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Kinetics and Mechanism of Ligand Isotopic Exchange of Tris(acetylacetonato)vanadium(III) in Acetylacetone and in Organic Solvents

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Tris(acetylacetonato)vanadium(III) undergoes ligand exchange in acetylacetone (Hacac) at 25–40 °C without side reactions. The exchange rate is expressed by rate = $(k_a + k_b[H_2O])$[complex] ([complex] ≈ 0.005 M, $[H_2O]$ = 0.01–0.2 M; M = mol dm^{-3}); $k_a = (1.36 \pm 0.12) \times 10^{-4}$ s^{-1} and $k_b = (6.6 \pm 1.5) \times 10^{-4}$ M^{-1} s^{-1} at 25 °C. The ΔH^* and ΔS^* are 17.5 ± 0.4 and 18.0 ± 1.3 kcal mol^{-1} and −17.5 ± 1.3 and −12.6 ± 1.3 cal K^{-1} mol^{-1}, respectively (cal = 4.18 J). No deuterium isotope effect was observed on the rate. Linear plot of k_0 vs. the concentration of free Hacac in acetonitrile and in neat Hacac suggests the predominant participation of the enol tautomer in the exchange. The rate-determining step seems to correspond to the formation of an intermediate containing a one-ended $acac^-$ and an Hacac (enol) or a water molecule for the k_a or k_b path, respectively, by the associative mechanism. The rate of exchange in dimethyl sulfoxide, acetonitrile, chloroform, methanol, and ethanol increased in this sequence by a factor of 10^3. The acceptor number of these solvents appears to be responsible for the different rates of exchange.

Introduction

Very little information is available concerning ligand substitution reaction of tervalent vanadium complexes. Only the reactions of $[V(H_2O)_6]^{3+}$ and $[V(Me_2SO)_6]^{3+}$ (Me_2SO = dimethyl sulfoxide) with unidentate ligands have been published,[2-7] and an associative mechanism is suggested.[2,4,7] Recently, the rate of ligand exchange of tris(acetylacetonato)vanadium(III) in $CDCl_3$ has been reported by NMR spectroscopy, but no definite mechanism has been proposed.[8]

On extending the kinetic studies of ligand-exchange reactions of tris(acetylacetonato) complexes of Fe^{III}, Cr^{III}, Co^{III}, etc. in acetylacetone (Hacac),[9,10] we have found a slow ligand exchange of $V(acac)_3$ in organic solvents including Hacac at 25 °C by the isotopic labeling method with ^{14}C. This paper deals with the kinetics, mechanism, and solvent effect on the rate of this exchange reaction by use of $V^{III}(acac\text{-}2\text{-}^{14}C)_3$ in various solvents in the presence of a large excess (≥10^3-fold) of free Hacac.

Experimental Section

Materials. The labeled acetylacetone Hacac-*2*-^{14}C and Hacac-*methylene*-$^2H_2$ (the deuterium content in the methylene moiety is 74%) were prepared and purified by the reported methods.[11,12] Tris(acetylacetonato)vanadium(III), $V(acac)_3$, was prepared from $V^{IV}O(acac)_2$,[13] Hacac, and zinc powder by Grdenič and Korpar-Cölig's method[14] and purified as follows. The precipitate was heated at 120 °C at ca. 1 mmHg (1 mmHg = 133 Pa) for a few hours to remove most of the byproduct $Zn(acac)_2$. The residue was twice recrystallized from benzene–hexane (1:3, v/v) to give brown crystals of $V(acac)_3$. The purity was examined by elemental analysis of C and H and melting point measurement.[15,16] The labeled complex, $V(acac\text{-}2\text{-}^{14}C)_3$, was prepared by the ligand-exchange method. The solution of $V(acac)_3$ (300 mg) in a mixture of Hacac-*2*-^{14}C (1 mL) and acetonitrile (1 mL) was allowed to stand for 1 day at room temperature and evaporated to dryness under a reduced pressure at room temperature to give dark yellow powder, which was twice recrystallized from the benzene–hexane mixture. The UV and visible absorption spectra in acetonitrile [λ_{max}, nm (log ϵ): 230 (4.00), 280 (4.29), 290 (4.27), 345 (3.90), 460 sh (2.53), 540 sh (1.76)] coincided with the reported data.[17,18] The specific counting rate was ca. 3×10^4 cpm mg^{-1} by use of a liquid scintillation counter with a counting efficiency ca. 80%.

Acetonitrile and Hacac were purified as mentioned before.[12] Methanol and ethanol were dehydrated with 3-Å molecular sieves and distilled. Chloroform was washed with aqueous sodium carbonate solution and water, dried with calcium chloride, and distilled. Dimethyl sulfoxide was dried with calcium hydride and distilled under a reduced pressure. Guaranteed grade 2,6-lutidine, trichloroacetic acid, and hexane were used without purification.

Kinetic Procedure. The complex in the reaction mixture was separated by evaporating free Hacac and the solvent in vacuo. The labeled complex (ca. 10 mg) and the solvent (10 mL of Hacac and Hacac-*methylene*-$^2H_2$ or a mixture of Hacac (1.9–9.7 M) with acetonitrile, methanol, ethanol, chloroform, or dimethyl sulfoxide (trichloroacetic acid or 2,6-lutidine was added whenever necessary)) were placed in each of the two sections of a branched glass-stoppered flask. The flask was kept in a thermostat (25.1 ± 0.1, 33.5 ± 0.1, 40.1 ± 0.1 or 48.0 ± 0.1 °C) for ca. 15 min and rotated to unite the contents of the two sections. The complex dissolved within 30 s. Five to seven portions (1.0 mL) of the solution were taken out at appropriate time intervals and swiftly poured into glass-stoppered tubes in an ice bath. The free Hacac and solvent were evaporated in vacuo at room temperature. The pure complex was recovered quantitatively as residue, which was dissolved in acetonitrile (5 mL). One milliliter of this solution was dissolved in toluene (14 mL) containing 0.1% *p*-terphenyl and 0.04% *p*-bis(5-phenyl-2-oxazolyl)benzene (POPOP) for scintillation pulse counting with a Nuclear Chicago Unilux IIA liquid scintillation counter.

Calculation of the Rate. The exchange rate R was calculated by the McKay equation (eq 1), where [complex] and [Hacac] stand for

$$R = \frac{3[\text{complex}][\text{Hacac}]}{3[\text{complex}] + [\text{Hacac}]} \frac{\ln [(x_0 - x_\infty)/(x_t - x_\infty)]}{t} = 3[\text{complex}] \ln (x_0/x_t)/t \quad ([\text{Hacac}] \gg [\text{complex}], x_\infty = 0) \quad (1)$$

the concentrations of the complex and acetylacetone, respectively. x is the specific counting rate of the recovered complex at the time indicated by the subscript. Plots of $\ln (x_0/x_t)$ against t were linear up to at least 50% completion of the exchange.

Kinetic runs under nitrogen atmosphere in two-necked flasks with Schlenk-type attachments gave the same rates. The solvent extraction method for the separation of the complex in the reaction mixture[10]

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Table I. Ligand-Exchange Rate of V(acac)$_3$ in Acetylacetone at 40.1 °C and in Acetonitrile at 48.0 °C

solvents	$10^3 \times$ [complex], M	$10^2 \times$ [H_2O], M	10^6R, M s^{-1}	10^4k_0, s^{-1}
Hacac	3.59	3.0	2.39 ± 0.06	6.65 ± 0.17
	7.46	2.9	5.06 ± 0.09	6.78 ± 0.12
CH_3CN	3.14	5.1	9.17 ± 0.16	2.92 ± 0.05
	5.01	9.6	16.7 ± 0.9	3.33 ± 0.18
		(5.1)		(2.79 ± 0.18)[a]

[a] Corrected value for [H_2O] = 5.1 × 10^{-2} M on the basis of k_0 vs. [H_2O] (cf. Figure 1).

also gave the same rates under otherwise equal experimental conditions.

Tautomerism of Acetylacetone. Acetylacetone is in tautomeric equilibrium between the enol and the keto form. The solvent containing a given amount of Hacac was allowed to stand for at least a few days at ca. 25 °C, to let the tautomerization reach equilibrium, and used for all the kinetic runs regardless of the experimental temperature. The enol fraction (f (%)) was determined by the UV and NMR spectroscopy.[19] The f value in the equilibrated state in neat Hacac decreases by 3% on rise of temperature by 15 °C in the present temperature region.[20] A similar decrease was estimated in acetonitrile (ca. 1 M Hacac) on the basis of the observed and reported[21] f values (vide infra, Figure 2, Table 3). The rate of tautomerization was smaller than that of the present exchange under the present experimental conditions, e.g., by a factor ca. 5 in neat acetylacetone[22] and in acetonitrile ([Hacac] = 1.9 M). Hence the change in f in the reaction mixture with progress of the exchange can be estimated to be less than 3% for all the kinetic runs even at temperatures different from 25 °C. The enol fraction measured in the equilibrated Hacac solution at 25 °C can be reckoned to represent those in the reaction mixtures at all the temperatures throughout the kinetic runs. Linear McKay plots in all the solvents also suggested that the possible small change in f did not affect the observed rate during the progress of kinetic runs, even if only one of the tautomers participated in the exchange.

Results

Verification of the Exchange Reaction. The visible absorption spectra of the reaction mixture remained unchanged for more than 10 half-lives of the exchange and were independent of the concentrations of H_2O (0.01–0.15 M) and Hacac (up to 9.7 M). The water content also remained constant. The McKay plots were linear, and no significant zero-time exchange was observed. Therefore, the decrease in the specific activity of the recovered complex corresponds to the exchange reaction

$$[V(*acac)_3] + Hacac \rightleftharpoons [V(acac)_3] + H*acac \quad (2)$$

where the asterisk denotes ^{14}C labeling.

Exchange Kinetics in Acetylacetone and in Acetonitrile. The exchange rate, R, was proportional to the concentration of the complex (Table I) and expressed by eq 3, where k_0 is the

$$R = k_0[complex] \quad (3)$$

observed first-order rate constant. It increased with increase in [H_2O] (Figure 1) and is expressed by eq 4. The k_a and

$$k_0 = k_a + k_b[H_2O] \quad (4)$$

k_b values were obtained from the intercepts and the slopes of the lines in Figure 1, respectively, and are shown in Table II, together with the activation parameters.

When Hacac-*methylene*-$^2H_2$ was used at 33.5 °C, the k_0, k_a, and k_b values did not change with those in the ordinary Hacac within the experimental error (Figure 1 and Table II).

The k_0 value increased with increase in the free-ligand concentration in acetonitrile up to 9.7 M (in neat Hacac) at 33.5 °C under a given concentration of water (Figure 2). The f value in the given system also increases with increase in [Hacac], particularly to a marked extent in more than 6 M solution, and can be extrapolated to the value in neat acetylacetone. The plot of k_0 value vs. the concentration of the enol tautomer ([enol]) in acetonitrile gave a straight line without an intercept (Figure 3). This fact indicates that the

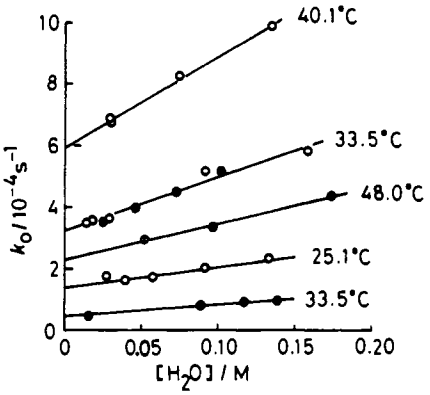

Figure 1. Influence of the water concentration and the deuterium isotope effect on the exchange rate constant (k_0) of V(acac)$_3$ ([complex] = (3–5) × 10^{-3} M): ○, in acetylacetone; ●, in acetylacetone-*methylene*-$^2H_2$; ⊕, in acetonitrile containing 1.93 M Hacac.

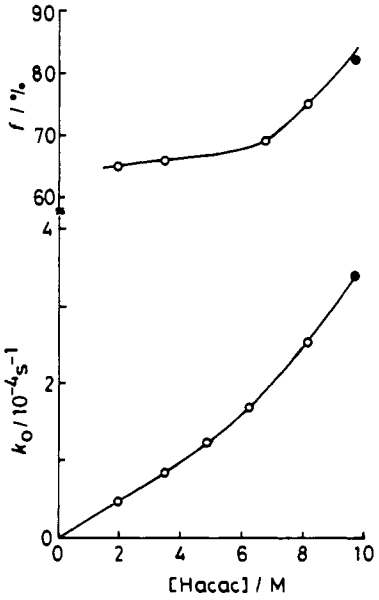

Figure 2. Influence of [Hacac] on k_0 and f: f, the enol fraction of Hacac in acetonitrile (○) and in neat acetylacetone (●) at ca. 25 °C; k_0 the exchange rate constant in the mixed solvent ([complex] ≈ 0.004 M) at 33.5 °C ([H_2O] = ca. 0.015 M for both curves).

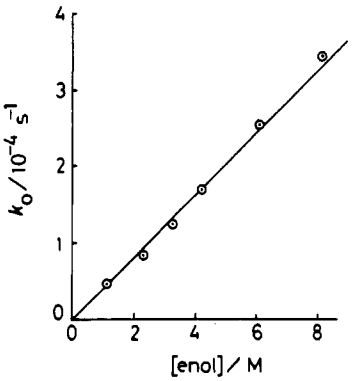

Figure 3. Plot of k_0 vs. [enol] (cf. Figure 2).

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Table II. Kinetic Data for the Ligand Exchange of V(acac)$_3$ in Acetylacetone and Acetonitrile[a]

solvents	parameters	rate const 25.1 °C	33.5 °C	40.1 °C	48.0 °C	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}
acetylacetone	$10^4 k_a$, s^{-1}	1.36 ± 0.12	3.20 ± 0.14, 3.09 ± 0.03[b]	5.87 ± 0.15		17.5 ± 0.4	−17.5 ± 1.3 (−21.7 ± 1.4)[c]
	$10^3 k_b$, M^{-1} s^{-1}	0.66 ± 0.15	1.67 ± 0.15, 1.80 ± 0.05[b]	2.96 ± 0.19		18.0 ± 1.3	−12.6 ± 4.6 (−16.7 ± 4.5)[d]
acetonitrile[b]	$10^4 k_a$, s^{-1}		0.50 ± 0.08		2.3 ± 0.2	ca. 19	ca. −14 (ca. −14)[c]
	$10^3 k_b$, M^{-1} s^{-1}		0.33 ± 0.06		1.2 ± 0.2	ca. 16	ca. −21 (ca. −22)[d]

[a] Errors are calculated at the 70% confidence level. [b] In acetylacetone-*methylene*-$^2H_2$. [c] For k_a' (=k_a/[enol]). [d] For k_b' (=k_b/[enol]).

Table III. Rate Constants of the Ligand Exchange of V(acac)$_3$ in Various Organic Solvents at 33.5 °C ([Hacac] = 1.93 M) and Their Parameters

solvents	10^3 × [complex], M	10^2 × [H_2O], M	k_0, s^{-1}	AN[a]	DN[b]	μ,[c] Debye	ϵ[d]	f,[g] %
methanol	3.5	6.7	6×10^{-2}	41.3	19.1	1.69	32.6[e]	74 (74)
ethanol	3.8	3.2	2×10^{-2}	37.1		1.67	24.3[e]	82 (82)
chloroform	4.8	13.5	6×10^{-4}	23.1		1.06	4.81[f]	87 (85)
acetonitrile	4.5	3.4	6×10^{-5}	19.3	14.1	3.94	37.5[f]	62 (67)
dimethyl sulfoxide	3.7	3.4	4×10^{-5}	19.3	29.8	4.3	48.9[f]	62 (76)

[a] Acceptor number.[28] [b] Donor number.[26] [c] Dipole moment. [d] Dielectric constant (1 Debye = 3.333×10^{-30} C m). [e] At 20 °C. [f] At 25 °C. [g] Enol fraction at 33 °C at 0.1 and 0.3 (in parentheses) mole fraction of Hacac.[21]

Table IV. Influence of Other Ingredients on the Observed First-Order Rate Constant in Acetylacetone at 33.5 °C

additions	[addition], M	10^3[complex], M	[H_2O], M	$10^4 k_0$, s^{-1}	$10^4 k_0$,[a] s^{-1}
2,6-lutidine	0.017	5.15	0.057	4.70 ± 0.27	4.15 ± 0.23
Me_2SO	0.016	3.75	0.019	4.17 ± 0.09	3.52 ± 0.17
	0.069	2.89	0.021	4.09 ± 0.12	3.55 ± 0.17
methanol	0.126	6.81	0.016	6.93 ± 0.11	3.47 ± 0.16
trichloroacetic acid	0.028	5.70	0.056	30.7 ± 3.8	4.14 ± 0.22

[a] The calculated k_0 value in pure acetylacetone (without other ingredients) at the given [H_2O] on the basis of the k_a and k_b values in Table II, using eq 4.

change in k_0 is due to the change in [enol] rather than to the medium effect.

Rate in Various Solvents and Influence of Acids and Bases. The k_0 values in methanol, ethanol, chloroform, acetonitrile, and dimethyl sulfoxide were calculated on the assumption that eq 3 holds for the exchange reactions in the following concentration regions: complex, 0.0035–0.0048 M; free ligand, 1.93 M; water, 0.032–0.135 M (Table III).

The influence of protic acids and bases was examined in neat acetylacetone. The k_0 value increased markedly on addition of trichloroacetic acid, but only to a negligible extent by that of 2,6-lutidine, dimethyl sulfoxide, and methanol (Table IV). NMR spectroscopy showed no change in enol fractions on addition of these reagents.

Discussion

Exchange Reaction in Acetonitrile and in Acetylacetone. The k_0 value in acetylacetone ([Hacac] = 9.7 M) and in acetonitrile ([Hacac] = 1.93 M) is commonly expressed by eq 4 in the presence of water. The ratio k_a/k_b[H_2O] is almost constant regardless of [Hacac] and temperature under the given [H_2O] (e.g., ca. 1.9 for [H_2O] = 0.1 M; cf. Table II and Figure 1). The activation enthalpies and entropies for k_a and k_b in acetylacetone are similar to those in acetonitrile (Table II). These facts as well as Figure 3 indicate that the exchange reactions in both media proceed similarly through two paths in these two media. The enol tautomer of Hacac must participate almost exclusively in the exchange reactions under the given conditions to give eq 5. One V(acac)$_3$ and one Hacac mol-

$$k_0 \approx k_0'[\text{enol}] \approx (k_a' + k_b'[H_2O])[\text{enol}] \qquad (5)$$

ecule in enol form participate in both paths, and one H_2O molecule also participates in the k_b path.

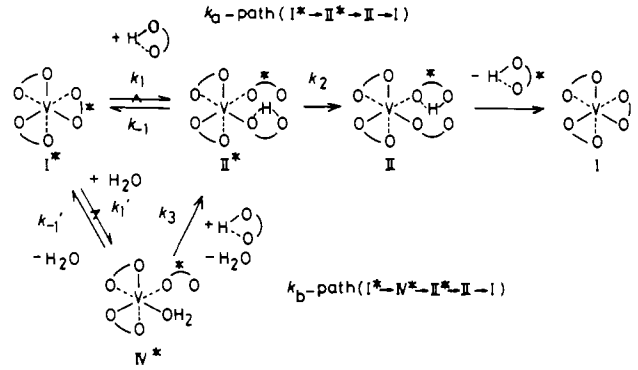

Figure 4. Plausible mechanism of the ligand exchange of V(acac)$_3$ in acetylacetone and in acetonitrile. I* and S denote V(*acac)$_3$ and the solvent molecule (Hacac or CH_3CN), respectively. (The enol tautomer of Hacac is suggested to participate predominatingly in the reaction.)

Plausible Mechanism. A plausible mechanism is illustrated in Figure 4, where I* denotes the original complex, V(*acac)$_3$. In the k_a path, the intermediate II* is formed from I* and Hacac (enol). II* is converted into II through the proton transfer from Hacac to *acac$^-$ on V^{III}, and II turns to I and H*acac. In the k_b path, complex I* and a water molecule produce intermediate IV*, which is converted into II*, the H_2O being replaced by the free Hacac (enol). II* undergoes similar changes as in the k_a path, to complete the exchange. Similar activation enthalpies and entropies for k_a and k_b in all the solvents shown in Table II suggest the participation of similar reaction routes and rate-determining steps in the two reaction paths. If the k_1 and the k_1' step are the slowest in the two

Table V. Kinetic Parameters for Ligand-Substitution Reactions of V^{III} Complexes in Aqueous and Nonaqueous Solutions at 25 °C[a]

no.	complexes	free ligands	solutions	k_{ex} or k_f, M^{-1} s^{-1}	k_s, M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}	ref
			Exchange (k_{ex})					
1	$[V(H_2O)_6]^{3+}$	H_2O	aq (μ = 1.0)	3×10^{2} [b]		6	−23	6
2	$[V(mal)_3]^{3+}$	$Hmal^-$	aq (μ = 1.0) pH 3-4	6×10^{-2} [c]		13	−12	29
3	$V(acac)_3$	Hacac	Hacac	1×10^{-5} (the k_a path)		18	−22	this work
			Anation (k_f) and Solvolysis (k_s[b])					
4	$[V(H_2O)_6]^{3+}$	NCS^-	aq (μ = 0.15)	1×10^{2}		8	−24	2, 3
			pH 1-1.6		3×10^{-2}	11	−23	
5	$[V(H_2O)_6]^{3+}$	$HC_2O_4^-$	aq (μ = 0.5) pH 0.3-1	1×10^{3}				7
6	$[V(H_2O)_6]^{3+}$	N_3^-	aq (μ = 1.0)	2×10^{2} [d]				4
			pH 0.4-1.3		4×10^{-1}	15	−4	
7	$[V(Me_2SO)_6]^{3+}$	NCS^-	Me_2SO	2×10^{2}	1×10^{-1}			5
8	$[V(Me_2SO)_6]^{3+}$	bpy	Me_2SO	1×10^{-1}		(12)	(−25)	
					3×10^{-4}			5
9	$[V(Me_2SO)_6]^{3+}$	ssa	Me_2SO	2×10^{-1}	1×10^{-4}			5

[a] Abbreviation: mal^{2-} = malonate, Me_2SO = dimethyl sulfoxide, bpy = 2,2'-bipyridine, ssa = "sulfosalicylic acid". [b] The rate constants are expressed by k (M^{-1} s^{-1}), the first-order rate constants being divided by the formal concentrations of the solvents ([H_2O] = 55 M, [Me_2SO] = 14 M, [Hacac] = 9.7 M). [c] The first-order rate constant is divided by [$Hmal^-$]. [d] pH 1.

paths, stationary-state conditions can be reasonably assumed with respect to II* and IV* to give eq 6 and 7. The con-

$$k_a = k_1[\text{enol}]\frac{k_2}{k_{-1} + k_2} \quad (6)$$

$$k_b[H_2O] = k_1'[H_2O]\frac{k_3[\text{enol}]}{k_3[\text{enol}] + k_{-1}'} \quad (7)$$

centration of the intermediate should be negligible as compared with that of the original complex (I* and I), since the visible absorption spectra of the complex in the reaction mixtures were constant regardless of the concentrations of water and Hacac (vide supra). On the assumptions $k_{-1} \ll k_2$ and $k_{-1}' \gg k_3$·[enol], eq 6 and 7 are further converted into eq 8 and 9,

$$k_a = k_1[\text{enol}] = k_a'[\text{enol}] \quad (8)$$

$$k_b[H_2O] = k_1'[H_2O]\frac{k_3[\text{enol}]}{k_{-1}'} = k_b'[H_2O][\text{enol}] \quad (9)$$

respectively. If k_2 were much smaller than k_{-1}, the proton-transfer rate should contribute to the rate (eq 6) and a deuterium isotope effect should be observed on the exchange rate.[9,12] However, the present exchange fails to give such an effect (Figure 1 and Table II). The intramolecular replacement of H_2O in IV* by the free end of the one-ended $acac^-$ (k_{-1}') can be much faster than the intermolecular replacement to give II* (k_3[enol]). Thus, the assumption is appropriate, and eq 5 is interpreted by eq 8 and 9. The k_1 and k_1' steps are the rate-determining steps, and the term $k_3[\text{enol}]/k_{-1}'$ represents the branching ratio for the accomplishment of the exchange from IV*.

The negative $\Delta S^{\ddagger}$ (Table II) and the first-order dependency of k_a on [enol] (Figure 3) suggest an associative mechanism to the rate-determining k_1 step.[9,12,23] The negative value of $\Delta S^{\ddagger}$ for k_b also suggests an associative attack of H_2O on V^{III} in the k_1' step. (The values of the activation parameters should reflect mainly the k_1' step, since the step is assumed to be much slower than the k_{-1}' and k_3 steps.)

Low reactivity of the keto tautomer in the exchange reaction[24] may be attributed to the difficulty of proton transfer

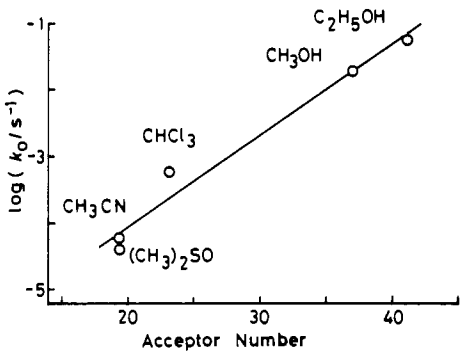

Figure 5. Plot of log k_0 (s^{-1}) vs. acceptor number.

in a II*-type intermediate containing a keto tautomer and an enolate as unidentates. Even if such an intermediate were formed, it should be a dead-end species.

The observed kinetic formulas could be also interpreted by considering the following possibilities: (i) The replacement of unidentate *$acac^-$ in II* or IV* by CH_3CN or free Hacac to give free H*acac can result in the ligand exchange. (ii) A water molecule can assist the proton transfer in the k_2 step (Figure 4). (iii) Hacac and H_2O may catalytically interact as proton donors with the original complex or some of the intermediates; e.g., formation of II* can be assumed for the k_a and k_b terms in eq 4 without and with the aid of a proton of H_2O in the k_1 step, respectively. However, these possibilities are excluded by the same reasons as discussed before.[25] Thus, the mechanism in Figure 4 is concluded to be the most plausible.

Effects of Solvent and Other Ingredients on the Rate. The rate was dependent on the solvent as shown in Table III. The k_0 value varies by a factor 10^3. There is no significant relationship between k_0 and f (the enol fraction at 33 °C in each solvent containing 0.1 and 0.3 mole fraction of Hacac[21]). The dielectric constant (ϵ), the dipole moment (μ), and the donor number (DN) do not correlate with k_0. On the other hand, the plot of log k_0 *vs.* the acceptor number (AN), the measure of the electrophilicity of a solvent molecule,[26] is linear (Figure

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5). The role of a solvent molecule may be understood by considering its interaction with the coordinated oxygen atom in $V(acac)_3$. The V–O bond is weakened, and the effective charge of the V^{III} ion increases through such an interaction to facilitate the formation of II* or IV* by the nucleophilic attack of Hacac or H_2O.[27]

The increase in k_0 in the presence of trichloroacetic acid in Hacac (Table IV) is also regarded as the acid catalysis, the proton interacting with the coordinated oxygen.[23]

Comparison with Related Reactions. Second-order rate constants and activation parameters of substitution reactions of $V^{III}O_6$-type complexes including ligand exchange (k_{ex}), anation (k_f), and solvolysis (k_s) are collected in Table V. The present k_{ex} (k_a) value is smaller by an order of 10^3–10^7 than the k_{ex}, k_f, and k_s values for the reactions of $[V(H_2O)_6]^{3+}$ and $[V(Me_2SO)_6]^{3+}$ with unidentate nucleophiles.[2-6] Such an inertness is in line with that in the exchange of malonato ligand in aqueous solution (cf. **2** in Table V).[29] The reaction product between $[V(Me_2SO)_6]^{3+}$ and 2,2′-bipyridine or sulfosalicylic acid in Me_2SO (**8** and **9** in Table V)[5] can contain the bidentate ligand as either unidentate or chelate. The small rate constants of the backward reactions suggest the presence of chelated species.

Most of the activation entropies in Table V are similar to one another. All these reactions seem to proceed via an associative rate-determining step, regardless of the dentate number of the ligands. (The anation of NCS^-,[2] N_3^-,[4] and $HC_2O_4^-$[7] for $[V(H_2O)_6]^{3+}$ was suggested to proceed via an associative mechanism). On the other hand, the ΔH^* values scatter and seem to be responsible for determining the mechanism.) The inertness of the present reaction is attributed to the large ΔH^* value.

The sequence of the exchange rates of $M^{III}(acac)_3$ in Hacac is obtained as follows:[9,10] $Fe^{III} > V^{III} \gg Co^{III} > Cr^{III} > Ru^{III} > Rh^{III}$. The first-order rate constant k_a value for V^{III} is 25 times smaller than for Fe^{III} and is larger than that for Co^{III} by a factor of 10^6, at 25 °C.

Registry No. $V(acac)_3$, 13476-99-8; Hacac, 123-54-6.

(27) Correlation of the acceptor number with parameters concerning reactions of complexes in solution has been demonstrated thermodynamically.[26] However, it has scarcely been discussed kinetically.
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Synthesis and Spectroscopic Study of η^5-$C_5H_5(CO)_2Fe[C(XR)YR]^+$ Carbene Complexes, Where X and Y Are O, S, Se, and/or NR

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A variety of $Cp(CO)_2Fe[C(XR)YR]^+$ (X = S; Y = O, S, Se) carbene complexes are readily available from $Cp(CO)_2Fe(CS)^+$ by reaction with RY^- to form $Cp(CO)_2FeC(=S)YR$, followed by alkylation with CH_3SO_3F or $CH_3SO_3CF_3$. Similar treatment of $CpFe(CO)_3^+$ leads to $Cp(CO)_2Fe[Y(CH_3)Ph]^+$ compounds rather than carbene complexes. The reactions of $Cp(CO)_2Fe[C(SCH_3)OCH_3]^+$ with alcohols and $Cp(CO)_2Fe[C(SCH_3)_2]^+$ with dithiols yield $Cp(CO)_2Fe[C(OR)OCH_3]^+$ and $Cp(CO)_2Fe[\overline{CS(CH_2)_nS}]^+$ (n = 2, 3) carbene complexes, respectively. The thiooxocarbene complex $Cp(CO)_2Fe[C(SCH_3)OCH_3]^+$ undergoes facile thermal rearrangement to a binuclear species, $[Cp(CO)_2Fe]_2SCH_3^+$. Reaction of $Cp(CO)_2Fe[C(SCH_3)_2]^+$ with $LiAlH_4$ yields $Cp(CO)_2Fe[C(SCH_3)_2H]$ which may be converted to an unstable secondary carbene complex, $Cp(CO)_2Fe[C(SCH_3)H]^+$, by reaction with CF_3SO_3H. These new carbene complexes, and other known carbene complexes, are studied by IR, ^1H NMR, and ^{13}C NMR spectroscopy to determine the electronic effects of the XR and YR groups; an order of relative π-stabilization ability is established (N ≫ Se ≥ S > O). Trends in the chemical shifts of the carbene carbons in the ^{13}C NMR spectra of the $Cp(CO)_2Fe[C(XR)YR]^+$ complexes are also observed.

Introduction

Transition-metal carbene complexes are of great interest as they are postulated as intermediates in catalytic processes, most notably in the Fischer–Tropsch reaction[2a] and in olefin metathesis.[2b] A better understanding of chemical, physical, and electronic factors which influence model carbene systems should lend insight into these catalytic processes. The interesting chemical behavior found for $Cp(CO)_2Fe[dithiocarbene]^+$ complexes[3] (Cp = η^5-C_5H_5) has prompted us to investigate the $Cp(CO)_2Fe[carbene]^+$ system further.

Carbon-13 NMR spectroscopy has proven to be a valuable tool in organometallic chemistry.[4-6] Analysis of carbene complexes by ^{13}C NMR spectroscopy is especially interesting because of the high sensitivity of the carbene carbon resonance to changes in the electronic environment.[7] In this report, we present the synthesis of a variety of iron carbene complexes incorporating O, S, and Se into the carbene ligands. These complexes, and other carbene complexes reported previously,[3,8] are analyzed by means of IR, ^1H NMR, and ^{13}C NMR spectroscopy with emphasis on the relative π-stabilization abilities of the heteroatoms in the carbene ligands.

Results and Discussion

Preparation of Carbene Complexes from $Cp(CO)_2Fe(CS)^+$. The bis(methylthio)carbene complex $\{Cp(CO)_2Fe[C(SCH_3)_2]\}PF_6$ (Ia) has been prepared in 69% yield from $Cp(CO)_2FeC(=S)SCH_3$ (which may be obtained from the re-

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