Kinetic Studies of Lewis Acidity. Part 2.[1] Catalysis by Tin(IV) Chloride, by Some Organotin(IV) Chlorides, and by Tin(II) Chloride of the Anionotropic Rearrangement of 1-Phenylprop-2-en-1-ol in Tetramethylene Sulphone Solution

Padraig C. Doolan, Peter H. Gore,* Robert Hollingworth, David N. Waters, and (in part) Ja'far Al-Ka'bi and Jameel A. Farooqi
Department of Chemistry, Brunel University, Uxbridge, Middlesex UB8 3PH

The kinetics have been measured for the rearrangement of 1-phenylprop-2-en-1-ol (**1**) to 3-phenylprop-2-en-1-ol (**2**) in tetramethylene sulphone solution, catalysed by various tin(IV) chloride species. The rate coefficients, k_n, at 313.2 K, per unit concentration of the catalyst, were: $SnCl_4$, 305; $PhSnCl_3$, 86.4; p-$MeC_6H_4SnCl_3$, 18.7; $MeSnCl_3$, 6.60; Pr^nSnCl_3, 5.36; $EtSnCl_3$, 4.69; Bu^nSnCl_3, 1.62; $(p\text{-}ClC_6H_4)_2SnCl_2$, *ca.* 3×10^{-2}; Ph_2SnCl_2, 5.1×10^{-3}; Et_2SnCl_2, 1.4×10^{-3}; Me_2SnCl_2, 4.3×10^{-4} $dm^3\ mol^{-1}\ s^{-1}$. The reaction catalysed by $SnCl_4$ was studied with a range of added compounds, *viz.* H_2O, LiCl, $LiClO_4$, and 1,8-bis(dimethylamino)naphthalene. Evidence was obtained for the involvement of both anhydrous $SnCl_4$ and its monohydrate as catalysts for the rearrangement. Tin(II) chloride has been found to be an effective catalyst for the rearrangement, with k_n (313.2 K) = 3.51 $dm^3\ mol^{-1}\ s^{-1}$. Addition of phosphoryl chloride to $SnCl_2$ causes a sharp increase in rate, with a maximum corresponding to the species $SnCl_2{\cdot}POCl_3$. The value of k_n (303.5 K) ≃ 1 200 $dm^3\ mol^{-1}\ s^{-1}$ makes this catalyst the most powerful yet found for the rearrangement.

The anionotropic rearrangement of 1-phenylprop-2-en-1-ol (**1**) to 3-phenylprop-2-en-1-ol (cinnamyl alcohol) (**2**) in anhydrous tetramethylene sulphone has been studied[1] in the presence of many metal and non-metal chloride catalysts, in an attempt to assess quantitatively their Lewis acidities. The kinetics of this molecular rearrangement (1) are presented here for a range of Sn^{IV} catalysts, and for Sn^{II} chloride.

$$\overset{\text{H}}{}\overset{\text{H}}{}\ H_2C{=}C{-}C(OH)Ph \rightleftharpoons HOCH_2{-}C{=}CPh \qquad (1)$$

(**1**) (**2**)

Previous quantitative studies of the Lewis acidities of Sn^{IV} chlorides of the type $RSnCl_3$ have been confined to measurements of equilibrium constants and the derivation of thermodynamic parameters related to the formation of complexes with Lewis bases. Species $RSnCl_3$ (R = Me, Bu^n, or Ph) have been studied in their reactions with a variety of such bases.[2] In each instance the halide was found to be only weakly acidic. Compounds $MeSnCl_3$ and Ph_2SnCl_2 were found in one study[2c] to be too weakly acidic for quantitative measurement.

Kinetic Studies with Sn^{IV} *Chloride.*—The results from our study of the rearrangement (1) in the presence of Sn^{IV} chloride have been briefly reported.[1] As with all these catalytic systems, the observed first-order coefficients (k_1) were directly proportional to the concentration of catalyst used, usually within a ten-fold range of concentrations. (The example for $SnCl_4$ is given in Table 1.) For purposes of comparison, therefore, a normalised second-order rate coefficient ($k_n = k_1$/[catalyst]) was preferred. The earlier study[1] showed that tin(IV) chloride was near the top of the sequence of catalytic strengths of chlorides studied, *viz.* $GaCl_3 > SnCl_4 > SbCl_5 > TiCl_4 > AlCl_3 \gg SbCl_3 \gg ZnCl_2$.

It was considered desirable to study the mechanism of catalysis by tin(IV) chloride in some detail.

Effect of added water. In any system using a powerful Lewis acid as catalyst there must be problems in achieving truly anhydrous conditions. Great care was therefore taken to exclude moisture from the solvent and the glassware used (*cf.* ref. 1), and replicability of rates was tested for, under standard conditions. Lack of careful handling, or deliberate addition of water, invariably caused a reduction in the observed rate coefficient, k_1. A purified solvent which allowed a maximum rate to be attained was consequently taken as representing 'anhydrous' conditions.

Addition, to $SnCl_4$ in anhydrous tetramethylene sulphone, of discrete quantities of water, in the range 1—15 times the

Table 1. Rate data and derived thermodynamic parameters for the anionotropic rearrangement of 1-phenylprop-2-en-1-ol (1.5×10^{-4} mol dm^{-3}) in tetramethylene sulphone solution, catalysed by tin(IV) chloride (1.0×10^{-4} mol dm^{-3}) with or without added water

[Added water] mol dm^{-3}	Rate coefft. $k_n/dm^3\ mol^{-1}\ s^{-1}$ [a–c]	$\Delta H^{\ddagger a}$ kJ mol^{-1}	$\Delta S^{\ddagger a}$ J K^{-1} mol^{-1}	$\Delta G^{\ddagger a}$ kJ mol^{-1}
0	305[d]	58.3	−80	83.3
1.0×10^{-4}	263	32.9	−162	83.7
2.0×10^{-4}	216	32.1	−166	84.2
5.0×10^{-4}	123	21.9	−203	85.7
1.0×10^{-3}	86.6	22.5	−205	86.6
1.5×10^{-3}	91.6	21.4	−208	86.4

[a] At 313.2 K. [b] k_1 measured in range 302—332 K; Arrhenius plots had correlation coefficients $r > 0.992$. [c] $k_n = k_1$ (computed)/[catalyst]. [d] Rate coeffts $10^2 k_1/s^{-1}$ with the anhydrous catalyst at 308.2 K (molarity of $SnCl_4$ in parentheses): 0.983 ± 0.05 (3.8×10^{-5}), 1.75 ± 0.02 (7.5×10^{-5}), 2.22 ± 0.10 (1.13×10^{-4}), 3.08 ± 0.15 (1.41×10^{-4}), 3.67 ± 0.27 (1.88×10^{-4}), 6.18 ± 0.05 (2.82×10^{-4}), and 7.52 ± 0.52 (3.76×10^{-4}).

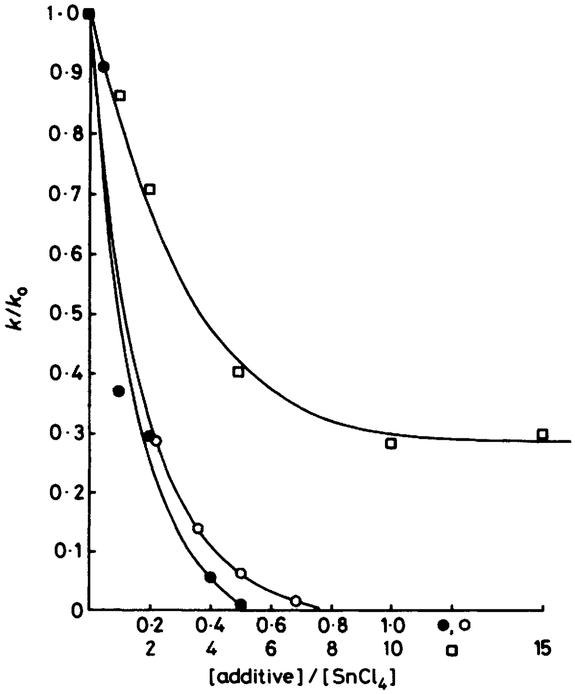


Figure. Reduction of the rate of anionotropic rearrangement of 1-phenylprop-2-en-1-ol, catalysed by tin(IV) chloride, on addition of various compounds; k, k_0 are rate coefficients in the presence, or absence, of additive, respectively. Points ●, ○, □ refer to addition of 1,8-bis(dimethylamino)naphthalene (at 307.8 K), lithium chloride (at 309.5 K), and water (at 313.2 K), respectively

concentration of $SnCl_4$, resulted in a reduction in the rate of rearrangement of substrate (**1**) (Table 1). A curve showing rate *vs.* the ratio $[H_2O]/[SnCl_4]$ is plotted in the Figure, for comparison with the effects of LiCl and 'proton sponge' on the rate (see later). The initial steep decline in rate is not maintained as the concentration of water is increased, and for values of $[H_2O]/[SnCl_4] \geqslant 10$ the rate levels off at 30% of the initial rate. The enthalpies of activation, $\Delta H^{\ddagger}$, are lowered thereby from *ca.* 58 to *ca.* 22 kJ mol^{-1}; therefore the observed reduction in rate must be due to the accompanying sharp decrease in the entropy of activation, $\Delta S^{\ddagger}$, from *ca.* -80 to *ca.* -200 J K^{-1} mol^{-1}. The activation parameters observed for the hydrated catalyst have low values (both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$), which correspond to those obtained for the Brønsted acid, $HCl{-}H_2O$,[1] whereas the high values for the parameters obtained for $SnCl_4$ under 'anhydrous' conditions are quite close to those observed for catalysis by other Lewis acids[1] under 'anhydrous' conditions. The data therefore indicate that addition of increasing amounts of water to the catalyst system causes a progressive conversion of $SnCl_4$ into less reactive hydrated forms.

The effect of the addition of water to a Lewis acid catalyst system for this rearrangement (1) has been examined previously,[3] for the case of BF_3 as catalyst and anhydrous dioxane as solvent. It was suggested there that the hydrate formed was available as a protic acid, *viz.* $H^{+}\,{}^{-}BF_3{\cdot}OH_2$, which exerted a weaker catalytic effect than did the anhydrous species.

The species $SnCl_4$ forms an adduct $SnCl_4{\cdot}S_2$ (**3**) (where S = tetramethylene sulphone) which has been characterised as a solid.[4] It is probable that, in solution in the anhydrous sulphone, this species is the predominant form in which the tin is present. The addition of water would be expected to lead to partial replacement of sulphone by water molecules in the co-ordination sphere of the tin atom. In the system $SnCl_4$–acetone the introduction of water has been shown[5] to give the species $SnCl_4{\cdot}2H_2O$. We postulate that in our system species such as $SnCl_4{\cdot}H_2O$, $SnCl_4{\cdot}S{\cdot}H_2O$ (**4**), and $SnCl_4{\cdot}2H_2O$ are formed in the presence of small amounts of water. The dihydrate would be expected to have little or no activity as an acid. Even at the highest concentration of added water the value of $[H_2O]/[S]$ is quite low (*ca.* 0.000 15). Moreover, the relative donor powers of tetramethylene sulphone and water are not very different.[6] This suggests that the $SnCl_4$ remains in large part uncombined with water [reaction (2)].

$$\underset{(\mathbf{3})}{SnCl_4{\cdot}S_2} + H_2O \rightleftharpoons \underset{(\mathbf{4})}{SnCl_4{\cdot}S{\cdot}H_2O} + S \qquad (2)$$

It might be expected that solutions of $SnCl_4$ in tetramethylene sulphone to which water has been deliberately added would exhibit eventual hydrolysis to SnO_2 and HCl,[7] these products having been shown to be formed by disproportionation of the initial co-ordination complexes. However, it was found that the catalytic activity of a solution of $SnCl_4$ and H_2O at 309 K, with the relatively large value of 23 for $[H_2O]/[SnCl_4]$, was constant over a 48 h period. Hydrolysis to SnO_2 and HCl is therefore not a factor here; in any case, although HCl is a catalyst[1] for the rearrangement (1), the rate calculated on the basis that 4 moles of HCl replace 1 mole of $SnCl_4$ is only *ca.* one seventh that found experimentally.

Effect of added 1,8-*bis*(*dimethylamino*)*naphthalene*. It has been reported that 1,8-bis(dimethylamino)naphthalene ('proton sponge'; p.s.) is a distorted molecule, the high internal strain of which is relieved by protonation; in consequence it has a high basicity, $pK_a = 12.34$.[8] The molecule is said to be an effective scavenger for protons; at the same time it is only weakly nucleophilic, not reacting *e.g.* with iodoethane.[8] It would be expected to be more efficient than the hindered non-nucleophilic base 2,6-di-t-butylpyridine,[9] which is a much weaker base ($pK_a = 3.58$). The effect of adding increasing amounts of p.s. to the catalyst $SnCl_4$ in tetramethylene sulphone was investigated, in the expectation that, should protic (Brønsted) acids be present, they would effectively be removed.

The data in Table 2 show that the addition of p.s., in a concentration only one tenth of that of the catalyst, causes a sharp drop in the rate coefficient for the rearrangement, to about one half its original value. Higher proportions, equivalent to *ca.* 50% of the $SnCl_4$, result in a lowering of the rate to less than 1% of the original value (Figure). This deactivating effect is much larger than the effect of adding water. If we accept the premise[8] that p.s. is only weakly nucleophilic, this dramatic reduction in rate cannot be due to a direct interaction between p.s. and $SnCl_4$. Rather, the effect may be interpreted as the deactivation of a very reactive catalytic species present at relatively low concentrations. Such a species could be the monohydrate (**4**), acting as a Brønsted acid; this would be removed by addition of p.s. It is assumed that this reaction is fast. The hydrate is likely to be present in the medium owing to the presence of adventitious water, but the greater part of this water will be uncomplexed (2).

If the equilibrium (2) is rapidly attained, removal of the acid (**4**) by addition of p.s. would shift the equilibrium to the right and all the $SnCl_4$ species present (assuming water to be in excess) would act effectively as the hydrate species (**4**). Once sufficient p.s. had been added to deactivate the Brønsted acid, there should then be no further catalytic activity. One would then expect a decline of the rate of rearrangement to zero, when increasing concentrations of p.s. are added, the point of intersection with the ordinate occurring at $[p.s.]/[SnCl_4] = 1$. The Figure shows that this is not observed: the initial decline in rate is much steeper and catalytic activity reaches *ca.* 0 at $[p.s.]/[SnCl_4] = 0.6$.

If, on the contrary, the forward rate of equilibrium (2) is similar to the rate of the rearrangement being studied, addition

Table 2. Rate coefficients of rearrangement of 1-phenylprop-2-en-1-ol (1.5×10^{-4} mol dm^{-3}) catalysed by tin(IV) chloride in tetramethylene sulphone solution, in the presence of added 1,8-bis(dimethylamino)naphthalene (p.s.), lithium chloride, or lithium perchlorate

Added p.s.[a]		Added LiCl[c]		Added $LiClO_4$[a,d]	
10^5 [p.s.]/mol dm^{-3}	$10^2\ k_1$/s^{-1}[b] (at 307.8 K)	10^4 [LiCl]/mol dm^{-3}	$10^2\ k_1$/s^{-1}[b] (at 309.5 K)	10^2 [$LiClO_4$]/mol dm^{-3}	$10^2\ k_1$/s^{-1}[b] (at 305.2 K)
0.5	2.43 ± 0.05	1.1	3.30 ± 0.02	1.0	1.73 ± 0.02
1.0	1.00 ± 0.01	1.8	1.60 ± 0.12	2.5	2.01 ± 0.12
2.0	0.78 ± 0.027	2.5	0.73 ± 0.00	4.9	2.77 ± 0.12
4.0	0.15 ± 0.013	3.4	0.20 ± 0.02	7.4	3.03 ± 0.07
5.0	0.027 ± 0.003	5.0	<0.01	9.5	3.57 ± 0.19
10	<0.001			13	4.18 ± 0.15

[a] [$SnCl_4$] = 1.0×10^{-4} mol dm^{-3}. [b] The quoted uncertainty refers to replicability within 3—5 kinetic runs. [c] [$SnCl_4$] = 5.0×10^{-4} mol dm^{-3}. [d] For zero added salt $k_1 = 1.43\ (\pm 0.03) \times 10^{-2}$ s^{-1}.

of p.s. would neutralise the corresponding amount of the acid (**4**), and in order to re-establish the equilibrium more catalyst (**4**) would be gradually formed. There would then be a gradual increase in rate as the rearrangement proceeded. This phenomenon was not observed.

It is therefore probable that the forward reaction of the equilibrium (2) is slow in comparison with the rearrangement. Addition of p.s. effectively removes the catalyst (**4**), and if this catalyst is very reactive, then the deactivation will take the form of a steep straight line, which would intersect the ordinate at a point well below [p.s.]/[$SnCl_4$] = 1.0. The Figure shows that the observed decline in activity is indeed steep, but the further, less dramatic, decline in rate observed, as more p.s. is added, is then likely to involve the deactivation of the other catalyst present, *viz.* species (**3**). This would mean that true Lewis acid catalysis also occurs.

Since direct deactivation of the species (**3**) appears to be ruled out (see before), one must seek an indirect mechanism which can achieve the same result. Free water molecules could react with the very basic p.s., to yield hydroxide ions [reaction (3)], which could be expected to co-ordinate strongly with, and thus to deactivate, molecules of the Lewis acid (**3**) [reaction (4)].

$$\text{p.s.} + H_2O \rightleftharpoons (\text{p.s.})H^+ + OH^- \qquad (3)$$

$$(\mathbf{3}) + OH^- \rightleftharpoons {}^-SnCl_4{\cdot}S{\cdot}OH + S \qquad (4)$$

Effect of added lithium chloride. In a recent investigation of the interaction of LiCl and $SnCl_4$ in tetramethylene sulphone solution (albeit at substantially higher concentrations than those used here) we showed, by conductimetry and Raman spectroscopy,[4] that the complexes $SnCl_5{}^-Li^+$ and $SnCl_6{}^{2-}2Li^+$ are formed at [LiCl]/[$SnCl_4$] = 1 and 2, respectively.

The addition of LiCl to $SnCl_4$ in tetramethylene sulphone produces a marked reduction in the rate of rearrangement, k_1 (Table 2). The shape of the curve of concentration *vs.* rate (Figure) is similar to that produced by p.s. (see before): the rate falls to near zero for concentrations of LiCl equal to 70—80% of the concentration of $SnCl_4$.

The steep downward curve (Figure) obtained for additions of less than equimolar amounts of LiCl indicates that the process here cannot be simply deactivation of the catalyst (**3**) by conversion into catalytically inactive chloride $SnCl_5{}^-$. More likely, the sharp decline in rate is due to a removal of a more highly active catalytic species, present in relatively low concentrations. If this species is (**4**), deactivation may proceed according to equation (5). However, complete deactivation of

$$(\mathbf{4}) + LiCl \rightleftharpoons SnCl_5{}^-Li^+ + S + H_2O \qquad (5)$$

the catalyst solution does not occur until the residual (*ca.* 30%) anhydrous species (**3**) has been converted, by further additions of LiCl, into inactive $SnCl_5{}^-$.

To summarise, two catalyst species, the anhydrous chloride (**3**) and the hydrate (**4**), appear to be involved in the rearrangement (1), but their relative importance cannot be specified on the present evidence.

Effect of added lithium perchlorate. The kinetic salt effect[10] was studied for the rearrangement (1) by measuring the rate for the $SnCl_4$–$[CH_2]_4SO_2$ system with additions of increasing concentrations of lithium perchlorate (Table 2). For concentrations up to 0.13 mol dm^{-3} of $LiClO_4$, *viz.* up to [$LiClO_4$]/[$SnCl_4$] = 1 300, there was a linear increase ($r = 0.9944$) in rate coefficient k_1, according to expression (6), where $k_1{}^\circ$ is the rate coefficient in the absence of $LiClO_4$.

$$k_1/k_1{}^\circ = 1.06 + 14.8\,[LiClO_4] \qquad (6)$$

For the solvolysis of aryl sulphonates in acetic acid solution, considered representative of a class of reactions in less polar solvents, it was found[10] that addition of $LiClO_4$ caused an increase in rate, accurately described by the linear relationship (7), where k_t is the solvolysis rate coefficient. This result has

$$k_t/k_t{}^\circ = 1 + b\,[LiClO_4] \qquad (7)$$

been described as a 'normal' salt effect,[10,11] with slope b characteristic of the substrate, but also dependent on the solvent. In solvents of this class, which include tetramethylene sulphone, the added salt is present not dissociated into ions, but as ion pairs. The rate-enhancing effect of added salts has been explained[11] in terms of a simple statistical-mechanical model based on dipole–dipole interaction between the salt ion pair and the transition-state ion pair. Although, as stated, $b(LiClO_4)$ shows some dependence on the substrate and the solvent used, the value (14.8 mol^{-1}) found for our reaction falls within the fairly narrow range observed[10] for other reactions. Our data, therefore, are consistent with a mechanism which involves the formation of a transition-state ion pair.

Kinetics Studies with Alkyl (*or Aryl*) *Derivatives of* Sn^{IV} *Chloride.—Monoalkyl* (*or monoaryl*) *tin*(IV) *chlorides.* Substitution of one chlorine atom in $SnCl_4$ by an organic group (alkyl or aryl) would be expected to modify its catalytic properties significantly. The results obtained for a series of compounds of type $RSnCl_3$ are summarised in Table 3. The compounds listed are all effective catalysts for the rearrangement (1), and the sequence of their activity is (R =) phenyl > *p*-tolyl > methyl > n-propyl > ethyl > n-butyl.

Table 3. Rate data and derived thermodynamic parameters for the anionotropic rearrangement of 1-phenylprop-2-en-1-ol (1.5×10^{-4} mol dm^{-3}) in tetramethylene sulphone solution, catalysed by alkyl- (or aryl-) tin(IV) chlorides

Catalyst	10^3 [catalyst] mol dm^{-3}	$10^3\ k_1/\mathrm{s}^{-1}$ [a,b] (computed)	$k_n/\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$ [a,c]	$\Delta H^{\ddagger}$ [a] kJ mol^{-1}	$\Delta S^{\ddagger}$ [a] J K^{-1} mol^{-1}	$\Delta G^{\ddagger}$ [a] kJ mol^{-1}
MeSnCl$_3$	1.03	6.80	6.60	36.6	−162	87.2
EtSnCl$_3$	0.79	3.71	4.69	29.3	−190	88.8
Pr^{n}SnCl$_3$	1.04	5.58	5.36	47.1	−130	87.7
Bu^{n}SnCl$_3$	1.17	1.89	1.62	33.9	−181	90.5
PhSnCl$_3$	0.133	11.5	86.4	54.4	−101	85.9
p-MeC$_6$H$_4$SnCl$_3$	0.124	2.32	18.7	32.7	−183	90.0

[a] At 313.2 K. [b] Measured in range 302—324 K. Arrhenius plots had correlation coefficients $r > 0.992$. [c] Normalised rate coefficient $k_n = k_1$ (computed)/[catalyst].

Table 4. Rate data and derived thermodynamic parameters for the anionotropic rearrangement of 1-phenylprop-2-en-1-ol (1.5×10^{-4} mol dm^{-3}) in tetramethylene sulphone solution, catalysed by dialkyl- (or diaryl-) tin(IV) chlorides

Catalyst	10^2 [catalyst] mol dm^{-3}	$10^5\ k_1/\mathrm{s}^{-1}$ [a] (computed)	$k_n/\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$ [b]	$\Delta H^{\ddagger}$ [c] kJ mol^{-1}	$\Delta S^{\ddagger}$ [c] J K^{-1} mol^{-1}	$\Delta G^{\ddagger}$ [c] kJ mol^{-1}
Me$_2$SnCl$_2$	9.79	4.22	4.3×10^{-4} [c]	42.3	−186	100.4
Et$_2$SnCl$_2$	10.1	14.3	1.4×10^{-3} [c]	51.6	−146	97.3
Ph$_2$SnCl$_2$	10.1	51.4	5.1×10^{-3} [c]	47.8	−147	93.9
(p-ClC$_6$H$_4$)$_2$SnCl$_2$	0.876	360	0.41 [d]			

[a] Temperature ranges: for Me$_2$SnCl$_2$, 391—413 K, r 0.985; for Et$_2$SnCl$_2$, 346—368 K, r 0.984; for Ph$_2$SnCl$_2$, 348—369 K, r 0.990; (p-ClC$_6$H$_4$)$_2$SnCl$_2$ studied only at 349 K. [b] $k_n = k_1$ (computed)/[catalyst]. [c] At 313.2 K. [d] At 349 K. Estimated k_n at 313.2 K is *ca.* 3×10^{-2} dm^3 mol^{-1} s^{-1}.

Anionotropy of 1-(p-*tolyl)prop-2-en-1-ol.* To examine further the role of the substrate in the anionotropic rearrangement, some experiments were conducted using 1-(p-tolyl)prop-2-en-1-ol (**5**). In the presence of acetic anhydride, this compound was

p-MeC$_6$H$_4$CH(OH)CH=CH$_2$ (**5**)   RCH(OH)CH=CHMe (**6**)

reported[12] to undergo isomerisation more rapidly than did substrate (**1**), but no quantitative data were obtained. More recently, for the related anionotropic rearrangement of alcohols (**6**; R = phenyl or p-tolyl) in dioxane–water, rate coefficients at 303 K of 3.07×10^{-2},[13] and 0.268 dm^3 mol^{-1} s^{-1},[14] respectively, were obtained.

The reaction of substrate (**5**) with catalyst SnCl$_4$ proved too rapid, and the weaker catalyst Pr^{n}SnCl$_3$ was consequently used. A rate coefficient $k_1 = 5.93\ (\pm 0.28) \times 10^{-3}$ s^{-1} was obtained for the rearrangement at 308.9 K, for [catalyst] = 1.04×10^{-3} mol dm^{-3}. The derived rate coefficient, $k_n = 5.70$ dm^3 mol^{-1} s^{-1}, is *ca.* 1.4 times that obtained for the parent alcohol (**1**) (extrapolated from data of Table 3, $k_n = 4.12$ dm^3 mol^{-1} s^{-1}, under the same conditions). The small enhancement of rate for the alcohol (**5**), due to electron release from the p-methyl group, is consistent with the role of the alcohol as a donor (*i.e.* Lewis base) in reacting with Lewis acids.

Dialkyl (*or diaryl*) *tin*(IV) *chlorides.* Kinetic studies were extended to the use of diorgano derivatives of SnCl$_4$. Previous work on the acidities of certain species R$_2$SnCl$_2$ [2b,15] relates to the formation of acid–base complexes. For the present system (Table 4) catalysts gave conveniently measurable rates, used at relatively high concentrations between 340 and 420 K. As can be gauged from the second-order rate coefficients, k_n, extrapolated to 313.2 K, these diorgano derivatives are appreciably weaker as catalysts than the mono-organo compounds.

It might be expected that alkyl (or aryl) substitution in the species SnCl$_4$ would have a progressive effect, *i.e.* that a second or subsequent substitution of a chlorine atom by an organic group would have a further acid-weakening effect similar to that of a first such group (see Table 5). However, the effect of a second substituent is dramatically greater than that of a first substituent of the same type. This can be regarded as due to an adverse steric effect, *viz.* steric hindrance to the formation of an acid–base complex involved in the reaction path. An analogous suggestion has been made[2c] for PhSnCl$_3$, though this halide behaves normally as a catalyst in the present system.

Table 4 includes some data for the catalyst bis-(p-chlorophenyl)tin(IV) chloride. It can be seen that substitution in the phenyl rings by a strong $-I$ group reverses electron-donation to the tin atom by the phenyl groups, and thereby increases its electron-accepting properties.

More detailed work using this catalyst had to be abandoned, as it was found that, even with care, the handling of the substance produced violent and persistent headaches in the operator (R. H.).

$\Delta H^{\ddagger}$–$\Delta S^{\ddagger}$ *Relationships.*—The foregoing observations that addition of water to SnCl$_4$ in tetramethylene sulphone caused regular and progressive reduction in both the enthalpy of activation, $\Delta H^{\ddagger}$, and the entropy of activation, $\Delta S^{\ddagger}$, point to a degree of compensation. It has previously[1] been shown that a similar straight line relationship exists for the anionotropic rearrangement (1), as catalysed by a series of metal and non-metal chlorides. The expression takes the form (8); recalculated

$$\Delta H^{\ddagger} = a + b\Delta S^{\ddagger} \qquad (8)$$

for 313.2 K, $a = 85.36$ kJ mol^{-1} and $b = 296$ K, with correlation coefficient $r = 0.9942$, and mean error in $\Delta H^{\ddagger}$ 2.8%.

The expression (8) is close to that observed for SnCl$_4$ and its hydrate (*viz.* $a = 80.73$ kJ mol^{-1}, $b = 288$ K); in fact a single straight line ($a = 85.83$ kJ mol^{-1}, $b = 305$ K, $r = 0.9910$) can be drawn for the data of twenty chloride catalysts we have examined. For SnCl$_4$ and its mono-organo derivatives the corresponding straight line has $a = 79.97$ kJ mol^{-1}, $b = 261$ K, $r = 0.9961$, with a mean error in $\Delta H^{\ddagger}$ of 2.3%.

It is recognised that a linear compensation line between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ may arise purely because of experimental errors or from statistical artefacts.[16] but these may contribute[17] less to

Table 5. Reduction of catalytic activity of tin(IV) and organotin(IV) chlorides on substitution by organic groups[a]

$SnCl_4$		$RSnCl_3$	
First organic substituent	Reduction factor[b]	Second organic substituent	Reduction factor[c]
Ph	3.5	Ph	17 000
p-MeC_6H_4	16		
Me	46	Me	15 300
Et	65	Et	3 300
Pr^n	57		
Bu^n	188		

[a] Data extrapolated to 313.2 K. [b] $k_n(SnCl_4)/k_n(RSnCl_3)$. [c] $k_n(RSnCl_3)/k_n(R_2SnCl_2)$.

Table 6. Rate coefficients for the anionotropic rearrangement of 1-phenylprop-2-en-1-ol (1.5×10^{-4} mol dm^{-3}) catalysed by mixtures of phosphoryl chloride and tin(II) chloride, for a total catalyst concentration of 1.09×10^{-4} mol dm^{-3}, in tetramethylene sulphone solution at 303.5 K

$\frac{10^5\,[SnCl_2]}{\text{mol dm}^{-3}}$	$\frac{10^5\,[POCl_3]}{\text{mol dm}^{-3}}$	k_1/s^{-1}
0	10.9	1.7×10^{-4}[a]
1.6	9.3	2.18×10^{-3}
3.7	7.2	3.67×10^{-2}
5.45	5.45	6.57×10^{-2}
7.2	3.7	2.85×10^{-2}
9.0	1.9	4.12×10^{-3}
10.9	0	1.9×10^{-4}[b]

[a] Extrapolated from data in ref. 1. [b] Extrapolated from the following rate coefficients ($10^3\,k_1/s^{-1}$) (T/K in parentheses) for the rearrangement of substrate (**1**), with $[SnCl_2] = 8.9 \times 10^{-4}$ mol dm^{-3}: 1.57 ± 0.08 (303.5), 1.87 ± 0.08 (308.4), 3.32 ± 0.07 (314.2), 4.88 ± 0.20 (318.2), and 6.55 ± 0.30 (323.1); derived parameters at 313.2 K were k_1 3.12×10^{-3} s^{-1}, $\Delta H^\ddagger$ 60.9 kJ mol^{-1}, $\Delta S^\ddagger$ -90.7 J K^{-1} mol^{-1}, $\Delta G^\ddagger$ 89.2 kJ mol^{-1}.

the correlation than an *a priori* dependence of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ on the same quantity, the rate k. The data available to us proved of insufficient precision to allow us to test for the existence of an isokinetic relationship,[16a,18] which could provide proof of a chemical causality between $\Delta H^\ddagger$ and $\Delta S^\ddagger$. The three diorganotin(IV) catalysis (see Table 4) were excluded from the set of twenty chloride catalysts since they do not fall on the correlation line, with deviations in $\Delta H^\ddagger$ of 14—31%. Such deviations may be the consequence of steric hindrance, as already postulated. Alternatively, the species R_2SnCl_2 may be such weak Lewis acids that they do not effectively co-ordinate with adventitious water, and thus are not able to generate Brønsted acids of the type H^+ $R_2\bar{S}nCl_2(OH)$. If so, one could interpret the very low activity of the R_2SnCl_2 catalysts as representing their true Lewis acidity, whereas the other catalysts examined, which form a coherent enthalpy/entropy data set, act to a substantial degree in the form of their catalytically more reactive hydrates.

Kinetic Studies with Sn^{II} *Chloride*.—Tin(II) chloride is not normally considered as acting as a Lewis acid, although it is known to be a weak Friedel–Crafts catalyst both in its anhydrous form[19] and as the dihydrate.[20] The anhydrous chloride proved to be a moderately effective catalyst for the anionotropy (**1**) (Table 6), with $k_n = 3.5$ dm^3 mol^{-1} s^{-1}, comparable with the activity of monoalkyltin(IV) chlorides (Table 3). This high reactivity, *ca.* 10^5 times as great as that of $ZnCl_2$,[1] is very surprising.

It was considered of interest to use our kinetic system to examine the possibility of interaction between tin(II) chloride and phosphoryl chloride. The latter has been shown to be an efficient catalyst, with k_n at 308.2 K *ca.* 83 dm^3 mol^{-1} s^{-1}.[1] It co-ordinates readily with metal chlorides, thereby acting as a Lewis base, in forming links through oxygen[21] to the metal atom. 1:1 Complexes have been shown to be formed with $AlCl_3$,[22] $GaCl_3$,[22] $SnCl_4$,[21] and $TiCl_4$.[21] Two of us[23] had shown that the complex $POCl_3{\cdot}ZnCl_2$[24] is a powerful catalyst for the rearrangement (1), being 10 times as effective as $POCl_3$ alone, and *ca.* 10^7 times as powerful as pure $ZnCl_2$.

The system $SnCl_2$–$POCl_3$ was studied in tetramethylene sulphone solution by the method of continuous variation (Job's method[25]), by monitoring the rate of rearrangement (1) (Table 6), for a total catalyst concentration of 1.09×10^{-4} mol dm^{-3}. A sharp maximum was observed for a catalyst corresponding to the species $SnCl_2{\cdot}POCl_3$. The activity of this catalyst corresponds to a k_n value at 303.5 K of *ca.* 1 200 dm^3 mol^{-1} s^{-1}. It is thus 4 times as reactive as $SnCl_4$, and indeed is quite the most effective catalyst found so far for the rearrangement. This novel interaction between $SnCl_2$ and $POCl_3$ merits more detailed study.

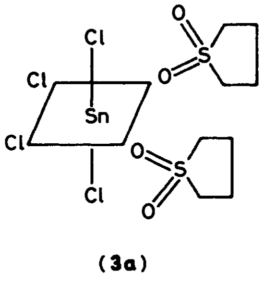
Mechanism of the Anionotropic Rearrangement of the Enol (**1**), *Catalysed by* Sn^{IV} *Chloride*.—A general mechanism for the rearrangement of the alcohol (**1**) has been outlined before;[1] the data presented in the present paper confirm the general conclusions reached earlier.

Recent work[4] on tin(IV) chloride in tetramethylene sulphone (S) showed that a crystalline complex, $SnCl_4{\cdot}S_2$ (**3**) having a *cis*-octahedral structure, may readily be isolated. In this complex, oxygen co-ordination by S occurs, and the structure is essentially retained in solution in S at 308 K. The molecular rearrangement is initiated by addition of the alcohol (**1**) to such a solution. On the basis of our earlier postulate,[1] complexation will then take place between the alcohol (**1**) and the tin atom of the catalyst, to give a species of type (**7**) [reaction (9)].

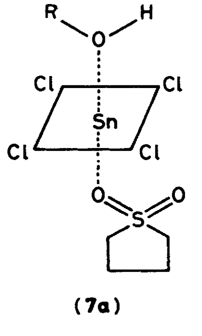
$$\underset{(\mathbf{3})}{SnCl_4{\cdot}S_2} + ROH \rightleftharpoons \underset{(\mathbf{7})}{SnCl_4{\cdot}ROH{\cdot}S} + S \qquad (9)$$

The *cis*-complex (**3**) can exist in two isomeric forms, in which those oxygen atoms of S which are not complexed to the tin atom are respectively *cis* or *trans* (**3a**) to each other. Nucleophilic replacement of one of these S molecules is likely to occur by a dissociative mechanism,[26] which normally involves a five-co-ordinate species.[27] Attack by a molecule of ROH (**1**) would involve a Berry pseudo-rotation mechanism,[27] and result in the formation of a *trans*-complex (**7a**).

The equilibrium (9) must be very rapidly established, in comparison with the rearrangement, since in no instance has a gradual build-up of the rate of rearrangement been observed. U.v. evidence[1] has suggested that the equilibrium (9) and the



(**3a**)



(**7a**)

corresponding one (10) involving the rearranged alcohol R′OH

$$\mathrm{SnCl_4{\cdot}R'OH{\cdot}}S + S \rightleftharpoons \underset{\mathbf{(3)}}{\mathrm{SnCl_4{\cdot}}S_2} + \mathrm{R'OH} \quad (10)$$

(**2**), strongly favour the complex (**3**), leaving the substrate and product alcohols present essentially in uncomplexed form.

Experimental

Materials.—The properties of pure tetramethylene sulphone and 1-phenylprop-2-en-1-ol (**1**) have been described.[1] 1-*p*-Tolylprop-2-en-1-ol (**3**) was prepared[12] from *p*-tolylmagnesium bromide and propenal, as an oil, b.p. 87—88 °C at 1.5 mmHg (lit.,[12] b.p. 120—122 °C at 10 mmHg), $n_D^{19.5}$ 1.5332. Literature methods were used for the preparation of trichloro(methyl)tin(IV),[28] trichloro(ethyl)tin(IV),[29] trichloro-(n-propyl)tin(IV),[30] trichloro-(n-butyl)tin(IV),[29] dichlorodimethyltin(IV),[31] dichlorodiethyltin(IV),[29] m.p. 84—85 °C (lit.,[29] 84—85 °C) (Found: Cl, 28.7. Calc. for $C_4H_{10}Cl_2Sn$: Cl, 28.6%), dichlorodiphenyltin(IV),[32] m.p. 41—42 °C (lit.,[32] 42—44 °C).

*Dichlorobis-*p*-chlorophenyltin*(IV). Tetrakis-*p*-chlorophenyltin(IV)[33] (20.1 g) and anhydrous tetrachlorotin(IV) (9.3 g) were heated at 180 °C for 3 h. The product was isolated and recrystallised (light petroleum); yield 92%; m.p. 86—87 °C (lit.,[34] 86.5 °C) (Found: C, 34.9; H, 2.3; total Cl, 33.5; ionisable Cl, 17.3. Calc. for $C_{12}H_8Cl_4Sn$, with 2 ionisable Cl: C, 34.9; H, 2.0; total Cl, 34.4; ionisable Cl, 17.2%).

Thin-layer Chromatography.—Impurities (*ca.* 0.1%) could readily be detected in catalysts by t.l.c., using the published procedure,[35] with benzene–acetone–acetic acid as developing solvent. R_F Values, and colours developed with dithizone (in parentheses) were: $SnCl_4$ 0, $MeSnCl_3$ 0.10 (red), $EtSnCl_3$ 0.17 (red), Pr^nSnCl_3 0.23 (red), Bu^nSnCl_3 0.25 (red), $PhSnCl_3$ 0.09 (red), *p*-$MeC_6H_4SnCl_3$ 0.10 (red), Me_2SnCl_2 0.17 (orange), Et_2SnCl_2 0.20 (orange), $Pr^n{}_2SnCl_2$ 0.33 (orange), $Bu^n{}_2SnCl_2$ 0.40 (orange), Ph_2SnCl_2 0.54 (orange), (*p*-$ClC_6H_4)_2SnCl_2$ 0.53 (orange), $Pr^n{}_3SnCl$ 0.74 (red), Ph_3SnCl 0.69 (red), Ph_3SnF 0.62 (red), $Pr^n{}_4Sn$ 0.80 (orange, after $KMnO_4$ degradation[35]), Ph_4Sn 0.77 (orange, after $KMnO_4$ degradation). Tin(II) chloride was not detected.

Kinetic Procedures.—Details of the experimental procedures, and the calculation of rate coefficients, have been given.[1] [Note. Equation (xiii) of ref. 1 is misprinted. For k_t read kt.] The reactant (**1**) was introduced into the solution of catalyst in tetramethylene sulphone, in the form of a stock solution (*ca.* 2×10^{-2} mol dm^{-3}) in the carrier solvent tetrachloromethane. The difference between rates ($SnCl_4$ as catalyst, at 306 K) in pure tetramethylene sulphone ($k_1 = 1.8 \times 10^{-2}$ s^{-1}) and in the normal reaction medium, 0.66% v/v CCl_4–$[CH_2]_4SO_2$ ($k_1 = 1.7 \times 10^{-2}$ s^{-1}), was ignored.

The wavelengths used in following the rearrangements were 284 nm for the alcohol (**1**) and 285.5 nm for the alcohol (**5**).

Acknowledgements

Scholarships to P. C. D. (S.E.R.C.) and to R. H. (International Tin Research Institute) are gratefully acknowledged.

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Received 24*th January* 1985; *Paper* 5/137