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KINETICS AND MECHANISMS OF INTERMOLECULAR LIGAND EXCHANGE

II. DIPHENYLTIN- AND DIMETHYLTINACETYLACETONATE WITH ACETYLACETONE *

THOMAS F. IGNACZ and NICK SERPONE *

Department of Chemistry, Sir George Williams Campus, Concordia University, 1455 de Maisonneuve Blvd., West, Montreal, Quebec H3G 1M8 (Canada)

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Summary

The kinetics and mechanisms of intermolecular ligand exchange of acetylacetonate (acac) groups between "bulk" free acetylacetone (enol form) and $R_2Sn(acac)_2$ (R = CH_3 or Ph) complexes have been re-investigated in chloroform-*d* (R = CH_3) and chlorobenzene (R = Ph) solutions by proton magnetic resonance spectroscopy using the total lineshape analysis in the temperature range: 12.7—37.0°C (R = CH_3; acac =CH— region), —1.4 to 19.6°C (R = CH_3; acac CH_3 region) and 25.9—48.0°C (R = Ph; acac =CH— region). The activation energies and entropies of activation are: for R = CH_3, 7.2 ± 0.7 kcal/mol and —30 ± 3 eu (acac CH_3), and 6.3 ± 0.6 kcal/mol and —32 ± 2 eu (acac =CH—); for R = Ph 8.8 ± 2.7 kcal/mol and —31 ± 9 eu (acac =CH—). Concentration dependence studies for both the $(CH_3)_2Sn(acac)_2$—Hacac and $Ph_2Sn(acac)_2$—Hacac systems indicate that the rate of acetylacetonate exchange is first-order in the concentration of $R_2Sn(acac)_2$ and zero order in the concentration of "bulk" free ligand. The intermolecular ligand exchange phenomenon is believed to involve coordination number lowering; viz. a Sn—O bond rupture as the rate-determining step to yield a five-coordinate intermediate species with a dangling unidentate acetylacetonate ligand.

Introduction

The mechanism(s) of intermolecular ligand exchange have often neither been verified nor shown to be completely unequivocal. In a study of the kinetics of ligand exchange between gold(III), gallium(III), thallium(III) and tin(IV) complexes and free acetylacetone, Glass and Tobias [1] proposed a mechanism, un-

* For part I, see ref. 7. Taken from a senior undergraduate thesis of T.F. Ignacz (1974—75).

substantiated by concentration dependence studies, in which the probable rate-determining step was postulated as being a metal—oxygen bond rupture, resulting in lowering of the coordination number.

In an analogous investigation of the ligand exchange reaction between InL_3 complexes (L = trifluoromethyl-β-diketonate ligands) and excess free ligand (HL), Tanner, Tuck and Wells [2] have proposed a mechanism similar to the one suggested by Adams and Larsen [3] for the ligand exchange between $M(dik)_4$ and Hdik, where dik is trifluoroacetylacetonate anion or acetylacetonate anion and M is Zr, Hf, or Th. The rate-determining step in the exchange reaction, however, 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 six-coordinate complex possessing two bidentate and two unidentate keto-enolate ligands.

Several studies [4—6] on the kinetics and mechanisms of environmental averaging processes on complexes of the type $R'R''M(acac)_2$ (M = Si, Ge, Sn; R' = CH_3 or Ph; R'' = CH_3, Ph or Cl; acac = $CH_3COCHCOCH_3^-$) have been reported from this laboratory. Serpone and Ishayek [7] have also recently reported their work on the intermolecular ligand exchange of acetylacetonate groups between diphenylbis(2,4-pentanedionato)tin(IV) and dimethylbis(2,4-pentanedionato)-tin(IV) in $CDCl_3$ and $CHBr_3$ solutions. A mechanism was described in which the rate-determining step involves a Sn—O bond rupture in the diphenyltin complex to yield a five-coordinate tin species with a dangling unidentate acetylacetonate ligand. Such a study had been undertaken in an effort to elucidate the mechanism(s) of intramolecular exchange processes in these and related complexes, albeit the results have not proven to be unequivocal.

To further clarify the mechanism(s) of intermolecular ligand exchange in $R_2Sn(acac)_2$-type complexes (R = Ph or CH_3), we have carried out a kinetic and mechanistic study on the ligand exchange between $(CH_3)_2Sn(acac)_2$ and 2,4-pentanedione (Hacac) in chloroform-*d* solutions, and between $Ph_2Sn(acac)_2$ and Hacac in chlorobenzene solutions.

Experimental

Materials and solvents

Diphenyldichlorotin, dimethyldichlorotin and thallous carbonate were purchased from Alfa Inorganics and were used as received. Acetylacetone (2,4-pentanedione) was Fisher Certified Reagent and was distilled prior to use. Reagent grade dichloromethane (Anachemia Chemical) and practical hexanes (Fisher Scientific) were dried over calcium hydride chips (Fisher Scientific) by refluxing for ca. 12 h and distilled prior to use. Fisher Certified Reagent chlorobenzene was purified and dried by distillation over molecular sieves (Fisher Scientific, Type 4-A) and stored over molecular sieves in a septum-capped bottle. Deuteriochloroform was prepared by a modified procedure [8] of Paulsen and Cooke [9] and was stored over molecular sieves in a septum-capped bottle. Thallium acetylacetonate was prepared according to standard procedures. Melting points were determined in capillaries, sealed under a dry nitrogen atmosphere with modelling clay, and are uncorrected.

The complex diphenylbis(2,4-pentanedionato)tin(IV) was prepared by reacting

diphenyldichlorotin with thallium acetylacetonate in dichloromethane in a dry nitrogen atmosphere according to literature methods [7,10]. M.p. 122—124°C; lit. [10], m.p. 125—126°C. The purity of the product was further ascertained by its infrared and NMR spectra.

Dimethylbis(2,4-pentanedionato)tin(IV) was obtained by an analogous established procedure [7,10]. M.p. 179—180°C; lit. [10], m.p. 177—178°C. The infrared and NMR spectra further verified the purity of the product.

Preparation of solutions and handling of data

Solutions were prepared in a dry nitrogen atmosphere in a glove-bag prior to each NMR investigation. The solutions were degassed according to the freeze-thaw-freeze method and the NMR sample tubes were flame-sealed in vacuo.

Concentration dependence studies were carried out on two series of solutions for each system under study. In the first series, the concentration of the metal complex was fixed at ca. 0.39 *M* for $(CH_3)_2Sn(acac)_2$ and ca. 0.38 *M* for $Ph_2Sn(acac)_2$; while the free ligand concentration was varied ($(CH_3)_2Sn(acac)_2$—Hacac system, 0.40—0.77 *M*; $Ph_2Sn(acac)_2$—Hacac system, 0.46—1.00 *M*). The second series involved a variation in the metal complex concentration ($(CH_3)_2Sn(acac)_2$, 0.07—0.40 *M*; $(C_6H_5)_2Sn(acac)_2$, 0.19—0.38 *M*) while the free ligand concentration remained constant at ca. 0.50 *M* ($(CH_3)_2Sn(acac)_2$—Hacac system) and at ca. 0.91 *M* [$Ph_2Sn(acac)_2$—Hacac system].

NMR spectra were recorded in $CDCl_3$/TMS and C_6H_5Cl/TMS solvents on a Varian A60-A NMR spectrometer operating at 60.00 MHz and equipped with a Model V-4343 variable temperature probe accessory and a Model V-6040 temperature controller accessory. Probe temperatures were obtained from the proton shift separations of methanol and ethylene glycol. All reported temperatures are based on the Van Geet equations [11].

The residence times of —CH= or $-CH_3$ proton(s) on a particular site were extracted from the NMR spectra recorded in the solvents and over the temperature ranges indicated: $(CH_3)_2Sn(acac)_2$, 12.7—37.0°C ($CDCl_3$) for the —CH=protons, —1.4 to 19.6°C ($CDCl_3$) for the $-CH_3$ groups, and $Ph_2Sn(acac)_2$, 25.9—48.0°C (C_6H_5Cl) for the —CH=protons. The computer fitting program required the following input parameters (for each temperature): $B(=\pi\delta\nu)$, where $\delta\nu$ is the chemical shift separation (in Hz) in the absence of exchange between the two resonance components of the exchanging system; p_A and p_B, the fractional populations at site A and at site B, respectively; T_{2A} and T_{2B} $(=1/\pi\ W_{1/2})$, the transverse relaxation times at site A and site B, respectively, in the absence of exchange, and $W_{1/2}$ is the full linewidth at one-half maximum height.

The chemical shift separations in the absence of exchange, $\delta\nu$, were obtained from a plot of $\delta\nu$ vs temperature (see ref. 4) in which the linear portion in the slow exchange region was extrapolated in the intermediate and fast exchange regions.

The fractional populations, p_A (metal—complex) and p_B (enol form of free ligand), were obtained from the molar concentration of each species, at the appropriate temperature. The concentration of the enol form of acetylacetone is dependent on the temperature and solvent. The percent enol content was estimated [12] over the required temperature range and in the appropriate solvents by NMR spectroscopy. The peak heights of the keto-methyl and enol-methyl

proton resonances were determined and a calibration plot of the percent enol vs temperature prepared.

The linewidths $W_{1/2}$ in the absence of exchange were obtained from the Sn—CH_3 proton resonance signal ($CDCl_3$) and from the acac—CH_3 signal (C_6H_5Cl) of $(CH_3)_2Sn(acac)_2$.

Results

The variable temperature spectra of the acetylacetonate methyl and methylene ring proton regions of the $(CH_3)_2Sn(acac)_2$—Hacac system in chloroform-*d* are illustrated in Fig. 1. Analogous spectra were obtained for the =CH— proton region of the diphenyltin/acetylacetone system, $Ph_2Sn(acac)_2$—Hacac, in chlorobenzene solutions.

The temperature-dependent residence times of the respective protons on the complexed ligand (τ_{cpd}) and on the free ligand (τ_{enol}) were estimated from the mean residence times, τ, using $\tau_{cpd} = \tau/p_{enol}$ and $\tau_{enol} = \tau/p_{cpd}$. These as well as the first-order rate constants, $k(= 1/\tau_{cpd})$, for the $(CH_3)_2Sn(acac)_2$—Hacac (enol

TABLE 1

TEMPERATURE-DEPENDENCE OF RESIDENCE TIMES FOR THE EXCHANGE OF acac GROUPS BETWEEN $R_2Sn(acac)_2$ AND Hacac

Temp. (°C)	τ_{cpd} (sec)	τ_{enol} (sec)	$k(= 1/\tau_{cpd})$ (sec^{-1})
R = CH_3 [a]*; =CH— region*			
37.0	0.0154	0.0195	65.1
24.6	0.0245	0.0316	40.8
21.4	0.0276	0.0357	36.2
18.6	0.0296	0.0384	33.8
16.0	0.0331	0.0432	30.2
12.7	0.0364	0.0476	27.5
—CH_3 region (acac)			
19.6	0.0438	0.0569	22.8
16.8	0.0510	0.0665	19.6
14.3	0.0540	0.0704	18.5
9.6	0.0651	0.0856	15.4
5.1	0.0803	0.1060	12.4
2.2	0.0998	0.1323	10.0
—1.4	0.1134	0.1509	8.82
R = Ph [b]*; =CH— region*			
48.0	0.306	0.795	3.27
45.5	0.341	0.890	2.93
42.5	0.452	1.181	2.21
41.1	0.357	0.938	2.80
39.1	0.383	1.010	2.61
36.9	0.422	1.137	2.37
34.7	0.447	1.191	2.24
33.3	0.506	1.346	1.98
30.6	0.631	1.680	1.58
28.3	0.891	2.373	1.12
25.9	0.830	2.211	1.20

[a] [$(CH_3)_2Sn(acac)_2$] 0.383 *M*; [Hacac] 0.563 *M*; $CDCl_3$ TMS. [b] [$Ph_2Sn(acac)_2$] 0.380 *M*; [Hacac] 1.100 *M*; C_6H_5Cl/TMS.

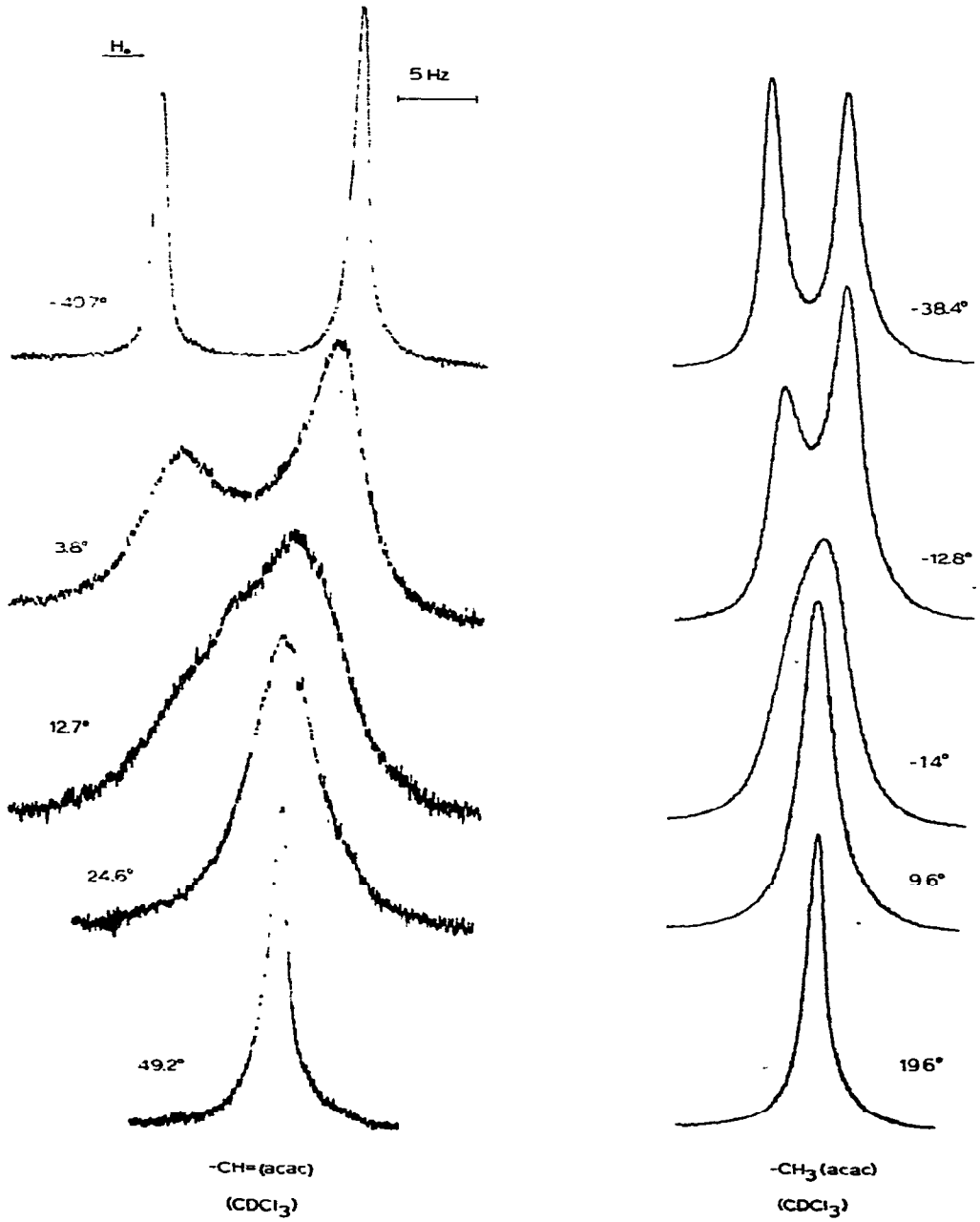

Fig. 1. NMR spectra for the acetylacetonate ring proton region and methyl region as a function of temperature for the intermolecular ligand exchange between $(CH_3)_2Sn(acac)_2$ and free acetylacetone (enol form).

TABLE 2

ARRHENIUS AND EYRING ACTIVATION PARAMETERS FOR THE INTERMOLECULAR EXCHANGE OF acac GROUPS BETWEEN $(CH_3)_2Sn(acac)_2$ AND Hacac; AND BETWEEN $Ph_2Sn(acac)_2$ AND Hacac

	$(CH_3)_2Sn(acac)_2$		$Ph_2Sn(acac)_2$
	$-CH_3$	$=CH-$	$=CH-$
E_a (kcal/mol)	7.2 ± 0.7 [a]	6.3 [b] ± 0.6 [a]	98.8 ± 2.7 [a]
log A	6.7 ± 0.6	6.2 [c] ± 0.5	6.5 ± 1.9
$\Delta H^{\neq}_{298}$ (kcal/mol)	6.6 ± 0.7	5.7 ± 0.6	8.2 ± 2.7
$\Delta S^{\neq}_{298}$ (e.u.)	−30 ± 3	−32 ± 2	−31 ± 9
$\Delta G^{\neq}_{298}$ (kcal/mol)	15.46 ± 0.05	15.23 ± 0.02	17.3 ± 0.1
k_{298} (sec^{-1})	29 ± 2	42 [d] ± 1	1.2 [e] ± 0.2

[a] Errors are estimated at the 95% confidence level. [b] Lit. [1], 7.6 ± 0.3 kcal/mol. [c] Lit. [1], 8.5. [d] 64 sec^{-1} at 40°C; lit. [1], 670 sec^{-1}. [e] 2.3 sec^{-1} at 40°C; lit. [1], 80 sec^{-1}.

TABLE 3

CONCENTRATION-DEPENDENCE OF THE RESIDENCE TIMES FOR EXCHANGE OF acac GROUPS BETWEEN $(CH_3)_2Sn(acac)_2$ AND Hacac [a]

$[(CH_3)_2Sn(acac)_2]$	[Hacac] [b]	τ_{cpd} (sec)	τ_{enol} (sec)	$k(=1/\tau_{cpd})$ (sec^{-1})
0.385	0.396	0.0259 [c]	0.0266 [c]	38.7
0.382	0.498	0.0339	0.0441	29.5
0.404	0.506	0.0269	0.0338	37.1
0.387	0.767	0.0289	0.0569	34.9
				Ave.: 34.6 ± 4.0 [d]
$[(CH_3)_2Sn(acac)_2]$	[Hacac] [b]	τ_{cpd} (sec)	τ_{enol} (sec)	$k(=1/\tau_{enol})$ (sec^{-1})
0.0738	0.434	0.0215 [c]	0.127 [c]	7.9
0.183	0.489	0.0289	0.0775	12.9
0.194	0.506	0.0342	0.0893	11.2
0.383	0.498	0.0339	0.0441	22.7
0.404	0.506	0.0269	0.0338	29.6

[a] $=CH-$ region; $CDCl_3$ solvent; 15.3°C. [b] Enol form. [c] Errors estimated to be approximately 10—15%. [d] One standard deviation.

TABLE 4

CONCENTRATION-DEPENDENCE OF THE MEAN RESIDENCE TIMES FOR EXCHANGE OF acac GROUPS BETWEEN $Ph_2Sn(acac)_2$ AND Hacac [a]

$[(C_6H_5)_2Sn(acac)_2]$	[Hacac] [b]	τ_{cpd} (sec)	τ_{enol} (sec)	$k(=1/\tau_{cpd})$ (sec^{-1})
0.381	1.651	0.103 [c]	0.447 [c]	9.7
0.380	1.004	0.286	0.754	3.5
0.391	0.983	0.213	0.538	4.7
0.382	0.655	0.217	0.365	4.6
0.385	0.462	0.128	0.154	7.8
				Ave: 6.1 ± 2.6 [d]
$[(C_6H_5)_2Sn(acac)_2]$	[Hacac] [b]	τ_{cpd} (sec)	τ_{enol} (sec)	$k(=1/\tau_{enol})$ (sec^{-1})
0.380	1.004	0.286 [c]	0.754 [c]	1.33
0.307	0.913	0.339	1.008	0.99
0.259	0.913	0.353	1.243	0.81
0.194	0.913	0.324	1.529	0.65

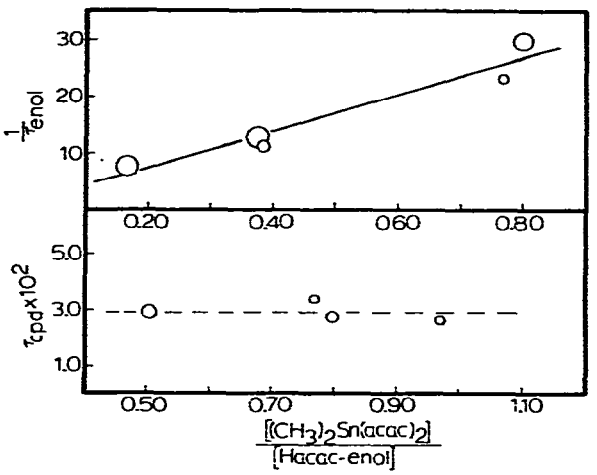

Fig. 2. Plots of the inverse mean lifetimes as τ_{cpd} and $1/\tau_{enol}$ as a function of the ratio of complex concentration to free ligand concentration (see text).

form; $CDCl_3$) and for the $Ph_2Sn(acac)_2$—Hacac (enol form; C_6H_5Cl) systems are presented in Table 1.

The Arrhenius energies of activation, E_a, and frequency factors, log A, were taken from the slope and intercept, respectively, of the linear least-squares plot of log k versus $1/T$. Values of E_a and log A, along with the Eyring activation parameters $\Delta G^{\neq}_{298}$, $\Delta H^{\neq}_{298}$, and $\Delta S^{\neq}_{298}$, and the extrapolated values of k at 298° K are summarized in Table 2. The activation entropies were calculated from the expression [13] $\Delta S^{\neq} = R[\ln A - \ln(RT/Nh)] - R$.

Results of the concentration dependence studies of the residence times for exchange of acetylacetonate groups between the dimethyltin- or diphenyltin-acetylacetonate, and the enol form of acetylacetonate are presented in Tables 3 and 4, respectively. Typical plots of $1/\tau_{enol}$ and τ_{cpd} as a function of $[(CH_3)_2Sn(acac)_2]/[Hacac\text{—}enol]$ for the dimethyltin—Hacac system ($CDCl_3$) are illustrated in Fig. 2.

Discussion

A common feature in both sets of spectra (Fig. 1) is that a temperature increase leads to a broadening and coalescence of the respective proton signals into a single, broad line (T_c of =CH— signals is 11° C and of the —CH_3 resonances is —4.5° C for the $(CH_3)_2Sn(acac)_2$—Hacac system; T_c for the =CH— signals of the $Ph_2Sn(acac)_2$—Hacac system is 27° C). In the high temperature limit, the resonance signals appear as single, sharp lines. Serpone and Ishayek [7] have attributed this coalescence behavior to a rapid intermolecular ligand exchange process. We hasten to point out that intramolecular exchange of acetylacetonate methyl groups in $(CH_3)_2Sn(acac)_2$ has not been observed (in $CDCl_3/CCl_4$ solvent) even at temperatures as low as —77° C [6] owing to very rapid rates of ex-

change, even though this complex exists as a mixture of *cis* and *trans* diastereomers [14]. In the case of *cis*-$Ph_2Sn(acac)_2$, coalescence of the two acac—CH_3 signals for the intramolecular exchange process occurs at —38°C ($CDCl_3$) [6], while the full linewidth ($W_{1/2}$) of the acac—CH_3 signal in chlorobenzene at —36°C is 2.5 Hz [12]. In the latter case, therefore, intermolecular exchange with acetylacetone was studied in a temperature range (see experimental) where the intramolecular exchange process was fast.

In a recent study from this laboratory, we [7] reported on the intermolecular acetylacetonate ligand exchange between $Ph_2Sn(acac)_2$ and $(CH_3)_2Sn(acac)_2$ complexes; the rate of exchange was found to be first-order in [$Ph_2Sn(acac)_2$]. The rate-determining step was identified as rupture of one Sn—O bond in the diphenyltin complex; E_a = 7.5 ± 1.5 kcal/mol, $\Delta S^{\neq}$ = —33 ± 5 eu and k_{25} = 3.8 sec^{-1} ($CDCl_3$ solutions). The energy of activation for the intramolecular exchange of methyl groups in $Ph_2Sn(acac)_2$ in chloroform-*d* solutions is 8.1 ± 0.3 kcal/mol, $\Delta S^{\neq}$ is —21.7 ± 1.4 eu, and k_{25} is 369 sec^{-1} [6]. The above values agree favorably well with those of Table 2 for the intermolecular ligand exchange between $R_2Sn(acac)_2$ (R = CH_3 or Ph) and Hacac, although the rate of exchange (k_{25} = 1.2 ± 0.2 sec^{-1}) is one order of magnitude slower than intramolecular exchange when R is Ph. Values of both energies of activation and activation entropies of Table 2 are remarkably similar to those referred to above suggesting that intra- and intermolecular exchange processes in these systems probably go over very similar potential energy surfaces. It is also noteworthy that intermolecular exchange in the dimethyltin—Hacac system is faster than in the diphenyltin—Hacac system; and exchange in both of these systems is faster than the analogous exchange between $(CH_3)_2Sn(acac)_2$ and $Ph_2Sn(acac)_2$. Presumably, this is a reflection of the increased difficulty in breaking a metal chelate ring as compared to the hydrogen bond in the proton "chelate" of acetylacetone [1]. While the role of the solvent ($CDCl_3$ vs. chlorobenzene) cannot be overlooked in these intermolecular exchange phenomena, faster exchange in the $(CH_3)_2Sn(acac)_2$—Hacac system is in accord with the greater lability of the dimethyltin—acetylacetonate complex (cf. refs. 6 and 7).

Another feature of Table 2 pertains to the rather large uncertainties in the values of the activation parameters for the intermolecular exchange in the $Ph_2Sn(acac)_2$—Hacac system. This may be the result of the uncertainties in the very small values of $\delta\nu$(2.75 Hz at —43°C; see e.g., refs. 15 and 16). Even more significant is the percent relative uncertainty in the average $k(= 1/\tau_{cpd})$ value of Table 4.

Two features are noted in Tables 3 and 4. First, the rate of transfer of an acetylacetonate ligand out of the metal complex, $(CH_3)_2Sn(acac)_2$ or $Ph_2Sn(acac)_2$, to the "bulk" of free ligand (enol form of acetylacetone) and represented as $1/\tau_{cpd}$, is independent of the concentration of free ligand. Second, the rate of transfer of an acetylacetonate ligand from the "bulk" of free enolate ligand to the complex $R_2Sn(acac)_2$ (R = CH_3 or Ph) and expressed as $1/\tau_{enol}$, indicates first-order dependence on the concentration of the dimethyltin- or diphenyltin-acetylacetonate complex. The dependence of the inverse mean lifetimes of acetylacetonate ligands on the two sites (complex and free ligand) on the concentrations of reactants is pictured in Fig. 2 for the $(CH_3)_2Sn(acac)_2$—Hacac system. An analogous plot is obtained for the $Ph_2Sn(acac)_2$—Hacac system. These

plots demonstrate that

$$\tau_{enol}^{-1} = \frac{k[R_2Sn(acac)_2]}{[Hacac—enol]} \text{ and } \tau_{cpd} = 1/k$$

and thus,

$$\text{Rate} = k[R_2Sn(acac)_2]$$

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 Fig. 2, $k = 32 \pm 5$ sec^{-1} (one standard deviation, 1σ) in fair agreement with $k = 34.6 \pm 4.0$ sec^{-1} (1σ), the average value of τ_{cpd}^{-1} of Table 3. A similar comparison for the $Ph_2Sn(acac)_2$—Hacac system yields $k = 4 \pm 1$ sec^{-1} (plot) in agreement with the average value of $k = 6.1 \pm 2.6$ (1σ) of Table 4.

The mechanism we propose is similar to the one we reported earlier for the ligand exchange in the $Ph_2Sn(acac)_2$—$(CH_3)_2Sn(acac)_2$ system [7], and to the one suggested by Tanner, et al. [2]. The first step involves rupture of a Sn—O bond in the $R_2Sn(acac)_2$ complex to yields a five-coordinate intermediate which is then thought to react with the enol form of acetylacetone. The complex is reformed following a fast proton transfer step between the two unidentate acetylacetonate ligands and eventual dissociation of one of these ligands from the tin atom. The remarkable similarity in the values of the activation parameters presented here and those reported earlier [7] for the intermolecular ligand exchange in $Ph_2Sn(acac)_2$—$(CH_3)_2Sn(acac)_2$ and for the intramolecular exchange in the $Ph_2Sn(acac)_2$ complex [6] (see above) leads us to believe that in the present systems, also, the rate-determining step is most probably the rupture of a Sn—O bond in the six-coordinate $R_2Sn(acac)_2$ complexes.

In a study of the ligand redistribution between C-14 labelled $Be(acac)_2$ and acetylacetone, Barabas [17] indicated that the measured rates of ligand exchange represent a composite of a mononuclear process and a bimolecular one, the relative extent of each being a function of the solvent used. Apparently, the contribution of the former process to the overall redistribution rate is negligible in chlorinated hydrocarbons, small in hydrocarbons and acetonitrile, and predominant in oxygenated solvents. This is in contrast to the present results and to our earlier findings [7] on the ligand exchange between $(CH_3)_2Sn(acac)$ and $Ph_2Sn(acac)_2$ in chlorinated solvents, and in contrast with the work of Tanner, Tuck, and Wells [3] on ligand exchange between InL_3 and HL. These studies show that in a variety of solvents used ($CDCl_3$, $CHBr_3$, chlorobenzene, CH_3CN, benzene, DMSO, and di-isopropylketone) the rate of ligand exchange is first order on the concentration of the complex and independent of free ligand concentration. Interestingly, the ligand exchange between the octa-coordinate $M(dik)_4$ and the free ligand Hdik (where dik = trifluoroacetylacetonate anion or acetylacetonate anion; and M = Zr, Hf, or Th) in benzene or chlorobenzene follow second order kinetics, the rate being first order with respect to both $[M(dik)_4]$ and [Hdik] (ref. 3).

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