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SOLVENT EFFECTS ON INITIAL AND TRANSITION STATES IN THE REACTION OF *m*-FLUOROPHENYLTRIETHYLTIN WITH MERCURIC CHLORIDE IN METHANOL AND METHANOL–WATER MIXTURES

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We have investigated solvent effects on the aromatic electrophilic substitution reaction of *m*-fluorophenyltriethyltin, 1, with mercuric chloride in order to obtain information about the polarity of the transition state. Second-order rate constants have been determined for the reaction of 1 with mercuric chloride in methanol and methanol–water mixtures at 25·0 °C, allowing determination of $\delta\Delta G^{\ddagger}$. Molar standard free energies of transfer (ΔG_t^0) for the same solvent mixtures have also been determined for 1 at 25·0 °C. Combination of our $\delta\Delta G^{\ddagger}$ and ΔG_t^0 values with literature data for ΔG_t^0 of $HgCl_2$ yield values of ΔG_t^0(TS), the standard free energy of transfer of the corresponding transition state (TS) in the reaction from methanol to aqueous methanol. It is shown that the reduction in activation energy accompanying replacement of methanol by water is due to initial state destabilization and not to TS stabilization. In fact, the TS is destabilized as methanol is replaced by water. Further analysis permits dissection of the free energies of transfer of the TS into electrostatic and non-electrostatic components. Comparison of these electrostatic components for the 1/$HgCl_2$ system with some model reactions shows that charge development in TS of 1/$HgCl_2$ is approximately 0·5 units of electronic charge.

INTRODUCTION

Mercuridestannylation reactions have been shown to be suitable for studies of salt and solvent effects.[1] From the effects of temperature, salts and solvents, we have proposed[2,3] that the S_E2 reaction of phenyltriethyltin by mercuric salts, reaction (1) (Y = H and X = Cl, I), proceeds via the rate-determining step which involves reaction of a π-complex.

$$YC_6H_4SnEt_3 + HgX_2 \rightarrow YC_6H_4HgX + XSnEt_3 \quad (1)$$

We have recently reported[4] the effects of substituents on reaction (1) in tetrahydrofuran, where it was found that the substituent effects could be correlated only in terms of Hammett σ constants; correlations were very poor with Brown σ^+ constants. Consistent with the results from other studies,[2,3] it was suggested that the rate-determining step involves the participation of a π-complex intermediate. Substituent effect studies on the reaction of aryltriethyltin compounds by mercuric acetate in tetrahydrofuran,[5] mercuridesilylation of aryltrimethylsilanes by mercuric acetate in acetic acid,[6] and the cleavage of aryl–tin bonds by iodine in carbon tetrachloride,[7] have also led to similar conclusions regarding the nature of the transition state in the reactions.

Solvent effects have proved to be of importance in elucidation of the mechanism of organic reactions.[1,8–15] Two main methods have been developed for the examination of solvent effects on rates. In the first method, rate constants, either as log k or $\Delta G^{\ddagger}$, are correlated with some solvent parameter(s). Of the various equations developed,[8–15] one of the most general is the solvatochromic equation formulated by Abraham, Kamlet, Taft and their coworkers,[9–13]:

$$\log P = \log P_0 + s\pi_1^* + a\alpha_1 + b\beta_1 + h\,\delta_{H^2}/100 \quad (2)$$

in which P is some property (e.g. rate constant), π^* is a measure of solvent polarity, α_1 the hydrogen-bond acidity, β_1 the hydrogen-bond basicity, and δ_{H^2} the solvent cohesive energy density. Equation (2) has been applied successfully to kinetics and equilibria.[12] Unfortunately, it cannot be applied to the present work because the various solvent parameters are only known for pure solvents.

Relevant to our work is the second method,[1,10,12,16]

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also developed by Abraham, which dissects solvent effects on $\log k$ or $\Delta G^{\ddagger}$ into contributions from the initial state (IS) and the transition state (TS) contributions through equation (3):

$$\Delta G_{t}^{0}(\mathrm{TS}) = \Delta G_{t}^{0}(\mathrm{HgCl_2}) + \Delta G_{t}^{0}(\mathbf{I}) + \delta\Delta G^{\ddagger} \quad (3)$$

where $\Delta G_{t}^{0}(\mathrm{X})$ denotes the standard free energy of transfer from the reference solvent 1 to solvent 2 of species X, $\delta\Delta G^{\ddagger} = \Delta G_{2}^{\ddagger} - \Delta G_{1}^{\ddagger}$, and TS represents the transition state in reaction (1). Abraham's method also allows further separation of solvent effects on $\Delta G_{t}^{0}(\mathrm{TS})$ into electrostatic (ΔG_{e}^{0}) and non-electrostatic (ΔG_{n}^{0}) contributions by equation (4):

$$\Delta G_{t}^{0} = \Delta G_{n}^{0} + \Delta G_{e}^{0} \quad (4)$$

where ΔG_{n}^{0} may be evaluated using an empirical relationship (equation (8)) published by Abraham and Johnston.[17] Comparison of the electrostatic contribution with those for various model reactions permits evaluation of the extent of charge separation in the TS. The present work deals with such evaluation of solvent influences on an aromatic electrophilic substitution. As far as we are aware no such studies have been reported for an aromatic electrophilic substitution reaction, and we report now our studies on the dissection of solvent effects on reaction (1) (Y = *m*-F and X = Cl) into IS and TS effects, and we use this dissection to characterize the TS according to the method of Abraham.[1] We chose this reaction because: (a) the rates of the reaction in a series of methanol–water mixtures could be followed conveniently; (b) the relevant thermodynamic data on mercuric chloride in a series of methanol–water mixtures are available;[16] and (c) there was interest in possible comparisons with related mercury-for-tin exchange in the aliphatic series.[1,16,17]

In order to apply equation (3), we have obtained pertinent $\delta\Delta G^{\ddagger}$ values from the determination of rate constants, and $\Delta G_{t}^{0}(\mathbf{1})$ by gas chromatographic head space analysis according to the method of Abraham.[16] $\Delta G_{t}^{0}(\mathrm{HgCl_2})$ for each of the solvent mixtures have previously been reported by Abraham.[16]

RESULTS AND DISCUSSION

Kinetic studies

The rates of reaction (1) (Y = *m*-F and X = Cl) in methanol and methanol–water mixtures were determined as described before.[2] In each kinetic run, which was monitored for up to at least 60% completion of the reaction, the second-order rate equation was obeyed. Values of k_2 (averaged over two or three runs) at 25·0 °C in methanol and methanol–water mixtures are given in Table 1.

Our previous studies concerning the effects of substituents on reaction (1) in tetrahydrofuran[4] did not include rate data for the **1**–$\mathrm{HgCl_2}$ system, the reaction chosen for the present studies, and we have determined the rate of the reaction at 25·0 °C as $k_2 = 0{\cdot}044$ l mol^{-1} s^{-1}. It was of interest to see whether or not the data point for the **1**–$\mathrm{HgCl_2}$ system could be included in the Hammett plot of $\log k/k_0$ versus σ constants:

$$\log k/k_0 = \rho\sigma \quad (5)$$

where k and k_0 are the rate constants for the substituted and unsubstituted compounds, respectively, and σ is the substituent constant characteristic of the substituents and ρ is the reaction constant indicating the relative need of the reaction for electron withdrawal or electron release. It was found that the rate data can be correlated with the substituent constants, σ (rate data for the unsubstituted compound and six substituted compounds were determined in previous work[4]), and a value of $\rho = -2{\cdot}60 \pm 0{\cdot}36$ is obtained for the reaction constant (correlation coefficient = 0·96), close to that without the point for the **1**–$\mathrm{HgCl_2}$ system ($\rho = -2{\cdot}91 \pm 0{\cdot}36$, correlation coefficient = 0·97). As before[4] there was no correlation between $\log k/k_0$ values and Brown σ^{+} constants, therefore our previous conclusion,[4] that the transition state of the rate-determining step for reaction (1) is not particularly polar, remains the same.

Table 1. Second-order rate constants for the reaction of **1** with $\mathrm{HgCl_2}$ in methanol–water mixtures at 25 °C

Solvent χ(MeOH)	Initial concentrations 10^4[**1**] (M)	10^4[$\mathrm{HgCl_2}$] (M)	k_2(l mol^{-1} s^{-1})[a]
1	5·85	2·96	6·39 ± 0·04
0·914	5·80	2·68	8·74 ± 0·11
0·800	3·95	2·06	19·54 ± 0·41
0·716	1·53	1·01	27·96 ± 1·63
0·640	1·66	0·81	47·66 ± 3·13
0·510	1·24	0·94	87·80 ± 6·44

[a] Errors shown are average deviations.

Standard free energies of transfer from methanol to methanol–water of 1

Free energies of transfer of **1** from methanol to methanol–water, $\Delta G_{t}^{0}(\mathbf{I})$, were determined through gas chromatographic head space measurement of the ratio of Henry's law constants, H_{2}^{0}/H_{1}^{0}:

$$\Delta G_{t}^{0} = RT\ln(H_{2}^{0}/H_{1}^{0}) \quad (6)$$

The relative values could be obtained through gas chromatographic measurements of the concentrations of **1** in methanol (solvent 1) and aqueous methanol (solvent 2) via equation (7):

$$H_{2}^{0}/H_{1}^{0} = (D_2/C_2)/(D_1/C_1) \quad (7)$$

where C_1 and C_2 denote molar concentrations of **1** in solvents 1 (methanol) and 2 (methanol–water), and D is the gas chromatography detector response for a sample of the vapour above the dilute solution of concentration C (assumed to approach infinite dilution). The values of ΔG_t^0 thus obtained are on the molar scale. Equation (7) is valid provided that the values of D/C have been extrapolated (if necessary) to zero concentration. Abraham[16] has shown for Et_4Sn that, within experimental error, the observed value of D/C may be taken as the limiting value provided that C is less than about 0·04 mol l^{-1}. In the present work, the actual values of concentration of **1** used in experiments to determine ΔG_t^0 ranged from 0·035 mol l^{-1} (solvent methanol) to 0·002 mol l^{-1} (aqueous methanol), so that extrapolation of the observed values of D/C to $C = 0$ was not necessary. Values of $\Delta G_t^0(1)$ averaged over at least two runs, along with some known values of ΔG_t^0 for tetra-alkyltins, and for $PhSnEt_3$ are given in Table 2. From Table 2, the sequence among the values of ΔG_t^0 is: $Pr_4^nSn > PhSnEt_3 > Et_4Sn$, which reflects the size of the solutes [molar volume values at 25 °C are: $V(Pr_4^nSn) = 266$, $V(PhSnEt_3) = 227$ and $V(Et_4Sn) = 119$ ml mol^{-1}. However, ΔG_t^0 values for **1** (molar volume = 232 ml mol^{-1} at 25 °C) are lower than those of $PhSnEt_3$ and Pr_4^nSn and are closer to the values of Et_4Sn, indicating the interactions of **1** with solvent through hydrogen bonding to the fluorine of **1**. On the other hand, when such interactions are not possible, as in the case of $PhSnEt_3$, the value of ΔG_t^0 increases with the size of the solute.[18]

As can be seen from Table 2, the values of ΔG_t^0 increase as methanol is replaced by water, indicating the destabilization of the solute in more aqueous systems. In contrast, the ΔG_t^0 values for $PhSnEt_3$, (Table 3) decrease significantly on going from methanol to acetone and ethyl acetate, indicating the stabilization of the system in these solvents.[18]

Table 3. Free energies of transfer (on the molar scale)[a] from methanol to acetone and ethyl acetate of $PhSnEt_3$ at 25 °C

Solvent	ΔG_t^0 (cal mol^{-1})
MeOH	0
Me_2CO	−1120
EtOAc	−1310

[a]From ref. 18 after correcting from the mole fraction scale to the molar scale.

Calculation of free energies of transfer from methanol to methanol–water mixtures of 1–$HgCl_2$ transition state

Combination of the values of ΔG_t^0 for **1** and $HgCl_2$ (given in Table 2) and $\delta\Delta G^{\ddagger}$ (calculated from data in Table 1), through equation (3) yields the values of ΔG_t^0(TS) shown in Table 4. Examination of the ΔG_t^0(IS) and ΔG_t^0(TS) values (Table 4) reveals that the reduction in $\Delta G^{\ddagger}$ as methanol is replaced by aqueous methanol is the result of IS destabilization rather than TS stabilization. Indeed, the TS is destabilized as the solvent is changed from methanol to aqueous methanol. These results are consistent with a transition state which overall is not particularly polar.

Comparison of ΔG_t^0(TS) values for $[1\text{–}HgCl_2]^{\ddagger}$ with those of the corresponding aliphatic reactions, i.e. $[R_4Sn\text{–}HgCl_2]^{\ddagger}$ (R = Et and n-Pr) in methanol–water mixtures,[16] should yield information regarding the polarity of the transition state; the relevant data are in Table 5. It is seen that the values of ΔG_t^0 (TS) for the aromatic reaction are much larger than the values for $[Et_4Sn\text{–}HgCl_2]^{\ddagger}$ and are comparable to those of $[Pr_4^nSn\text{–}HgCl_2]^{\ddagger}$, indicating that the transition state involving tetraethyltin is more polar than the aromatic

Table 2. Free energies of transfer (on the molar scale) of **1**, Et_4Sn, Pr_4^nSn and $PhSnEt_3$ from methanol to methanol–water mixtures at 25 °C

Solvent χ(MeOH)	ΔG_t^0 (cal mol^{-1}) **1**[a]	Et_4Sn[b]	Pr_4^nSn[b]	$PhSnEt_3$[c]
1	0	0	0	0
0·914	250 ± 40	310	390	440
0·800	980 ± 14	810	1010	
0·716	1300 ± 80	1220	1580	
0·640	1750 ± 30	1650	2150	
0·510	2600 ± 70	2450	3200	

[a]This work; errors shown are average deviations.
[b]From ref. 16.
[c]From ref. 18 after correcting from the mole fraction scale to the molar scale.

Table 4. Free energies of transfer (on the molar scale) from methanol to methanol–water of **1**, $HgCl_2$, and $[I\text{–}HgCl_2]^{\ddagger}$ at 25 °C

Solvent χ(MeOH)	$\delta\Delta G^{\ddagger a}$	ΔG_t^0 (cal mol^{-1}) **1**[b]	$HgCl_2$[c]	$[1\text{–}HgCl_2]^{\ddagger}$
1	0	0	0	0
0·914	−186	250	73	140
0·800	−662	980	187	510
0·716	−874	1300	294	720
0·640	−1190	1750	412	970
0·510	−1552	2600	619	1670

[a]Calculated from data in Table 1.
[b]From Table 2.
[c]From ref. 16.

Table 5. Calculation of values of ΔG_e^0 for the transfer from methanol to methanol–water of transition states[a] in cal mol^{-1} at 25 °C

	χ(MeOH)[b]	0·914	0·800	0·716	0·640	0·510
$[Et_4Sn{-}HgCl_2]^{\ddagger}$[c]	ΔG_t^0	10	150	330	600	1100
	ΔG_n^0	380(420)	990(1080)	1540(1670)	2090(2270)	3100(3370)
	ΔG_e^0	−370(−410)	−840(−930)	−1210(−1340)	−1490(−1670)	−2000(−2270)
	$Z^{\pm}$	0·66(0·73)	0·64(0·71)	0·63(0·70)	0·61(0·68)	0·58(0·66)
$[Pr^n_4Sn{-}HgCl_2]^{\ddagger}$[c]	ΔG_t^0	110	420	790	1220	2010
	ΔG_n^0	450(460)	1170(1200)	1810(1850)	2450(2500)	3660(3770)
	ΔG_e^0	−340(−350)	−750(−780)	−1020(−1060)	−1230(−1280)	−1640(−1760)
	$Z^{\pm}$	0·60(0·62)	0·57(0·59)	0·53(0·55)	0·50(0·52)	0·47(0·51)
$[\mathbf{1}{-}HgCl_2]^{\ddagger}$[d]	ΔG_t^0	140	510	720	970	1670
	ΔG_n^0	420(450)	1100(1160)	1700(1800)	2300(2430)	3420(3620)
	ΔG_e^0	−280(−310)	−590(−650)	−980(−1080)	−1330(−1460)	−1750(−1950)
	$Z^{\pm}$	0·49(0·55)	0·45(0·49)	0·51(0·56)	0·54(0·59)	0·51(0·56)

[a] The values of ΔG_n^0 and ΔG_e^0 calculated for $V = 62$ ml mol^{-1} (ref. 23) and 90 ml mol^{-1} (ref. 24) (in parentheses) for $HgCl_2$.
[b] For transfer from methanol to methanol–water of the specified mole fraction.
[c] From ref. 17.
[d] This work; the values of ΔG_n^0 and ΔG_e^0 have been calculated from equation (4) using ΔG_t^0 (TS) values from Table 4.

counterpart. On the other hand, it has been shown that the increase in solvolysis rate of t-butyl chloride[1,16,19] (S_N1 model) or 2-chloroethylmethyl sulphide[20] (k_Δ model) as the solvent is changed from methanol to aqueous methanol is due both to an increase in the free energy of the reactants and to a reduction in the free energy of the corresponding TS. Recently, Goncalves *et al.*[21] have reported on the dissection of solvent effects on $\Delta G^{\ddagger}$ into contributions from IS and TS for t-butyl halides in monoalcohols and dialcohols. Consistent with the polar nature of transition states, it was found that the solvation of the TS is more important than that of the IS, the effect being larger for dialcohols than for monoalcohols. In contrast, the increase in solvolysis rate of n-butyl bromide on addition of water to methanol is due almost entirely to destabilization of the IS. These different patterns result because of greater charge development for the S_N1 and k_Δ processes as compared to the S_N2 and S_E2 processes. Non-electrostatic factors dominate for all of the initial states, although electrostatic factors dominate for the S_N1 and k_Δ transition states.

Calculation of the electrostatic contribution in transfer from methanol to methanol–water mixtures

Dissection of ΔG_t^0(TS) into electrostatic and non-electrostatic contributions can be accomplished through equation (4) by first calculating the non-electrostatic term with an empirical formula of Abraham and Johnston[17] describing the dependence of this term on molar volume:

$$\Delta G_n^0 = a_0 + a_1 V^{1/3} + a_2 V^{2/3} + a_3 V + a_4 V^{4/3} + a_5 V^{5/3} \tag{8}$$

where V is the molar volume of the solute under investigation and a_0 to a_5 are empirical constants. Abraham and Johnston[17] determined these constants for different methanol–water mixtures by fitting ΔG_n^0 values for non-polar non-electrolytes into a binomial expression of the form of equation (8). In assigning a molar volume to the $[\mathbf{1}{-}HgCl_2]^{\ddagger}$, we have followed Abraham and Johnston,[17] and Weal,[22] where the transition state volume decreases by 8 ml mol^{-1} (as in the case of S_E2 and S_N2 transition states); this gives a molar volume of 286 ml mol^{-1} [based on the reported[23] value of $V(HgCl_2) = 62$ ml mol^{-1}] for $[\mathbf{1}{-}HgCl_2]^{\ddagger}$ or 314 ml mol^{-1} [based on the reported[24] value of $V(HgCl_2) = 90$ ml mol^{-1}]. Insertion of these values into equation (8) gives the required values of ΔG_n^0 which are given in Table 5 along with the values of ΔG_e^0.

Abraham and Johnston[17] have suggested that the value of ΔG_e^0 for an electrically neutral transition state can be taken as a measure of charge separation in the transition state. By comparing the value of $\Delta G_e^0[\text{t-BuCl}]^{\ddagger} = -6{\cdot}32$ kcal mol^{-1}, for transfer from methanol to water with those of alkylammonium ions[1,17] (as a reference state with one unit of fully developed charge separation), the charge separation in the transition state was calculated as $z = 0{\cdot}85$. Further, it was assumed that the value of z for $[\text{t-BuCl}]^{\ddagger}$ remains constant in transfer to other methanol–water mixtures. Comparison of ΔG_e^0 values for $[\mathbf{1}{-}HgCl_2]^{\ddagger}$, $[Et_4Sn{-}HgCl_2]^{\ddagger}$ and $[Pr^n_4Sn{-}HgCl_2]^{\ddagger}$ with those of $[\text{t-BuCl}]^{\ddagger}$ in the same solvents results in z values in all the solvents studied, as shown in Table 5.

From Table 5, the average value of z of about 0·5 for the $[\mathbf{1}{-}HgCl_2]^{\ddagger}$ indicates that the transition state for the aromatic reaction is less polar that those of the aliphatic counterparts. We have already shown for the reaction of $PhSnEt_3$ with $HgCl_2$ in methanol[2] that the reactive electrophile is mainly $HgCl_2$, and that $HgCl^+$ has little contribution as the effective electrophile. Thus, the above value of z represents the approximate polarity of the transition state of the rate-determining step for reaction (1). It is suggested that the value of z is consistent with the results of previous studies (i.e. substituent effects,[4] salt effects,[2] solvent effects, and temperature[2,3]), and the transition state for reaction (1) is far removed from highly polar δ-complex, and is nearer to a π-complex. The value of z for reaction (1) is higher than those of solvolytic reactions[1] for a variety of primary alkyl halides (ranging from 0·27 to 0·40) but close to the values of z for the Menschutkin reaction of trimethylamine with methyl iodide[1] ($z = 0{\cdot}42$) and Pr^iBr solvolysis[1] ($z = 0{\cdot}51$).

EXPERIMENTAL

Chemicals. 1-Bromo-3-fluorobenzene and triethyltin bromide were obtained from Aldrich Chemical Co. and were used without further purification. Methanol from Aldrich was distilled from magnesium. Solutions of methanol–water mixtures were made by weight using deionized, distilled water. Mercuric chloride was treated as described previously,[3] and *m*-fluorophenyltriethyltin (**1**) was prepared by the action of *m*-fluorophenylmagnesium bromide on triethyltin bromide.[25] The product was distilled at 74–76 °C/0·2–0·3 mmHg, and both the proton NMR and GLC analyses were consistent with *m*-florophenyltriethyltin as the only observable species present.

Kinetics. Rates were determined spectrophotometrically by following the concentration of mercuric chloride at different intervals, as described previously.[2] Mercuric chloride concentrations were calculated as described by Abraham and Johnston.[26] In this method the absorbance (D) of a methanol solution at 315 nm using 1 cm cells is related to the mercuric chloride concentration by the equation: $D = 10124{\cdot}0\,[HgCl_2] + 0{\cdot}036$. This calibration equation was determined previously[26] for the substitution reactions of tetra-alkyltins with mercuric salts in methanol as the reaction solvent. However, since the concentrations employed for reaction (1) were much lower than those of the aliphatic reactions, for each kinetic run the value of the intercept was adjusted using a known concentration of mercuric chloride. The new intercept was then used in the calculation of mercuric chloride concentrations at different time intervals.

Chromatographic studies. Chromatographic analyses to determine $\Delta G_t^0(\mathbf{1})$ were carried out as described by Abraham[16] using a Hewlett Packard 5830A gas chromatograph with a flame ionization detector. The column used was a 3 m column of 0·5% Carbowax 20 M/3·5% SE30 on Anakrom ABS 80–100 mesh support. The concentration of **1** ranged from 0·035 M for solvent methanol to 0·002 M for solvent methanol/water of mole fraction methanol 0·51. Flasks of 150–200 ml capacity containing the solute solution (normally 10 ml) were sealed with septa and maintained by thermostat at 25·0 ± 0·1 °C to equilibrate; tests showed that equilibration was rapid, but about 1 h was allowed to lapse before measurements were made. The pressure inside each flask was maintained at atmospheric pressure by piercing the septum with a narrow hypodermic needle. To prevent condensation of the solvent on the inside of the septum caps, the flasks were covered with a thin plastic sheet so that the sheet lay on top of the septum caps. Vapour samples (1·5 ml) were withdrawn, expanded (to 2 ml) and then chromatographed. Each set of analyses usually consisted of three solutions of which one was a fresh solution of the solute in methanol.

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