The Effect of Lithium Perchlorate on the Reactants and the Transition State in a Bimolecular Electrophilic Substitution

By M. H. ABRAHAM* and T. R. SPALDING

(*The Joseph Kenyon Laboratories, University of Surrey, London, S.W.*11)

WE have found that the substitution of tetraalkyltins by mercuric iodide, in solvent 96% methanol, proceeds by the rate-determining bimolecular reaction (1; R = Et, Bu^n).

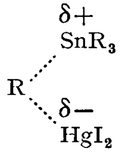
$$R_4Sn + HgI_2 \rightarrow R_3SnI + RHgI \qquad (1)$$

The observed molecularity suggests that either mechanism S_E2 or mechanism S_Ei is operating, leading to transition states (I) and (II) respectively. Positive kinetic salt effects would be expected for mechanism S_E2, but not for mechanism S_Ei (see ref. 1), and we have determined the k/k_0 values at 40° (Table), where k and k_0 are the second-order rate constants in the presence, and in the absence, of lithium perchlorate respectively.

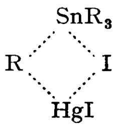
TABLE

Kinetic salt effects, and activity coefficients, in reaction (1)

M-LiClO$_4$	k/k_0	γ^{R_4Sn}	γ^{HgI_2}	$\gamma^{\ddagger}$
(a) R = Et				
0	1	1	1	1
0·016	1·02	1·015	1·015	1·01
0·059	1·11	1·06	1·06	1·01
0·081	1·13	1·08	1·08	1·03
0·107	1·18	1·10	1·10	1·03
0·161	1·31	1·16	1·16	1·03
0·262	1·47	1·27	1·27	1·10
0·392	1·59	1·43	1·44	1·29
0·503	1·80	1·58	1·59	1·40
0·670	2·04	1·84	1·86	1·68
(b) R = Bu^n				
0	1	1	1	1
0·049	1·06	1·06	1·05	1·05
0·102	1·19	1·12	1·10	1·04
0·128	1·30	1·16	1·12	1·00
0·241	1·56	1·32	1·25	1·06



(I)



(II)

The effect of added salt may be discussed in terms of equation (2), where γ^A is the molar activity coefficient of component A, and where $\gamma_0^A = 1$ in the absence of added salt. All of the

$$k = k_0 \cdot \gamma^{R_4Sn} \cdot \gamma^{HgI_2}/\gamma^{\ddagger} \qquad (2)$$

reactants (Et_4Sn, Bu^n_4Sn, and HgI_2) are salted-out by lithium perchlorate, Setschenow's equation,[2] $\log(S/S_0) = \alpha\,[LiClO_4]$, being followed up to at least a one molar concentration of lithium perchlorate. Since the reactants are but sparingly soluble in 96% methanol, their activity coefficients may be obtained[2] by use of the equation $\gamma = S_0/S$. These coefficients, at 40°, are recorded in the Table. From the activity coefficients of the reactants, and the observed values of k/k_0, the activity coefficient of the transition state, $\gamma^{\ddagger}$, can be calculated from equation (2).

It is evident that there is a large, positive kinetic salt effect (see Table), but also that this is due to the effect of the salt on the reactants. Up to about 0·25 M-lithium perchlorate there is little effect on the transition state, and above this concentration of salt, the transition state is actually destabilised by lithium perchlorate. The salt effect on the transition state does not follow Setschenow's equation, and hence the transition state is not behaving as a non-electrolyte (such as Et_4Sn, Bu^n_4Sn, and HgI_2). Rather the behaviour of the transition state is intermediate between that of the three non-electrolytes we have studied, and that expected for electrolytes.

We conclude that the transition states in reaction (1, R = Et, Bu^n) must be polar, with some separation of charge, and that reaction (1) proceeds by mechanism S_E2 *via* an "open" transition state such as (I).

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[1] M. H. Abraham and J. A. Hill, *J. Organometallic Chem.*, 1967, **7**, 11.
[2] F. A. Long and W. F. McDevit, *Chem. Rev.*, 1952, **51**, 119.