Kinetics of the Hydrolysis of Some Dihalogenotin(IV) β-Diketonates

By **Malcolm J. Frazer** † and **L. Ian B. Haines**, Department of Chemistry, The Polytechnic of North London London N7 8DB

The kinetics of the hydrolysis of the compounds $[SnX_2(acac)_2]$ (X = Cl, Br or I; acacH = acetylacetone) and $[SnCl_2(ke)_2]$ (keH = benzoylacetone, dibenzoylmethane, or trifluoromethylacetylacetone) are reported. The reactions all follow second-order kinetics and have negative entropies of activation. For the $[SnX_2(acac)_2]$ compounds the enthalpies of activation decrease in the order Cl > Br > I and those for the compounds $[SnX_2(ke)_2]$ are in the order benzoylacetone ~ dibenzoylmethane > trifluoromethylacetylacetone. The mechanism of the reaction is discussed.

A LARGE number of dihalogenometal β-diketonates have been reported. In particular tin(IV) complexes of the type $[SnX_2(acac)_2]$ (X = F, Cl, Br, or I) are well authenticated[1-3] and their physical properties have been thoroughly investigated.[1,4] However, apart from n.m.r. studies of the exchange of the methyl groups between the two non-equivalent sites in the complexes,[1,5] there is little kinetic information on compounds of this type. Indeed, there is little information on the kinetics of substitution reactions of octahedral tin(IV) complexes.[6,7] In view of the possibility of associative mechanisms for the halide exchange reactions of tin(IV) complexes,[6] we have investigated the hydrolysis of some dihalogenotin(IV) β-diketonates.

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† *Present address:* School of Chemical Science, University of East Anglia, University Plain, Norwich NOR 88C.

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EXPERIMENTAL

$[SnCl_2(acac)_2]$,[2] $[SnBr_2(acac)_2]$,[2] and $[SnI_2(acac)_2]$ [4,8] were prepared as described in the literature. Bis(trifluoromethylacetylacetonato)copper(II) $[Cu(tfacac)_2]$, bis(benzoylacetonato)dichlorotin(IV) $[SnCl_2(bzac)_2]$, and dichlorobis(dibenzoylmethanato)tin(IV) $[SnCl_2(bzbz)_2]$ were prepared by reaction of metal halide with 2 mol equiv. of the appropriate ligand.

$[SnCl_2(tfacac)_2]$ Was prepared by the reaction of stannic chloride (3·4 mmol) and $[Cu(tfacac)_2]$ (3·3 mmol) in chloroform (200 cm^3). After vigorous stirring (5 min), the $CuCl_2$ was filtered off and the solvent removed (25 °C/0·1 mmHg) to leave a viscous oil. Recrystallization attempts were unsuccessful, but the oil crystallised to a white solid after being stirred for *ca.* 10 days (Found: C, 24·4; H, 1·8; Sn, 23·7. Calc. for $C_{10}H_8Cl_2F_6O_4$: C, 24·2; H, 1·6; Sn, 23·9%).

Standard solutions of water in chloroform were prepared by adding weighed amounts of distilled water to dry chloroform and stirring for 1—2 h. The water content was checked by the Karl-Fischer procedure.[9]

Method of Studying Reaction Rates.—A 1-cm silica cell was baked in an oven and allowed to cool in a dry atmosphere. It was filled with a solution of water in chloroform of the appropriate concentration. The cell was placed in the thermostatted cell compartment of a spectrophotometer maintained at the required temperature. The cell was allowed to equilibrate for 15—20 min, removed, and *ca.* 20 μg of the solid tin complex was added and quickly dissolved in the solvent to give a concentration of complex of *ca.* 5×10^{-5} mol dm^{-3} (measured by initial absorbance reading). The cell was returned to the cell compartment and reaction monitored by the change in absorbance of the reaction solution (absorbance maxima used are given in the Table).

Spectral data and activation parameters [a] for the hydrolysis of tin(IV) complexes

Complex	λ_{max}/nm	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	k_2 (at 30 °C) [b]/ dm^3 mol^{-1} s^{-1}
$[SnCl_2(acac)_2]$	303	71·9 ± 3·4	−48·5 ± 10·0	8·80 ± 0·57
$[SnBr_2(acac)_2]$	305	55·6 ± 5·4	−98·7 ± 17·6	1·51 ± 0·19
$[SnI_2(acac)_2]$	308	27·6 ± 4·0	−166·1 ± 12·1	0·155 ± 0·007
$[SnCl_2(bzac)_2]$	335	71·1 ± 4·2	−52·3 ± 12·6	10·3 ± 0·7
$[SnCl_2(bzbz)_2]$	367	72·0 ± 4·2	−51·9 ± 13·0	7·46 ± 1·24
$[SnCl_2(tfacac)_2]$	310	49·4 ± 2·5	184·1 ± 8·4	0·743 ± 0·006

[a] Data for $[SnCl_2(tfacac)_2]$ obtained at 10, 20, and 30 °C. Data for all other complexes obtained at 30, 40, and 50 °C. [b] Average of at least 5 determinations.

*Hydrolysis with Oxygen-*18*-enriched Water.*—Hydrolysis of the complex with oxygen-18-enriched water was carried out by dissolving *ca.* 0·1 g of the tin complex in 5 cm^3 of dry chloroform and adding 0·1 g of 5% oxygen-18-enriched water. The mixture was then stirred vigorously until the spectrum of an aliquot, suitably diluted with dry chloroform, showed that hydrolysis was complete. The mixture was then filtered and the chloroform removed by evaporation on a steam-bath to leave a mixture of water and the free ligand. The mass spectrum of this mixture was obtained.

RESULTS AND DISCUSSION

Although it has been reported that $[SnCl_2(acac)_2]$ and $[SnBr_2(acac)_2]$ in chloroform have absorbance maxima in the u.v. spectra at 273 nm,[4] we found that solutions of these complexes in dry chloroform have absorption maxima at 303 and 305 nm, respectively. In wet chloroform, however, the spectra of the complexes gradually disappear and are replaced by the spectrum of the free acetylacetone (absorbance maximum 275 nm).

Measurement of the absorption spectra of reactants and products for each of the reactions studied showed that the product corresponds to 2 mol equiv. of free ligand per mol equiv. of tin(IV) complex in the original reaction mixture. Attempts to isolate tin-containing hydrolysis products yielded only stannic oxide (confirmed by elemental analysis) and this was the only tin-containing species found in the mass spectrum of reaction mixtures in which hydrolysis was complete. The reaction being followed must, therefore, be the hydrolysis of the complexes producing hydrogen halide, free ligand, and stannic oxide, which may be hydrated [equation (1)].

$$[SnX_2(ke)_2)] + (n + 2)H_2O \longrightarrow SnO_2,nH_2O + 2HX + 2keH \qquad (1)$$

With the concentration of water greatly in excess of the concentration of the complex and monitoring the reaction at the λ_{max} of the tin(IV) complex (Table), it was generally found that plots of log $(A_t - A_\infty)$ (where A_t and A_∞ are the absorbances at time = t and time = ∞, respectively) against time gave straight lines for up to five half-lives. In all cases plots of the observed pseudo-first-order rate constants, obtained at a particular temperature, against concentration of water gave straight lines passing through the origin. The rate equation for the hydrolysis reaction under the conditions used is therefore that given in equation (2).

$$\text{Rate} = k[SnX_2(ke)_2][H_2O] \qquad (2)$$

At lower concentration of water (less than a *ca.* 100- to 200-fold excess of water over complex) the slope of the logarithmic plot decreased with time and below a *ca.* 50-fold excess of water the reaction did not go to completion as shown by the absorbance of the reaction solution. In these cases, the initial slope of the logarithmic plot was used to obtain a first-order rate constant. Since the concentrations of water in these solutions was much greater than that needed for a first-order excess, the explanation for this retardation is not simply reduction in the concentration of water in the reaction mixture owing to reaction with the complex. It therefore appeared that the reaction was retarded by one of the products.

Addition of free ligand to reaction mixtures to give

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concentrations up to $0{\cdot}3$ mol dm^{-3} failed to produce any measurable inhibition of the reaction. However, addition of chloroform saturated with the appropriate hydrogen halide (to give solutions of hydrogen halide of up to $0{\cdot}02$ mol dm^{-3}) to reaction solutions in which 0 to 80% reaction had occurred stopped further reaction completely, though there was no detectable reversal of the reaction. A likely explanation of this inhibition is that the hydrogen halide interacts with the water[10] preventing reaction of water with the complex.

The Table lists the second-order rate constants for the hydrolysis of the compounds studied together with the enthalpies and entropies of activation calculated by a least-squares procedure.

One very clear feature of the reactions studied is the very marked similarity of the enthalpies and entropies of activation of the reactions of $[(SnCl_2(acac)_2]$, $[SnCl_2(bzac)_2]$, and $[SnCl_2(bzbz)_2]$. Previous kinetic studies on the hydrolysis of the d^0 systems $[Si(bzbz)_3]^+$, tris(tropolonato)silicon(IV), and dichlorobis(tropolonato)tin(IV) indicated that the cationic species react by initial attack by water on the β-carbon atom of the chelating ligand.[11] An earlier report also suggested that $[Si(acac)_3]^+$ hydrolysis occurs *via* an associative mechanism.[12] If an associative mechanism of this type were operating in the present case one would expect that a stepwise replacement of the methyl groups on the β-carbon atom of the ligand by phenyl groups would cause some reduction in the rate on steric grounds. The electronic effect of these groups is probably quite small.

Mass spectral analysis of the products of the reactions using oxygen-18-enriched water showed no enrichment of the ligand by oxygen-18. This indicates that attack by water on the β-carbon atom of the ligand cannot be the rate-determining step.

The decrease in the enthalpies of activation in the series $[SnCl_2(acac)_2]$, $[SnBr_2(acac)_2]$, $[SnI_2(acac)_2]$ argues against an associative reaction. The second-order kinetics might be caused by a dipole–dipole interaction between the complex prior to the rate determining step [equations (3) and (4)].

$$[SnX_2(ke)_2] + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [SnX_2(ke)_2]\ldots\ldots H_2O \qquad (3)$$

$$[SnX_2(ke)_2]\ldots\ldots H_2O \xrightarrow{k_2} \text{products} \qquad (4)$$

The rate equation for this mechanism is given in equation

$$-\frac{d[SnX_2(ke)_2]}{dt} = \frac{k_2\dfrac{k_1}{k_{-1}}[SnX_2(ke)_2][H_2O]}{1 + \dfrac{k_1}{k_{-1}}[H_2O]} \qquad (5)$$

(5) which, when $k_1[H_2O]/k_{-1} \ll 1$, reduces to a second-order rate equation. The exact nature of the second step in the reaction is not totally clear though it presumably requires a considerable amount of bond breaking, probably of the tin–halogen bond.

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