

The Acid Cleavage of Mixed Allyltin(IV) Compounds

G. PLAZZOGNA, V. PERUZZO and G. ROSSETTO

Istituto di Chimica Analitica, Via Marzolo 1, 35100 Padova, Italy

Received May 30, 1978

Our interest in the allyltin derivatives stems from their potential synthetic application in the organic and organometallic field due to high reactivity of the tin–allyl bond [1–3]. Specifically the application to the preparation of a variety of disubstituted distannoxanes involves primarily the protonolytic cleavage of the tin–allyl bond.

In previous papers [4–7] the protonolysis of the tin–allyl bond has been shown to proceed predominantly by a S_E2' mechanism. The present note deals with the kinetic effect of the variation in the nature of the substituents on the tin atom. The following selected allyltin compounds have been considered: tri-*n*-butylallyltin, *n*-butyl-di-vinylallyltin, trivinylallyltin and di-*n*-butylallyltin chloride; the rate of protonolysis and the activation parameters have been determined.

Results and Discussion

The kinetics of acid cleavage reaction of allyltin compounds in methanol can be studied by following spectrophotometrically the disappearance of the broad, intense, allyltin peak at 225 nm.

The spectral data of the considered compounds are shown in Table I. It was observed that allyltin compounds react with hydrogen chloride to form propene and trialkyltin chloride. Except where otherwise indicated, the methanolic solutions contained 4% by volume of water.

In such conditions the acids are completely dissociated at the concentrations used [8]. The reaction was verified to be first order in acid concentration (10^{-3} – 10^{-2} *M*) and in substrate (10^{-4} – 10^{-3} *M*) under pseudo-first order conditions (acid in excess). The first order rate law was obeyed up to >90% of completion. Repeated determinations of k_{obs} suggested an average deviation of about $\pm 3\%$. Changes of initial substrate concentration in the range 10^{-4} to 5×10^{-3} *M* produced no measurable change in k_{obs} . Second-order rate constants, k_2 , are given by $k_{\text{obs}}/[H^+]$. The kinetic results for the allyltin derivatives are given in Table I together with the activation enthalpies and entropies. When water was added (from 0 to 2.25 *M*) to the methanol, the rates decreased. The addition of water depresses the acidity of medium. When perchloric acid was used as proton source for tributyl-allyltin the rates ($0.336 M^{-1} \text{sec}^{-1}$) were practically the same as those observed with HCl ($0.321 M^{-1} \text{sec}^{-1}$). It may be thought, as previously suggested [5], that the counterion is not involved in the transition state.

Regarding the effects of the substituents at the tin atom on the reaction rates (see Table I), it is to be noted that the rate decreases markedly when a butyl is replaced by a vinyl group, whereas the entropies of activation increase in the same order, thus suggesting a progressive decrease of the transition state solvation.

This trend can be explained taking into account the greater electron donating ability of the vinyl groups with respect to the butyl groups owing to a possible d–p interaction. In fact, increasing the electron releasing capacity of groups bonded to the tin will decrease the Lewis acidity of the tin and make solvation less effective in the transition state. Moreover, if solvation of the substrates in the transition state is a stabilizing factor, also the small increase of enthalpies becomes reasonable.

An examination of Table II shows that, for the $Bu_2SnClCH_2CH=CH_2$ compound, the values of the

TABLE I. Rate Constants of Protonolysis for Allyltin Compounds in Methanol–Water (4%), Activation Parameters and Spectral Data.

Substrate	$k_2 (M^{-1} \text{sec}^{-1})$				ΔH^\ddagger (Kcal mol ⁻¹)	ΔS^\ddagger (cal mol ⁻¹ K ⁻¹)	λ_{max} (nm)	λ^a (nm)	ϵ^b Reactants ($M^{-1} \text{cm}^{-1}$)
	18 °C	22 °C	26 °C	29 °C					
$Bu_3SnCH_2CH=CH_2$	0.165	0.222	0.321	0.371	13.2	–16.6	225	225	8550
$Bu(CH_2=CH)_2SnCH_2CH=CH_2$	0.021	0.033	0.046	0.059	16.0	–11.2	225	230	6910
$(CH_2=CH)_3SnCH_2CH=CH_2$	0.011	0.015	0.023	0.030	16.5	–10.8	223	230	6870
$Bu_2Sn(Cl)CH_2CH=CH_2$							222	225	7690

^aAnalytical wavelength. ^bRelative to the analytical wavelength.

TABLE II. Rate Constants of Protonolysis for $\text{Bu}_2\text{Sn}(\text{Cl})\text{CH}_2\text{CH}=\text{CH}_2$ in methanol and Methanol-Water (4%) at Variable $[\text{NaCl}]$, $[\text{HCl}]$ and $[\text{HClO}_4]$, $T = 26^\circ\text{C}$.

Solvent	$[\text{NaCl}] \times 10$ (M)	$[\text{HCl}] \times 10^3$ (M)	$[\text{HClO}_4] \times 10^3$ (M)	$k_{\text{obs}} \times 10^5$ (sec^{-1})	k_2 ($M^{-1} \text{sec}^{-1}$)
Methanol	—	2.88	—	10.94	0.038
	—	4.32	—	16.42	0.038
	—	5.76	—	22.46	0.039
	—	7.20	—	28.08	0.039
Methanol-Water (4%)	—	3.5	—	0.91	
	—	5.0	—	1.65	
	—	6.0	—	2.04	
	—	9.0	—	3.94	
	—	—	2.51	0.26	
	—	—	5.03	0.30	
	—	—	7.08	0.33	
	—	—	10.60	0.40	
	0.297	—	—	5.8	2.80
	0.470	—	—	"	3.95
	0.704	—	—	"	5.31
	1.070	—	—	"	7.55

rate in methanol are consistent with a second-order kinetic law, while in methanol-water it seems that the reaction mechanism becomes complicated. In fact the equation $k_{\text{obs}} = k_2[\text{H}^+]$ is no longer obeyed and moreover the value of k_{obs} is dependant on the nature of the acid used. The observed rate constants, k_{obs} , increase linearly with the concentration of Cl^- provided a constant salt ($[\text{NaCl}] + [\text{NaClO}_4]$) and $[\text{HClO}_4]$ concentration is used. This dependence may suggest that also the Cl^- species can be present in the reaction mechanism and the observed rate constants should be governed by an equation of the type: $k_{\text{obs}} = k_1 + k_2[\text{H}^+] + k_3[\text{H}^+][\text{Cl}^-]$.

The values $k_1 = 2.75 \times 10^{-6} \text{ s}^{-1}$, $k_2 = 1.1 \times 10^{-4} M^{-1} \text{ s}^{-1}$ can be obtained by plots of k_{obs} against $[\text{HClO}_4]$ and hence $k_3 = 4.9 \times 10^{-1} M^{-2} \text{ s}^{-1}$.

Experimental

Allyltin compounds have been prepared from the allylmagnesium bromide and the appropriate organotin chloride in ethyl ether [9].

Dibutylallyltin chloride was prepared by reacting equimolecular amounts of dibutyldiallyltin and dibutyltin dichloride as previously reported [3]. U.V. spectra were recorded with a Unicam SP 800 instrument.

Absorbance readings in the kinetic procedure were taken on a Carl Zeiss M4 QIII single beam spectrophotometer. All other chemicals were reagent grade and were used without further purification.

Acknowledgments

The authors thank C.N.R. for financial support.

References

- 1 E. W. Abel and S. Moorhouse, *J. Chem. Soc. Dalton*, 1706 (1973) and references therein.
- 2 V. Peruzzo and G. Tagliavini, *J. Organometal. Chem.*, 66, 437 (1974).
- 3 G. Tagliavini, V. Peruzzo, G. Plazzogna and D. Marton, *Inorg. Chim. Acta*, 24, L47 (1977) and references therein.
- 4 H. G. Kuivila and J. A. Verdone, *Tetrahedron Lett.*, 119 (1964).
- 5 J. A. Verdone, J. A. Mangravite, N. M. Scarpa and H. G. Kuivila, *J. Am. Chem. Soc.*, 97, 843 (1975).
- 6 J. A. Mangravite, J. A. Verdone and H. G. Kuivila, *J. Organometal. Chem.*, 104, 303 (1976).
- 7 M. M. Kreevoy, P. J. Steinwand and V. Kayser, *J. Am. Chem. Soc.*, 88, 124 (1966).
- 8 T. Shedlovsky and R. L. Kay, *J. Phys. Chem.*, 60, 151 (1956).
- 9 W. J. Jones, W. C. Davies, S. T. Bowden, C. Edwards, V. E. Davies and L. H. Thomas, *J. Chem. Soc.*, 1446 (1947).