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Kinetics and Mechanisms of Intermolecular Ligand Exchange. I. Diphenyltin and Dimethyltin Acetylacetonates[1]

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The kinetics and mechanisms of intermolecular ligand exchange of acetylacetonate (acac) groups between $(C_6H_5)_2Sn(acac)_2$ and $(CH_3)_2Sn(acac)_2$ have been investigated in deuteriochloroform and bromoform solutions by ^1H nmr spectroscopy in the temperature ranges 17.5–58.5° ($CDCl_3$) and 57–102° ($CHBr_3$). The activation energies and entropies of activation are 7.5 ± 1.5 kcal/mol ($CDCl_3$), 5.4 ± 0.9 kcal/mol ($CHBr_3$), −33 ± 5 eu ($CDCl_3$), and −42 ± 3 eu ($CHBr_3$), respectively. Concentration dependence studies in $CHBr_3$ indicate that the rate of acetylacetonate exchange is first order in $(C_6H_5)_2Sn(acac)_2$ and zero order in $(CH_3)_2Sn(acac)_2$ concentration. A mechanism is proposed in which the rate-controlling step, in contrast to earlier studies, is identified as a metal–oxygen bond rupture in $(C_6H_5)_2Sn(acac)_2$ to yield a five-coordinate tin species with a dangling unidentate acetylacetonate ligand.

Introduction

Mechanistic studies of intramolecular configurational rearrangement phenomena in six-coordinate chelate complexes continue to be a subject of great interest in inorganic chemistry.[2] These studies have been mainly centered on keto-enolate ($R\text{-}COCH_2CO\text{-}R$) complexes, but more recently also on dithiocarbamate[3] and tropolonate[4] complexes of transition metals. In contrast, mechanisms of intermolecular ligand exchange in metal β-diketonate complexes have received relatively little attention. The lack of information stems from the very slow rates of exchange on the nmr time scale. But where intermolecular exchange can be followed by nmr spectroscopy, those studies may, in some cases, unravel the mechanisms of intramolecular rearrangement phenomena.

The first such study on β-diketonate complexes was reported by Adams and Larsen,[5] who investigated the kinetics of ligand exchange between $M(dik)_4$ and the free ligand Hdik [where dik = trifluoroacetylacetonate anion (tfac) or acetylacetonate anion (acac); and M = Zr, Hf, or Th]. Rates of exchange of zirconium and hafnium trifluoroacetylacetonates with the free ligand in benzene and chlorobenzene and of the metal acetylacetonates with the free ligand in chlorobenzene were observed to be first order in both metal complex and free ligand. The first step in the proposed mechanism involved an M–O bond rupture in the eight-coordinate $M(acac)_4$ complex in rapid equilibrium with a seven-coordinate species; the rate-controlling step was suggested as resulting from M–O bond rupture in the eight-coordinate species containing three bidentate and two unidentate acetylacetonate ligands.

In a related study, Glass and Tobias[6] investigated the exchange behavior of several organometallic acetylacetonate complexes [metal is tin(IV), gold(III), gallium(III), and thallium(III)]. They proposed a similar mechanism as that of Adams and Larsen;[5] however, no concentration dependence studies were conducted to substantiate it. A more recent study[7] on the ligand exchange between indium(III) β-diketonates and the corresponding free ligand suggests that the rate of exchange, in this system, is first order in the concentration of the complex. A similar mechanism as the one reported earlier[5] was proposed but the rate-determining step was identified as the rotation of one monodentate ligand about a partial double bond prior to intramolecular proton transfer to a second monodentate ligand in the species containing two bidentate and two unidentate β-diketonate ligands.

Radioactive tracer studies have also been employed to follow isotopic ligand exchange in aluminum(III),[8] palladium(II),[9] and beryllium(II)[10] acetylacetonate with ^{14}C-labeled acetylacetonate. A feature in these studies is that exchange occurs through several paths but one path common to all is first order in the concentration of the complex. This first-order path involves an M–O bond rupture in a rapid equilibrium step to yield a species with a unidentate acetylacetonate; the rate-controlling step was identified as rupture of the remaining metal–oxygen bond in the unidentate ligand.

In an earlier communication,[11] we reported our findings on the stereochemistry of $(C_6H_5)_2Sn(acac)_2$ and some preliminary studies on the configurational rearrangement processes. In an effort to elucidate the mechanism(s) of configurational rearrangements in the above complex and in other organometallic (Sn, Ge, Si) complexes, we have undertaken a detailed kinetic and mechanistic study on the ligand exchange between $(C_6H_5)_2Sn(acac)_2$ and $(CH_3)_2Sn(acac)_2$ in deuteriochloroform and bromoform.

Experimental Section

Materials. Reagent grade 2,4-pentanedione (Fisher) and diphenyltin dichloride and dimethyltin dichloride (Alfa Inorganics) were used as received. Deuteriochloroform was prepared by a modified method[12] of that of Paulsen and Cooke.[13] Bromoform (Canlab) was purified by distillation over molecular sieves (Type 4A) just prior to use. Dichloromethane and hexane were refluxed over calcium hydride and distilled therefrom prior to use.

Diphenylbis(2,4-pentanedionato)tin(IV). This compound was

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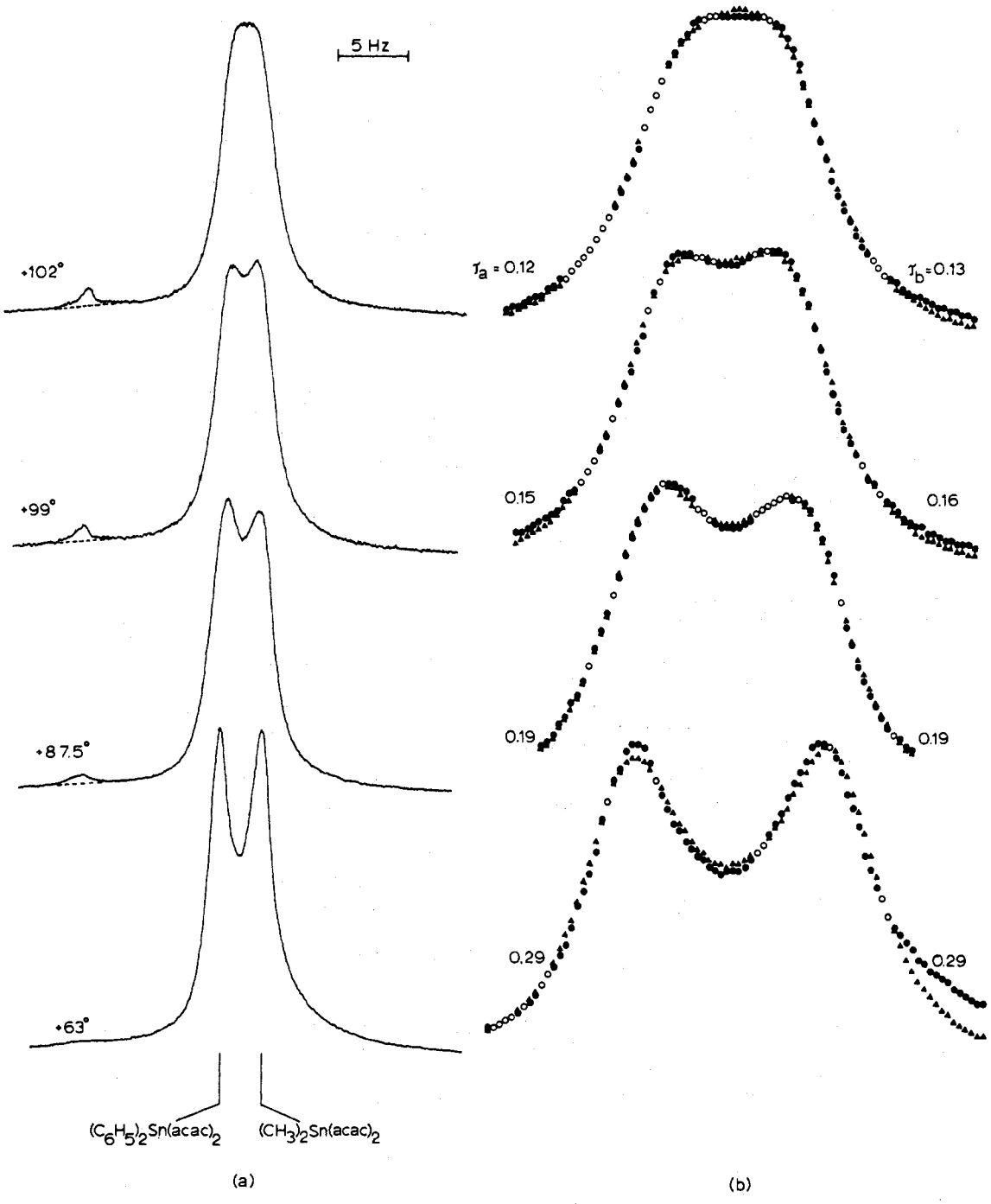

Figure 1. Nmr spectra for the acetylacetonate methyl proton region as a function of temperature in the ligand exchange between $(C_6H_5)_2Sn(acac)_2$ and $(CH_3)_2Sn(acac)_2$ in bromoform: (a) experimental spectra; (b) comparison of experimental and calculated nmr spectra; solid circles represent experimental points, solid triangles represent calculated points, and open circles denote a perfect fit of experimental and calculated points.

prepared in a manner similar to that described in the literature[14,15] by allowing diphenyltin dichloride to react with sodium acetylacetonate in dry dichloromethane. The desired white crystals were recrystallized from dry dichloromethane–hexane solutions and dried *in vacuo*; mp 124–126°; lit.[14] mp 125°; lit.[15] mp 125–126°. The purity of the product was further ascertained from its infrared and nmr spectra.

Dimethylbis(2,4-pentanedionato)tin(IV). This product was also prepared[16] by allowing dimethyltin dichloride and sodium acetylacetonate to react in dry dichloromethane. Recrystallization was accomplished in dry dichloromethane–hexane solutions; the compound was dried *in vacuo*; mp 179–180°; lit.[16] mp 177–178°. The purity of this compound was checked from its infrared and nmr spectra.

Preparation of Solutions. Because of possible hydrolysis[14] of $(C_6H_5)_2Sn(acac)_2$ and $(CH_3)_2Sn(acac)_2$, the complexes were handled and the solutions prepared entirely under anhydrous conditions in a dry nitrogen atmosphere in a glove bag. The dimethyltin complex was weighed (0.03505 g, 0.1010 mmol) in a 1.00-ml dry volumetric flask to which was added 0.04836 g (0.1026 mmol) of the diphenyltin compound and enough deuteriochloroform–10% v/v TMS solvent to yield a 1.00-ml solution. This solution was transferred to a dry 9-in. nmr precision tube which was subsequently sealed *in vacuo*. A similar 1.00-ml solution of 0.03471 g (0.1000 *M*) of $(CH_3)_2Sn(acac)_2$

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and 0.04649 g (0.0987 *M*) of $(C_6H_5)_2Sn(acac)_2$ was prepared in bromoform–10% v/v TMS solvent.

To determine the format of the rate law, two series of solutions were prepared in bromoform. One series consisted of five solutions all with a fixed concentration of $(C_6H_5)_2Sn(acac)_2$ (*ca.* 0.1 *M*) and varying concentrations of $(CH_3)_2Sn(acac)_2$ (0.06–0.15 *M*). The other series also consisted of five solutions in which the concentration of $(CH_3)_2Sn(acac)_2$ was kept constant at *ca.* 0.1 *M* and the concentration of $(C_6H_5)_2Sn(acac)_2$ was varied in the range 0.8–0.16 *M* (see Results and Discussion).

Measurement of Nmr Spectra. Variable-temperature proton magnetic resonance spectra were obtained with a Varian Associates HA-100 high-resolution spectrometer operating at 100 MHz. The spectrometer was equipped with a variable-temperature probe accessory, Model V-4343, and a temperature controller accessory, Model V-6040. Spectra were recorded in the frequency sweep mode in the temperature ranges −32 to +59° ($CDCl_3$) and +36 to +102° ($CHBr_3$). Temperatures were determined in the usual way with the calibrated charts supplied by Varian Associates.

Treatment of Nmr Spectra. Nmr spectra were subjected to computer fitting, but first they were converted into digital form. Digitization of a spectrum was accomplished with the aid of a Hewlett-Packard (H-P) 2114A computer, an Analog/Digital (A/D) converter, a Moseley Autograph Model 7001AM X-Y recorder, a Hewlett-Packard G-2B null detector, and a Hewlett-Packard Type F-3B line follower. Signals from the line follower were converted into digital form by the A/D converter as a series of points of an X-Y plot (intensity *vs.* frequency in hertz). These points were recorded on paper tape. The digitized spectra were then transferred from paper tape to magnetic tape using the H-P 2114A computer, an H-P Model 2020 digital tape unit, and an H-P Model 2737A punch tape reader. The computer (CDC 6400) fitting program requires initial trial values of the following parameters: τ_A, the lifetime of a nucleus on site A; τ_B, the lifetime on site B; the chemical shift, with respect to some arbitrary zero, of the nucleus at site A and that of the nucleus at site B to yield $\delta\nu_0$ in absence of exchange; the line width in the absence of exchange; and finally a scaling factor. Line widths at half-maximum amplitude of the acetylacetonate methyl resonance of $(CH_3)_2Sn(acac)_2$ were used as the line widths in the absence of exchange at each temperature; this parameter was kept fixed in the fitting program while the others were, in general, allowed to vary.

Results and Discussion

Proton Nmr Spectra and Kinetics of Ligand Exchange. The acetylacetonate methyl proton region in the variable-temperature nmr spectra for an equimolar mixture of $(C_6H_5)_2Sn(acac)_2$ and $(CH_3)_2Sn(acac)_2$ in bromoform is presented in Figure 1a. In Figure 1b, we compare the calculated and experimental spectra along with the residence times in site A, the site in diphenyltin acetylacetonate, and in site B, the site in dimethyltin acetylacetonate. Similar results were obtained for the methyl region in the variable-temperature nmr spectra of an equimolar mixture of $(C_6H_5)_2Sn(acac)_2$ and $(CH_3)_2Sn(acac)_2$ in deuteriochloroform. Downfield from the acetylacetonate methyl proton signals (Figure 1a) appears a very small resonance which increases in intensity with increase in temperature. This resonance persisted in the room-temperature nmr spectrum of the sample recorded after the 102° spectral run and is attributed to a small decomposition impurity from the diphenyltin complex which seemingly decomposes to an extent <1% at and above *ca.* 80°.

A common feature in the bromoform and deuteriochloroform nmr spectra is that as the temperature is increased, the methyl proton resonance signals of both the diphenyltin and dimethyltin acetylacetonate complexes broaden and then coalesce into a single, broad line (T_c = 37.5° in $CDCl_3$; T_c = 102° in $CHBr_3$). If the temperature is increased further, the methyl region appears as a single, sharp line. To ascertain that this coalescence behavior is not merely the result of varying temperature dependences of the acetylacetonate methyl proton chemical shifts in the two complexes, the proton chemical shifts were determined as a function of temperature for both the deuteriochloroform and bromoform samples. The results show a linear dependence[17,18] of the proton shifts on temperature and also that differences in chemical shifts are constant, within experimental error, in the temperature range studied. Thus, coalescence is attributed to a rapid intermolecular exchange process which interchanges acetylacetonate groups between the two complexes $(C_6H_5)_2Sn(acac)_2$ and $(CH_3)_2Sn(acac)_2$.

Values of the residence times τ_A and τ_B for an acetylacetonate methyl group in $(C_6H_5)_2Sn(acac)_2$ and $(CH_3)_2Sn(acac)_2$, respectively, along with the chemical shifts, $\delta\nu_0$, as well as the inverse mean lifetimes, expressed as $1/2\tau$ ($\tau = \tau_A\tau_B/(\tau_A + \tau_B)$), are tabulated in Table I for deuteriochloroform and are summarized in Table II for the bromoform samples.

Arrhenius activation energies, E_A, and frequency factors, A, were obtained from the slope and intercept, respectively, of the least-squares straight lines of log k *vs.* $1/T$ plots (Figure 2), where $k = (2\tau)^{-1}$ is the first-order rate constant for exchange. Activation entropies, $\Delta S^{\ddagger}$, at 25° were calculated from the relation

$$\Delta S^{\ddagger} = R[\ln A - \ln (RT/Nh)] - R \quad (1)$$

The activation parameters and extrapolated values of k at 25° are listed in Table III.

The results are subject to some small systematic errors because the line widths in absence of exchange are temperature dependent throughout the temperature range in which spectra were recorded. Errors estimated at the 95% confidence level and reported in Table III for the activation parameters represent the scatter of points from the least-squares lines; they do not include small systematic errors from the estimation of line widths in the absence of exchange. However these line widths differ only by about 0.10 Hz (0.89–0.99 Hz in $CDCl_3$; 0.87–0.96 Hz in $CHBr_3$) in the temperature range for which kinetic data are reported; thus, systematic errors are expected to be less than those listed in Table III. Further, errors propagated into E_A, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ from the uncertainty in τ values are estimated to be about 10–15%. Jones and Fay[12,19] have observed that overestimating T_2'' (in the absence of exchange) and therefore underestimating W'' (line width in absence of exchange) lead to lower E_A and more negative $\Delta S^{\ddagger}$ values.

The rate of ligand exchange at 25° is faster in deuteriochloroform although E_A is slightly larger. The difference in rates of exchange is ascribed to differences in the entropies of activation: −33 eu in $CDCl_3$, −42 eu in $CHBr_3$. Since a tin–oxygen bond rupture is necessary to bring about exchange, the difference, though small, in the two energies of activation of Table III probably arises from (a) greater solvation of the ground state of both complexes by deuteriochloroform, (b) a solvent-assisted tin–oxygen bond rupture, (c) a transition state in which the sixth coordination site is occupied by a solvent molecule, and (d) interaction of HCX_3 with the basic site of the dangling ligand. Presumably, either or both of processes (c) and (d) are more favorable in deuteriochloroform. Whatever the effects of the solvent on the ground state of the complexes and on the transition state (or intermediate), they cannot simply be related to differences in dipole moments[20] of the solvents as these are nearly

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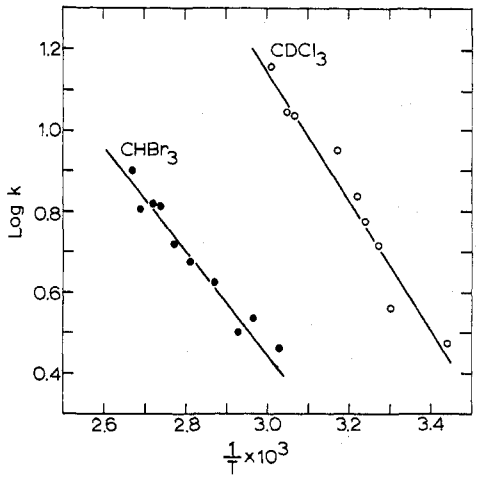

Figure 2. log k *vs.* $1/T$ plots for acetylacetonate ligand exchange between $(C_6H_5)_2Sn(acac)_2$ and $(CH_3)_2Sn(acac)_2$ in deuteriochloroform and bromoform; $k = 1/2\tau$ is the first-order rate constant for the exchange process.

Table I. Temperature Dependence of Mean Residence Times for Exchange of Acetylacetonate Groups between $(C_6H_5)_2Sn(acac)_2$ and $(CH_3)_2Sn(acac)_2$ in Deuteriochloroform[a]

Temp, °C	τ_A,[b] sec	τ_B,[b] sec	k (=1/2τ),[c] sec^{-1}	$\delta\nu_0$, Hz
58.5			14[d]	3.08[e]
55			11[d]	3.08[e]
53	0.096	0.089	11	3.02
42	0.10	0.12	9.0	3.24
37.5 (T_c)	0.13	0.14	6.9	3.19
35.5	0.17	0.17	5.9	3.03
32.5	0.19	0.20	5.2	2.95
30	0.26	0.28	3.7	3.05
17.5	0.32	0.36	3.0	3.11

[a] $[(C_6H_5)_2Sn(acac)_2] = 0.103\ M$; $[(CH_3)_2Sn(acac)_2] = 0.101\ M$. [b] Errors estimated to be about 10–15%. [c] Literature[6] value 4.0 sec^{-1} at 40°. [d] Calculated from the Piette-Anderson [*J. Chem. Phys.*, 30, 899 (1959)] expression $1/2\tau = 2\pi P_A P_B(\delta\nu_0)^2/(W^* - W'')$ where $P_A = 0.496$, $P_B = 0.504$, $\delta\nu_0 = 3.08$ Hz (in the absence of exchange), $W^* = 1.92$ Hz (the line width during exchange), and $W'' = 0.89$ Hz (line width in the absence of exchange). [e] Average of $\delta\nu_0$ values from computer-fitted spectra.

Table II. Temperature Dependence of Mean Residence Times for Exchange of Acetylacetonate Groups between $(C_6H_5)_2Sn(acac)_2$ and $(CH_3)_2Sn(acac)_2$ in Bromoform[a]

Temp, °C	τ_A,[b] sec	τ_B,[b] sec	k (=1/2τ), sec^{-1}	$\delta\nu_0$, Hz
102 (T_c)	0.12	0.13	7.9	3.76
99	0.16	0.16	6.4	3.63
94.5	0.15	0.15	6.6	3.81
92	0.15	0.16	6.5	3.87
87.5	0.19	0.19	5.3	3.65
83	0.21	0.21	4.7	3.58
75	0.24	0.24	4.2	3.63
68	0.31	0.32	3.2	3.51
64	0.29	0.29	3.4	3.64
57	0.34	0.35	2.9	3.65

[a] $[(C_6H_5)_2Sn(acac)_2] = 0.099\ M$; $[(CH_3)_2Sn(acac)_2] = 0.100\ M$. [b] Errors estimated to be about 10–15%.

the same [1.01 D ($CHCl_3$), 0.99 D ($CHBr_3$)] nor to differences in the dielectric constants[20] of the solvents [4.806 (20°) for $CHCl_3$; 4.39 (20°) and 3.71 (100°) for $CHBr_3$].

Mechanism of the Intermolecular Exchange Process. To elucidate the mechanism of acetylacetonate exchange between $(C_6H_5)_2Sn(acac)_2$, site A, and $(CH_3)_2Sn(acac)_2$, site B, values of the mean residence times τ_A and τ_B were determined as a function of the concentrations of $(CH_3)_2Sn(acac)_2$ and $(C_6H_5)_2Sn(acac)_2$, respectively. Two series of solutions were prepared in bromoform (see Experimental Section). Results of the total line shape analysis are listed in Tables IV and V, along with the inverse mean lifetimes, $1/\tau_A$ and $1/\tau_B$, of the acetylacetonate ligand on sites A and B, and $\delta\nu_0$ values from computer-calculated nmr spectra.

Table III. Arrhenius and Eyring Activation Parameters for the Intermolecular Exchange of Acetylacetonate Groups between $(C_6H_5)_2Sn(acac)_2$ and $(CH_3)_2Sn(acac)_2$

Parameters	Solvents: Deuteriochloroform (T_c = 37.5°)	Solvents: Bromoform (T_c = 102°)
E_A, kcal/mol	7.5 ± 1.5[a]	5.4 ± 0.9
log A	6.05 ± 1.08	4.02 ± 0.57
$\Delta H^{\ddagger}_{298}$, kcal/mol	6.9 ± 1.5	4.8 ± 0.9
$\Delta S^{\ddagger}_{298}$, eu	−33 ± 5	−42 ± 3
$\Delta G^{\ddagger}_{298}$, kcal/mol	16.65 ± 0.09	17.37 ± 0.15
k_{298}, sec^{-1}	3.8 ± 0.6	1.1 ± 0.3

[a] Errors are estimated at the 95% confidence level.

Two features are noteworthy in Tables IV and V. First, the rate of transfer of an acetylacetonate ligand out of $(C_6H_5)_2Sn(acac)_2$ to $(CH_3)_2Sn(acac)_2$, expressed as $1/\tau_A$, is independent of the concentration of $(CH_3)_2Sn(acac)_2$ (Table IV). Second, the rate of transfer of an acetylacetonate ligand out of $(CH_3)_2Sn(acac)_2$ to $(C_6H_5)_2Sn(acac)_2$, expressed as $1/\tau_B$, shows first-order dependence on the concentration of the diphenyltin complex (Table V). The dependence of the inverse mean lifetimes of acetylacetonate ligands on sites A and B on the concentrations of reactants is pictured in Figure 3. These plots indicate

$$\tau_B^{-1} = \frac{k[(C_6H_5)_2Sn(acac)_2]}{[(CH_3)_2Sn(acac)_2]} \tag{2}$$

$$\tau_A^{-1} = k \tag{3}$$

where k is the observed first-order rate constant for the ligand-exchange process. From the slope of the linear least-squares analysis on the five points of the plot (top) of Figure 3, $k = 4.6 \pm 1.2$ sec^{-1} (1σ) in good agreement with $k = 4.4 \pm 0.3$ sec^{-1} (1σ), the average value of $1/\tau_A$ of Table IV.

The mechanism we propose resembles that of Adams and Larsen[5] for the ligand exchange between $M(acac)_4$ [M = Zr, Hf] and acetylacetone. The first step involves rupture of a Sn-O bond in the $(C_6H_5)_2Sn(acac)_2$ complex to yield a five-coordinate intermediate which then is thought to react with a similar five-coordinate species formed from a rapid equilibrium step from $(CH_3)_2Sn(acac)_2$. The mechanism is described in Scheme I. Applying the usual steady-state analysis we get

$$d[A^*]/dt = k_1[A] - k_{-1}[A^*] - k_2[A^*][B^*] = 0 \tag{4}$$

from which

$$[A^*] = \frac{k_1[A]}{k_{-1} + k_2K[B]}$$

where $[B^*] = K[B]$. The rate of ligand exchange is given by

$$\frac{d[C]}{2dt} = k_2[A^*][B^*] = \frac{Kk_1k_2[A][B]}{k_{-1} + k_2K[B]} \tag{5}$$

whence

$$\frac{1}{\tau_A} = \frac{1}{[A]}\frac{d[C]}{2dt} = \frac{k_1k_2K[B]}{k_{-1} + k_2K[B]} \tag{6a}$$

$$\frac{1}{\tau_B} = \frac{1}{[B]}\frac{d[C]}{2dt} = \frac{k_1k_2K[A]}{k_{-1} + k_2K[B]} \tag{6b}$$

Scheme I

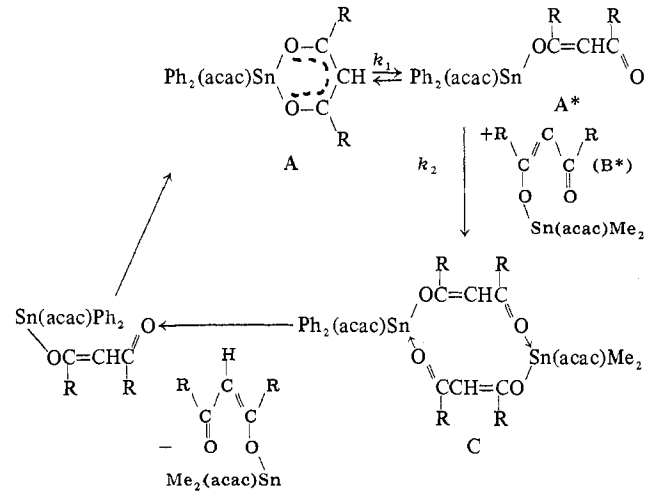

Table IV. Dependence of the Inverse Mean Lifetime $1/\tau_A$ on the Concentration of $(CH_3)_2Sn(acac)_2$ in Bromoform at 70°

[A],[a] *M*	[B],[a] *M*	τ_A,[b] sec	τ_B,[b] sec	$1/\tau_A$, sec^{-1}	$\delta\nu_0$, Hz
0.1005	0.1530	0.22	0.30	4.5	3.68
0.1003	0.1341	0.23	0.28	4.4	3.73
0.0999	0.1154	0.21	0.23	4.8	3.70
0.0987	0.1000	0.26	0.25	3.9	3.68
0.0981	0.0605	0.23	0.14	4.3	3.49

[a] A = $(C_6H_5)_2Sn(acac)_2$; B = $(CH_3)_2Sn(acac)_2$. [b] Error estimated to be about 10–15%.

Table V. Dependence of the Inverse Mean Lifetime $1/\tau_B$ on the Concentration of $(C_6H_5)_2Sn(acac)_2$ in Bromoform at 70°

[A],[a] *M*	[B],[a] *M*	[A]/[B]	τ_A,[b] sec	τ_B,[b] sec	$1/\tau_B$, sec^{-1}	$\delta\nu_0$, Hz
0.1613	0.0977	1.6506	0.22	0.14	7.1	3.72
0.1373	0.1004	1.3678	0.20	0.16	6.3	3.46
0.1194	0.0982	1.2161	0.32	0.26	3.9	3.61
0.0987	0.1000	0.9864	0.26	0.25	4.0	3.68
0.0822	0.0966	0.8505	0.25	0.27	3.7	3.71

[a] A = $(C_6H_5)_2Sn(acac)_2$; B = $(CH_3)_2Sn(acac)_2$. [b] Error estimated to be about 10–15%.

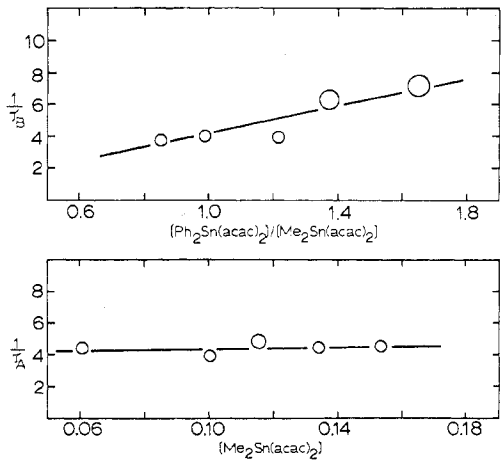

Figure 3. Plots of the inverse mean lifetimes $1/\tau_A$ and $1/\tau_B$ (see text) as a function of concentration.

Equations 6 lead to two different expectations: case i if $k_2K[B] \gg k_{-1}$

$$1/\tau_A = k_1; \quad 1/\tau_B = k_1[A]/[B] \tag{7}$$

and case ii if $k_{-1} \gg k_2K[B]$

$$1/\tau_A = k_2KK_1[B]; \quad 1/\tau_B = k_2KK_1[A] \tag{8}$$

Case i thus yields expressions for τ_A^{-1} and τ_B^{-1} consistent with those obtained experimentally (Figure 3); it is concluded that $k_2 \gg k_{-1} > k_1$ and thus k_1 is the rate-controlling step. The rate law can be expressed as $R = k_1[A]$ from eq 5.

Therefore, the rate-determining step in the ligand-exchange process between $(C_6H_5)_2Sn(acac)_2$ and $(CH_3)_2Sn(acac)_2$ appears to be rupture of one Sn-O bond in the six-coordinate diphenyltin complex. Such a case has not been reported before but has been suggested by several workers as a first step in the intramolecular environmental averaging processes in transition and post-transition metal complexes.[2,19] The kinetic data presented here, unfortunately, do not preclude a mechanism in which the rate-determining step is identified as rotation of one monodentate ligand (in species A*) about a partial double bond in the O-C-C-C-O moiety of the acetylacetonate unidentate ligand.[21]

The strongest evidence against rotation of the dangling acetylacetonate ligand in the A* species as the rate-controlling step arises from studies on the stereochemical lability of some triorganosilicon acetylacetonates.[22] These complexes possess an open-chain enol-ether structure and give rise to configurations in which the uncoordinated carbonyl oxygen atom is positioned either cis or trans to the siloxy group. Apparently, cis isomers undergo a rapid, intramolecular rearrangement process which interchanges the allylic and acetyl CH_3 groups on the acetylacetonate moiety. This rearrangement is believed to occur *via* a five-coordinate silicon intermediate; however, a similar process for the trans isomers is restricted by rotation about the C=C bond[23] as no broadening of the acetylacetonate methyl lines for the trans isomer of $(CH_3)_3Si(acac)$ was observed in the temperature range −70 to +120°.[22]

In addition, the data do not preclude a solvent-assisted path in the rupture of a Sn-O bond. That the solvent does not play an insignificant role is suggested by comparison of activation parameters in $CDCl_3$ and $CHBr_3$ (see Table III). Values of $\Delta S^{\ddagger}$ for the ligand-exchange process are rather low, −42 eu ($CHBr_3$) and −33 eu ($CDCl_3$) for a reaction involving a bond rupture rate-determining step. Brown[24] has pointed out that entropies of activation should be positive for a dissociative mechanism and negative for an associative one, in the absence of strong solvent effects. These low negative values of $\Delta S^{\ddagger}$ exclude complete dissociation of an acetylacetonate ligand and probably reflect the fact that the free end of the unidentate acetylacetonate ligand in species A* remains close to its original coordination site, bromoform

(21) The steps in such a mechanism are

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* \xrightarrow{k_{rot}} A^*_{rot} \xrightarrow{B^*_{rot}} C \rightarrow \ldots$$

If the rate of ligand exchange is defined by $d[A^*_{rot}]/dt = k_{rot}[A^*]$, where A^*_{rot} is the "rotated form" of A*, then one obtains expressions for τ_A^{-1} and τ_B^{-1} and the rate as $\tau_A^{-1} = k_{rot}k_1/(k_{-1} + k_{rot})$, $\tau_B^{-1} = k_{rot}k_1[A]/(k_{-1} + k_{rot})[B]$, and rate $= k_1k_{rot}[A]/(k_{-1} + k_{rot})$ which are also consistent with eq 2 and 3.

(22) T. J. Pinnavaia, W. T. Collins, and J. J. Howe, *J. Amer. Chem. Soc.*, 92, 4544 (1970); J. J. Howe and T. J. Pinnavaia, *ibid.*, 91, 5378 (1969).

(23) The nmr spectra of the trans isomers reveal a -CH= multiplet, two acetylacetonate methyl doublets, and a Si-CH_3 singlet.[22]

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being more effective in keeping the free end near this site. This also would explain the larger value of $\Delta S^{\ddagger}$ in $CDCl_3$ since this solvent, in its attempt to coordinate to the "vacant" sixth position, would force the free end away from its original site, thus leading to an increase in $\Delta S^{\ddagger}$.

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Contribution from the Institute "Ruder Boskovic," Zagreb, Croatia, Yugoslavia

Pentaaquo(3-chloropyridine)chromium(III) and Pentaaquo(3-cyanopyridine)chromium(III) Ions. The Preparation, Characterization, and Kinetics of the Aquation[1]

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The pentaaquo(3-chloropyridine)chromium(III) and pentaaquo(3-cyanopyridine)chromium(III) ions were prepared by the reduction of the corresponding pyridine adducts of diperoxychromium(VI) species with acidic ferrous perchlorate followed by the separation on a cation-exchange column. These pyridinyl nitrogen-bonded complexes aquate according to the rate law $-d \ln [Cr(3\text{-}Xpy)^{3+}]/dt = k_0 + k_{-1}/(H^+)$ at different temperatures studied. In 1 M ionic strength ($HClO_4$ + $NaClO_4$) the activation parameters for the 3-chloropyridine complex and 3-cyanopyridine complex have the values: $\Delta H_0^{\ddagger}$ (kcal mol^{-1}) 26.3 ± 0.5 and 23.9 ± 0.6, $\Delta S_0^{\ddagger}$ (cal mol^{-1} deg^{-1}) −1.6 ± 1.3 and −5.2 ± 1.7, $\Delta H_{-1}^{\ddagger}$ (kcal mol^{-1}) 33.5 ± 0.1 and 31.7 ± 0.2, $\Delta S_{-1}^{\ddagger}$ (cal mol^{-1} deg^{-1}) 13.7 ± 0.4 and 11.3 ± 0.6. The corresponding specific rates extrapolated to 25° are k_0 (sec^{-1}) 1.6×10^{-7} and 1.3×10^{-6} and k_{-1} (M sec^{-1}) 1.6×10^{-9} and 1.1×10^{-8}. A linear correlation between log k_0 or log k_{-1} and pK_a's of a series of the substituted pyridine ligands is found. A comparison with the similar finding for a series of uninegative ligands is made and the mechanistic implications discussed.

Introduction

The linear relationship between the logarithm of rate of aquation and the logarithm of stability constant has revealed useful insights on modes of spontaneous[2-5] and assisted[6,7] aquation of transition metal complexes. A particular linear free energy relationship (LFER) is the one involving reactivity and basicity.[8] Linear correlations between the free energy of activation for the aquation[9-16] or another octahedral substitution reaction[17-19] and the pK_a of the leaving[9-15,19] or nonleaving[16-18] ligand is often found. This kind of LFER offers less direct insight into mechanism of substitution reactions; however, comparisons of the correlations obtained for different series of ligands related to the same moiety might prove more useful.

This paper deals with 3-chloropyridine and 3-cyanopyridine complexes of monosubstituted chromium(III), aquation of which was studied as a function of acidity and temperature. Acquisition of these data together with those previously published on analogous pyridine[20] and 3-picoline[21] complexes enabled us to make a correlation between the reactivity and the basicity of the leaving pyridine ligands. A comparison with the similar analysis of the reactivity of the complexes with uninegative ligands[14] is made.

Experimental Section

Preparation of Pentaaquo(3-chloropyridine)chromium(III) and Pentaaquo(3-cyanopyridine)chromium(III) Ions. These complex ions were prepared by the reduction of the respective pyridine adducts of diperoxychromium(VI) species with acidic ferrous perchlorate solution, followed by the separation on a cation-exchange resin. The procedure was analogous to the one reported for the preparation of pentaaquo(3-picoline)chromium(III) ion.[21] The concentration of pentaaquo(3-chloropyridine)chromium(III) ion[22] or pentaaquo(3-cyanopyridine)chromium(III) ion[22] in 3 M perchloric acid solution obtained in this way was $1\text{–}3 \times 10^{-2}$ M. The solution stored at −5° did not change for an extended period of time. Aquation of the complex ions to a certain degree was observed when, for the purpose of kinetic studies at low acidity, cooled (0°) stock solutions were reduced to 0.1 M $HClO_4$ by titration with cooled 3 or 1 M potassium hydroxide.

Other Materials. Laboratory grade 3-chloropyridine (Fluka) was distilled and a middle fraction with bp 146–147° was used. Labora-

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