

## KINETICS OF THE LIGAND EXCHANGE BETWEEN ORGANO-GOLD(III), -GALLIUM(III), -THALLIUM(III), AND -TIN(IV) ACETYLACETONATES AND FREE ACETYLACETONE\*

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### SUMMARY

The rate of the exchange of the acetylacetonate ligand between several organometallic acetylacetonates and the proton chelate, acetylacetonate, have been studied using pmr spectroscopy. The order of increasing exchange rate is  $\text{Cl}_2\text{Sn}(\text{acac})_2 \ll (\text{CH}_3)_2\text{Au}(\text{acac}) \simeq (\text{CH}_3)\text{ClSn}(\text{acac})_2 \simeq (\text{CH}_3)_2\text{Ga}(\text{acac}) < (\text{C}_6\text{H}_5)_2\text{Sn}(\text{acac})_2 < (\text{CH}_3)_2\text{Sn}(\text{acac})_2 < (\text{CH}_3)_2\text{Tl}(\text{acac})$ . Since the rate of intramolecular exchange appears to be much greater than that for intermolecular exchange, the diorgano-tin(IV) and thallium(III) chelates should be very non-rigid molecules at room temperature. The rate of exchange of acetylacetonate between  $(\text{CH}_3)_2\text{Sn}(\text{acac})_2$  and  $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{acac})_2$  is slower than the exchange between either complex and acetylacetonate.

### INTRODUCTION

A large number of organometallic acetylacetonates have been synthesized, and many of these have been described in a recent review<sup>1</sup>. Some additional information on these compounds can be found in a comprehensive review on  $\beta$ -diketonates<sup>2</sup>. Many of these organometallic acetylacetonates are neutral molecules; and generally, they are quite soluble in most organic solvents.

Proton magnetic resonance spectroscopy is a particularly useful technique for the determination of the structures of such organometallic chelates. In order to use this technique, however, it is necessary to work under experimental conditions where the organometallic molecule is stereochemically rigid. Studies on organotransition metal aquo complexes which have metal electronic configurations usually associated with very inert behavior, e.g.,  $d^6$  and  $d^8$ , have shown that alkyl groups labilize the other ligands in the first coordination sphere<sup>3,4</sup>. Consequently, it is likely that most of the organo-heavy metal chelates are quite non-rigid at room temperature. Several years ago, we cited the occurrence of a single acetylacetonate methyl proton resonance for  $(\text{CH}_3)_2\text{Sn}(\text{acac})_2$  as support for the *trans* structure<sup>5</sup>. Although the *trans* structure is certainly correct as was also shown by the Raman and infrared spectra<sup>5</sup>, it is now evident that such organotin compounds are sufficiently non-rigid at room tempera-

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ture so that intramolecular ligand exchange would lead to coalescence of non-equivalent ligand proton resonances. Consequently, the PMR spectra recorded at room temperature are not suitable for establishing the structures of such complexes. Upon lowering the temperature of the  $(\text{CH}_3)_2\text{Sn}(\text{acac})_2$  solutions to  $-92^\circ$ , we have observed no changes in the PMR spectrum which are in conflict with the assignment of the *trans* structure. Replacement of the two methyl groups by, *e.g.*, two chloride ligands gives a much more "rigid" molecule. In this case the stable structure is the *cis* isomer, and the non-equivalent acetylacetonate protons can be observed at room temperature in PMR spectra<sup>6</sup>.

In order to obtain information on the lability of coordinated  $\beta$ -diketonate ligands, we have carried out a survey of the rates of exchange of the acetylacetonate ligand between the organometallic chelate and the proton chelate, *i.e.*, the enol form of acetylacetonate itself. These measurements have been made, in part, with acetylacetonate itself as the solvent, so pseudo first order rate constants for the exchange reactions are obtained. In a subsequent communication more detailed kinetic studies on certain selected molecules will be reported<sup>7</sup>.

Although there have been several studies on intramolecular exchange of  $\beta$ -diketonate ligands with non-equivalent protons<sup>8-14</sup>, there appears to have been only one study<sup>15</sup> on the exchange of the ligand between a complex and the free  $\beta$ -diketonate. We have chosen this latter type of experiment in order to obtain general information on the lability of several chelates which have symmetrical structures. Although these intermolecular exchange rates will be distinctly different from the rates of intramolecular exchange it is hoped that both will exhibit similar trends as the metal is varied.

## EXPERIMENTAL

### *Preparation of organometallic acetylacetonate complexes*

#### *Dimethylbis(2,4-pentanedionato)tin(IV)*<sup>5</sup>

A benzene solution of acetylacetonate was treated with excess anhydrous dimethyltin(IV) oxide, the mixture was filtered to remove excess  $(\text{CH}_3)_2\text{SnO}$ , and the solvent was evaporated in a stream of nitrogen to yield colorless crystals. The product was recrystallized from anhydrous benzene, m.p.  $181-183^\circ$ , lit.<sup>16</sup>  $177-178^\circ$ \*. The PMR spectrum and integrals were identical to those originally reported<sup>5</sup> indicating that a pure sample had been obtained.

The compound was also prepared by dissolving  $(\text{CH}_3)_2\text{SnO}$  and acetylacetonate in water with excess sodium hydroxide. A white precipitate was formed when 6 *M* nitric acid was added slowly to give  $\text{pH} \approx 8$ . The product was washed with water and recrystallized from chloroform.

#### *Chloromethylbis(2,4-pentanedionato)tin(IV)*

Methyl stannic acid<sup>17</sup> and acetylacetonate were dissolved in water with excess ammonia. Hydrochloric acid (6 *M*) was added slowly until a white precipitate formed

\* The melting points were obtained using a sealed tube. When the compound is heated slowly in the open air on a Fisher-Johns apparatus, no definite melting point is observed, and this led to our original report<sup>5</sup>.

at pH  $\approx$  5. The product was collected on a frit and recrystallized from chloroform; m.p. 133–135° (dec.).

*Dichlorobis(2,4-pentanedionato)tin(IV)*<sup>18</sup>

This compound was isolated from the aqueous solution used in the preparation of Cl(CH<sub>3</sub>)Sn(acac)<sub>2</sub> by the further addition of 6 M hydrochloric acid until pH  $\approx$  2. The white product was collected on a frit and recrystallized from chloroform. The PMR spectrum was identical to that reported previously<sup>6,19–21</sup>.

*Diphenylbis(2,4-pentanedionato)tin(IV)*<sup>5</sup>

Anhydrous diphenyltin(IV) oxide was refluxed with acetylacetone for four hours. The unreacted oxide was removed by filtration, and the solvent was removed using a rotary evaporator. The PMR spectrum was identical to that reported previously<sup>5</sup>.

*Dimethyl(2,4-pentanedionato)gold(III)*<sup>22</sup>

This compound was prepared as described previously<sup>23</sup> and recrystallized from ligroin.

*Dimethyl(2,4-pentanedionato)gallium(III)*<sup>24</sup>

The preparation of this compound has been described previously<sup>25</sup>.

*Dimethyl(2,4-pentanedionato)thallium(III)*<sup>26</sup>

Trimethylthallium<sup>27</sup> was dissolved in ether with excess acetylacetone. The ether was evaporated with a stream of nitrogen, and the white product was recrystallized from benzene. (Analysis: Found: C, 25.2; H, 3.92; Tl, 61.2%. C<sub>7</sub>H<sub>13</sub>O<sub>2</sub>Tl calcd.: C, 25.2; H, 3.93; Tl, 61.3%). The PMR spectrum in a benzene solution was identical to that reported previously<sup>28</sup>.

*Chloroform*

The chloroform used as a solvent in the NMR experiments was freed of ethanol by shaking it with concentrated H<sub>2</sub>SO<sub>4</sub>, separating the acid fraction, and distilling the CHCl<sub>3</sub> from anhydrous CaSO<sub>4</sub>.

*Proton magnetic resonance spectra*

A Varian A-60 spectrometer with a V6020 heat exchanger and V6040 variable temperature controller was used. In addition an external oscillator, Hewlett Packard 3300A function generator, and a counter, Hewlett Packard 3734A, were employed. Sample tubes, Varian 905370, sealed with 3/16" "Caplug" closures (available from Protective Closures Co., Buffalo, N. Y. 14216) were used, since an air-tight and sometimes pressure-tight seal was required.

The field sweep was calibrated using the side-band technique with an external oscillator. Care was taken so that the calibration was not influenced by the *r-f* power level. Accurate measurements of line position were made by bracketing the resonance of interest with sidebands of the other resonance line from which the shift was to be measured. Accuracy is believed to be  $\pm 0.2$  cps.

TABLE I  
PROTON MAGNETIC RESONANCE DATA AND EXCHANGE PARAMETERS

Site a (Concn. M)	Site b (Concn. M)	$P_a$	Solvent	Resonance site	$\delta_{10}^a$ (cps)	$W^*$ cps ( $T^\circ K$ )	$W^{**}$ cps
$Cl_2Sn(acac)_2$ (0.41 M)	Hacac (-)	0.05	Hacac	$\gamma$ -CH(acac) complex	15.6	0.44(351) 0.40(364) 0.42(372) 0.43(378)	0.33
$(CH_3)_2Auacac$ (1.19 M) <sup>b</sup>	Hacac (-)	0.17-0.21	Hacac	$\gamma$ -CH(acac) complex	11.1	0.58(313) 0.58(339) 0.92(353) 1.00(357) 1.32(364) 1.27(365) 1.48(370) 1.87(378)	0.58
$(CH_3)ClSn(acac)_2$ (0.40 M)	Hacac (-)	0.20	Hacac	$CH_3(acac)$ complex	2.0	0.45(313) 0.60(330) 0.75(339) 0.94(353)	0.45
$(CH_3)_2Ga(acac)_2$ (1.18 M)	Hacac (-)	0.05	Hacac	$\gamma$ -CH(acac) complex	3.2	0.48(308) 0.63(336) 1.00(351) 1.60(364) 2.00(372)	0.48
$(CH_3)_2Sn(acac)_2$ (0.23 M)	Hacac (-)	0.17	Hacac	$\gamma$ -CH(acac) complex	4.5	0.37(308) 0.77(346) 1.15(360) 1.65(365)	0.37
$(C_6H_5)_2Sn(acac)_2$ (0.21 M)	$(C_6H_5)_2Sn(acac)_2$ (0.21 M)	0.48	$CHCl_3$	$\gamma$ -CH(acac)( $C_6H_5$ ) <sub>2</sub> Sn <sup>IV</sup> complex	3.6	1.6(313)	0.65
$(C_6H_5)_2Sn(acac)_2$ (0.52 M)	Hacac (0.65 M enol)	0.52	$CHCl_3$	$\gamma$ -CH(acac)( $CH_3$ ) <sub>2</sub> Sn <sup>IV</sup> complex	3.6	2.1(313)	0.65
$(CH_3)_2Sn(acac)_2$ (0.28 M)	Hacac (0.21 M enol)	0.50	$CHCl_3$	$\Sigma$ $\gamma$ -CH(acac)	8.4	2.42(313)	0.66
		0.50		$\Sigma CH_3(acac)$	6.6	1.33(313)	0.60
		0.52		$\Sigma \gamma$ -CH(acac)	14.3	coal.(251) 7.7(255) 3.7(266) 3.2(274) 0.45 2.0(280) 1.5(291) 0.45(313)	0.45
		0.52		$\gamma$ -CH(acac) separation	---	14.3 <sup>b</sup> (217) 13.6 <sup>b</sup> (229) 12.3 <sup>b</sup> (236)	
		0.44	$CH_3OH$	$\Sigma CH_3(acac)$	5.2	coal.(236) 2.0(247) 1.0(266) 0.90(374) 0.60	0.60
				$\Sigma CH_3(acac)$	9.2	2.5(191) 1.80(206) 0.98(227) 0.52(266)	0.52

<sup>a</sup> Concentration determined by signal integration at each temperature, as slight decomposition occurred above 80°. Initial concentration given. <sup>b</sup> Values for  $\delta_{10}^{en}$  the separation of the two resonances in cps during exchange.

For line width measurements the  $r$ - $f$  field was reduced to as low a level as possible while employing the maximum scale expansion and sweep time. Several traces were made of each absorption line, and the values of the width at half intensity were averaged. The values obtained by this method are believed accurate to  $\pm 0.1_5$  cps (average deviation from mean).

Integrals were measured at low  $r$ - $f$  power levels and rapid sweep times so that chemically different protons would respond in a like manner.

Temperature measurements were made using a copper-constantan thermocouple inserted to the bottom of an empty spinning NMR sample tube. They were reproducible to better than  $0.5^\circ$ .

## RESULTS

The line width parameters are collected in Table 1. The following standard equations<sup>29</sup> were used to evaluate the lifetimes  $\tau_m$ . For fast exchange (1) was used.

$$1/\tau_m = \frac{4\pi P_a P_b (\delta\nu_0)^2}{(W^* - W'')} \quad (1)$$

For intermediate exchange where  $\tau_m \delta\nu_0 \approx 1$ , equation (2) was used.

$$1/\tau_m = \sqrt{2\pi(\delta\nu_0^2 - \delta\nu_{ex}^2)} \quad (2)$$

When coalescence of peaks was observed, (3) was employed.

$$1/\tau_m = \sqrt{2\pi(\delta\nu_0)} \quad (3)$$

With slow exchange, equation (4) was used.

$$1/\tau_m = \frac{\pi(W_a^* - W_a'')}{(1 - P_a)} \quad (4)$$

TABLE 2

LIGAND EXCHANGE REACTIONS AND RATES AT  $40^\circ$

System	Solvent	$1/\tau_a$ sec <sup>-1</sup> (rad.)	$E_a$ kcal·mole <sup>-1</sup>	Log $A$ sec <sup>-1</sup> (rad)	$r^a$
1 Cl <sub>2</sub> Sn(acac) <sub>2</sub> + Hacac	Hacac	≤0.6	—	—	—
2 (CH <sub>3</sub> ) <sub>2</sub> Au(acac) + Hacac	Hacac	0.088	13 ± 1.0	8.1	0.989 <sup>b</sup>
3 (CH <sub>3</sub> )ClSn(acac) <sub>2</sub> + Hacac	Hacac	0.094	16 ± 2.5	10.2	0.994 <sup>b</sup>
4 (CH <sub>3</sub> ) <sub>2</sub> Ga(acac) + Hacac	Hacac	0.10	15 ± 2.5	9.9	0.992 <sup>c</sup>
5 (CH <sub>3</sub> ) <sub>2</sub> Sn(acac) <sub>2</sub> (0.23 M) + (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Sn(acac) <sub>2</sub> (0.21 M)	CHCl <sub>3</sub>	4.0	—	—	—
6 (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Sn(acac) <sub>2</sub> (0.52 M) + Hacac (0.65 M, enol)	CHCl <sub>3</sub>	80	—	—	—
7 (CH <sub>3</sub> ) <sub>2</sub> Sn(acac) <sub>2</sub> (0.28 M) + Hacac (0.25 M, enol)	CHCl <sub>3</sub>	670	7.6 ± 0.3	8.5	0.992 <sup>b</sup>
8 (CH <sub>3</sub> ) <sub>2</sub> Tl(acac)(0.15 M) + Hacac (0.20 M, enol)	CH <sub>3</sub> OH	2430	3.2 ± 0.8	6.1	0.984 <sup>d</sup>

<sup>a</sup>  $r \equiv$  Pearson correlation coefficient. <sup>b</sup> > 99% confidence level. <sup>c</sup> 90% confidence level. <sup>d</sup> 80% confidence level.

In these expressions,  $P_a$  and  $P_b$  are the fractional populations of the sites a and b, the complex and the enol form of acetylacetonate, respectively,  $W^*$  is the full width at half intensity of the resonance under conditions of exchange,  $W''$  is the width in the absence of exchange,  $\delta\nu_0$  is the separation of the two resonances in cps, and  $\delta\nu_{ex}$  is the separation of the two signals under conditions of exchange in cps.

The values of the parameters in the absence of exchange  $\delta\nu_0$  and  $W''$  are reported at various temperatures. For the slow exchange systems (Nos. 1,2,3,4)  $\delta\nu_0$

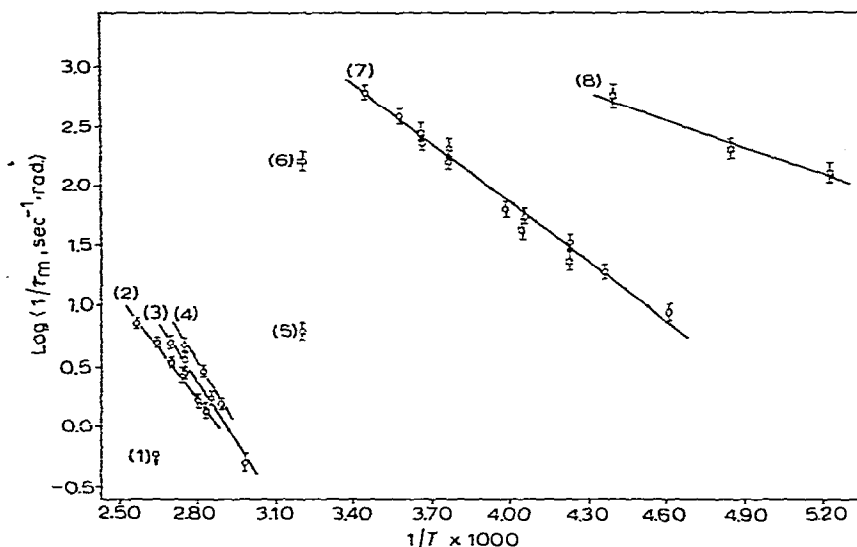


Fig. 1. Determination of the activation energies for exchange in the systems listed in Table 2.

was measured directly, usually at the lowest temperature, for each set of data. For the fast exchange systems, the values were derived from the difference in chemical shifts of the pure components measured separately. The accuracy of this procedure was checked with  $(CH_3)_2Sn(acac)_2$  where the system cooled to  $-60^\circ$  gave  $\delta\nu_0$  directly. The temperature dependence of  $\delta\nu_0$  is, in general, small (within the experimental error) in the systems where it could be measured directly (Nos. 1,2,3,4,7).

The small amount of the keto form of acetylacetonate present plays no role in the exchange as evidenced by its unchanged PMR spectrum as the temperature is changed. The concentration of the enol form present was determined by integration of the keto and enol signals.

The values for the pseudo first order rate constants  $1/\tau_a = P_b/\tau_m$  are listed in Table 2. Fig. 1 shows plots of  $\log(1/\tau_m)$  versus  $1/T$  used to obtain values for the activation energy of exchange. The linear equation  $\log 1/\tau_m = E_a/RT + \log A$  was fitted to the data by least squares. The errors estimated for the  $E_a$  values were determined graphically by drawing the lines of maximum and minimum slope through a given set of data whose maximum variance at each point was calculated by assigning the average experimental error to each parameter in the rate equations. The correlation coefficient,  $r$ , was calculated as a measure of the goodness of fit. Where four or more data sets were available, the fit was found to be better than the 99% confidence level.

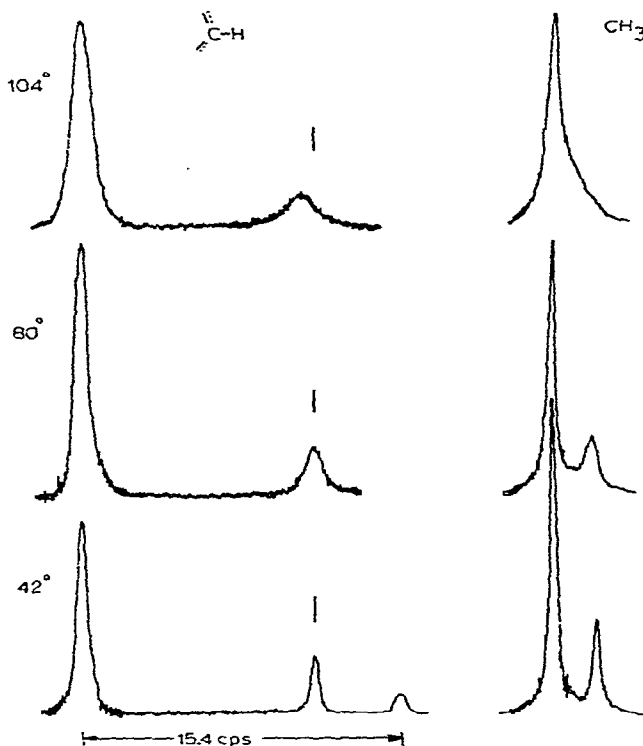
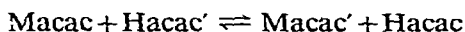


Fig. 2. PMR spectrum of  $(\text{CH}_3)_2\text{Au}(\text{acac})$  in Hacac as a function of temperature, acac (enol) resonances shown.

#### DISCUSSION

The rates of the exchange of acetylacetonate between the proton chelate and the organometallic chelates span a wide range of values. The rates were approximately the same for the reactions with  $(\text{CH}_3)_2\text{Au}(\text{acac})$ ,  $(\text{CH}_3)_2\text{Ga}(\text{acac})$ , and  $(\text{CH}_3)\text{ClSn}(\text{acac})_2$ , and the activation energies were also almost the same. The reactions of the gold(III) and gallium(III) compounds are particularly simple, since they are of the type



The rates for these two compounds at  $40^\circ$  are relatively slow even in pure acetylacetonate. The similarity in the rates reflects the fact that in spite of the large difference in the masses of the metal atoms and the fact that the coordination about gold is essentially square planar while that about gallium is tetrahedral,  $(\text{CH}_3)_2\text{Au}^{\text{III}}$  and  $(\text{CH}_3)_2\text{Ga}^{\text{III}}$  are remarkably similar in much of their chemistry<sup>25,30</sup>.

One non-organometallic compound  $\text{Cl}_2\text{Sn}(\text{acac})_2$  was included to demonstrate the effect on lability of introducing alkyl groups into the first coordination sphere. The rate of exchange between acetylacetonate and this compound was too slow to be measured even at  $105^\circ$ . Since this molecule shows two methyl proton resonances of equal intensity, only the single  $\gamma$ -proton resonance of  $\text{Cl}_2\text{Sn}(\text{acac})_2$  and that of Hacac were used in studying the exchange process. Although Kawasaki and Tanaka<sup>19</sup>

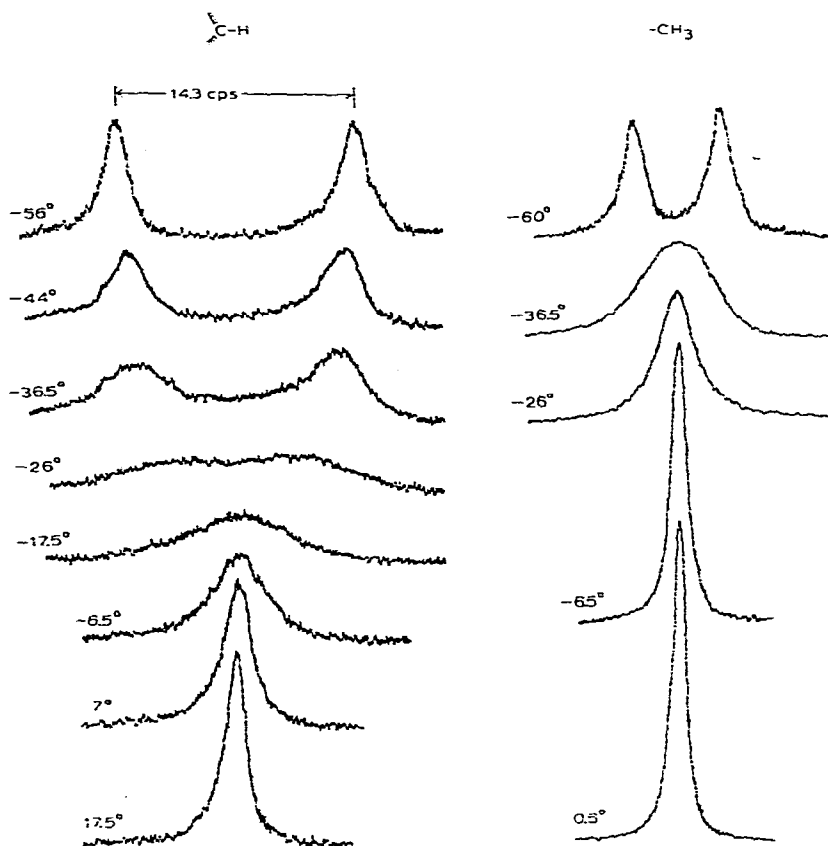


Fig. 3. PMR spectrum of  $(\text{CH}_3)_2\text{Sn}(\text{acac})_2 + \text{Hacac}$  (enol) in chloroform solution as a function of temperature, acac resonances shown.

considered only one ligand and discussed reasons for distortion therein, Smith and Wilkins<sup>6</sup> considered the symmetry of the entire molecule and correctly attributed the splitting of the methyl resonance to the *cis* molecular structure. This has been discussed further by Faller and Davison<sup>20</sup> who showed that the two methyl proton resonances can be coalesced while maintaining the tin proton spin-spin coupling. This demonstrates that the coalescence arises from an intramolecular rather than an intermolecular exchange. It is likely that these intramolecular exchange processes are in general much faster than the intermolecular exchanges as is the case here.

Replacement of one chloride of  $\text{Cl}_2\text{Sn}(\text{acac})_2$  with a methyl group to give  $(\text{CH}_3)\text{ClSn}(\text{acac})_2$  leads to a marked increase in the lability of the coordinated acetylacetonate ligands. The pseudo first order rate constant of  $9.4 \times 10^{-2} \text{ sec}^{-1}$  for the exchange in acetylacetonate solution was sufficiently fast to be measured. It has been suggested<sup>31</sup> that this compound which has the *cis* structure in solution at low temperatures isomerizes at *ca.*  $0^\circ$  and exists entirely as the *trans* isomer at  $20^\circ$ .

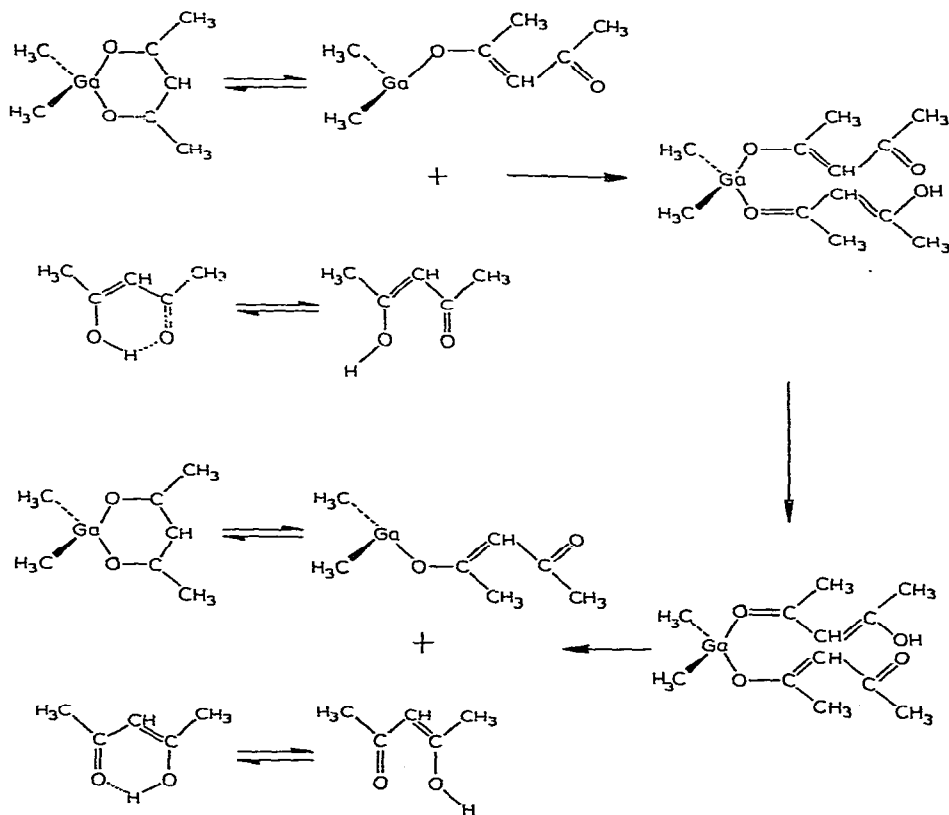
Replacement of the second chloride by a methyl group to give  $(\text{CH}_3)_2\text{Sn}(\text{acac})_2$  increases the acetylacetonate lability greatly, and the *trans* rather than the *cis* structure becomes the thermodynamically favored one. The intermolecular exchange rate is so



rapid even at  $-60^\circ$  that it is necessary to study the reaction with dilute chloroform solutions so that it is sufficiently slow on the NMR time scale. With 0.25 *M* acetylacetonate in the  $\text{CHCl}_3$  solution, the reaction is still 6700 times faster than the exchange with  $(\text{CH}_3)_2\text{ClSn}(\text{acac})_2$  in acetylacetonate. Replacement of the two methyl groups by phenyl groups giving  $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{acac})_2$  leads to a small reduction in the rate of exchange. Chemically, the phenyl derivatives appear to be somewhat more stable than the alkyl derivatives.

The most labile complex was the dimethylthallium(III) acetylacetonate. Unfortunately, because of its low solubility in chloroform, it was necessary to study the exchange in methanol solution. This may affect the rate by stabilizing a partly dissociated chelate.

A reasonable mechanism for the exchange of a coordinated  $\beta$ -diketonate with the ligand conjugate acid has been suggested by Adams and Larsen<sup>15</sup>. Using  $(\text{CH}_3)_2\text{Ga}(\text{acac})$  as an example, this would involve the following steps. It is likely that the rate



determining step(s) involve breaking of the metal–oxygen bonds. It is unlikely that the rates are governed entirely by the strengths of the metal–oxygen bonds. If the totally symmetric metal–oxygen bond stretching frequency is taken as a measure of bond strength, these are not greatly different. For the compounds  $(\text{CH}_3)_2\text{Ga}(\text{acac})$ ,  $(\text{CH}_3)_2\text{Au}(\text{acac})$ , and  $(\text{CH}_3)_2\text{Sn}(\text{acac})_2$ , the values are 454 (ref. 25), 445 (ref. 23), and 415  $\text{cm}^{-1}$  (ref. 5).

Exchange of the acetylacetonate between the two tin chelates  $(\text{CH}_3)_2\text{Sn}(\text{acac})_2$  and  $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{acac})_2$  is appreciably slower than the exchange of either compound with free acetylacetone. This probably reflects the increased difficulty in breaking a metal chelate ring compared to the hydrogen bond in the proton chelate, acetylacetone.

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