ORGANOMETALLIC COMPOUNDS

V[*]. KINETICS OF PHENYL–TIN CLEAVAGE BY A CHELATING AGENT

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Previous work[1] has established the scope of tin–phenyl cleavage of diphenyltin dichloride by such chelating agents (HCh) as acetylacetone, benzoylacetone, dibenzoylmethane, salicylaldehyde, and 8-quinolinol (HOx). At temperatures about 150°, compounds of the type $Cl_2Sn(Ch)_2$ are produced quantitatively. The present communication reports the results of an investigation of the kinetics of the cleavage reaction.

EXPERIMENTAL

Materials

The ligands (Eastman White Label) were recrystallized from benzene–petroleum ether and diphenyltin dichloride (Columbia Chemicals, Inc.) was recrystallized from petroleum ether. The melting point of the purified material was used as a criterion of purity.

Diphenyltin dibromide, prepared by the method of Pedley and Skinner[2], was obtained as white crystals, m.p. 37–38° (petroleum ether, b.p. 90–110°) reported m.p. 37°. (Found: Br, 37.01, $C_{12}H_{10}Br_2Sn$ calcd.: Br, 36.92 %.)

Dichlorobis(8-quinolinolato)tin(IV), prepared using the previously described method[1], was recrystallized from benzene–petroleum ether, and the purity was verified by chloride analysis (Found: Cl, 14.71. $C_{18}H_{12}Cl_2N_2O_2Sn$ calcd.: Cl, 14.84 %.)

Dibromobis(8-quinolinolato)tin(IV) was prepared similarly; yellow crystals, m.p. 352° dec. (dimethyl sulfoxide–methanol). (Found: C, 37.94; H, 2.24; Br, 27.91. $C_{18}H_{12}Br_2N_2O_2Sn$ calcd.: C, 38.13; H, 2.12; Br, 28.21 %.)[**]

Dimethyl sulfoxide, reagent grade, was stored over molecular sieves until needed.

Procedure

Diphenyltin dihalide and 8-quinolinol were dissolved separately in 50-ml portions of dimethyl sulfoxide. The solutions were allowed to reach thermal equilibrium and were mixed in a 3-neck flask, which was equipped with an efficient condenser, and which was placed in a constant-temperature bath. Maximum temperature variation during a run was 0.5°. Aliquot portions were withdrawn periodically and the reaction quenched by cooling.

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[*] Part IV, see ref. 1.

[**] Carbon, hydrogen analyses performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Reaction rates were measured spectrophotometrically using a Bausch and Lomb Spectronic 20 colorimeter with matched cells. Pseudo first-order rate law was obeyed up to 90% of reaction, and rate constants, k_{obs}, (Table 1) were calculated from the relationship $k_{obs} = 2.303\ m$, where m is the slope of the linear relationship $-\log_{10}(D_\infty - D_t)$ *vs* time (sec), and D_∞ and D_t are the optical densities at infinity and time, t, respectively.

The optical densities were measured at 800 and 805 mμ for the diphenyltin dichloride and diphenyltin dibromide systems respectively. Of the compounds of the type $Cl_2Sn(Ch)_2$ that have been reported, the one for which Ch is 8-quinolinolate (Ox) is the most stable and for this reason was selected for extensive study. Spectrophotometric measurements indicate that $Cl_2Sn(Ox)_2$ or $Br_2Sn(Ox)_2$ does not decompose during the time and at the temperatures involved in the runs summarized in Table 1. Moreover, in all cases, the infinity spectrum indicates the formation of $Cl_2Sn(Ox)_2$ or $Br_2Sn(Ox)_2$ is complete.

Some rate constants were determined conductometrically, using a model

TABLE 1

SPECIFIC RATE CONSTANTS FOR TIN–PHENYL CLEAVAGE OF DIPHENYLTIN DICHLORIDE[a] AND DIPHENYLTIN DIBROMIDE BY 8-QUINOLINOL IN DIMETHYL SULFOXIDE

Diphenyltin dichloride				*Diphenyltin dibromide*			
t (°C)	[HOx] (10^2 M)	*Added salt* (10^2 M)	$10^3 k_{obs}$ (sec^{-1})	*t* (°C)	[HOx] (10^2 M)	*Added salt* (10^2 M)	$10^3 k_{obs}$ (sec^{-1})
178.3	1.00	—	1.41	172.0	1.00	—	3.81
178.6	2.00	—	1.66	172.4	3.00	—	4.15
178.8	2.00	—	1.70	177.9	1.00	—	3.92
178.0	3.00	—	2.15	177.8	1.00	—	4.01
178.8	3.00	—	2.17	177.9	3.00	—	4.35
178.1	4.00	—	2.36	178.0	3.00	—	4.28
178.5	4.00	—	2.44	192.0	1.00	—	5.32
184.1	4.00	—	3.36	192.1	1.50	—	5.44
184.0	4.00	—	3.41	191.3	3.00	—	5.48
188.1	4.00	—	3.56	191.8	4.00	—	5.44
188.0	4.00	—	3.68	191.8	4.00	—	5.58
187.9	2.00	—	2.39	192.0	3.00	2.00[b]	4.22
191.8	1.00	—	2.39	191.8	3.00	2.00[b]	4.34
192.1	1.00	—	2.42	192.0	1.00	2.00[d]	2.11
193.3	2.00	—	2.56	191.7	3.00	2.00[d]	3.39
193.1	3.00	—	3.16				
192.2	4.00	—	3.73				
192.1	4.00	2.00[b]	3.73				
191.8	4.00	2.00[b]	3.75				
191.8	3.50	0.50[c]	3.68				
192.0	2.00	2.00[c]	3.46				
191.8	4.00	0.50[d]	2.96				
191.8	4.00	1.00[d]	2.53				
191.8	4.00	1.50[d]	2.10				
193.2	4.00	2.00[d]	1.82				
192.0	4.00	2.00[d]	2.03				
191.8	4.00	—	1.94[e]				
192.3	4.00	—	2.24[e]				

[a] Concentration of diphenyltin dichloride or dibromide 1×10^{-2} M in all runs. [b] $(C_2H_5)_4NBr$ present. [c] 8-Quinolinol hydrochloride present. [d] $(CH_3)_4NCl$ present. [e] Conductometric method used.

RC-16B2 conductivity bridge, dipping platinum black electrodes (cell constant 0.123 cm^{-1}) and measuring the conductivity of the quenched aliquot portions. It was found that $-\log(R_\infty - R_t)$ was a linear function of time; R_∞ and R_t are the resistances at infinity and time, t, respectively. The following are molar conductivity data for dimethyl sulfoxide solutions: 8-Quinolinol 0.810 (0.01 M), $(C_6H_5)_2SnCl_2$, nil (1 × 10^{-2} M), $Cl_2Sn(Ox)_2$ 42.0 (1 × 10^{-3} M), $(C_6H_5)_2SnBr_2$, 2300 (1.00 × 10^{-3} M), $Br_2Sn(Ox)_2$, 230 ohm^{-1}·cm^2·moles^{-1} (1.00 × 10^{-3} M).

It was not possible to study the reaction using other solvents because the boiling points were too low (*e.g.*, dibutyl ether, benzene, toluene, xylene) or because the materials were insoluble, or because the spectrum of the solvent interfered (*e.g.*, nitrobenzene).

DISCUSSION

First order rate law is followed during tin–phenyl cleavage of diphenyltin dihalide by 8-quinolinol in dimethyl sulfoxide. However, at the reactant concentration ratios, $[HOx]/[(C_6H_5)_2SnCl_2]$, studied (1)–(4), there is a dependence of k_{obs} on the concentration of 8-quinolinol. At 192°, this dependence is best described by the equation

$$\text{rate} = (k_1 + k_2\,[HOx]^2)[(C_6H_5)_2SnCl_2]$$

where k_1 is 2.25 × 10^{-3} sec^{-1} and k_2 is 0.925 (Fig. 1). At a lower temperature (178°) this relationship is valid for the reactant ratios 1, 2, 3 and the value of k_2 is substantially the same. Similar results are noted for diphenyltin dibromide systems.

It is believed that the formation of $Cl_2Sn(Ox)_2$ is due to the following set of reactions and that a similar series may be written for the dibromo analogue.

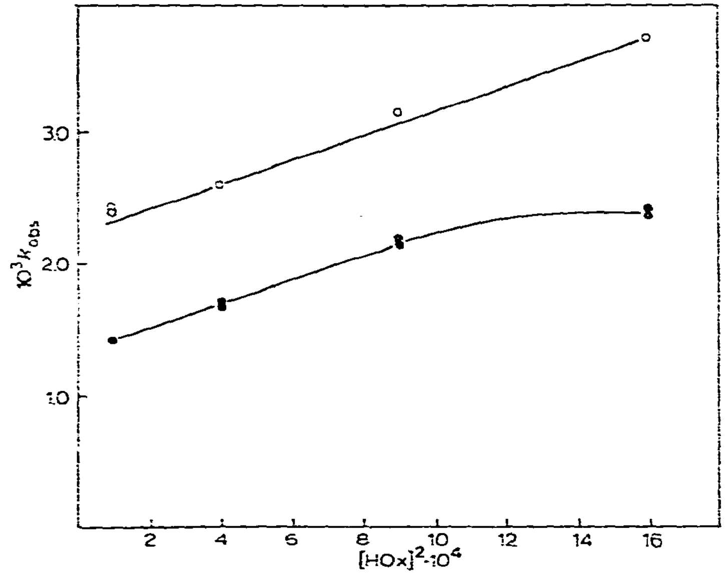

Fig. 1. Variation of k_{obs} for tin–phenyl cleavage of diphenyltin dichloride with [8-*quinolinol*]^2 at 192° (open circles) and 178° (closed circles).

$$(C_6H_5)_2SnCl_2 \xrightarrow{k_1} n\ \mathrm{Cat}^+ + Cl^-,\ \text{where Cat}^+ \text{ is } [(C_6H_5)_2SnCl_2(C_6H_5)_2SnCl]^+ \tag{1}$$

$$n\ \mathrm{Cat}^+ \xrightarrow{k} \text{products} \tag{1a–n}$$

$$(C_6H_5)_2SnCl_2 + 2\ HOx \underset{}{\overset{K_{eq.}}{\rightleftharpoons}} (C_6H_5)_2SnCl_2\cdot(HOx)_2 \tag{2}$$

$$(C_6H_5)_2SnCl_2\cdot(HOx)_2 \xrightarrow{k_2} \text{products} \tag{2a–n}$$

In effect, it is suggested that there are two cleavage paths. The first involves, as a rate-determining step, the formation of a coordination entity, $[(C_6H_5)_2SnCl_2(C_6H_5)_2SnCl]^+$, which is followed by a series of rapid recombination steps. The second involves a rapid formation of a second coordination entity, $C_6H_5SnCl_2\cdot(HOx)_2$, which undergoes intramolecular tin–phenyl cleavage. The following evidence is offered in support of the proposed mechanism.

The kinetic data are in accord with such a mechanism; k_2 in the rate expression would be equal to $k_2' K_{eq}$. Moreover, the presence of chloride ion, supplied as tetramethylammonium chloride, causes a marked decrease in the value of k_{obs} for those runs for which $[HOx]/[(C_5H_6)_2SnCl_2]$ is 4. Over the range of chloride investigated, the value of log k_{obs} appears to be a linear function of $[Cl^-]^{1/2}$ or of $\mu^{1/2}$. This effect is due to mass-law retardation and not to a general ionic-strength effect because the substitution of bromide for chloride ion caused no reduction in the observed rate constant. This observation is in accord with the suggested mechanism which involves reaction between ions and molecules, not between ions.

The lack of effect on rate of added bromide ion deserves further comment. If chlorine–bromine interchange occurred between bromide ion and diphenyltin dichloride, a mass-law effect should be observed. That it is not, may be attributed to an unfavorable equilibrium. However, the equilibrium should be favorable for the reversed situation, *i.e.* the effect of added bromide ion and chloride ion on the rate of cleavage of diphenyltin dibromide, which is suppressed both by added bromide or chloride ion. The rate of replacement of bromide in diphenyltin dibromide by chloride ion is much faster than the rate of cleavage of diphenyltin dibromide. For a chloride/diphenyltin dibromide ratio of 2, the value of $10^3\ k_{obs}$ is the same as that for diphenyltin dichloride at HOx/tin ratios of 3 (3.39 *vs* 3.16) and 1 (2.11 *vs* 2.39, 2.42). These data also serve to indicate the lack of an effect of added bromide ion on the rate of cleavage of diphenyltin dichloride.

The nature of the dissociative process is suggested by existence of a two-term rate-law expression, by the effect of added halide ion, and by the relative values of k_1 for the diphenyltin-dichloride and -dibromide systems. The retardive effect on rate by added chloride ion has been examined in some detail. At a reactant ratio $[HOx]/[(C_6H_5)_2SnCl_2]$ of 4 and at 192°, there is a linear dependence of k_{obs} and $1/[Cl^-]^n$ where n is 0.5 but not 1.0 or 2.0. This would suggest a dissociation represented by eqn. (1), where n Cat$^+$ is $1/2[(C_6H_5)_2SnCl_2(C_6H_5)_2SnCl]^+$. The rate of formation of product by this process would be equal to $k_1[(C_6H_5)_2SnCl_2]_T F$, where F is the fraction of cations Cat$^+$ that undergo tin–phenyl cleavage and by applying the steady-state approximation, F is found to be equal to $1/(m[Cl^-]^{1/2} + 1)$.

Also, the formation of a species of the type n Cat$^+$ should occur more readily with diphenyltin dibromide than with the dichloride and this is reflected in the relative values of $10^3 k_{obs}$ which are (at 192°) 5.35 and 2.25 for diphenyltin dibromide and dichloride, respectively.

The formation of a second coordination entity, $(C_6H_5)_2SnX_2 \cdot 2HOx$, is suggested by the second term of the two term rate expression, by analysis of the spectra of the solutions at various stages of reaction, and by the effect of added 8-quinolinolium ion. The two-term rate expression suggests only the stoichiometry. The formation of an adduct is postulated rather than an entity such as $(C_6H_5)_2Sn(Ox)_2$ or $(C_6H_5)_2Sn(Ox)Cl$. The last two compounds have been prepared previously and their spectra in dimethyl sulfoxide were measured, and analysis of the spectra of the reaction mixture at various stages of reaction indicates that these compounds are not present in significant quantities. Furthermore, the rate is essentially the same whether measured by the spectrophotometric or the conductivity method. This is suggestive evidence that the reaction does not involve complex formation with the concommitant liberation of highly mobile hydronium and chloride ions.

Finally, the insensitivity of log k_{obs} to ionic strength does not necessarily support the suggestion that a preliminary step (2) involves coordination by 8-quinolinol, not by 8-quinolinolate ion, but at 192° and a reactant concentration ratio of 4.0, there appears to be no general acid dependence. The addition of 8-quinolinol hydrochloride appears to have no effect on the value of k_{obs}, though there is a slight reduction when 50 percent of 8-quinolinol is present as the hydrochloride. Thus it would appear that a rate-determining step is not dependent upon a pre-equilibrium dissociation of 8-quinolinol.

The function and structure of the entity $(C_6H_5)_2SnX_2 \cdot 2HOx$ are of considerable interest. It appears that the formation of this entity would serve to activate the electrophilic proton and the incipient phenyl carbanion. Such a view has been advanced recently by Dessy and co-workers[3] and aids in an understanding of the present cleavage study as well as others reported in the literature[3]. There are, moreover, many examples of the role of coordination in orienting ligands[4]. Such a phenomenon appears to be in operation here, though it is not possible to determine the structure or coordination number. There is a slight preference for an eight-coordinate species because such compounds are known[5], because the incipient 8-quinolinolate moiety is more likely to be bidentate than unidentate, and because the proximity of a phenyl and a coordinated hydroxy group seems reasonable for effective reaction.

An examination of the temperature dependence of ln k_{obs} provides further support for the proposed mechanism. The Arrhenius equation is obeyed over only a relatively narrow temperature range, 184–192° although the reaction has been measured over the range 178–192°. Moreover, there is a minimum reaction temperature; below 150° spectrophotometrically discernable reaction does not occur. The non-adherence to the Arrhenius equation could have several interpretations. Experimental technique does not appear to be at fault, for the precision is good. The choice of the Arrhenius equation was not in error; the adherence is equally poor for the corrected form of the equation[6].

$$T \ln k = T \ln A - E/R$$

The final interpretation, that the reaction is complicated and that the observed rate constant is a function of more than one rate constant, is most reasonable.

Although $\ln k_{obs}$ *vs* $1/T$ does not follow the Arrhenius equation, a plot of $\ln k_1$ *vs* $1/T$ does, where the values of k_1 are obtained as the intercept from Fig. 1. The following activation parameters are obtained for diphenyltin dichloride for what is apparently the dissociative process at 192°: E, 15 kcal/mole; ΔH^*, 14 kcal/mole; and ΔS^*, −43 e.u.*. The large negative value for the entropy of activation would be expected if the activated state is an ion pair, particularly one which is more highly solvated than the reactants.

Finally, the possibility that this is a chain reaction which has as the first step the homolytic cleavage of a tin–carbon bond has been considered and has been rejected. There is no spectrophotometric evidence of biphenyl, though this would be an expected and readily discernable product. There is no difference observed when the reaction is carried out in clear or darkened vessels.

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SUMMARY

The kinetics of tin–phenyl cleavage of diphenyltin dichloride by 8-quinolinol (HOx) in dimethyl sulfoxide have been determined at 178–192°. The rate of formation of the product, $Cl_2Sn(Ox)_2$, is given by the expression, rate $= k_{obs}[(C_6H_5)_2SnCl_2]$, where $k_{obs} = k_1 + k_2[HOx]^2$. The two-term expression reflects a dissociative mechanism and a mechanism which involves formation and decomposition of $C_6H_5SnCl_2 \cdot 2HOx$. A mass-law retardation effect is demonstrated by the addition of chloride ion, though the addition of bromide ion causes no alteration in the rate. It appears that the second mechanism consists of a nucleophilic attack by 8-quinolinol followed by activation of electrophilic proton and incipient phenyl carbanion through coordination.

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* The corresponding values for the dibromide are 9 kcal/mole, 8 kcal/mole and −53 e.u. The pertinent equations and error analyses is given elsewhere[6].