for radioassay (>99% octane by gas chromatography). Completeness of the alcoholysis was checked by performing a similar experiment with untagged alcohol, introducing radiotagged alcohol after the hour long stirring period, and allowing the mixture to react for an additional 16 hours. Radioassay of product octane indicated that the reaction with the tagged alcohol was less than 1%.

Alcoholysis experiments were also performed in which a stoichiometric amount of the alcohol was added dropwise to a solution of the aluminum alkyl in hexane, using an apparatus as described above. In three such experiments performed with isobutyl alcohol at 0° the observed radioactivity of the octane was 56 ± 1% of that calculated. With methanol at 50° the activity was 86% of the expected. A similar experiment performed with tris(2-ethylhexyl)aluminum at 70° gave octane with 99% of the calculated activity.

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Kinetics of tin–phenyl cleavage by 8-quinolinol under ansolvous conditions

Recently, the kinetics of the formation of compounds of the type X_2SnOx_2, where $X = Cl, Br$, $Ox = 8$-quinolinolate, were studied using dimethyl sulfoxide solutions[1].

$$(C_6H_5)_2SnX_2 + 2\,HOx \rightarrow X_2SnOx_2 + 2\,C_6H_6 \qquad (1)$$

The rate of formation of product obeys a pseudo-first-order law and the observed rate constants, k_ψ, vary as a function of the concentration of 8-quinolinol. The appropriate rate expression is:

$$\text{rate} = k_\psi[(C_6H_5)_2SnCl_2] = (k_1 + k_2[HOx]^2)\,[(C_6H_5)_2SnCl_2]$$

Evidence has been presented[1] that the two-term rate expression reflects two cleavage paths. However, there is considerable uncertainty about the role of solvation in either cleavage path, and, for reasons cited earlier[1], it was not possible to study cleavage rates in a variety of solvents. Accordingly, it seemed appropriate to study the rate of tin-phenyl cleavage by manometric methods as rate of benzene evolution and to determine whether the reaction occurs at the same rate in the absence of solvent.

Pertinent rate data, measured by the manometric method for tin–phenyl cleavage of diphenyltin dichloride by 8-quinolinol, are summarized in Table 1. Better than 4% precision for duplicate runs was obtained using the monometric method, and the validity of the method is supported by the following considerations. The thermal stability of the reactants was investigated. It was found that 8-quinolinol cause no discernible change in pressure; the decomposition of diphenyltin dichloride does occur at a low rate over a three-hour period, but it was not deemed necessary to correct for the low rate. That this assumption was justified was evidenced by the fact that essentially the same value of k_ψ was obtained when the amount of diphenyltin dichloride was changed from 1.00 mmole to 10.0 mmole while the 8-quinolinol-to-tin ratio remained constant.

As was the case with kinetic runs using dimethyl sulfoxide, a first-order-rate law is followed during tin-phenyl cleavage by 8-quinolinol in the absence of solvent. For the present study as before, the values of the pseudo-first-order rate constants show the same pendence on the concentration of 8-quinolinol.

The values of $10^3\ k_1$ at 192°, which reflect a substrate dissociation process, are 2.25 ± 0.04 and $\frac{1}{2}(3.73\pm0.20)$ sec^{-1} for the dimethyl sulfoxide and ansolvous runs, respectively. It may be noted that there is a 10–20% decrease in the value of k_1 in the absence of solvent. Considering the error limits, this is probably not a real effect, and if the current view that cleavage reactions always involve a push–pull mechanism and solvent participation is correct, it is surprising that the effect is not greater. Admittedly, there is evidence for a Sn–O bond in dimethyl sulfoxide solutions of dimethyltin nitrate[2] and there is good reason to believe that diphenyltin dichloride

TABLE 1

PSEUDO-FIRST-ORDER RATE CONSTANTS (k_ψ) FOR TIN PHENYL CLEAVAGE OF DIPHENYLTIN DICHLORIDE BY 8-QUINOLINOL

t(°C)	$[HOx]/[(C_6H_5)_2SnCl_2]$[a]	$10^3\ k_\psi$(sec^{-1})
180.4	2.00	5.00
180.4	2.00	4.61
179.5	3.00	7.76
192.1	1.00	4.73
192.3	1.00	4.67
192.5	1.50	6.03
191.9	1.75	6.77
191.9	2.00	6.96
192.1	2.00[b]	7.42
192.0	3.00	29.0
192.3	3.00	33.4
201.4	2.00	7.81
201.4	2.00	7.38

[a] 1.00 mmole diphenyltin dichloride used in all runs; [b] 10.0 mmole diphenyltin dichloride used.

is strongly solvated by dimethyl sulfoxide at room temperature. However, it is evident from our results that the dissociative processes occur with little assistance from coordinated solvent, probably because the tin compound is much less strongly solvated at the boiling point of dimethyl sulfoxide which was attained in the cleavage runs. It is surprising that the effect is not greater. The best indication that the transition states for the solvent and ansolvous processes are the same is given by the entropy of activation data which are −43 and −56 eu, respectively. This is taken as evidence that both states represent a similar degree of probability, and that the transition state requires a high degree of orientation.

It would be desirable to be able to compare the rate of cleavage in solution *vis-a-vis* under ansolvous conditions for diphenyltin difluoride, dichloride, dibromide, and diiodide. Unfortunately, this has not been possible. The difluoride is polymeric, and a comparison would not be valid. The cleavage of diphenyltin dibromide was studied using dimethyl sulfoxide solution, but under ansolvous conditions the rates are too great to measure accurately at present. Diphenyltin diiodide appears to undergo decomposition, particularly in dimethyl sulfoxide solution, and cleavage rates could not be measured.

General procedure

The general procedure for the kinetic studies consisted in packing millimolar quantities of reactants into a 9 mm (i.d.) Pyrex tube which was then sealed at both ends with paraffin wax. The tube was then suspended in the neck of the pre-heated reaction vessel by means of the glass lip at the upper end of the tube. The vessel (which consisted of a modified 500 ml-r.b. flask with three standard-taper tubes for attachment to vacuum line and to manometer and for addition of sample tube) was rapidly evacuated prior to the initiation of the reaction caused by the melting and mixing of the reactants. The pressure obtained was less than 1 mm Hg. Manometer readings (± 0.1 mm) were read by one person and recorded by a second at 5-second intervals. The zero time represented the first pressure change. For all runs, there was an initial induction period, during which the increase in pressure was slight, while mixing occurred. This was followed by a reaction period, during which time the increase in pressure was substantial. For the latter period, pseudo-first-order rate constants, k_ψ, were obtained as $k_\psi = 2.303\, m$ where m is the slope of the linear plot of $-\log(P_\infty - P_t)$ *vs.* time, t, sec^{-1}; P_∞, P_t represent the final and current manometer readings respectively.

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