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Preparation and Ligand Isotopic Exchange of Tris(acetylacetonato)-tin(IV) Perchlorate in Acetonitrile

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Tris(acetylacetonato)tin(IV) perchlorate $[Sn(acac)_3]ClO_4$ was prepared in crystalline state in acetylacetone (Hacac) and its structure was verified. It is stable in dehydrated acetonitrile (AN) at room temperature. It undergoes hydrolysis in the presence of a large amount of water (*e.g.*, 10^{-4} mol dm^{-3} complex against 10^{-1} mol dm^{-3} water) in two steps: The first, fast step gives a product $[Sn(acac)_2(OH)(H_2O)]ClO_4$, which slowly undergoes further hydrolysis or polymerization to give eventually a gelatinous precipitate. The ligand isotopic exchange with Hacac[^{14}C] can be measured in $\simeq 10^{-2}$ mol dm^{-3} complex solution in AN containing 0.03—0.12 mol dm^{-3} water below −20 °C. The rate is independent of free Hacac concentration. The dependence of the rates of the hydrolysis and the ligand isotopic exchange on water concentration is expressed by: rate$=A[\text{complex}][H_2O]^2/(1+B[H_2O])$, where the A values are 0.15 and 0.30 dm^6 mol^{-2} s^{-1} at −20 °C, ΔH^{*} and ΔS^{*} being (50 ± 8) and (36 ± 20) kJ mol^{-1}, and (-60 ± 20) and (111 ± 40) J mol^{-1}K^{-1}, respectively. There seems to be a common rate-determining step in which one acac$^-$ ligand dissociates with the action of water. The intermediate gives rapidly the original complex in the presence of excess Hacac. Otherwise it undergoes further hydrolysis in the presence of an overwhelming amount of water. The large ionic radius of tin(IV) should be responsible for the rapid water substitution as compared with the corresponding octahedral silicon(IV) and germanium(IV).

Tris(β-diketonato) complexes are common for a wide variety of transition and non-transition metal ions, and their structures and properties have been studied intensively.[1] Several workers[2] including ourselves[3,4] have investigated the kinetics of ligand substitution (including racemization and isomerization) of tris(β-diketonato) complex cations of Group 4 elements, *i.e.* silicon(IV), germanium(IV) and titanium(IV). It seems interesting to compare their properties with those of tin(IV) analogue, for which tris-bidentate octahedral complexes of β-diketonates are left unknown.

The tin(IV) complex containing acetylacetonate (acac$^-$) was first prepared by Dilthey,[5] and it was formulated as a salt of the cation $[Sn(acac)_3]^+$. However, Rosenheim *et al.*[6] gave the formula $[Sn(acac)_2Cl_2]$ to the complex, and this form was confirmed by White.[7] Similar complexes of the type $[Sn(acac)_2X_2]$ (X=halide, methyl, and phenyl) were synthesized and their rapid site-exchange was examined by NMR.[8] Tropolonate (trop$^-$), one of the related diketonates, gave chargeless complexes with coordination numbers 7 and 8, $[Sn(trop)_3X]$ (X=chloride and phenyl) and $[Sn(trop)_4]$.[9]

We have synthesized a new compound tris(acetylacetonato)tin(IV) perchlorate $[Sn(acac)_3]ClO_4$ in crystalline state and studied its hydrolysis and ligand isotopic exchange in acetonitrile.

Experimental

Materials. *Tris(acetylacetonato)tin(IV) Perchlorate*: Dichlorobis(acetylacetonato)tin(IV) (4.1 g, 0.011 mol) prepared by the method of Morgan and Drew[10] was dissolved in Hacac (60 cm^3) and treated with silver perchlorate (4.3 g, 0.021 mol) in Hacac (50 cm^3). The precipitate (silver chloride) was filtered off, and diethyl ether (120 cm^3) was added to the filtrate to give colorless needles. They were filtered off, washed with diethyl ether, dried, and recrystallized from Hacac solution (110 cm^3) by adding diethyl ether (250 cm^3). Yield, 50% on the basis of $[Sn(acac)_2Cl_2]$. The colorless crystals melt at 221—223 °C with decomposition. Found: C, 34.94; H, 4.11; Sn, 23.3%. Calcd for $C_{15}H_{21}O_{10}ClSn$: C, 34.95; H, 4.10; Sn, 23.0%. This compound contained no chloride ions.

The complex is insoluble in diethyl ether, tetrahydrofuran, chlorobenzene, acetic acid, and hexane. It is soluble in Hacac and was recrystallized from it. It is also soluble in the following solvents: easily in acetone, acetonitrile (AN), nitromethane, and dichloromethane; slightly in ethanol, ethyl acetate, and 1,1,2,2-tetrachloroethane. In all the seven solvents the recrystallization was unsuccessful, presumably owing to water contained as an impurity. Water, chloroform, and dimethyl sulfoxide rapidly decomposed the complex to give white precipitate and Hacac.

Hydrolysis Product: An AN solution (20 cm^3, containing *ca.* 0.1 M water; M=mol dm^{-3}) of the complex ($\simeq 10^{-2}$ M) was mixed with diethyl ether (60 cm^3) and set aside for 1 h. Colorless precipitate appeared gradually. They were filtered off, washed with diethyl ether, and dried *in vacuo*. This product (Product A) absorbed the moisture from air and decomposed into Hacac and brownish white solid.

Other Reagents: Acetonitrile was refluxed with diphosphorus pentoxide and distilled. The procedure was repeated until the water content fell to *ca.* 0.005 M. Commercially available pure hexane was used without further purification. The labeled compound Hacac[^{14}C] was prepared as in reference.[11] The specific activity was 0.01 mCi/g.

Kinetic Procedure. *Hydrolysis in Acetonitrile*: Kinetic runs were carried out in a quartz cell in a thermostated jacket, which was placed in a spectrophotometer Hitachi 124. A co-necked glass tube with two branched bottoms containing the complex solution ($\simeq 10^{-4}$ M, 5 cm^3) and AN (containing 0.01 to 0.6 M water, 5 cm^3) was cooled to −25 °C and both liquids were mixed. The solution was pippeted into the quartz cell at given temperatures (−11.8, −13.7, −17.3, and −20.0 °C). Methanol was used as coolant which was circulated through the jacket from HAAKE KT 33 thermostat. Dry nitrogen was blown on the surface of the cell to avoid freezing. The change in absorption was followed at 315 or 250 nm.

Ligand Isotopic Exchange: The complex solution in AN (0.05 to 0.1 M, 5 cm^3) containing 0.05 M Hacac and the radioactive Hacac solution in AN (0.01 to 0.1 M, 5 cm^3) were introduced separately into the two branched bottoms of a co-necked flask with a stopper, and cooled in a thermostat. Both solutions were mixed after *ca.* 30 min to let the exchange reaction start.

At appropriate time intervals, portions (*ca.* 1 cm^3 each) were pippeted quickly into chilled hexane (*ca.* 5 cm^3) in a thin glass tube at −55 °C. (Only the enol tautomer is partly extracted into the hexane phase.4)) After 30 to 40 s, the hexane layer (*ca.* 3 cm^3) was separated and allowed to stand for 24 h at room temperature until the keto-enol equilibrium was reached. One cm^3 portion was diluted 10 folds with hexane and the extinction measured at 273 nm to find the concentration of Hacac. Another 1 cm^3 portion was mixed with anisole containing 0.4% *p*-terphenyl and 0.01% *p*-bis(5-phenyl-2-oxazolyl)benzene (POPOP) to be submitted to β-activity counting. The specific activity (x) of the extracted Hacac was known from these data.

Calculation of the Exchange Rate. The rate of isotopic exchange was calculated according to McKay's formula (Eq. 1).

$$R = -[3ab/(3a+b)][\ln(1-F)]/t \qquad (1)$$

where a and b are the complex and the ligand concentration, respectively, and t and F are the lapse of time and the extent of reaction at time t, respectively. The F values were calculated by $(x_0-x_t)/(x_0-x_\infty)$ where the suffixes denote the time lapse until the quenching of reaction.

Acetylacetone is present in tautomeric enol-keto equilibrium in AN, and the percentages of enol form are 62 and 67 in AN, at room temperature and −10 °C, respectively. The interconversion rate constant between enol and keto is *ca.* 10^{-5} s^{-1} at −10 °C, being much slower than the present isotopic exchange.12) The experimental x_∞ coincided with the value calculated on the assumption that only the enol form of free Hacac participates in the exchange. All the calculations were therefore made on this assumption, the b values being set to be equal to 0.62 time of the gross free Hacac concentration. This factor is based upon the enol percentage of Hacac in AN at room temperature. (The Hacac solution for kinetic runs were prepared, set aside for more than 24 h at room temperature, and cooled immediately before use.) The $\log(1-F)$ *vs.* t diagrams are linear until *ca.* half exchange time, and seems to concave on further progress of the reaction. The R values used in the following discussion are those obtained at the initial linear part of McKay plots.

Apparatuses. Hitachi 124 Spectrophotometer with a low temperature jacket and Hitachi 323 were used for recording the UV absorption spectra at −10 to −20 °C, and at room temperature, respectively. Nuclear Chicago Unilux II-A Liquid Scintillation Counter was employed for recording the β-activity of ^{14}C. The water content was measured by Karl Fischer titration. Metrohm E 365 B Konduktoskop with EA 608 bright platinum electrodes was used for conductivity measurements. Hitachi EPI-2G Infrared Spectrophotometer and Varian A-60 Spectrometer were used for recording the IR absorption and NMR spectra, respectively.

Results and Discussion

Structure and Ultraviolet Absorption. The properties of the complex are summarized in Table 1. The relation between molar conductivity and concentration showed that the tin(IV) complex was a 1:1 electrolyte as those of silicon(IV), germanium(IV) and titanium(IV). The IR absorption (KBr disk) was very similar to those of the corresponding silicon(IV) and germanium(IV) complexes, with C=O stretching and ClO$_4^-$ bands in 1500—1570 cm^{-1} region and at 1100 cm^{-1}, respectively. Proton NMR spectrum in acetonitrile[$^2H_3$] (CD$_3$CN) gave two singlets at 2.32 and 6.18 ppm (*vs.* TMS), corresponding to methyl and methylidyne protons of the coordinated acetylacetonates. These properties suggest

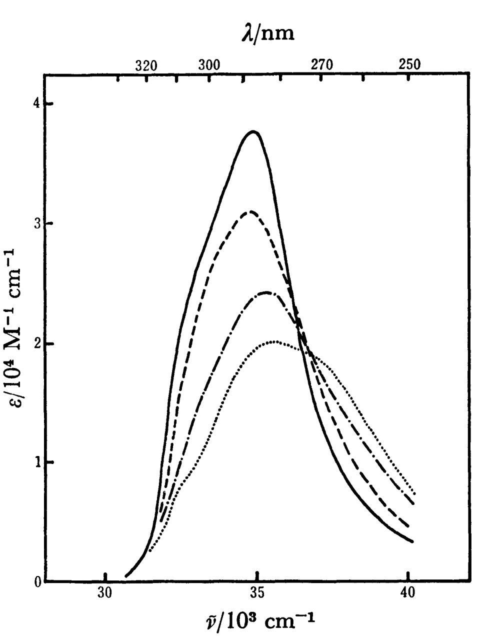


Fig. 1. Ultraviolet absorption spectrum of [Sn(acac)$_3$]ClO$_4$ in acetonitrile. Complex, ≃10^{-4} M; water, 0.1 M; at 25 °C.
——Freshly prepared, ----1 h after,
-·-·-3 h after, ------10 h after.

TABLE 1. PROPERTIES OF [M(acac)$_3$]ClO$_4$ (M=Si, Ge, AND Sn) AND [Sn(acac)$_2$Cl$_2$]

Central ion	Si(IV)c)	Ge(IV)e)	Sn(IV)	[Sn(acac)$_2$Cl$_2$]
Molar conductivitya)				
Λ (complex)/S cm^2 M^{-1}	161	152	153	
UV absorption peakb)				
$\tilde{\nu}$/10^3 cm^{-1}	32.7 (sh)	32.8 (sh)	32.5 (sh)	32.2 (sh)f)
(ε/10^4 M^{-1} cm^{-1})	34.4 (≈3.5)	34.7 (3.55)	34.7 (≈3.8)	33.3 (≈1.5)f)
IR absorption peakc)				
$\tilde{\nu}$/cm^{-1} C=O–M	1550—1570	1530—1570	1530—1570	
ClO$_4^-$	1100	1100	1100	
NMR peak (solvent)d)	(CDCl$_3$)	(CDCl$_3$)	(CD$_3$CN)	(CDCl$_3$)
δ/ppm CH$_3$	2.30	2.33	2.32	2.11, 2.20
=CH–	6.28	6.18	6.18	5.97 (or 5.69g))

a) Complex concentration: 5×10^{-4} M, at 25 °C. b) In acetonitrile, at 25 °C. c) In KBr disk.
d) Tetramethylsilane: δ=0.0 ppm. e) Ref. 3. f) In benzene. g) Ref. 13.

that the tin(IV) complex has a common octahedral tris-chelate type structure.

The UV absorption spectrum is shown in Fig. 1. The pattern of a freshly prepared AN solution is very similar to those of silicon(IV) and germanium(IV) analogues in the absence of water (<0.01 M). There is an absorption peak at 34700 cm^{-1} (288 nm) with a shoulder at 32500 cm^{-1} (305 nm). In a complex solution ($\simeq 10^{-4}$ M) containing >0.1 M water at room temperature, the extinction coefficient decreased with time in the wavelength range 280—330 nm, and increased at 250—275 nm. Such a change seems to be due to hydrolysis of the complex cation. An isosbestic point at 278 nm was observed only in the initial period.

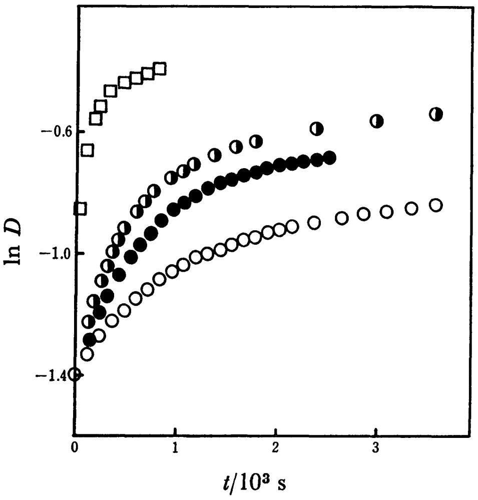


Fig. 2. Increase in extinction at 250 nm in acetonitrile at −17.3 °C. Complex, 7.4×10^{-5} M; water, 0.070 M (○), 0.094 M (●), 0.106 M (◑), 0.267 M (□).

Hydrolysis. The increase in extinction at 250 nm is illustrated in Fig. 2. At least two steps should be involved. The rate of the first fast step, which is apparent up to *ca.* 15 min in the diagram (−17.3 °C), increases with increase in water content, while the second step seems to be rather insensitive to it under the given conditions. Electrolytic conductivity of the solution remained unchanged throughout these periods.

Product of the First Step of Hydrolysis: Product A (see Experimental) seems to be a salt of hydrolysis product in the first step. This colorless solid deteriorated in atmosphere and its properties were not correctly known. The UV absorption spectrum in AN gave a peak at 34100 cm^{-1} (293 nm) with a shoulder around 33000 cm^{-1} (305 nm). The overall pattern is similar to that of the original complex, but the location and the intensity of the peak (ε=*ca.* 15000 $M^{-1} cm^{-1}$ respect to the metal)are obviously different. The IR absorption in Nujol mull and KBr pellet indicated the presence of OH and/or H_2O, coordinated C=O of acetylacetonate, and perchlorate.

The proton NMR spectrum in CD_3CN (*ca.* 0.05 M) gave a group of peaks at *ca.* 2.2, and apparently broad peaks at *ca.* 3.7 and 6.1 ppm *vs.* TMS at room temperature. The signals at *ca.* 2.2 and 6.1 ppm seem to come from methyl and methylidyne of coordinated $acac^-$, respectively. These chemical shifts are similar to those of *cis*-$[Sn(acac)_2Cl_2]$.[13]

One sample of Product A gave an analytical result, C, 25.10; H, 3.85; and ash 38.7%. (Calcd for $[Sn(OH)(acac)_2(H_2O)]ClO_4$, $C_{10}H_{17}O_{10}ClSn$: C, 26.6; H, 3.8; ash as SnO_2, 33.4%). There seems to be an overall trend that the carbon content decreases but the hydrogen and the ash percentages increase with increase in time lapse between the initiation of reaction and precipitation of Product A from AN solution. These results and constant electrolytic conductivity seem to indicate that the hydrolysis proceeds as Eq. 2 at the initial stage.

$$[Sn(acac)_3]^+ + 2H_2O \rightleftharpoons [Sn(OH)(acac)_2(H_2O)]^+ + Hacac \qquad (2)$$

Product A should consist mainly of the perchlorate salt of this cation or its hydrate and contains small amounts of the products of further hydrolysis.

Reverse Reaction of the First Step: When the solution of Product A in CD_3CN ($\simeq 0.05$ M) was treated with Hacac to produce *ca.* 1 M solution at room temperature, six sharp proton peaks appeared immediately in NMR spectrum. Four of them, at 2.05, 2.18, 3.65 and 5.61 ppm, correspond to the signals of free Hacac, and two remaining singlets coincided with the coordinated $acac^-$ in the original complex $[Sn(acac)_3]^+$ (Table 1). When Product A (*ca.* 2 g) was dissolved in Hacac (*ca.* 5 cm^3) at room temperature and immediately treated with diethyl ether (20 cm^3), crystalline $[Sn(acac)_3]ClO_4$ was obtained.

All these facts tell that the reverse reaction of Eq. 2 is very rapid in the presence of a large excess of Hacac. (UV absorption spectroscopy is not useful, because excessive Hacac gives an intense absorption in $\simeq 300$ nm region).

Kinetics of the First Step: Apparent rate constants of the first "fast step," k_h, were obtained by the Guggenheim plot of the absorbance at 250 or 315 nm in AN. When the water concentration was less than 0.05 M in the presence of *ca.* 10^{-4} M complex, the hydrolysis was very slow below −10 °C, and the rate was measured

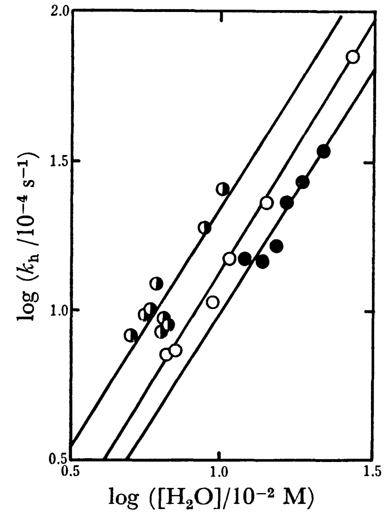


Fig. 3. Apparent hydrolysis rate constant k_h *vs.* water content in acetonitrile in log-log scale.
● −20.0 °C, ○ −17.3 °C, ◑ −11.8 °C.

in AN containing more than 0.05 M water at −10 to −20 °C. First order rate law was obeyed with respect to the complex concentration; rate=k_h[complex].

The observed k_h increases with increase in water content, as illustrated in the log-log plot of Fig. 3. The overall gradient is *ca.* 1.7 in the water concentration range 0.05 to 0.3 M. Various attempts were made to find an appropriate formula which fits the observed data. Linear plot of $[H_2O]/k_h$ *vs.* $1/[H_2O]$ indicated that Eq. 3 is a good approximation for the kinetic data in the given water concentration region.

$$k_h = A[H_2O]^2/(1+B[H_2O]) \qquad (3)$$

The A values were calculated to be 0.15, 0.20, 0.27 and 0.34 $M^{-2}\,s^{-1}$ at −20.0, −17.3, −13.7 and −11.8 °C, respectively, and $\Delta H^{\neq}$ and $\Delta S^{\neq}$ therefore (50±8) kJ mol^{-1} and (60±20) J $mol^{-1}\,K^{-1}$, respectively. The observed deviation from 2 in the gradient of Fig. 3 seems to be due to the contribution of $B[H_2O]$ term in the denominator, which remains in the vicinity of unity.

The Second Step: The "slow step" of the hydrolysis was not investigated in detail. Since the electrolytic conductivity remained unchanged in this step, either further hydrolysis to give *e.g.* $[Sn(OH)_2(acac)(H_2O)_2]^+$ or polymerization to give *e.g.* $[(acac)_2Sn(\mu\text{-}OH)_2Sn(acac)_2]^{2+}$ may take place. The apparent rate constant which was rather insensitive to the water concentration (Fig. 2) was *ca.* $1\times10^{-5}\,s^{-1}$ at −20 °C. When the complex solution ($\simeq10^{-2}$ M) was set aside in atmosphere for 24 h or treated with a large amount of water, gelatinous precipitate appeared, which were found to be hydrated tin(IV) hydroxide, *i.e.* olation product of tin(IV). Hence the product of the second step can be a binuclear tin(IV) complex.

Ligand Isotopic Exchange. Figure 4 gives log $(1-F)$ *vs.* t diagrams, in which Hacac in enol form is reckoned to participate in the exchange (see Experimental). These diagrams are linear without intercepts for at least $F<0.7$. The UV absorption of the reaction mixture remained unchanged during these periods. Therefore isotopic exchange must take place exclusively whenever the water concentration is of the same order with the complex concentration ($\simeq10^{-2}$ M).

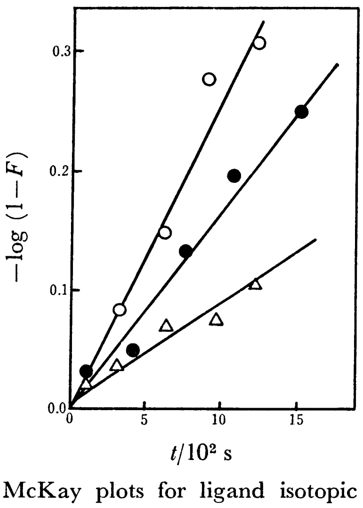


Fig. 4. McKay plots for ligand isotopic exchange of $[Sn(acac)_3]ClO_4$ in acetonitrile at −20.4 °C. Complex, 0.03 M; Hacac (enol), 0.06 M; water, 0.027 M (△), 0.045 M (●), 0.058 M (○).

Table 2. McKay's R values and the rate constants k_x of ligand isotopic exchange of $[Sn(acac)_3]ClO_4$ in acetonitrile at −20.4 °C[a)]

[Sn] / 10^{-2} M	[L] / 10^{-2} M	$[H_2O]$ / 10^{-2} M	R / 10^{-6} M s^{-1}	k_x / 10^{-4} s^{-1}	[Acid] / 10^{-2} M
2.3	0.90	4.4	8.6±0.9	3.8±0.4	
2.6	1.8	2.6	4.1±0.3	1.6±0.2	
3.9	1.9	2.6	5.3±1.0	1.4±0.3	
6.7	1.8	5.9	32.9±4.3	4.9±0.6	
2.4	2.1	3.6	8.3±1.8	3.6±0.8	
2.4	2.1	4.4	6.1±0.3	2.5±0.1	
3.0	4.4	2.7	4.0±1.4	1.4±0.5	
2.5	5.2	3.6	8.8±1.3	3.6±0.5	
2.5	6.1	5.8	18.3±5.6	7.2±2.2	
2.9	6.2	2.7	5.1±2.5	1.7±0.9	
3.0	6.2	3.1	4.7±0.9	1.6±0.3	
3.0	6.2	7.1	32.5±3.5	11.0±1.2	
3.0	6.2	12.1	56.1±1.8	19.0±0.6	
5.1	6.1	2.9	11.1±4.1	2.2±0.8	
3.0	6.9	3.3	10.0±3.9	3.4±1.3	
5.6	7.2	4.2	28.4±2.6	5.1±0.5	
3.9	7.7	3.1	10.9±2.0	2.8±0.5	
5.6	10.1	6.9	48.2±5.1	8.7±0.9	
3.9	7.7	3.2	16.8±0.9	4.3±0.2	1.5[b)]
3.2	6.4	3.5	17.2±0.6	5.5±0.2	5.1[c)]
3.2	6.4	3.8	18.6±1.4	5.9±0.5	10.2[c)]

a) Concentration: complex, [Sn]; enol form of Hacac, [L]; water, $[H_2O]$; acid, [Acid]. b) Acetic acid. c) Trichloroacetic acid.

Adjustment of water concentration was extremely difficult at a low temperature, and the experimental error is larger than the ordinary kinetic studies. Table 2 gives McKay's R values obtained in the presence of varying concentration of the complex, Hacac and water, at −20.4 °C. They are proportional to the complex concentration, and first order rate constant k_x is expressed by Eq. 4.

$$k_x = R/a \qquad (4)$$

The ligand concentration gives only a small influence on the rate constant. On the other hand, the water concentration gives greater effect on k_x than others do; Fig. 5 shows the plot of k_x *vs.* the water concentration on log-log scale. The overall gradient calculated by the method of least squares is *ca.* 1.7 in the range from 0.03 to 0.12 M water. A similar plot at −28.1 °C gave a similar pattern.

There seems to be a remarkable trend, however, that the gradient becomes greater than unity in <0.05 M water. This tendency can be more clearly expressed by the plot of $k_x/[H_2O]$ *vs.* $[H_2O]$ in Fig. 6. The $k_x/[H_2O]$ values increase almost linearly with increase in water concentration in <0.05 M solution, and seem to approach a limiting value in the range >0.05 M. Such an observation leads to two possible interpretations of participation of water as in the following.

If the original complex interacts with one mole of water to give an encounter complex, which undergoes isotopic exchange with the aid of another mole of water, the rate formula can be written as Eq. 5.

$$k_x = A'[H_2O]^2/(1+B'[H_2O]) \qquad (5)$$

When the water concentration is small, Eq. 5 is reduced

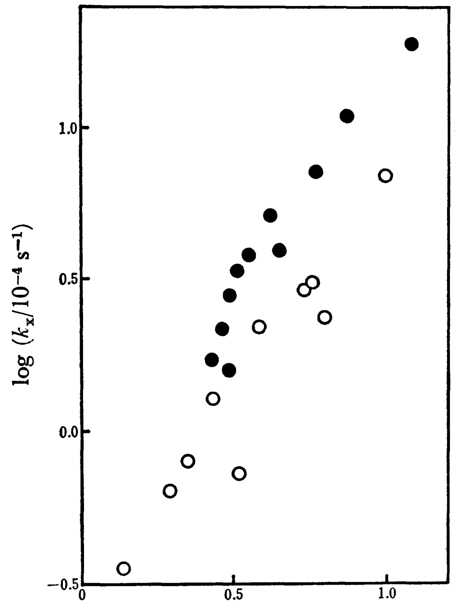
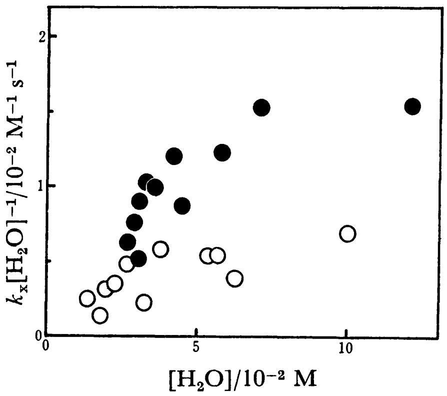


Fig. 5. Influence of water concentration on ligand isotopic exchange rate constant k_x at −28.1 (○) and − 0.4 °C (●). Complex, 0.03 M: Hacac (enol), 0.06 M.



Dig. 6. Plots of k_x/[H$_2$O] against [H$_2$O] at −28.1 (○), and −20.4 °C (●). Complex, 0.03 M; Hacac (enol), 0.06 M.

to a second order rate formula as Eq. 6.

$$k_x = A'[H_2O]^2 \qquad (6)$$

On the other hand, when the water concentration becomes >0.05 M, the term B'[H$_2$O] in the denominator becomes sufficiently large and the k_x/[H$_2$O] approaches a limiting value.

$$k_x/[H_2O] = (A'/B') \qquad (7)$$

Equation 5 has the same pattern as Eq. 3 for the hydrolysis of the present complex. The A' value is *ca.* 0.3 M^{-2} s^{-1} in the water concentration range 0.05 to 0.12 M at −20.4 °C. (*cf.* A=0.15 M^{-2} s^{-1} for the hydrolysis). The activation enthalpies and entropies for the A' are $\Delta H^{\neq}$=(36±20) kJ mol^{-1} and $\Delta S^{\neq}$=(111±40) J mol^{-1} K^{-1}, respectively. They have rather large experimental errors since the data were obtained only at −28.1 and −20.4 °C.

Another interpretation can be encountered by assuming significant change in activity coefficient of water in AN.[14] Nevertheless we tend to favor the first consideration on the basis of the discussions given below.

Acetic and trichloroacetic acid enhance the isotopic exchange as seen in Table 2. The extent of the catalytic action of these weak and strong acids does not differ much from each other, and does not depend on their concentration. It seems the acid catalysis has reached almost saturation under the given conditions.

The Reaction Mechanism. The isotopic exchange does not proceed appreciably in the absence of water below 0 °C, and the original complex itself does not seem to undergo ligand isotopic exchange. The hydrolysis and the isotopic exchange were studied in different concentration regions of the complex and water in AN. However, the apparent exchange rate constant A' is only twice as large as the apparent hydrolysis rate A at −20 °C, and the activation parameters are similar to each other within the experimental errors. These facts suggest that these two reactions might proceed *via* a common route. A plausible mechanism is visualized in Fig. 7.

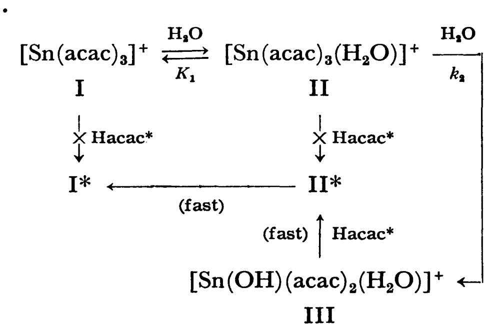


Fig. 7. Plausible mechanism of hydrolysis and ligand isotopic exchange of [Sn(acac)$_3$]$^+$ ion in acetonitrile. I* and II* are the same species with I and II respectively with labeled acac$^-$.

The original complex interacts rapidly with water to give an intermediate (II, for the structure, *vide infra*). Then II undergoes reaction with another molecule of water to give III, the main component of Product A (see Experimental). In the isotopic exchange reaction, excessive free Hacac rapidly reacts with III to restore II*. In the absence of free Hacac and in the presence of a large excess of water (experimental condition for the hydrolysis), III is subject to further reaction with water or to polymerization, to make the hydrolysis irreversible. Thus the isotopic exchange and hydrolysis seem to have a common intermediate and a common rate-determining step (A=k_2K_1=A').

The rate-determining step II→III should involve the break of a metal-ligand bond with the aid of water. The water molecule should play a unique role, because the solvent AN brings about neither solvolysis nor isotopic exchange.

Structure and Role of Intermediate II: Intermediate II can be either a six-coordinated species with one unidentate and two bidentate acac$^-$ and a water molecule as ligands, or a seven-coordinated species with three bidentates and a water molecule. In the former case the break of the remaining bond with the aid of water would be the rate-determining step. If II were seven-coordinated, water-assisted break of a metal-ligand bond followed by rapid break of another Sn–O bond of the same acac$^-$ would be rate-controlling. Alternatively, the seven-coordinated species can be in rapid equilibrium to give a small amount of the six-coordinated species with one unidentate acac$^-$ which can behave similarly as in the former case.

Present experimental data cannot discriminate these possible mechanisms, and we can only discuss the most probable route by analogie. Seven- and eight-coordinated tin(IV) complexes with oxygen donors are known in crystalline state,9) and the presence of a seven-coordinated intermediate is not unlikely. Homologous complexes $[Si(acac)_3]^+$ and $[Ge(acac)_3]^+$ are claimed to produce intermediates with a unidentate acac$^-$ on racemization and isotopic exchange. It was discussed that unidentate acac$^-$ is stabilized in the complexes with highly charged central metal ions such as aluminium(III), gallium(III), silicon(IV), and germanium(IV).3,15) Thus we tend to consider that intermediate II would be mostly present as seven-coordinated species and produce a small amount of unidentate acac$^-$ by rapid equilibrium, and that the break of the remaining Sn–O bond of the unidentate acac$^-$ would be responsible in determining the rate of hydrolysis and isotopic exchange. Assistance of water at this step can be substantiated either by attacking the intermediate as nucleophile or by blocking the vacant coordination site of the intermediate to retard the recombination of Sn–O.

Comparison with Related Complexes. Other members of 4B family, silicon(IV) and germanium(IV), give homologous complexes $[M(acac)_3]^+$ with acetylacetonate, and the structures are very similar to $[Sn(acac)_3]^+$. However, those two complexes are much more inert than the corresponding tin(IV) complex, and the ligand isotopic exchange is measurable over 100 °C in AN. The dependence of their rates upon various factors is significantly different from the present complex, and they are resistive against hydrolysis even at elevated temperatures.3) They were resolved into enantiomers, and their racemizations were found to proceed similarly at a measurable rate without the assistance of water between 40 and 60 °C, presumably *via* an intermediate with a unidentate acac$^-$.

Frazer and Haines found that the related tin(IV) complexes $[Sn(acac)_2X_2]$ (X=Cl, Br, and I) undergo hydrolysis below 0 °C to liberate acac$^-$ in chloroform. The rate law was:

$$\text{rate} = k[H_2O][Sn(acac)_2X_2] \qquad (8)$$

where the complex and water concentration were $\simeq 5 \times 10^{-5}$ and 0.005—0.01 M, respectively. They proposed a mechanism involving an association pre-equilibrium between the complex and water, and a rate-determining attack of this water molecule to break Sn–O bond.16) The role of water molecule seems to be different from that in the present reactions, but the labile interaction with water is common. The large octahedral ionic radius of tin(IV) ion may be responsible for the difference among silicon(IV), germanium(IV), and tin(IV).

Titanium(IV), a member of 4A family, also gives a tris(acetylacetonato) complex $[Ti(acac)_3]^+$ with a similar structure, which readily undergoes hydrolysis in hydrous solvents. The rate of ligand isotopic exchange is measurable in the same temperature region as the tin(IV) complex, although details of the kinetic behavior remains unknown.4) The similar lability towards hydrolysis and isotopic exchange seems to owe to the similarity in the octahedral ionic radius.

An iso-electronic cation indium(III) also gives a complex $[In(acac)_3]$, which is very sensitive to hydrolysis. Its ligand isotopic exchange is immeasurably fast at −20 °C in tetrahydrofuran.17) Another d^{10} cation, gallium(III) gives also $[Ga(acac)_3]$ and the ligand isotopic exchange rate is measurable at $\simeq$0 °C. However, the dependence on various factors is different from the present case.18) It seems as if the charge and the ionic radius of the central metal ion is very important in determining the kinetic behavior of non-transition metal complexes.

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14) If the exchange proceeds *via* an entirely different route involving only one mol of water, the rate formula can be written as: $k_x = k_f \gamma [H_2O]$ where γ stands for the activity coefficient of water in AN. If γ decreases in $<$0.05 M solution, k_x *vs.* $[H_2O]$ diagrams can assume apparently second order dependence as shown in Fig. 5. No information is available concerning the activity coefficient of a very small concentration of water in AN at −20 °C. However, such a solution may be approximated to an AN solution of ice and a significant decrease in activity coefficient cannot be necessarily unreasonable.

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