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OXIDATION OF ORGANODITIN COMPOUNDS BY TRIS(1,10-PHENANTHROLINE)IRON(III) PERCHLORATE

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Summary

The kinetics of the oxidation of organoditin compounds by tris(1,10-phenanthroline)iron(III) perchlorate in acetonitrile have been studied. The reaction leads to the cleavage of the tin—tin bond with the concomitant reduction of two moles of iron(III) complex per mole of organoditin compound reacted. The reaction obeys a second-order rate law, first-order with respect to both distannane and the iron(III) complex, and the reactivity order is $Ph_6Sn_2 < Me_3SnSnPh_3 < Me_6Sn_2 < Bu_6Sn_2$. Such a trend appears to be mainly attributable to the influence of the organic group R in favouring the tendency of the tin atoms to donate electrons to the oxidizing agent. An outer-sphere redox mechanism involving two one-electron transfer redox steps is proposed.

Introduction

Organoditin compounds are known to undergo oxidative tin—tin bond cleavage with several reagents, according to reactions of type (1),

$$R_6Sn_2 + XY \rightarrow R_3SnX + R_3SnY \qquad (1)$$

where XY can be a halogen or some other covalent molecule, e.g. CF_3I [1]. Metal ions that are readily reduced can also cause this kind of oxidative bond cleavage [1—3]. The reactions involved in these processes are usually interpreted in terms of S_E mechanism, implying normally [4—7], through not always [3], an electrophilic attack of XY on a tin atom. From another point of view these reactions can be regarded as electron-transfer redox processes, particularly when the reaction products exhibit oxidation numbers unquestionably different from those exhibited by the reacting species. The possibility of organoditin compounds undergoing electron-transfer redox reactions is also suggested by the proven existence of reversible redox systems of type (2) [8,9].

$$R_6Sn_2 \rightleftharpoons 2\,R_3Sn^+ + 2\,e \qquad (2)$$

Thus, the oxidative reactions of distannanes can be simply explained in terms of the usual electron-transfer redox mechanism, involving inner- or outer-sphere activated complexes [10], according to whether bonding interactions between the reactants in the activated complex are significant or not. The best way of investigating the factors affecting the reactivities of distannanes would appear to be to obtain kinetic data relevant to outer-sphere rather than inner-sphere redox processes [10]. In this connection, an outer-sphere redox mechanism is likely to operate when the oxidizing reagent is such that strong direct interactions with the metal atoms of the organoditin compound are prevented by a suitable choice of the ligands bonded to the central metal atom. We have tried to realize such a situation by choosing a rather bulky oxidizing agent, which lacks any potential bridging group, thus making unfavourable a direct attack on the tin atoms of distannanes.

We report here a kinetic investigation of the oxidation of some organoditin compounds (Bu_6Sn_2, Me_6Sn_2, $Me_3SnSnPh_3$, Ph_6Sn_2) by tris-(1,10-phenanthroline)iron(III) perchlorate, $[Fe(Phen)_3](ClO_4)_3$ [sometimes indicated as Fe^{III} in the following], in acetonitrile.

Experimental

Materials

Hexamethylditin (Me_6Sn_2), hexabutylditin (Bu_6Sn_2), and hexaphenylditin (Ph_6Sn_2) (Schuchardt materials) were purified either by distillation (Bu_6Sn_2), by recrystallization from light petroleum (b.p. 60—80°) at —78° (Me_6Sn_2) or by precipitation from chloroform by addition of ethanol (Ph_6Sn_2). Trimethyltriphenylditin ($Me_3SnSnPh_3$) was prepared according to the literature procedure [11].

Tris(1,10-phenathroline)iron(III) and iron(II) complexes were prepared as described by Sutin and Gordon [12] and kept in the dark.

Acetonitrile was purified and dried by the standard methods [13].

Preparation of the reaction mixtures, stoichiometry of the reactions and evaluation of the reaction rates.

Stock solutions of both organoditin compounds and iron complexes were prepared by weight in black-painted flasks and used immediately after their preparation. The distannane solutions were standardized by $AgNO_3$ titration [14] or, having determined the stoichiometry of the reactions under investigation, by the spectrophotometric evaluation of the amount of iron(III) complex reacted with a given volume of stock solution of distannane. The solutions of the iron(II) and iron(III) complexes exhibit absorption spectra which are very similar, qualitatively and quantitatively, to those obtained when the complexes are dissolved in aqueous sulfuric acid, and the solutions are stable for the time necessary to carry out the kinetic experiments [less than 2% decomposition of iron(III) complex in one hour at 35°]. The reactions were followed spectrophotometrically. Relatively slow reactions were carried out by mixing appropriate volumes of thermostatted stock solutions of the reactants directly in

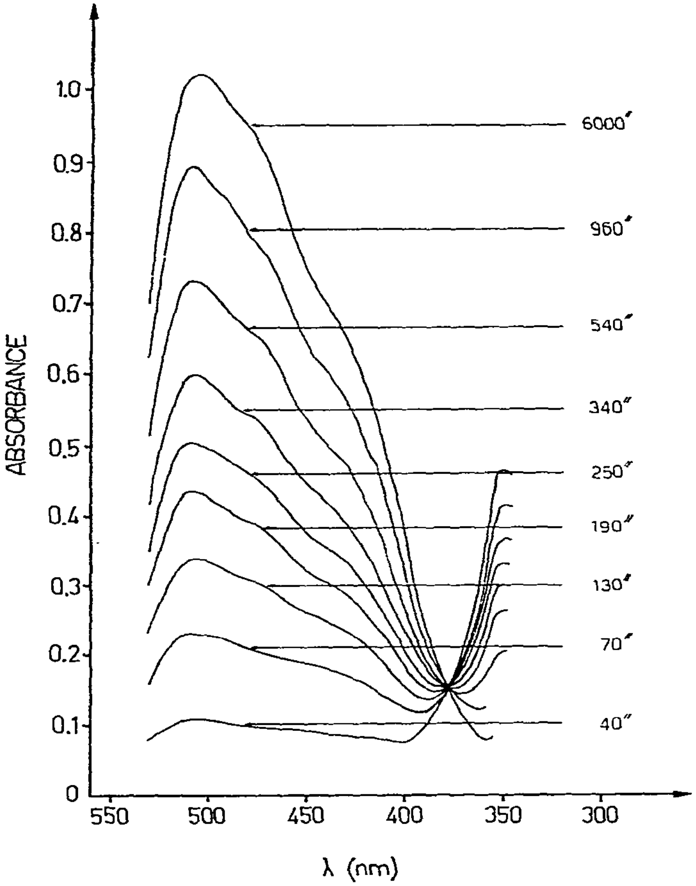

Fig. 1. Changes in the absorption spectrum of a solution initially containing Ph_6Sn_2 (8.65×10^{-5} *M*) and $[Fe(Phen)_3](ClO_4)_3$ (1.00×10^{-4} *M*) in acetonitrile at 20°.

1 cm silica cells maintained in the thermostatted cell compartment of an Optica CF4R recording spectrophotometer. The reactions were followed by recording, at suitable time intervals, the spectra of the reacting mixture in the wavelength range 550—350 nm, where a strong change of absorbance occurs during the reaction and also at an isosbestic point at 378 nm (Fig. 1). Fast reactions were carried out by means of a stopped-flow apparatus. In this case the change of transmittance with time was followed at 510 nm.

The reaction involves the reduction of iron(III) to iron(II), as shown by the analysis of the spectral changes of the reacting mixture with time. An experiment carried out using a reacting mixture initially containing Fe^{III} 5.0×10^{-5} *M* and Ph_6Sn_2 1.67×10^{-4} *M* showed that all the iron(III) is reduced at the end of the reaction, whereas when Fe^{III} 1.00×10^{-4}*M* and Ph_6Sn_2 3.35×10^{-5} *M* are used the final spectrum shows that 6.65×10^{-5} *M* iron(II) is present at the end of the reaction. Similar results were obtained with the other organoditin compounds, and are consistent with the stoichiometric equation (3), where the form of the tin-containing reaction product is postulated on the basis of the usual behaviour of distannanes toward oxidation. Ph_3Sn^+ has also been experimentally detected in the products of a reaction carried out with concentrations of reactants much higher than those used in the kinetic experiments ($[Ph_6Sn_2] = 7.0 \times 10^{-4} M$; $[Fe^{III}] = 1.4 \times 10^{-3} M$).

$$R_6Sn_2 + 2[Fe(Phen)_3](ClO_4)_3 \rightarrow 2R_3Sn^+ClO_4^- + 2[Fe(Phen)_3](ClO_4)_2 \qquad (3)$$

Addition of a stoichiometric amount of $NaBPh_4$, followed by water, led to the quantitative separation of $[Fe(Phen)_3](BPh_4)_2$. After rapid filtration, the solution was treated with a large excess of NaCl and extracted with benzene. After fast evaporation of benzene at room temperature under vacuum a whitish powder was recovered which analyzed correctly for Ph_3SnCl.

Whenever possible the kinetic experiments were carried out using organoditin compounds in sufficiently large excess to realize pseudo-first-order conditions. The pseudo-first-order rate constants, k_{obs}, were determined from the slopes of the plots of log $[D_t - D_\infty]$ against time, where D_t and D_∞ are the absorbances of the reaction mixture at time t and at the end of the reaction, respectively. When pseudo-first-order conditions were not realizable the concentrations of the reagents at different times were first evaluated from the absorption spectra, the stoichiometry of the reaction being known. The concentrations evaluated at different times were found to obey relationship (4) where X is the concentration of iron(III) reacted at time t.

$$k_2 t = 2\frac{2.303}{2[R_6Sn_2]_0 - [Fe^{III}]_0} \cdot \log \frac{[(Fe^{III})]_0 \cdot (2[R_6Sn_2]_0 - X)}{2[R_6Sn_2]_0 \cdot ([Fe^{III}]_0 - X)} \qquad (4)$$

The ranges of concentrations explored in the individual cases are as follows: (a) $[Bu_6Sn_2]_0$, 6.60×10^{-5}–2.50×10^{-4} M; $[Fe^{III}]_0$, 2.00×10^{-5} –$3.00 \times 10^{-5} M$; (b) $[Me_6Sn_2]_0$, 8.35×10^{-5}–$2.33 \times 10^{-4} M$; $[Fe^{III}]_0$, 2.35×10^{-5}–3.60×10^{-5} M; (c) $[Me_3SnSnPh_3]_0$, 5.00×10^{-5}–2.50×10^{-4} M; $[Fe^{III}]_0$, 2.00×10^{-5}–$3.00 \times 10^{-5} M$; (d) $[Ph_6Sn_2]_0$, 2.00×10^{-5}–1.67×10^{-4} M; $[Fe^{III}]_0$, 2.50×10^{-5}–1.00×10^{-4} M. The limits of the ranges used were imposed either by the low solubility of the organoditin compounds or by the impossibility of following the kinetics with the available equipment. The reaction rates were evaluated at two temperatures (20 and 35°). At least seven kinetic runs were carried out at each temperature and for each organoditin compound.

Results and discussion

The organoditin compounds examined undergo oxidation by tris(1,10-phenanthroline)iron(III) perchlorate according to the non-complementary redox reaction (3), which follows the second order rate law (5). The values of k_2 are listed in Table 1 together with the activation parameters. The form of the rate law, together with the stoichiometry of the reaction, implies an overal redox process involving two one-electron redox steps, consistent with the general behaviour of tris(1,10-phenanthroline)iron(III) as a one-electron oxidant [15,16], even when it reacts with a two-electron reductant [17]. Such a mech-

TABLE 1

SECOND-ORDER RATE CONSTANTS, k_2, AND ACTIVATION PARAMETERS[a] FOR THE OXIDATION OF ORGANODITIN COMPOUNDS BY TRIS (1,10-PHENANTHROLINE)IRON(III) PERCHLORATE IN ACETONITRILE

organoditin compound	t (°C)	k_2 ($l \cdot mole^{-1}, s^{-1}$)	ΔH^* (kcal/mole)	ΔS^* ($cal \cdot {}^\circ K^{-1} \cdot mole^{-1}$)
Ph_6Sn_2	35	106	12.7	− 8
	20	34.8		
$Me_3SnSnPh_3$	35	1400	9.5	−13
	20	602		
Me_6Sn_2	35	52000	8.5	− 9
	20	24200		
Bu_6Sn_2	35	130000	7.8	−10
	20	64500		

[a] Errors: k_2, ± 3%; ΔH^*, ± 1 kcal/mole; ΔS^*, ± 3 cal $^\circ K^{-1} \cdot mole^{-1}$.

$$-\frac{d[Fe^{III}]}{dt} = k_2 \cdot [R_6Sn_2] \cdot [Fe^{III}] \qquad (5)$$

anism must involve an organotin radical as an intermediate, and can be described by the following set of reaction steps:

$$R_6Sn_2 + Fe^{III} \xrightarrow{slow} R_6Sn_2^{\cdot+} + Fe^{II} \qquad (6a)$$

$$R_6Sn_2^{\cdot+} + Fe^{III} \xrightarrow{fast} 2R_3Sn^+ + Fe^{II} \qquad (6b)$$

$$R_6Sn_2^{\cdot+} \xrightarrow{fast} R_3Sn^+ + R_3Sn^\cdot \qquad (6c)$$

$$R_3Sn^\cdot + Fe^{III} \xrightarrow{fast} R_3Sn^+ + Fe^{II} \qquad (6d)$$

On the basis of the Frank—Condon principle, the electron-transfer step (6a) is more likely than the alternative step (7). In order to confirm the details of the

$$R_6Sn_2 + Fe^{III} \rightarrow R_3Sn^+ + R_3Sn\cdot\ Fe^{II} \qquad (7)$$

mechanism (6) we have tried to determine how the reaction products affect the reaction rate. Two kinetic runs were carried out at 35° using reacting mixtures initially containing the same concentrations of the reagents ($[Ph_6Sn_2]_0$ 2.0×10^{-5} M; $[Fe^{III}]$ 1.0×10^{-4} M), but with one containing also the reaction products ($[Ph_3SnClO_4]$ 1.7×10^{-2} M; $[Fe^{II}]$ 2.0×10^{-4} M). The resulting k_2 values were 99.2 $l \cdot mol^{-1} \cdot s^{-1}$ and 98.8 $l \cdot mol^{-1} \cdot s^{-1}$, respectively, showing that the reaction products have no significant kinetic effect. This may be due to the reactivity of the radical intermediate, either $R_6Sn_2^{\cdot+}$ or $R_3Sn\cdot$, which is so great that any kinetic effect of the reaction products under the experimental conditions used is not detectable.

The reactivity order of the organoditin compounds examined, $Ph_6Sn_2 < Me_3SnSnPh_3 < Me_6Sn_2 < Bu_6Sn_2$, appears to be essentially due to the changes in the enthalpy of activation, although there is possibly some entropic contribution for the asymmetric organoditin compound. A fairly good linear correlation exists between the log k_2 and the E_0 values of the redox couple (2). The slope is 0.5 when E_0 is expressed in kcal/mole but, although this might be consistent with the theoretical expectation for an outer-sphere redox process [10], a discussion on this basis is limited by the fact that the E_0 values were evaluated

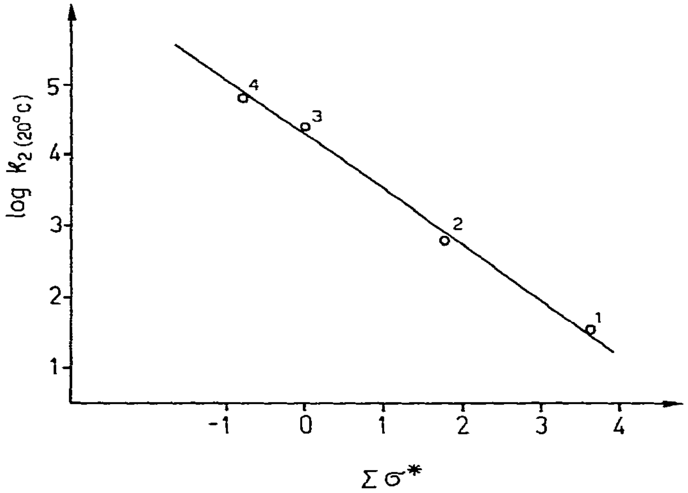

Fig. 2. Relationship between $\Sigma\sigma^*$ and log k_2 for the oxidation of Ph_6Sn_2 (1), $Me_3SnSnPh_3$ (2), Me_6Sn_2 (3) and Bu_6Sn_2 (4) by tris(1,10-phenanthroline)iron(III) perchlorate in acetonitrile at 20°.

in benzene/methanol mixtures [9], not in acetonitrile. Among the factors that in principle may contribute to produce the observed reactivity trend the most important ones should be (a) the relative tendencies of tin atoms to donate electrons, (b) the changes in the steric hindrance and (c) the energy required to elongate the tin—tin bond to the length required in the activated complex. It is reasonable to expect that the first factor is related to the electron-repelling ability of the R groups bonded to the tin atoms. In this context it is found (Fig. 2) that log k_2 for the entire series of organoditin compounds linearly correlates with the sum of the Taft σ^* values ($\Sigma\sigma^*$) of R, according to relationship (8). Such a linear relationship, with a negative value for the slope, suggests

$$\log k_2 = -1.29\ \Sigma\sigma^* + 4.22 \qquad (8)$$

that the relative tendency of the tin atoms to donate electrons is actually a primary effect in determining the observed reactivity trend. A rather peculiar result is that the asymmetric distannane also fits relationship (8), although the presence of different groups (Ph and Me) on two different tin atoms could suggest a reactivity rather similar either to Ph_6Sn_2 or to Me_6Sn_2. A similar result was previously found in the reactions of these same compounds with I_2 [5], and was interpreted in terms of a solvent-assisted mechanism. However, such a result may be due to a cooperative effect of Me and Ph groups in influencing the energetic level of the electrons to be transferred. Further work on other asymmetric organoditin compounds will be necessary to confirm such an interpretation.

The change in the steric hindrance of the group R does not appear to be important in determining the observed reactivity trend. In fact, if steric requirements were important, the reactivity of Me_6Sn_2 should be higher than that of Bu_6Sn_2. In addition, the values of log k_2 would hardly be expected to give a correlation with $\Sigma\sigma^*$ because of the intervention of a variable steric contribution [18,19]. The approximate constancy of the entropy of activation seems also to be consistent with a constant steric contribution along the entire series. The absence of a discriminating steric contribution probably implies the occurrence of one of the following possibilities: (a) the reactants do not approach closely in the activated complex; (b) the reaction center on the distannane is largely available for a direct attack by the oxidizing agent. The latter hypothesis is unlikely to apply in the case under examination because of the kind of iron(III) complex used. In fact, if such a bulky oxidizing agent closely approached the tin atoms before the electron transfer, a variable steric contribution to the rate would likely be found, which would be particularly high for Ph_6Sn_2. This contribution, as noted above, does not appear to be present. Thus the best mechanism for the reactions under examination seemingly involves an outer-sphere redox process in which the reactants do not approach closely before the electron transfer. The activated complex exhibits only weak interactions between the acceptor orbitals of the oxidizing agent and the donor orbitals of the organoditin molecule.

The energy required to elongate the tin—tin bond to meet the requirements of the activated complex does not appear to contribute significantly to the differences between the reactivities of the various distannanes. If such a contribution were important one would rather expect Ph_6Sn_2 to be more reactive than Me_6Sn_2 [E(Sn—Sn) = 36.3±2.4 kcal/mole for Ph_6Sn_2 [20] and 39 kcal/mole for Me_6Sn_2 [21]]. Even in terms of the tin—tin bond strength (an indication of which is given by the tin—tin force constants, 1.17 mdyne/Å for Ph_6Sn_2 [22] and 1.39 mdyne/Å for Me_6Sn_2 [23]), one would expect a contribution to the rate in favour of Ph_6Sn_2 rather than of Me_6Sn_2.

References

1 H. Gilman, W.H. Atwell and F.K. Cartledge, Advan. Organometal. Chem., 4 (1966) 1, and references therein.
2 R.E. Dessy, W. Kitching and T. Chivevers, J. Amer. Chem. Soc., 88 (1966) 453.
3 G. Tagliavini, S. Faleschini and E. Genero, Ric. Sci., 36 (1966) 717.
4 S. Boué, M. Gielen and J. Nasielski, Bull. Soc. Chim. Belg., 73 (1964) 864.
5 G. Tagliavini, S. Faleschini, G. Pilloni and G. Plazzogna, J. Organometal. Chem., 5 (1966) 136.
6 H.C. Clark and C.J. Willis, J. Amer. Chem. Soc., 82 (1960) 1888.
7 G.A. Razuvaev, N.S. Vyazankin and Yu.I. Dergunov, Zh. Obshch. Khim., 30 (1960) 1310.
8 G. Tagliavini and L. Doretti, Chem. Commun., (1966) 562.
9 L. Doretti and G. Tagliavini, J. Organometal. Chem., 12 (1968) 203, and references therein.
10 F. Basolo and R.G. Pearson, Mechanisms of Inorganic Reactions, Wiley, New York, 2nd ed., Chap. 6.
11 C.A. Kraus and R.H. Bullard, J. Amer. Chem. Soc., 48 (1926) 2131.
12 N. Sutin and B.M. Gordon, J. Amer. Chem. Soc., 83 (1961) 70.
13 A. Weissberger, Organic Solvents, Interscience, New York, 1955.
14 G. Tagliavini, Anal. Chim. Acta, 34 (1966) 24.
15 A.G. Sykes, Advan. Inorg. Chem. Radiochem., 10 (1967) 153 and references therein.
16 D.P. Keeton and A.G. Sykes, J. Chem. Soc., Dalton Trans., (1972) 2530.
17 J.S. Littler and I.G. Sayce, J. Chem. Soc., (1964) 2545.
18 R.W. Taft Jr., J. Amer. Chem. Soc., 74 (1952) 3120.
19 H.K. Hall Jr., J. Amer. Chem. Soc., 79 (1957) 5441.
20 D. Keiser and A.S. Kana'an, J. Phys. Chem., 73 (1969) 4264.
21 T.L. Cottrell, The Strengths of Chemical Bonds, Butterworths, London, 2nd ed., 1958, p. 259, quoted in ref. 20.
22 P.A. Bulliner, C.O. Quicksall and T.G. Spiro, Inorg. Chem., 10 (1971) 13.
23 B. Fontal and T.G. Spiro, Inorg. Chem., 10 (1971) 9.