C. Since the Hacac was kept at room temperature for a long time before use, dissolved and cooled immediately before mixing, 0.80 time of the concentration of Hacac was taken as b. (Preferential participation of the enol form in the exchange was also reported for the system $[Ti(acac)_3]^+$ *vs.* Hacac in AN.[12]) The calculated x_∞ value on this basis coincided with the experimental value. Hence the participation of the keto-form in the ligand exchange reaction was not taken into consideration.

Results

Absorption Spectrum. Selbin measured the visible absorption spectrum of $[VO(acac)_2]$ in various solvents, and found that the difference in wave numbers ($\Delta\nu$) between the two absorption peaks in 600—800 nm region was characteristic of the solvents.[1] Gutmann found a good correlation[13] between $\Delta\nu$ and the donor number[2] of the solvent. We have measured the visible absorption spectrum of $VO(acac)_2$ in Hacac and found two peaks at 13980 and 17120 cm^{-1} with ε values 39 and 33 cm^{-1} M^{-1}, respectively. From the difference in wave numbers of these peaks the donor number of Hacac can be calculated to be 20 at room temperature.

Gutmann measured the absorption spectra of $VO(acac)_2$ in dichloromethane containing varying amounts of organic solvents and calculated the formation constants of one to one adducts between $VO(acac)_2$ and the solvent molecules.[14] We have applied this method to the present system and obtained the formation constants of $[VO(acac)_2 \cdot Hacac]$ to be 0.14 and 0.19 M^{-1} at 25 and −33 °C, respectively, the corresponding $\Delta G°$ values being 4.8 and 3.3 kJ mol^{-1}.

In the reaction mixtures additivity law in the UV absorption spectrum was obeyed between $[VO(acac)_2]$ and Hacac. Since the concentrations of both the complex and Hacac were very low, the concentration of the adduct should be too small to be reflected in the absorption spectrum.

Kinetic Data. The visible and UV absorption spectra of the reaction mixture in DCE remained unchanged during the course of the kinetic runs. McKay plots of the runs gave straight lines with very small intercepts, which seemed to be separation-induced. Hence it was verified that the ligand exchange reaction took place exclusively throughout the reaction time. The gradients were determined by the least square method, and the experimental errors in R values calculated on 70% confidence level to be *ca.* 10%. McKay plots were linear in the presence of donor solvents, too.

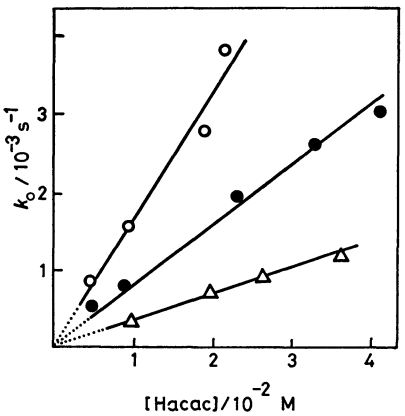

Fig. 1. Dependence of the observed first-order rate constants upon the concentration of free Hacac in enol form in DCE.
-○-: −25.0, -●-: −33.0, -△-: −39.8 °C.

The R was linearly dependent on a in the range between 0.0127 and 0.030 M and the first order rate constant k_0 ($=R/a$) can be the measure of rate of the present ligand exchange. Figure 1 indicates that k_0 increases linearly with increase in b, and the intercept is zero within experimental error. Hence Eq. 2 holds for the range of b from 0.0046 to 0.041 M.

$$R = k_0 a = k_2 ab. \quad (2)$$

The activation parameters obtained from k_2 values at −39.8, −33.0, and −25 °C are listed in Table 1.

Table 1. Rate constants and activation parameters for the substitution reaction of oxovanadium(IV) complexes

System	Method	t/°C	k/s^{-1}	ΔH^*/kJ mol^{-1}	ΔS^*/J $mol^{-1}K^{-1}$
$[VO(H_2O)_5]^{2+}$—H_2O in H_2O[a]	^{17}O NMR	25	520	57.2	−6.3
(same)[b]	^{17}O NMR	25	$\approx 10^{11}$	—	—
$[VO(H_2O)_5]^{2+}$—gly^- in water { formation[c]	Stopped flow	25	1300 M^{-1}	50.2	−16.7
{ dissoc.	Calcd	25	460	54.8	−10.0
$[VO(gly)(H_2O)_4]^+$ in water[d]	T-jump	25	37	—	—
(chelation)	Stopped flow	25	35	—	—
$[VO(acac)_2]$—Hacac* in DCE[e]	Label	−33	0.071 M^{-1}	47.6±1.7	−61.9±8.4
$[VO(acac)_2]$ in DCE+DMSO[f]	Label	−33	0.0038 M^{-1}	71.9±10	−4±40

a) Substitution at the basal site. b) At the apical site; both Ref. 4. c) Ref. 5. d) Ref. 18. e) Present study f) Present study in 0.0643 M DMSO.

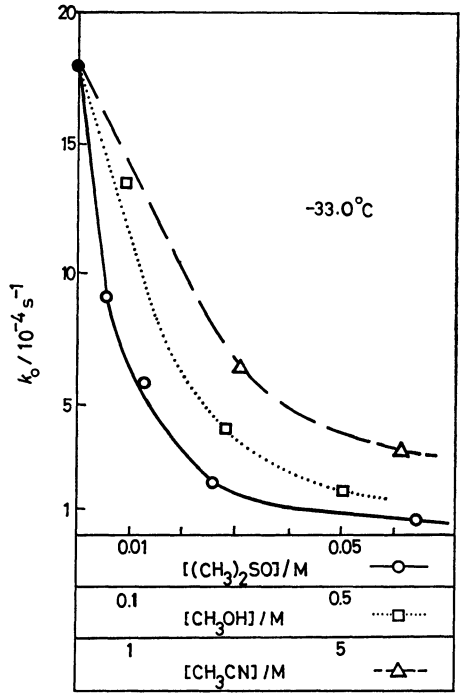

Fig. 2. Decrease in rate of the isotopic exchange on addition of donor solvents to the DCE solution.
—○—: DMSO, ···□···: methanol, ---△---: AN, at −33.0 °C, [Hacac]=0.0222 (—○—, ···□···), 0.0218 M (---△---).

The ligand exchange becomes slower on addition of donor solvents to the DCE solution (Fig. 2). The extent of retardation increases in the following sequence (Eq. 3). (Gutmann's donor numbers are shown in the parentheses).

$$\underset{\text{NM}}{\underset{(2.7)}{CH_3NO_2}} < \underset{\text{AN}}{\underset{(14.1)}{CH_3CN}} < \underset{\text{MeOH}}{\underset{(19)}{CH_3OH}} < \underset{\text{DMF}}{\underset{(26.6)}{HCON(CH_3)_2}} < \underset{\text{DMSO}}{\underset{(29.8)}{(CH_3)_2SO}} \quad (3)$$

NM gave only a negligible effect. The extent of retardation by all the other donor solvents increased with increase in their concentrations in DCE. The dependence of k_0 upon b was similar to Eq. 2 in DCE containing DMSO as indicated in Fig. 3. The k_2 and activation parameters in 0.0643 M DMSO in DCE are shown in Table 1.

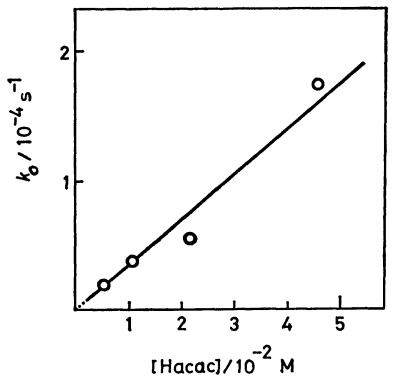

Fig. 3. Dependence of the first-order rate constant upon the concentration of free Hacac in enol form in DCE containing DMSO. At −33.0 °C, [DMSO]=0.0643 M.

Acid and base catalysis were not examined, because trichloroacetic and *m*-toluic acid caused rapid decomposition of [VO(acac)$_2$], and pyridine hindered the separation of the complex in the reaction mixture.

The deuterium isotope effect was measured in a system [VO(acac[^{14}C])$_2$] *vs.* Hacac[^2H] to find the ratio $k_H/k_D=1.3\pm0.2$ at −33 °C in DCE.

Discussion

The basal and the apical site of a square pyramidal structure are not equivalent to each other, and the known rates of substitution at these two sites are different from each other. All the known data support that the substitutions at the apical and the basal site take place with rate constants $>$ *ca.* 10^7,[3,4,15] and 10^2—10^3 s^{-1},[4-6,15,16] respectively.

Since the absorption spectra of the reaction mixtures remained unchanged, no other reactions than isotopic exchange have taken place. The influence of donor solvents is characteristic, and the reaction mechanism is discussed separately in their absence and presence.

In Dichloroethane. We have considered that the interaction between [VO(acac)$_2$] and Hacac reflected in the visible absorption spectra must be due to the addition of the free ligand at the basal position of [VO(acac)$_2$] to give *cis*-[VO(acac)$_2$(Hacac)].[17] The interaction at the basal site can involve either a direct addition or an intramolecular rearrangement, in which the free ligand first associated at the apical site rearranges to the basal site. In either case substitutions at the basal site must proceed much faster than the present isotopic exchange. Hence we consider that the exchange would proceed through the adduct, as shown in Eq. 4.

$$[VO(acac)_2] + Hacac^* \overset{K_L}{\rightleftharpoons} cis[VO(acac)_2(Hacac^*)] \quad (4)$$

$$cis[VO(acac)_2(Hacac^*)] \xrightarrow{k_{ex}} cis[VO(acac^*)_2(Hacac)]. \quad (5)$$

Thus the observed rate constant k_0 should be expressed by

$$k_0 = R/a = k_2 b = k_{ex}K_L b, \quad (6)$$

and the k_{ex} values are calculated to be 0.37 and 63 s^{-1} at −33 and 25 °C, respectively.

For the exchange of acac$^-$ to be completed, the reaction of Eq. 5 should involve two steps, *i.e.* transfer of a proton from the incoming Hacac to the coordinated acac$^-$, and the following chelation of the deprotonated unidentate ligand. The calculated k_{ex} (63 s^{-1}) at 25 °C is similar to that of the rate of chelation of unidentate glycinate in water[18] (Table 1). If the proton transfer itself were the rate determining step, isotope effect should be significant between Hacac and Dacac. Experiments gave a ratio $k_H/k_D=1.3\pm0.2$. Decisive conclusion is difficult because of the large experimental error, but the proton transfer does not seem to be an

independent rate determining step. Chelation associated with the proton transfer would be responsible in determining the k_{ex}.

The $\Delta H^{\ddagger}$ value for the overall k_2 in DCE is rather small, and the $\Delta S^{\ddagger}$ is large in minus. These suggest an associative mechanism at the rate determining step. When the incoming Hacac at the basal site undergoes chelation to eliminate the old ligand, associative attack by the free end upon the old V–O bond, which is in consonance with the proton transfer, would be responsible in determining the rate (Fig. 4).

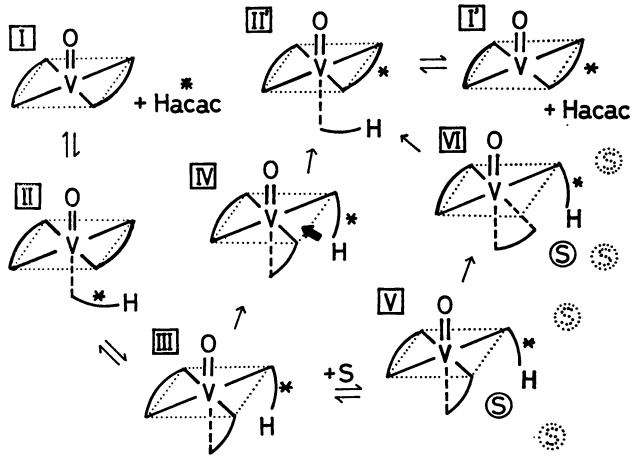

Fig. 4. Plausible reaction mechanism of the ligand exchange in DCE in the absence and the presence of donor solvents. S, donor solvent molecule; arc-like curves, acac$^-$; *, ^{14}C-labelled ligands; thick broken line, weak interaction.

Solvent Effect. In the presence of donor solvents the rate of exchange decreases. The extent is better correlated with Gutmann's donor number than with other parameters such as dielectric constant and dipole moment. Hence a direct interaction between the complex and the donor solvent should be taken into consideration. The kinetics were closely studied with DMSO as a model. The interaction can be understood in two ways: one is to reckon the competition between DMSO and free Hacac towards the coordination site of the complex as responsible, and presumes no difference in the actual route of isotopic exchange; the other is to anticipate a different mechanism in the presence of DMSO.

If the exchange proceeded through the same route as Eqs. 4 and 5, and DMSO molecule behaved as merely a rival of Hacac for the coordination site, the kinetic formula should be modified as Eq. 7, where K_S stands for the formation constant of the adduct [VO(acac)$_2$(DMSO)],

$$k_0 = k_2 b = k_{ex} K_L b/(1+K_S[S]), \qquad (7)$$

where [S] stands for the concentration of donor solvent. If this were valid, the plot of $1/k_2$ *vs.* [S] should give a straight line. However, the diagram is concave upwards. The activation parameters in the presence and the absence of DMSO differ significantly as shown in Table 1. Hence we have to consider that the contribution of competition should be small, not necessarily be ignored, and a different mechanism should be operating in the presence of donor solvent.

The large $\Delta H^{\ddagger}$ and almost zero $\Delta S^{\ddagger}$ in the presence of DMSO suggest that the exchange would proceed *via* a dissociative mechanism. If DMSO molecules interact with intermediate III in Fig. 4 to give an outer-sphere coordination (V), the nucleophilic attack of the free end of unidentate Hacac upon the V–O bond of the leaving acac$^-$ would be disturbed, so that the associative mechanism would not function any more. Hence a dissociative cleavage of the V–O bond of the leaving acac$^-$, which is accompanied by the proton transfer from the incoming Hacac, would become responsible for the exchange (VI in Fig. 4). (A dissociative mechanism could operate on the adduct [VO(acac)$_2$(DMSO)], but such a route would operate independently of the free Hacac concentration to bring about an intercept on Fig. 3. Absence of intercept on Fig. 3 excludes such a route.) Thus we can conclude that the main role of a donor solvent molecule should be an outer sphere coordination to the intermediate, which hinders the progress of associative rate-determining step of the exchange. Formation of an inactive adduct as [VO(acac)$_2$(DMSO)] would give only a minor contribution, if not necessarily nothing.

Haake and Pfeiffer introduced a new parameter, number of solvent participation, n.[19] This figure indicates the number of solvent molecules which interact with the substrate complex to inhibit the attack of a nucleophilic reagent upon the substrate. The n values were measured in the present system to be 1.6, 0.6, and 1 to 2 (depending on the concentration of methanol), for DMSO, AN and methanol in DCE, respectively. The non-integral figures reflect the complexicity with which the donor solvent molecules interact with the substrate. They may compete with Hacac in the formation of II (Fig. 4), and more than one molecule can interact with III to give V. Hence the n values do not seem to contradict our reaction mechanism.

The authors thank the Ministry of Education for financial support.

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