Journal of Organometallic Chemistry, 239 (1982) 307—312
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

AROMATIC SUBSTITUTION. THE EFFECT OF ALCOHOLIC SOLVENTS ON THE REACTION OF PHENYLTRIETHYLTIN WITH MERCURY(II) SALTS

MOHAMMAD REZA SEDAGHAT-HERATI *, and PARVIN NAHID
Department of Chemistry, Isfahan University of Technology, Isfahan (Iran)

(Received May 27th, 1982)

Summary

Second-order rate constants are reported for the cleavage of the phenyl—tin bond of phenyltriethyltin by mercury(II) salts in ethanol, propan-1-ol, propan-2-ol and butan-1-ol. It is shown that the reactivity order for the mercury(II) salts is $HgI_3^- \ll HgI_2 < HgCl_2$. Activation parameters are reported, and on the basis of the low values of activation enthalpies the presence of an intermediate π-complex is suggested for the reactions.

Introduction

It has been shown that salt and solvent effects studies are important in elucidation the mechanism of aliphatic electrophilic substitution reactions in which metal—carbon bonds are cleaved by metal-containing reagents [1]. Such studies have been widely carried out on these reactions. In contrast the number of reports describing salt and solvent effects studies on the related aromatic electrophilic substitution reactions is very small. In previous work [2], it was shown that reaction 1 (X = Cl and I) in methanol follows second-order kinetics, and proceeds via an intermediate π-complex through a transition state that is not particularly polar.

$$PhSnEt_3 + HgX_2 \rightarrow PhHgX + XSnEt_3 \qquad (1)$$

The present work deals with a study of solvent effects on reaction 1 (X = Cl and I). By studies similar to those in methanol [2], we determined the rate constants for the above reaction in ehtanol, propan-1-ol, butan-1-ol and propan-2-ol. These solvents were chosen, because of the possibility of comparing the solvent effects with those in the related aliphatic substitution reaction 2 (X = Cl and I) studied by Abraham et al. [3].

$$Et_4Sn + HgX_2 \rightarrow EtHgX + XSnEt_3 \qquad (2)$$

The S_E2 reaction of phenyltriethyltin with mercury(II) salts

In earlier work [2], we have determined rate constants for reaction 1 (X = Cl and I) in the solvent methanol, and have now extended these measurements to the solvents ethanol, propan-1-ol, butan-1-ol and propan-2-ol. Rates were determined at 298 and 273 K, the progress of the reactions being monitored as before [4]. In each kinetic run, the normal second-order rate equation was followed. With mercury(II) iodide as the electrophile, reaction 1 (X = I) was followed by a fast equilibrium 3 (X = I), entirely analogous to the equilibria observed in aliphatic substitutions [5].

$$Et_3SnX + HgX_2 \overset{K}{\rightleftharpoons} Et_3Sn^+ + HgX_3^- \qquad (3)$$

In these cases the second-order rate constant was obtained by evaluating the value of K on a trial and error basis by use of a computer programme. (This programme was written based on data taken from the literature [6].) In the case of reaction 1 (X = Cl) in butan-1-ol, application of the normal second-order rate equation showed that the values of k_2 decreased during the reaction. Hence the data were treated as in the case of reaction 1 (X = I). It was found that the experimental second-order rate constants remained almost constant by taking $K = 0.1$. On the other hand, in the case of reaction 2 (X = Cl) in butan-1-ol no complex formation between Et_3SnCl and $HgCl_2$ takes place [3]. It seems likely that for reaction 1 (X = Cl) in butan-1-ol equilibrium 3 (X = Cl) does not exist, and the value of K is to be regarded as a correction factor. The reason why the values of k_2 decreased during the reaction was not investigated. Average values

TABLE 1

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF $PhSnEt_3$ WITH MERCURY(II) HALIDES [a, b]

Solvent	Initial concentrations		k_2 (l mol^{-1} s^{-1})	
	$10^5[PhSnEt_3]$ (*M*)	$10^5[HgX_2]$ (*M*)	273.15 K	298.15 K
A with $HgCl_2$				
MeOH	8.0	4.0	29.80 [c]	
MeOH	4.0	2.0		103.40 [c]
EtOH	10.0	5.0		24.40
EtOH	20.0	10.0	5.84	
Pr^nOH	20.0	10.0	4.22	13.19
Pr^iOH	20.8	10.1	2.81	10.62
Bu^nOH	40.0	20.0	3.91	11.42
B with HgI_2				
MeOH	8.0	4.0	4.12 [c]	23.90 [c]
EtOH	10.0	5.0		4.78
EtOH	20.0	12.0	1.00	
Pr^nOH	40.0	20.0	0.81	3.36
Pr^iOH	40.0	20.0	0.53	2.67
Bu^nOH	80.0	40.0	0.30	1.68

[a] Rate constants uncorrected for solvent contraction from 298 K; all runs carried out at least in duplicate. [b] This work except where indicated. [c] From ref. 2.

of the rate constants (from between 2 to 4 separate runs) for reaction 1 (X = Cl and I) in various alcoholic solvents for two different temperatures (298 and 273 K) are shown in Table 1.

Influence of the substrate and reactant

The k(Ph)/k(Et) at 298 K for the solvents studied are given in Table 2. From the very high values of the ratios, it may be deduced that in the solvents studied it is the phenyl group that is cleaved from tin by the mercury(II) halides. For similar cleavages in the solvent methanol this was shown to be the case by product analyses [2].

The effect of an excess of I^- on reaction 1 (X = I) in the solvents used was to stop the substitution. Thus the order of reactivity of mercury(II) salts towards phenyltriethyltin in the solvents used is $HgI_3^- \ll HgI_2 < HgCl_2$. This sequence is similar to that found for reaction 2 (X = Cl and I) in the same solvents [3]. This sequence also shows that nucleophilic assistance by I^- is not important in either aliphatic or aromatic substitutions.

The relative reactivities of mercury(II) salts towards Et_4Sn and $PhSnEt_3$ are given in Table 3. A polar transition state has been suggested for the reaction between Et_4Sn and the mercury(II) salts, with no reduction in charge separation as the alcohol solvent becomes less polar [3]. In contrast the transition state for the reaction between $PhSnEt_3$ and the mercury(II) salts is less polar, as the studies of salt and solvent effects in methanol [2] and the values of activation parameters in the solvents used (Table 4) would suggest. However, since the relative reactivities of the mercury(II) halides remain almost unchanged on going from methanol to butan-1-ol, it is suggested that the polarities of the transition state for reaction 1 remains much the same in the various alcoholic solvents used.

Activation parameters

It was proposed [2] that the low values of $\Delta H^{\neq}$ for the reaction between $PhSnEt_3$ and the mercury(II) halides in methanol (Table 4) are indicative of an initial π-complex formation between the two reactants. Indeed where this process of complex formation is not possible, high values of $\Delta H^{\neq}$ are obtained. Thus for the Et_4Sn/HgX_2 system in methanol the values of $\Delta H^{\neq}$ are 14.10 and 12.80 kcal mol^{-1} on the mol fraction scale for chloride and iodide respectively [4,7]. The work of Reutov et al. [8] on a series of reactions of $RSnMe_3$ (R = Ph, C_6F_5, $CH_2{=}CH$ and Me) with $HgCl_2$ in methanol also shows that the activation enthalpies for compounds with a π-complexing organic group are much lower than for compounds of the type Me_4Sn. The values of $\Delta H^{\neq}$ for $PhSnEt_3/HgX_2$ (X = Cl and I) in other solvents (Table 4) are also low, and we suggest that a π-complex (as in methanol) between the reactants is present as a reaction intermediate; this is then followed by the usual σ-complex. It has indeed, been demonstrated that mercury(II) halides form molecular complexes with aromatic hydrocarbons [9].

From the values of $\delta\Delta G^{\neq}$ (Table 5) in the alcoholic solvents it would seem at first sight that the polarity of the $PhSnEt_3$ transition state is higher than that of

TABLE 2

COMPARISON OF THE EASE OF CLEAVAGE OF THE Ph—Sn AND Et—Sn BONDS FOR THE REACTIONS OF $PhSnEt_3$ AND Et_4Sn WITH HgX_2 at 298.15 K [a, b]

Solvent	$k(Ph)/k(Et)$ with $HgCl_2$	$k(Ph)/k(Et)$ with HgI
MeOH	1.24×10^5 [c]	3.77×10^4 [c]
EtOH	7.86×10^4	1.98×10^4
Pr^nOH	5.33×10^4	2.18×10^4
Bu^nOH	5.82×10^4	1.48×10^4

[a] Observed rate constants statistically corrected where necessary. [b] Rate constants for the reaction of Et_4Sn and HgX_2 have been taken from ref. 3. [c] From ref. 2.

TABLE 3

RELATIVE REACTIVITIES OF MERCURY(II) HALIDES TOWARDS $PhSnEt_3$ AND Et_4Sn AT 298.15 K

	With Et_4Sn [a]		With $PhSnEt_3$ [b]	
	$HgCl_2$	HgI_2	$HgCl_2$	HgI_2
MeOH	1	0.76	1	0.23
EtOH	1	0.78	1	0.20
Pr^nOH	1	0.62	1	0.25
Pr^iOH	1		1	0.25
Bu^nOH	1	0.58	1	0.15

[a] From ref. 3. [b] Data from Table 1.

TABLE 4

ACTIVATION PARAMETERS [a] FOR THE CLEAVAGE OF $PhSnEt_3$ BY MERCURY(II) HALIDES

Solvent	$\Delta G^{\ne}$	$\Delta H^{\ne}$	$\Delta S^{\ne}$
A with $HgCl_2$			
MeOH	12.81 [b]	7.4 [b]	—18.2 [b]
EtOH	13.88	8.7	—17.5
Pr^nOH	14.39	6.8	—25.5
Pr^iOH	14.53	8.0	—21.9
Bu^nOH	14.60	6.3	—27.7
B with HgI_2			
MeOH	13.68 [b]	9.2 [b]	—14.9 [b]
EtOH	14.85	9.5	—17.8
Pr^nOH	15.20	8.6	—22.1
Pr^iOH	15.35	9.9	—18.4
Bu^nOH	15.73	10.6	—17.4

[a] Activation parameters at 298.15 K calculated after converstion of rate constants (Table 1) (uncorrected for solvent contraction from 298.15 K) to units of mol fraction^{-1} s^{-1}, $\Delta G^{\ne}$ (±0.02) and $\Delta H^{\ne}$ (±0.4) in kcal mol^{-1}, and $\Delta S^{\ne}$ (±1.2) in cal K^{-1} mol^{-1}. Quoted errors are standard deviations for a 4% error in the rate constants. [b] From ref. 2.

TABLE 5

THE EFFECT OF VARYING THE ALCOHOL SOLVENTS ON $\Delta G^{\neq}$ (kcal mol^{-1}) FOR THE REACTIONS OF $PhSnEt_3$ AND Et_4Sn WITH MERCURY(II) HALIDES

Solvent	$PhSnEt_3$ [a] $\delta\Delta G^{\neq}$ [c]	Et_4Sn [b] $\delta\Delta G^{\neq}$ [c]
A with $HgCl_2$		
MeOH	0.00	0.00
EtOH	1.07	0.80
Pr^{n}OH	1.58	1.10
Pr^{i}OH	1.72	
Bu^{n}OH	1.79	1.34
B with HgI_2		
MeOH	0.00	0.00
EtOH	1.17	0.79
Pr^{n}OH	1.52	1.20
Pr^{i}OH	1.67	
Bu^{n}OH	2.05	1.51

[a] Calculated from second-order rate constants in Table 1, on the mol fraction scale. [b] Taken from ref. 3, and on the mol fraction scale. [c] $\delta\Delta G^{\neq} = \Delta G^{\neq}$ (alcoholic solvent) — $\Delta G^{\neq}$ (methanol solvent).

the Et_4Sn transition state. However, in order to reach a firm conclusion, these values must be dissected into initial state and transition state contributions.

Experimental

Phenyltriethyltin was made as before [2]. Mercury(II) chloride and iodide were recrystallised from methanol. Alcohols were dried over anhydrous phosphorous pentoxide and distilled.

Kinetic measurements were carried out by Abraham's method [4] of withdrawing aliquots of the reaction mixture and quenching them by addition to 2.5×10^{-3} *M* potassium iodide in a methanol/water mixture of mol fraction methanol 0.91. The formed HgI_3^- was determined through its absorbance at 315 nm. Spectrophotometric measurements were made with a Perkin—Elmer UV-VIS double beam spectrophotometer. Because the solutions for analyses contained large quantities of the solvents, new calibrations were constructed (except for ethanol) as follows. Solutions of mercury(II) chloride with appropriate concentrations for each solvent (at least 7 points) were prepared. Solu-

TABLE 6

CALIBRATION VALUES USED IN THE CALCULATIONS OF THE RATE CONSTANTS [a] (all for 315 nm)

Solvent	Calibration values		Dilution factor
Pr^{n}OH	$D = 1.0303 \times 10^4$	HgX_2 — 0.0014	10.0
Pr^{n}OH	$D = 1.0805 \times 10^4$	HgX_2 — 0.0075	3.6
Pr^{i}OH	$D = 1.0294 \times 10^4$	HgX_2 — 0.0011	10.0
Bu^{n}OH	$D = 1.0182 \times 10^4$	HgX_2 — 0.0032	10.0
Bu^{n}OH	$D = 1.0388 \times 10^4$	HgX_2 + 0.0001	5.0

[a] For ethanol as solvent, the calibration values in methanol [4] (at 315 nm) were used.

tions were quenched (dilutions were according to the dilutions used in the kinetic run) as for the aliquot portions of the reaction mixture (see above). Absorbance measurements were then made on these solutions at 315 nm. A plot of absorbance (*D*) against the formal concentration of mercuric salt in the quenched sample in each case yielded an excellent straight line at the wavelength used. Calibration values are given in Table 6.

Acknowledgment

We thank Mr. M. Davarpanah for invaluable help with the computer programmes.

References

1 M.H. Abraham, Electrophilic Substitution at a Saturated Carbon Atom, in C.H. Bamford and C.F.H. Tipper (Eds.), Comprehensive Chemical Kinetics, Elsevier, Amsterdam, 1973, Vol. 12.
2 M.H. Abraham and M.R. Sedaghat-Herati, J. Chem. Soc. Perkin II, (1978) 729.
3 M.H. Abraham and P.L. Grellier, J. Chem. Soc. Perkin II, (1975) 623.
4 M.H. Abraham and G.F. Johnston, J. Chem. Soc. A, (1970) 188, 193.
5 M.H. Abraham and T.R. Spalding, J. Chem. Soc. A, (1968) 2530.
6 M.H. Abraham, P.L. Grellier, M.J. Hogarth, T.R. Spalding, M. Fox and G.R. Wickham, J. Chem. Soc. A, (1971) 2972.
7 M.H. Abraham and M.J. Hogarth, J. Chem. Soc. A, (1971) 1469.
8 A.N. Kashin, I.P. Beletskaya, A.Ts. Malkhasyan and O.A. Reutov, J. Org. Chem. (USSR), 9 (1973) 1127.
9 I. Eliezer and P. Avinur, J. Chem. Phys., 55 (1971) 2300; I.M. Vezzosi, G. Peyronel and A.F. Zanoli, Inorg. Chim. Acta, 8 (1974) 229.