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REACTIONS AT HIGH PRESSURE 13 ; VOLUME PROFILES FOR THE BROMINOLYSES OF TETRA-ALKYLSTANNANES[1].

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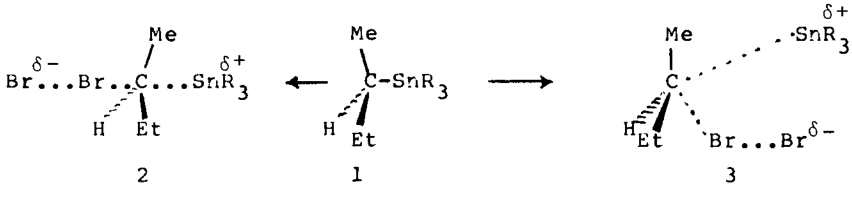
Abstract: Volumes of activation and of reaction have been measured for the S_E2 brominolyses in cyclohexane of SnR_4, R= Et,1-Bu and 2-Bu and lie in the range, respectively -50 to -60 and +20 to +35 cm^3mol^{-1}.

The volume of activation for iodinolysis of tetramethyltin, $\Delta V^{\neq} = -50\ cm^3mol^{-1}$ was previously reported [2]. On the basis of similarity to volumes of activation for Menshutkin reactions [3] this was interpreted as indicative of a similar transition state ,2, resulting in inversion of configuration . The stereochemistry of brominolysis of tin leaving groups at carbon has now been examined using optically active 2-butyl derivatives from which it appears that retention of configuration is usual,inversion only being observed when the remaining SnR_3 moiety is very bulky, e.g. R= neopentyl [4]. That being so it seems likely that our volume of activation may correspond to the front-face attack at carbon .It is known that S_E2 reactions at carbon may take place at either front or rear faces unlike their nucleophilic counterparts so it cannot be assumed that a change of reagent from iodine to bromine will be accompanied by no change of mechanism . In order to check whether values of $\Delta V^{\neq}$ are of similar magnitude for brominolysis we have carried out measurements on three stannanes including $2\text{-}Bu_4Sn$, and have also measured volumes of reaction for the better comparison,calculated from partial molar volumes of the individual reagents and



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products. Results are summarised in Tables 1 and 2 .

Table 1

Rate Constants, $10^3k_2/M^{-1}s^{-1}$, and Volumes of Activation, $\Delta V^{\neq}/cm^3mol^{-1}$ for Brominolyses of R_4Sn in Cyclohexane at 25°C.

R = Et		R = 1-Bu		R = 2-Bu	
p/bar	k_2	p/bar	k_2	p/bar	k_2
1	5.83	1	4.12	1	24.7
200	8.00	190	5.33	200	33.3
400	13.0	300	6.67	280	35.8
550	17.7	380	9.00	310	44.2
650	24.7	480	12.0	420	52.5
750	31.3	600	16.7	480	58.5
770	32.0	700	22.0	580	70.0
				700	88.3
$\Delta V^{\neq}$	-56		-65		-47

Table 2

Partial Molar Volumes, $\overline{V}$/ cm^3mol^{-1}, of Reagents and Products and Volumes of Reaction, $\Delta\overline{V}$: (cyclohexane, 25°C).

R =	Et	1-Bu	2-Bu
R_4Sn	197.3	333.5	319.4
R_3SnBr	197.7	292.9	304.0
RBr	76.9	119.1	109.7
$\Delta\overline{V}$	+20	+23	+36

The more positive volume of activation for 2-Bu_4Sn is paralleled by a more positive volume of reaction so that the difference between this and the other alkyltins lies in a product property. Consequently, all volumes of activation point to a similar transition state. If one regards the intrinsic volume of the transition state as mid way between those of reagents and products, then the electrostrictive volume changes are of the order -70 cm^3mol^{-1} indicative of an extremely high dipole moment even allowing for the fact that the solvent, cyclohexane, is of low dielectric constant. This may be compared with -60 for the volume of reaction of a Menshutkin quaternisation in this solvent [5] and must correspond to essentially full charge formation in the transition state of the S_E2 reaction. This must now be regarded as characteristic values for the retention mode,3; volume parameters for inversion are yet to be established.

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