REACTIONS AT HIGH PRESSURE, IV[1]: IODODESTANNYLATION OF TETRAMETHYLTIN

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The detailed mechanisms of aliphatic S_E2 reactions exemplified by the halogen cleavage of organometallic compounds have proved difficult to establish[2] and no reaction geometry seems to be consistently favoured as is the case for the S_N2 reaction. Stereochemical studies show that retention often occurs as in the bromodemercuration of many secondary alkyl mercuribromides[3] although inversion can also occur as in the bromodestannylation of $RSn(neoC_5H_{11})_3$[4], the transition states being depicted as I and II respectively.

$$S_E2(ret)open \qquad\qquad S_E2\ (inv.)$$
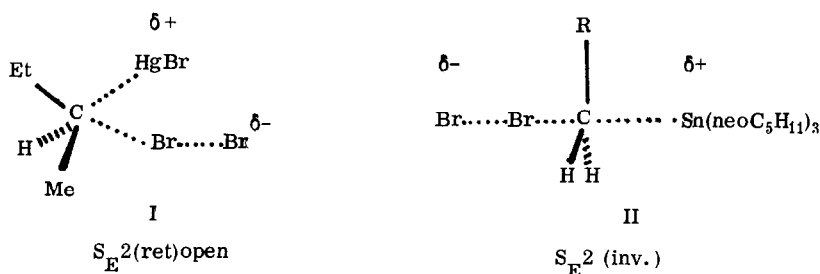
It seemed to us likely that these two pathways could be differentiated by an examination of the pressure dependence of the rates, no data for S_E reactions having hitherto been published. Iododestannylation of tetramethyltin is known to proceed via a highly dipolar transition state on account of the very large solvent sensitivity of the rates.[5] The inversion route proceeding from neutral substrates would lead to a transition state which closely resembles that for the Menschutkin quaternisation reaction and for which, in aprotic media, activation volu mes in the range -40 to -50 cm^3 are commonly found.[6, 7, 8] This figure contains contributions from bond-making (about -10 cm^3)[9] and from solvent electro-striction. The latter, the major factor should be most pronounced when the charge-developing centres are both exposed to solvation and are not directly interacting. This would be the case for the S_E2 (inv) transition state; by comparison, the S_E2(ret) geometry prevents full solvation on account

of the crowding between electrophile and leaving group at the front face and the juxtaposition of
positive and negative centres which may even be bridged by the departing iodide ion (the 'closed'
transition state though probably not implicated in this reaction).   This should result in a substantially
less negative volume of activation.

We now report rates of iododestannylation of tetramethyltin in dibutyl ether.   Measurements
were made at 29.1° by a sampling technique using initial concentrations of iodine (0.003M) and
tetramethyltin (0.1M) to give first order kinetics at pressures up to 1000 atmos beyond which rates
became inconveniently fast.   Second order rate constants were obtained taking into account the
solvent compressibility.

Table.   Pressure-rate data.

Pressure/ atmos.	k_2/ $L. mol^{-1} min^{-1}$	Pressure/ atmos.	k_2/ $L. mol^{-1} min^{-1}$
1	0.0542	760	0.216
246	0.0831	900	0.266
300	0.0915	930	0.268
450	0.128	985	0.283
607	0.157	1095	0.338

A considerable rate acceleration with pressure was observed, the data fitting the equation 1,

$$\ln k_2 = -2.936 + (2.029 \times 10^{-3}) P - (2.97 \times 10^{-7}) P^2 \qquad\qquad 1$$

with a correlation coefficient of 0.9987, Figure.   This leads to a volume of activation,
$\Delta V_o^{\neq} = -50 \text{ cm}^3$.   This value is at the extreme end of the range of those observed for quaternisations
and therefore by our argument above appears to fit an inversion pathway rather than retention.
Abraham and coworkers[10] have recently published reactivity profiles for iododestannylation of a series
of tetra-alkyltins in methanol and concluded that these reactions adopt the S_E2 (inv) pathway.   While
a change of solvent cannot allow one to rule out a change of mechanism (although this seems unlikely)
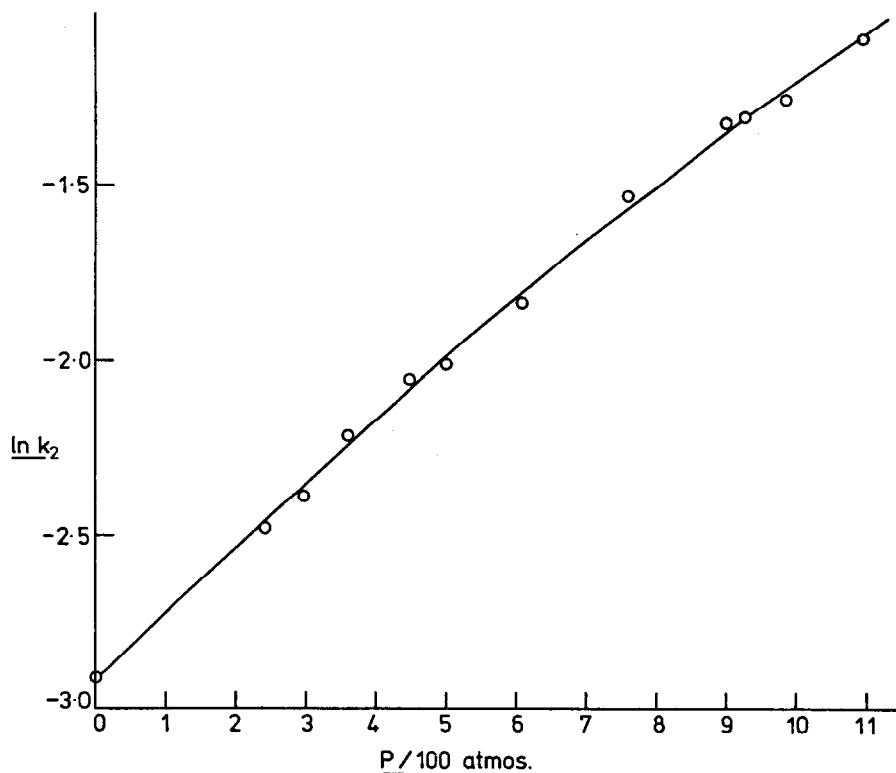
Figure: Pressure effect on the rate of I_2 + $SnMe_4 \longrightarrow$ MeI + $SnMe_3I$;

The curve corresponds to equation 1, the points are experimental.

t h i s   study does appear to complement the reactivity profile approach and to confirm these workers'

conclusions.   Further confidence in results from activation volumes in this field will await the study

of a greater variety of reaction types.

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