Journal of Organometallic Chemistry, 288 (1985) 289–294
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

HOMOLYTIC SUBSTITUTION IN TRIALKYLTIN IODIDES BY PHOTOCHEMICALLY GENERATED IODINE ATOMS

II *. MECHANISTIC INTERPRETATION

L. VERDONCK, P.H. DE RYCK, S. HOSTE and G.P. VAN DER KELEN

Laboratorium voor Algemene en Anorganische Chemie, Rijksuniversiteit Gent, Krijgslaan 281, B-9000 Gent (Belgium)

(Received December 18th, 1984)

Summary

From analysis of feature of the reactions of trialkyltin iodides with iodine in terms of the charge-transfer mechanism, it is concluded that the fragmentation step is rate limiting. This view is shown to be compatible with current theories (RRKM or QET) of unimolecular reactions.

Introduction

From a study of homolytic substitution in trialkyltin iodides by photochemically generated iodine atoms

$$R_3SnI + I^{\cdot} \xrightarrow{k_2} R_2SnI_2 + R^{\cdot}$$

it was concluded that the charge-transfer model, involving ion-pair formation, provides a valid basis for describing the mechanism of this reaction [1].

Consideration of the blue shift, the charge transfer band maximum, and values of the formation constants led to the conclusion that the halide atom is the preferred donor site in the R_3SnX molecule [2]. Analysis of the thermodynamic data for the donor–acceptor complexes of the type $[R_3SnI \cdot I_2]$, using Mulliken's Resonance Structure Theory [3], led to assessment of the various energy contributions to the charge transfer [4]. Furthermore, PES data suggest that electron transfer from the nonbonding electrons of the halogen atom in the trialkyltin compound to I_2 [4] or to photochemically generated free iodine radicals is very likely.

In contrast, in the analogous reactions of tetraalkyltin compounds, it is believed that charge-transfer interaction takes place from the alkyl–tin σ-bond [5]. This is in keeping with the fact that the HOMO in R_4Sn has predominantly σ-bonding

---

* For part I see Ref. 1.

0022-328X/85/$03.30

TABLE 1

COLLECTED EXPERIMENTAL DATA FOR R_4Sn AND R_3SnI

R	R_4Sn			R_3SnI			
	I_D (eV) [a]	E_p (eV) [b]	log k	I_D (eV) [c]	E_p (V) [c]	log k_2 [d]	$\sigma^{\star}\cdot\Delta H_f$ [e] (kcal mol^{-1})
1 methyl	9.69	2.48	4.72	8.95	0.710	1.92	0
2 ethyl	8.90	1.76	6.43	8.64	0.760	4.41	−2.85
3 n-propyl	8.82		6.41	8.61	0.710	3.89	−2.42
4 isopropyl	8.64	1.51	6.30	8.48		4.70	−3.34
5 n-butyl	8.76	1.75	6.43	8.54	0.680	3.64	−1.47
6 isobutyl	8.68	1.77	5.74	8.51		2.63	−1.71
7 s-butyl	8.45	1.45	6.41	8.39	0.715	4.18	−2.73

[a] I_D = first ionization potential. see C.L. Wong, K. Kochida, A. Gin, M.A. Weiner, J.K. Kochi, J. Org. Chem., 44 (1979) 3979. [b] E_p = anodic peak potential, see R.J. Klinger and J.K. Kochi, J. Am. Chem. Soc., 102 (1980) 4790. [c] Ref. 7. [d] Ref. 8. [e] ΔH_f values for $Me^{\cdot}$, $Et^{\cdot}$ and $i\text{-}Pr^{\cdot}$: F.A. Houle and J.L. Beauchamps, J. Am. Chem. Soc., 101 (1979) 4067; for n-But.: J.M. Williams and W.H. Hamill, J. Chem. Phys., 49 (1968) 4467; for n-Pr. and i-Bu.: S.W. Benson, Thermochemical Kinetics, John Wiley, 1976, pp. 299; for s-Bu.: D.M. Golden and S.W. Benson, Chem. Rev., 69 (1969) 125.

character [10,22]. There are, however, additional differences with respect to corresponding tetraalkyltin compounds. For example, although the formation constants for the charge transfer complex are small for the iodides [6], they are at least an order of magnitude larger than those estimated for the corresponding tetraalkyltin compounds [7,8]. Moreover, the range of reaction rates for analogous compounds containing other alkyl groups relative to those for the methyl derivate is 1–594, compared to 1–51 for the corresponding tetraalkyltin compounds; the absolute rates for the iodination of R_3SnI are much lower than those for iodination of R_4Sn (Table 1). An explanation for these differences is proposed below.

Discussion

There is evidence that in the radical chain mechanism homolytic substitution (S_H2) of a trialkyltin iodide by a photochemically generated iodine atom is the rate-limiting process [1,9]. Furthermore the charge transfer model represents the homolytic substitution as a multi-step process in which the initial reaction is an electron transfer from the trialkyltin iodide to the iodine atom within a $[R_3SnI \rightarrow I^{\cdot}]$ donor–acceptor complex [5,7,8]:

$$[R_3SnI \rightarrow I^{\cdot}] \xrightarrow{k_a} [R_3SnI^{+\cdot} I^-] \qquad (1)$$

The second step consists of the unimolecular fragmentation of the trialkyltin iodide cation [11] (eq. 2,3) followed by very rapid product formation (eq. 4,5).

$$[R_3SnI]^{+\cdot} I^-] \begin{cases} \xrightarrow{k_{f_1}} R_2SnI]^+ I^- + R^{\cdot} & (2) \\ \xrightarrow{k_{f_2}} R_3Sn]^+ I^- + I^{\cdot} & (3) \end{cases}$$

$$R_2SnI]^+ I^- \xrightarrow{\text{fast}} R_2SnI_2 \qquad (4)$$

$$R_3Sn]^+ I^- \xrightarrow{\text{fast}} R_3SnI \qquad (5)$$

The fragmentation and product-formation reactions 3 and 5 could not be detected since they cannot be distinguished from simple exchange with iodine. However the occurrence of reaction 3 and 5 has been demonstrated indirectly in a study of the reaction between Et_3SnBr and iodine atoms, in which Et_3SnI and Et_2SnI_2 as well as Et_2SnBr_2 are formed [9].

There were, however, some experimental observations which prompted us to doubt the rate-determinating nature of the ion-pair formation process for the R_3SnI, viz.:

(1) Since in the charge transfer formulation the ease of oxidation of the donor molecule is the dominant factor for homolytic substitution [12], a rough prediction of the relative reaction rate in a series of corresponding compounds can be made by use of ionisation energies. Examination of the ionization energy (I_D) data collected in Table 1 reveals that R_3SnI derivatives would be expected to react slightly faster with I atoms than the corresponding R_4Sn which is the opposite of the experimental facts (Table 1). Furthermore, a random redistribution is obtained when I_D values are plotted versus log k_2.

(2) A linear correlation between the E_p and I_D data, such as was observed for the R_4Sn series (viz. $E_p = 0.76\ I_D +$ constant) is not found for the R_3SnI series. On the contrary, within experimental error E_p is almost constant (Table 1).

We are thus led to suggest that the unimolecular fragmentation of the $R_3SnI^{+\cdot}$ ions must also be considered as a potential rate limiting step. If the cleavage of the Sn–alkyl bond to give a radical $R^\cdot$ (reaction 2) is rate limiting, there should be a correlation between the rate constant k_2 and thermodynamic parameters relating to the formation of the alkyl radical, for instance the formation enthalpy $\Delta H_f(R^\cdot)$ (see Table 1). There is, indeed, a linear correlation between ΔH_f and the $\sigma^\star$ parameter for the inductive effect of the R group [13], viz. $\log k_2 = 1.89 - 0.85(\sigma^\star \cdot \Delta H_f(R^\cdot))$ (see Fig. 1). This strongly favours the fragmentation as the rate-determinating step.

The corresponding $R_4Sn^{+\cdot}$ ions, on the other hand, are assumed to fragment very

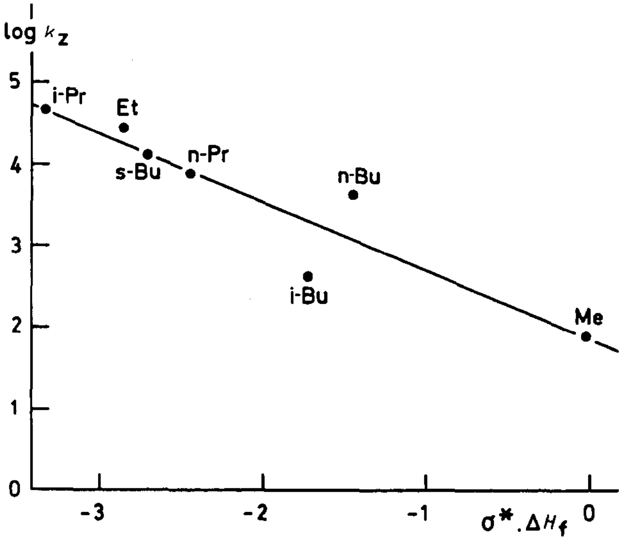
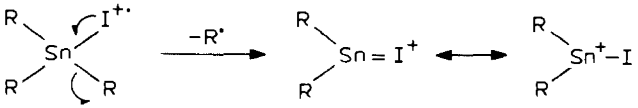


Fig. 1. Correlation diagram of $\log k_2$ vs. $\sigma^\star \cdot \Delta H_f(R^\cdot)$.

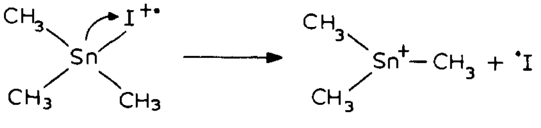
rapidly [5]. The question then arises of how this can be accomodated within the commonly used concepts of unimolecular fragmentation, such as the statistical Riece–Ramsperger–Kassel–Marcus (RRKM) [14,15] or the allied Quasi-Equilibrium Theory (QET) [16–18]. Moreover since the species under consideration is a polyatomic charged species, the charge localization theory [19–21] must also be considered.

The concept of charge-radical localization assumes that the site of lowest ionization potential is the preferred site of charge localization. It is then assumed that the electron deficiency "triggers" the fragmentation, relating the preferred site of charge localization to the preferred mode of fragmentation. This concept has been very successful in organic chemistry but has also been severely criticized since the second premise is inconsistent with the QET. In the QET it is assumed that the excited molecular ion does not usually decompose immediately into the fragment ions, but can undergo several, or many, vibrations before decomposition. It is further assumed that during these vibrations there is a high probability of radiationless transitions, and extensive electron reorganisation which results in a distribution of the excitation energy in a completely random fashion. An important consequence is that a reactive ion can have no memory of its mode of formation. A particular ion with a given internal energy and electron distribution should react in the same manner regardless of the way it has been formed (charge transfer, electron impact, etc.). On the other hand randomization, although proceeding very fast, nevertheless takes some time and occurs typically in a time of psec (10^{-12} sec) so that faster decomposition reactions are not subject to randomization. In this case the localized electron deficiency probably "triggers" the fragmentation. Simple direct bond cleavages are of this type. Since in the R_4Sn compounds the HOMO has predominantly σ-bonding character [10,22], the molecular ion formed by electron transfer will fragment immediately by a single direct tin–alkyl bond cleavage to form the very stable $R_3Sn^+(IV)$ ion [23] and an alkyl radical. The activation energies for the reverse reaction (tin–alkyl bond formation) are known to be very small [14,19]. In these cases the relative stabilities of products reflect the relative bond strengths. Thus the mode of decomposition of mixed tetraalkyltin compounds should reflect the relative strengths of the various alkyltin compounds present. This has been confirmed by experiment [6], the following preferential cleavage being found: t-But > i-Pr > Et > Me.

In contrast, decompositions including rearrangements and/or electron shifts are assumed to require more than 10 psec allowing partial or total energy randomization and electronic reorganization. Since the HOMO in the R_3SnI compounds has predominantly lone pair character, the electron deficiency arising from electron transfer has to be localized primarily on the iodide atom, i.e. $R_3SnI^{+\cdot}$. Subsequent electronic rearrangement, involving a double electron shift, results in alkyl radical cleavage with formation of a species represented by two canonical forms with the charge localized, respectively, on the heteroatom iodine and on the metallic tin atom:



Since the arguments concerning the relationship between preferential cleavage and bond strength apply, alkyl cleavage is preferred. This has been demonstrated by the relative abundancies of the $R_2SnX]^+$ and $R_3Sn]^+$ ions in the mass spectra of R_3SnX (R = alkyl, X = halogen) compounds [24–26], where the $R_2SnX]^+$ peak is generally observed as the base peak. However for Me_3SnI, the $Me_3Sn]^+$ fragments are more abundant than the $Me_2SnI]^+$ fragments, indicating preferential electron pair shift resulting in elimination of an iodine radical:



Apparently in this case the charge localization on iodine "triggers" the fragmentation, probably because the bond energy difference between the Sn–I and $Sn–CH_3$ bonds is minimal [27]. Furthermore, in the photoelectron spectra of the R_3SnI [7], the bands assigned to the ionisation of the Sn–C and Sn–I σ-bond electrons are well separated, except in the case of Me_3SnI for which they are merged. In all other cases the bond strength criterion is valid, i.e. irrespective of the electron distribution in the molecular ion, the fragmentation of lowest energy will be favoured.

We conclude that the theory of unimolecular reactions provides an acceptable basis for explaining the behaviour of the trialkyltin iodides, in particular for the fact that the rate-determining step is the fragmentation.

References

1 P.H. De Ryck, L. Verdonck and G.P. Van der Kelen, Int. J. Chem. Kinet., in press.
2 L. Verdonck, S. Hoste, G.G. Herman, W. Lippens and G.P. Van der Kelen, Spectrochim. Acta A, 40 (1984) 215.
3 (a) R.S. Mulliken, J. Am. Chem. Soc., 74 (1952) 811; b. R.S. Mulliken, J. Phys. Chem., 56 (1952) 801.
4 S. Hoste, G.G. Herman, W. Lippens, L. Verdonck and G.P. Van der Kelen, Spectrochim. Acta, to be published.
5 S. Fukuzumi and J.K. Kochi, J. Org. Chem., 45 (1980) 2654.
6 S. Hoste, G.G. Herman, F.F. Roelandt, W. Lippens, L. Verdonck and G.P. Van der Kelen, Spectrochim. Acta A, 39 (1983) 959.
7 S. Fukuzumi and J.K. Kochi, J. Phys. Chem., 84 (1980) 608.
8 S. Fukuzumi and J.K. Kochi, J. Am. Chem. Soc., 102 (1980) 2141.
9 L. Verdonck, E. Saccasijn, P.H. De Ryck, S. Hoste and G.P. Van der Kelen, Bull. Soc. Chim. Belg., 93 (1984) 1037.
10 A.E. Jonas, G.K. Schweitzer, F.A. Grim and I.A. Carlson, J. Electron Spectrosc., 1 (1972/73) 29.
11 Charge localization on a specific atom requires the knowledge of the electron deficient site; if not known the charge is marked as $]^+$; see also in the text in the discussion of the charge localization theory.
12 S. Fukuzumi and J. Kochi, J. Phys. Chem., 84 (1980) 2246.
13 For similar correlations see for instance: S. Fukuzumi and J.K. Kochi, J. Am. Chem. Soc., 104 (1982) 7599 and C.K. Hancock, E.A. Meyers and B.J. Yager, ibid., 83 (1961) 4211.
14 R.A. Marcus, and O.K. Rice, J. Phys. Colloid. Chem., 55 (1951) 894.
15 R.A. Marcus, J. Chem. Phys., 20 (1952) 359.
16 W. Forst, Theory of Unimolecular Reactions, 1973, Acad. Press, New York and London.
17 H.M. Rosenstock, M.B. Wallenstein, A.L. Wahrhaftig and H. Eyring, Proc. Nat. Acad. Sci. USA, 38 (1952) 667.
18 H.M. Rosenstock, Advances in Mass Spectrometry, Vol. 4, The Institute of Petroleum, London, 1968.

19 C.J. Cummings and W. Bleakny, Phys. Rev., 58 (1940) 787.

20 H. Budzikiewicz, C. Djerassi and D.H. Williams, Mass Spectrometry of Organic Compounds, 1967, Holden Day, San Francisco.

21 (a) D.H. Williams, Mass Spectrometry, Vol. 1, 1971, The Chemical Society, London; (b) Vol. 2, 1973, The Chemical Society, London; (c) R.A.W. Johnstone, Mass Spectrometry, Vol. 3, 1975, The Chemical Society, London; (d) Vol. 4, 1977, The Chemical Society, London.

22 T.P. Fehlner, J. Ulman, W.A. Nugent and J.K. Kochi, Inorg. Chem., 15 (1976) 2544.

23 S. Boue, M. Gielen and J. Nasielski, Bull. Soc. Chim. Belges, 77 (1968) 43.

24 M. Gielen and G. Mayence, J. Organomet. Chem., 12 (1968) 363.

25 M. Gielen and M. De Clercq, J. Organomet. Chem., 47 (1973) 351.

26 M. Gielen and G. Mayence, J. Organomet. Chem., 46 (1972) 281.

27 A.L. Yergey and F.W. Lampe, J. Am. Chem. Soc., 87 (1965) 4204.