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A ^{13}C-NMR and Infrared Investigation of Dihalobis(2,5-pentanedionato)tin(IV) Complexes

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The mechanism of exchange in the series of fluxional (dynamic) molecules $M(dik)_2X_2$ (where M = Sn, Ti; X = halogen, alkoxide; dik = acetylacetonate (acac)) or a related anion of acac has been the subject of some controversy [1]. Two mechanisms are said to be likely for this process; these are a multistep twist or a one bond rupture mechanism of a metal–oxygen bond in a chelate ring. The twist mechanism has been demonstrated in a few cases to be the exchange process; *e.g.*, $M(\alpha\text{-}C_3H_5T)_3$ (T is tropolonate anion and M is Al, Co or Ga) [2–4]. In other cases the mechanism is uncertain but generally the twist mechanism has been supported.

We have recently reported carbon-13 nuclear magnetic resonance (NMR) data as well as infrared (IR) data on the titanium acetylacetonate complexes, $Ti(acac)_2X_2$, which are seemingly in support of the bond rupture mechanism [5].

In this paper we report the carbon-13 NMR parameters for similar tin acetylacetonate complexes and show that this data taken together with the previously reported ^{1}H-NMR [6], infrared [6], and the recently reported crystal structure of $Sn(acac)_2Cl_2$ [7] can also be interpreted in terms of a bond rupture mechanism.

The proton NMR data for $Sn(acac)_2X_2$ (X = F, Cl, Br, or I) has been reported by Jones and Fay who have made a detailed kinetic analysis of the data [6].

TABLE I. Coalescence Temperatures (T_0) and Chemical Shift Differences ($\Delta\nu$) for $Sn(acac)_2X_2$.[b]

Compound	Methyl Protons[a]		Methyl Carbon		Carbonyl Carbon	
	T_c	$\Delta\nu$	T_c	$\Delta\nu$	T_c	$\Delta\nu$
$Sn(acac)_2F_2$	28	4.79	15	1.47	24	3.42
$Sn(acac)_2Cl_2$	82	5.41	53	0.44	93	13.18
$Sn(acac)_2Br_2$	78	5.63	56	0.85	85	10.25
$Sn(acac)_2I_2$	61	5.83	48	1.95	56	3.91

[a] Ref. 6. [b] T_c, °C; $\Delta\nu$, Hz.

We have shown by a simple kinetic analysis that the carbon-13 data and H-1 data both have the same kinetic behaviour. The analysis follows the procedure of Kessler [8] and uses the chemical shift difference in the non-exchanging region ($\Delta\nu$) to calculate an exchange rate k_c (equation 1).

$$k_c = \frac{\pi\Delta\nu}{\sqrt{2}} \qquad (1)$$

From this the free energy of activation, $\Delta G^\ddagger$, may be calculated (equation 2):

$$\Delta G^\ddagger = 4.57\, T_c(10.32 + \log T_c/k_c) \qquad (2)$$

The carbon-13 data for these compounds are reported in Table I while Table II contains the calculated $\Delta G^\ddagger$ for all compounds. The agreement between proton and carbon data is evident.

The hypothesis which we forwarded for the titanium compounds was based on the *trans* effect of the halides; the halide which exerts the greatest *trans* effect should have the weakest Ti–O bond and thus the fastest rate of reaction. Table III lists rate constants and selected infrared frequencies for $Sn(acac)_2X_2$ [9]. The assignments are those of Jones and Fay save for the fluoride complex. They have assigned the Sn–O frequencies at 597 and 465 cm^{-1} and the frequencies Sn–F at 586 and 571 cm^{-1}. We believe that the highest Sn–O should be exchanged with one of the Sn–F frequencies to give the assignments in the Table. The Sn–O frequency near 460 cm^{-1} shows little halogen variation and is assigned to the Sn–O *trans* to another oxygen of the acac ligand. The other Sn–O frequency shows a halogen dependence and is assigned to the Sn–O *trans* to the halide. The infrared data exactly parallels the rate data. A relatively large change in k, from fluoride to iodide, is paralleled by the fairly large frequency change whereas the small change in the rate constant from bromide to chloride is in agreement with the infrared data.

TABLE II. Free Energies of Activation, $\Delta G^\ddagger$ (kcal/mol), for $Sn(acac)_2X_2$.

Compounds	Methyl Protons	Methyl Carbon	Carbonyl Carbon
$Sn(acac)_2F_2$	16.19	16.14	16.17
$Sn(acac)_2Cl_2$	19.13	19.13	19.10
$Sn(acac)_2Br_2$	18.88	18.88	18.84
$Sn(acac)_2I_2$	17.91	17.88	17.89

TABLE III. Rate Constants and Selected Infrared Frequencies (Nujol) for $Sn(acac)_2X_2$.[a]

	$Sn(acac)_2F_2$	$Sn(acac)_2Cl_2$	$Sn(acac)_2Br_2$	$Sn(acac)_2I_2$
k 25 °C, Sec^{-1}	8.0	1.5×10^{-1}	2.1×10^{-1}	6.3×10^{-1}
ν(Sn–O), cm^{-1}	564(s)	592(s)	585(s)	583(s)
ν(Sn–O), cm^{-1}	468(s)	460(s)	456(s)	451(m)
ν(Sn–X), cm^{-1}	600(s) 580(s)	334(s)	264(s)	185(m)

[a] Ref. 9.

Furthermore, definitive support for this mechanism is available from the recent published crystal structure determination of $Sn(acac)_2Cl_2$ [7]. Two different Sn–O distances are reported with the Sn–O *trans* to chloride being 0.013 Å longer than that for Sn–O *trans* to another oxygen. Additional ^{13}C-NMR work is underway on complexes which are not amenable to proton spectroscopy because of the complexity of the proton spectrum [10].

Experimental

The $Sn(acac)_2X_2$ complexes were prepared as previously reported [6]. The ^{13}C NMR were taken on a JEOL-FX60Q NMR spectrometer. All samples were run in either $CDCl_3$ or $CDCl_2CDCl_2$ with TMS used as an internal standard. The coalescence temperatures data are accurate to ±1.0 °C. The infrared spectra were taken on Beckman IR-13 spectrophotometer.

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