Assisted Acetolysis of Tributyltin Hydride

BY RAYMOND E. DESSY,[1] THOMAS HIEBER,[2] AND FRANK PAULIK[3]

A kinetic and mechanistic investigation of the acetolysis of tributyltin hydride in DMSO and DMSO–diglyme mixtures in the presence of halide ion is first order in hydride and acetic acid, and first order and catalytic in halide ion. It is suggested that the mechanism involves the pre-rate-determining coordination of halide ion on tin, a process which activates the hydride ion in question, making attack by acetic acid occur more readily. This process of activation is termed assistance. Evidence is accumulating in the cleavage of C–M and H–M linkages that nucleophilic attack at the metal atom, as well as the electrophilic attack at carbon or hydrogen, is important. The effect of solvent and anion structure assistor action is discussed.

Although considerable effort has been expended on the reaction of organometallic compounds, very little is known about the mechanism of formation of carbon–metal bonds or the mechanism of cleavage of these bonds.

Dessy and Paulik have pointed out[4] that, just as electrophilic assistance to substitution processes is evident when lone pairs are available near the reaction site, as in the silver-ion catalyzed solvolysis of alkyl halides, nucleophilic assistance to electrophilic substitution processes should be most evident in those compounds where an element possessing an incomplete octet, or one capable of expanding its octet, is near the reaction site. This criterion is met perfectly by organometallic compounds where the metal atom gives rise not only to this "electron deficiency," but through its electropositive nature permits bond polarization to occur, making the metal more susceptible to nucleophilic attack and generating an incipient carbanion through such polarization—a position susceptible to electrophilic attack.

It has also been pointed out[4] that in acidolysis reactions electrophilic attack alone will be observed if (a) the anion of the acid is incapable of coordinating with the metal atom, such as might be the case with sulfate or perchlorate; or (b) the solvent is capable of hydrogen bonding with a potential nucleophile, such as might be the case with halide ion in alcohol or alcohol–water solvents. It is obvious that nucleophilic assistance will be most evident in the reactions of organometallic compounds in aprotic environments when a strong nucleophile is present. Kinetic evidence for such participation in the acetolysis of phenylcarbomethoxymercury in DMSO in the presence of halide ion has been found.[5] The reaction is first order in organomercurial, halide ion, and acid. A pre-rate-determining equilibrium involving halide ion and organomercurial substrate is indicated. Three items—*the assistor, a poor anion solvating reaction medium, and the open p- or sp^x-hybrid orbitals on mercury*—are involved.

In the case of mercury one is dealing with an element possessing a filled d-subshell and having open p- or sp^x-hybrid orbitals available. It seemed of interest to investigate the elements which had no available sp^x-hybrid orbitals, but available empty d-orbitals, and those which contained no available d-orbitals, and open p- or sp^x-hybrid orbitals, for evidence of such nucleophilic assistance at the metal in the cleavage of C–M bonds. Evidence in these three strikingly different cases would indicate that the phenomenon of nucleophilic assistance is widespread throughout the periodic table. Work on the latter case, involving unsymmetrical organoboranes, is in progress, but sufficient evidence is now available from kinetic studies of the assisted

acetolysis of tributyltin hydride to indicate that nucleophilic participation is clearly observable in organometallic compounds containing a metal having the former characteristics where coordination requires the "expansion of the octet." It is the purpose of this paper to present these details.
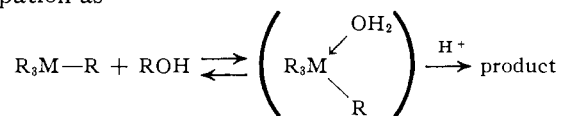
There appears to be a correlation between this study and the reports in the literature concerning the acidolysis of carbon–metal bonds involving Si, Ge, Sn, or Pb and the base-catalyzed reaction or acidolysis of silicon–hydrogen bonds.

Eaborn[6] has studied the acidolysis of C–Si, C–Ge, C–Sn, and C–Pb bonds using aryltrialkylmetal compounds as substrates. In these systems, in aqueous alcoholic perchloric acid or sulfuric acid in acetic acid–water, the acidolysis follows a Hammett correlation, $\log k/k_0 = \rho(\sigma + r(\delta^+ - \sigma))$, the value of r steadily decreasing from 0.7 to 0.4 as one proceeds from Si to Sn. From an observation of the large positive ρ-values, it is suggested that in these cases the reaction involves predominantly electrophilic attack on carbon, while the monotonic decrease in r is attributed to increasing amounts of nucleophilic attack on the metal atom by solvent.

In the system

$$ArMR_3 \xrightarrow[\text{HClO}_4]{\text{EtOH, HOH}}$$
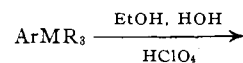
the relative rates of cleavage of the aryl group from the metal are $1:36:3.5 \times 10^5:2 \times 10^8$ for Si, Ge, Sn, and Pb, respectively. Eaborn has pictured the solvent participation as

$$R_3M{-}R + ROH \rightleftharpoons \left(R_3M\begin{smallmatrix} \nearrow OH_2 \\ \searrow R \end{smallmatrix} \right) \xrightarrow{H^+} \text{product}$$

suggesting its importance for Sn and Pb particularly.

Dessy and Kim have studied the cleavage of C–Hg bonds in hydrochloric acid–DMSO–dioxane systems and found a similar Hammett correlation with $r = 0.5$.[7]

In this particular case, it is suggested that pre-rate-determining coordination of halogen on mercury leading to an assistance of the electrophilic proton attack on carbon is involved. Evidence that supports this view of nucleophilic participation at the metal is suggested[8] in the data derived from a study of the mechanism of formation of C–Hg bonds from acetylenes, RC≡CH, and HgX_2, where a four-center mechanism seems to be involved. This reaction is related, via the principle of microscopic reversibility, to the cleavage of the same bond.

The base-catalyzed reaction of trialkylsilicon hydrides has been studied by Steward,[9] Kaplan and Wilz-

(1) Alfred P. Sloan Fellow.
(2) National Institute of Health Predoctoral Research Fellow.
(3) Texaco Corporation Predoctoral Fellow.
(4) R. E. Dessy and F. Paulik, J. Chem. Educ., **40**, 185 (1963).
(5) R. E. Dessy and F. Paulik, J. Am. Chem. Soc., **85**, 1812 (1963).

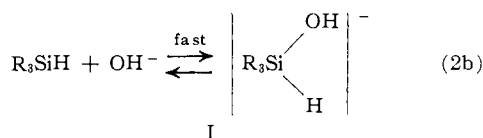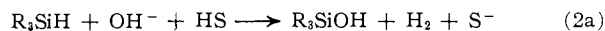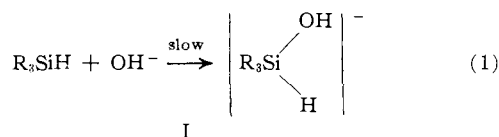(6) (a) C. Eaborn and K. C. Pande, J. Chem. Soc., 1566 (1960); (b) F. B. Deans and C. Eaborn, ibid., 2299 (1858); (c) E. Eaborn and K. C. Pande, ibid., 297 (1961); (d) C. Eaborn and J. A. Waters, ibid., 542 (1961).
(7) R. E. Dessy and J. Kim, J. Am. Chem. Soc., **83**, 1167 (1961).
(8) R. E. Dessy, W. L. Budde, and C. Woodruff, ibid., **84**, 1172 (1962).

bach,[10] and Sommer.[11] The area is a rather complex one, but three mechanisms have been proposed involving the often used $OH^--EtOH-HOH$ system.

$$R_3SiH + OH^- \xrightarrow{\text{slow}} \left| R_3Si\begin{matrix} OH \\ \\ H \end{matrix} \right|^- \quad (1)$$

I

$$I + HS \xrightarrow{\text{fast}} R_3SiOH + H_2 + S^-$$

$$R_3SiH + OH^- + HS \longrightarrow R_3SiOH + H_2 + S^- \quad (2a)$$

$$R_3SiH + OH^- \xrightleftharpoons{\text{fast}} \left| R_3Si\begin{matrix} OH \\ \\ H \end{matrix} \right|^- \quad (2b)$$

I

$$I + HS \xrightarrow{\text{slow}} R_3SiOH + H_2 + S^-$$

The second-order kinetics, first order in base and silicon hydride, and the presence of small deuterium isotope effects ($k^{SiH}/k^{SiD} = 1.2-1.5$) have led Kaplan and Wilzbach[10] to prefer a transition state

$$\left| R_3Si\begin{matrix} OH \\ | \\ --H---H--S \end{matrix} \right|^{*-}$$
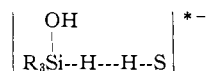
in which the bond between the hydrogen atoms is almost complete in the transition state.

Steward and Pierce,[9] exploring the area by means of the Taft equation, have suggested that structure-reactivity correlations are best made by assuming two limiting reaction mechanisms—(1) predominating when strained rings or electron-withdrawing groups are involved around silicon, while (2a) predominates when electron donors are present. In the alkyl series the effect of polar substituents on the base-catalyzed hydrolysis of organosilicones is appreciable ($\sigma^* = 4.27$), although in the acid-catalyzed reaction it is quite small ($\sigma^* = 0.77$).
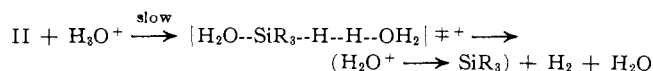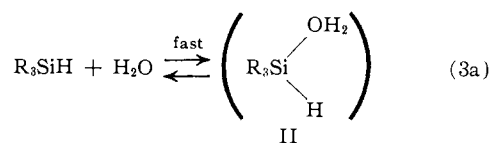
The closest example to the reaction in question is the decomposition of trialkylsilicon hydrides by hydrogen chloride in aqueous ethanol. In order to avoid the effect of trace amounts of water, Eaborn[12] employed 95% ethanol. The reaction appears to be first order in acid and first order in silicon hydride, and p-substitution in phenyldimethylsilicon hydride has remarkably little effect on the rate, which is consistent with the results of Steward and Pierce in the alkyl series, the rate ratio p-Cl:H:p-CH₃ being 1.2:1:0.85. The addition of water decreased the rate of reaction, a fact attributed to the drop in the acidity function. Interestingly enough, added LiCl increased the rate of reaction far more than might be expected from a salt effect. Finally, the observation that the acid decomposition in anhydrous dioxane is accelerated by the addition of water (despite the drop in acidity function (*sic*)) and the presence of a solvent isotope effect ($k^{H_2O}/k^{D_2O} = 2$) led to the suggestion that one of the following mechanisms was involved.

(9) (a) O. W. Steward and O. R. Pierce, *J. Am. Chem. Soc.*, **83**, 4932 (1961); (b) O. W. Steward and O. R. Pierce, *ibid.*, **83**, 1916 (1961); (c) O. W. Steward and O. R. Pierce, *ibid.*, **81**, 1983 (1959).
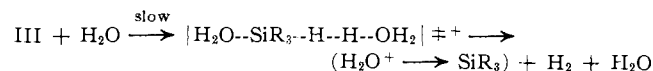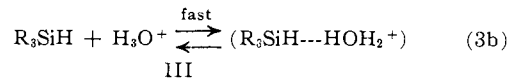
(10) L. Kaplan and K. E. Wilzbach, *ibid.*, **77**, 1297 (1955).

(11) (a) L. H. Sommer and O. F. Bennett, *ibid.*, **79**, 1008, 3295 (1957); (b) L. H. Sommer, W. P. Barie, and D. Weyenberg, *ibid.*, **81**, 251 (1959); (c) L. H. Sommer, D. Weyenberg, and P. G. Campbell, Abstracts of Papers, 135th National Meeting of the American Chemical Society, Boston, Mass., April, 1959, p. 23M.

(12) J. E. Baines and C. Eaborn, *J. Chem. Soc.*, 1436 (1956).

$$R_3SiH + H_2O \xrightleftharpoons{\text{fast}} \left(R_3Si\begin{matrix} OH_2 \\ \\ H \end{matrix} \right) \quad (3a)$$

II

$$II + H_3O^+ \xrightarrow{\text{slow}} |H_2O--SiR_3--H--H--OH_2| \mp^+ \longrightarrow$$
$$(H_2O^+ \longrightarrow SiR_3) + H_2 + H_2O$$

or

$$R_3SiH + H_3O^+ \xrightleftharpoons{\text{fast}} (R_3SiH---HOH_2^+) \quad (3b)$$

III

$$III + H_2O \xrightarrow{\text{slow}} |H_2O--SiR_3--H--H--OH_2| \mp^+ \longrightarrow$$
$$(H_2O^+ \longrightarrow SiR_3) + H_2 + H_2O$$

In latter reviews Eaborn[13] tended to favor 3b as the most likely mechanistic pathway, although the hydrogen bonding involved in the pre-rate-determining intermediate is rather unusual.

It is of value to point out that it was felt by this author[13] that the work of Taketa, Kumada, and Tarama[14] involving the acidic ethanolysis of triethylsilane, which indicated that *both* chloride ion and oxonium ion were involved in the rate-determining step, was improbable.

Experimental

Apparatus.—The most convenient method for following the rate of this reaction ($R_3MH + HA \rightarrow H_2 + R_3MA$) was to measure the change in pressure (due to hydrogen gas evolution) with respect to time at a constant volume. The instrument used in the kinetic studies was a modified Thomas–Van Slyke–Folch manometric apparatus. The reaction vessel, to be connected to the manometer, consisted of a 100-cc. flat-bottomed flask with a side arm for attachment and a stopcock fitted with a rubber septum for injection of the acetic acid by means of a 10-cc. hypodermic syringe. Stirring of the reaction mixture was accomplished by a magnetic stirrer.

The temperature regulating system consisted of a large water bath under constant agitation in which a bimetallic thermoregulator and heating unit were immersed. Water from the bath was circulated through the gas chamber jacket and around the reaction vessel by means of a centrifugal circulating pump. Temperature control was maintained within 0.1° at 31.4°.

Description of Reagents.—After purification, all materials were stored in calcium chloride desiccators until used. All solvents were flushed with nitrogen gas as a precaution against oxidation of the hydride solution.

Solvents.—Diglyme (diethylene glycol dimethyl ether, Matheson Coleman and Bell) was dried over and distilled from LiAlH₄ at atmospheric pressure. The pure material boiled at 160–161°. Dimethyl sulfoxide (DMSO, Matheson Coleman and Bell) was dried over calcium hydride and fractionally distilled at atmospheric pressure and reduced pressure. The fraction taken distilled at 189–190° (atmospheric pressure) or at 45° at 1.0 mm. Glacial acetic acid (du Pont, reagent grade) was refluxed with potassium permanganate for 6 hr. in order to oxidize any aldehydes present. The acid was then dried over and distilled from magnesium perchlorate at atmospheric pressure. This procedure yielded glacial acetic acid having a boiling point of 117.0–118.0°. Trifluoroacetic acid (Matheson Coleman and Bell) was distilled at atmospheric pressure before use. Hydrochloric acid (du Pont, reagent grade) was used as received. Ethyl ether (Mallinckrodt, reagent grade anhydrous) was dried over and distilled from LiAlH₄.

Assistors.—The alkali metal salts employed in these studies were commercially available, reagent grade materials. The salts included NaF, NaC₂H₃O₂, NaBr, NaI, LiCl, LiBr, LiClO₄, and KSCN. They were dried at temperatures of 130–150° for several hours before use. Triphenylphosphine (Metal and Thermit Corp.) was recrystallized three times from absolute ethanol. The material obtained after recrystallization was a white solid melting at 78–80°. Triphenylphosphine oxide (Metal and Thermit Corp.) was recrystallized once from methylcyclohexane (Phillips Petroleum), giving a white crystalline material melting at 153–154°. Tri-n-butyltin hydride was prepared from bis-(tri-n-butyltin) oxide, by reduction with lithium aluminum

(13) C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London, 1960.

(14) A. Taketa, M. Kumada, and K. Tarama, *Bull. Inst. Chem. Res., Kyoto Univ.*, **31**, 260 (1953).

hydride (deuteride) according to the method of Considine.[15] The pure hydride boiled at 99–101 (5 mm.), with $n^{19}D$ of 1.4735.

Treatment of Data.—All runs were made under conditions that were pseudo-first order in hydride, with acid concentrations 10 to 20-fold that of the hydride substrate. Plots of log $(P_\infty - P)$ vs. t led to pseudo-k_1's. Division by the acetic acid concentration gave second-order rate constants, k_2, while division by the initial assistor concentration, if present, led to the k_3 values presented.

A typical run, followed to 99% of the expected hydrogen evolved, which obeyed a first-order plot to 80% reaction, appears below.

Conditions.—Tri-n-butyltin hydride (0.067 M), acetic acid (0.67 M), lithium chloride (0.067 M) in DMSO-diglyme (1:1) at 31.4°. From the free volume of the apparatus a pressure change of 35.43 cm. was expected (a).

Pressure, cm.	Time, min.: sec.	$(P - P_0) = x$, cm.	$(a - x)$, cm.
15.00	0:00	0.00	35.43
23.30	0:30	8.30	27.13
30.10	1:00	15.10	20.33
39.10	2:17	24.10	11.33
44.10	3:45	29.10	6.33
47.10	5:25	32.10	3.33
49.70	8:22	34.70	0.73
50.43	10:15	35.43	0.00

Results and Discussion

Although any derivative of a group IV element might have been employed in a study to determine the importance of nucleophilic attack on the metal atom in cleavage of a M–X bond, the M–H bond has unique characteristics. In comparison to M–R bonds, it has a high degree of polarity which will more sharply elicit nucleophilic assistance if it is present. In comparison with M–Cl bonds it has the attribute of not involving

of preparation, and polarizability suggested tin. Although triphenyltin hydride would have been most preferable, the problems posed in purification led to the final selection of tributyltin hydride. The desirable solvent properties of dimethyl sulfoxide, or diglyme, particularly their ability to dissolve inorganic materials and not to solvate anions, suggested their use in the study of the acidolysis of tributyltin hydride. A preliminary survey of possible acids led to the findings that trifluoroacetic acid reacted very slowly with the tributyltin hydride in diglyme. Hydrochloric acid reacted much too rapidly, while the substituted phenols were too sluggish in their attack. Acetic acid finally gave a manageable system.

The results of the initial study of the $(C_4H_9)_3SnH$–HOAc–DMSO system are given in Table I. Runs I-A-1 and I-A-2 clearly show that the reaction, yielding hydrogen and tributyltin acetate, run under pseudo-first-order conditions, is first order in hydride and in acid. Pseudo-first-order plots were well behaved over the first 40% of the reaction, from which the slopes used to calculate k_2 were derived. After this point the reaction appeared to deviate in a positive manner, running its course more rapidly than might be expected from the rate law. This was finally traced to an autocatalytic term, involving the product $(C_4H_9)_3SnOAc$, as run I-H indicates. The addition of $LiClO_4$ to the reaction leads to the observance of a small positive salt effect, run I-G. This might be due to a direct effect of bulk solvent dielectric, or to a specific effect of perchlorate ion, but the autocatalytic findings would suggest that liberation of small amounts of acetate ion which exert a specific effect themselves is the most probable source.

TABLE I[a]

$$(C_4H_9)_3SnH + HOAc + assistor \xrightarrow[DMSO]{31.4°} (C_4H_9)_3SnOAc + H_2$$

Run	$((C_4H_9)_3SnH$, M	(HOAc), M	Assistor	(Assistor), M	k_2, l./mole-sec.	k_3, l.²/mole²-sec.
I-A-1	0.093	0.93	. . .	. . .	6.3×10^{-5}	. . . .
I-A-1	.090	.90	. . .	. . .	6.4×10^{-5}	. . . .
I-A-2	.064	.128	. . .	. . .	6.9×10^{-5}	. . . .
I-A-2	.082	.164	. . .	. . .	6.5×10^{-5}	. . . .
I-B	.051	.51	LiCl	0.051	4.7×10^{-3}	9.5×10^{-2}
I-B	.051	.51	LiCl	.051	4.6×10^{-3}	9.3×10^{-2}
I-C-1	.046	.46	LiBr	.046	9.4×10^{-4}	2.0×10^{-2}
I-C-1	.046	.46	LiBr	.046	9.9×10^{-4}	2.1×10^{-2}
I-C-2	.049	.58	LiBr	.035	7.7×10^{-4}	2.2×10^{-2}
I-C-3	.062	1.24	LiBr	.062	1.2×10^{-3}	2.0×10^{-2}
I-D	.062	0.62	NaBr	.062	1.4×10^{-3}	2.2×10^{-2}
I-E	.059	.59	NaI	.059	1.1×10^{-4}	. . . .
I-F	.078	.78	KSCN	.078	2.4×10^{-4}	. . . .
I-G	.049	.49	LiClO₄	.098	9.2×10^{-5}	. . . .
I-H	.045	.45	$(C_4H_9)_3SnOAc$	.045	1.1×10^{-4}	. . . .
I-J	.058	.58	$(C_6H_5)_3P$	.058	1.1×10^{-4}	. . . .
I-K	.052	.52	$(C_6H_5)_3P{\rightarrow}O$	.104	1.8×10^{-4}	. . . .
	$((C_4H_9)_3SnD)$, M					
I-B-d	0.071	0.71	LiCl	0.071	5.5×10^{-3}	7.8×10^{-2}
I-B-d	0.071	0.71	LiCl	0.071	5.6×10^{-3}	7.9×10^{-2}

[a] Tributyltin hydride in DMSO, at the concentrations employed before mixing with the reacting solutions, was found to be an emulsion from which reproducible aliquots could be taken as indicated by the observed rate constants. Complete solution was effected upon addition of the final reactant, acetic acid in DMSO.

possible $d\pi$–$p\pi$ bonding. The dihydrides and trihydrides of group IV elements have complex chemistry, as Kuivila[16] has so elegantly shown, so that a trialkyl or aryl metal hydride seemed most appropriate. Again, to elicit the greatest degree of nucleophilic participation, it seemed advantageous to employ one of the more massive, and therefore more polarizable elements of group IV, and the compromise between stability, ease

(15) W. Considine and J. J. Ventura, *Chem. Ind.* (London), 1683 (1962).
(16) A. K. Sawyer and H. G. Kuivila, *J. Am. Chem. Soc.*, **82**, 5958 (1960).

Runs I-B, C, and D indicate that the addition of the halogen ions Cl⁻ and Br⁻ results in an increase in the observed k_2. The pseudo-first-order plots obtained under chloride ion catalysis are linear for over 80% of the course of the reaction, since under these circumstances the contribution by autocatalysis is too small to detect. In bromide ion runs only the initial 40% of the reaction was used in calculations of rate constants to avoid the autocatalysis term. The fact that even though stoichiometric amounts of halogen ion are em-

TABLE II

$$(C_4H_9)_3SnH + HOAc + assistor \xrightarrow[\text{DMSO-diglyme}]{31.4°} (C_4H_9)_3SnOAc + H_2$$

Run	$((C_4H_9)_3SnH)$, M	(HOAc), M	Assistor	(Assistor), M	k_2, l./mole-sec.	k_3, l.²/mole²-sec.
II-A	0.114	1.14	...	...	2.56×10^{-5}	....
II-A	.114	1.14	...	...	2.42×10^{-5}	....
II-B	.067	0.67	LiCl	0.067	1.30×10^{-2}	1.95×10^{-1}
II-B	.067	.67	LiCl	.067	1.37×10^{-2}	1.92×10^{-1}
II-C-1	.067	.67	LiBr	.067	2.29×10^{-3}	3.41×10^{-2}
II-C-2	.067	.67	LiBr	.134	4.46×10^{-3}	3.37×10^{-2}
II-C-2	.067	.67	LiBr	.134	4.54×10^{-3}	3.42×10^{-2}
II-C-3	.067	1.34	LiBr	.067	2.23×10^{-3}	3.37×10^{-2}
II-C-3	.067	1.34	LiBr	.067	2.20×10^{-3}	3.32×10^{-2}
II-D	.067	0.67	NaBr	.067	2.24×10^{-3}	3.38×10^{-2}
II-D	.067	.67	NaBr	.067	2.27×10^{-3}	3.40×10^{-2}
II-E	.067	.67	NaI	.067	1.18×10^{-4}	1.77×10^{-3}
II-E	.067	.67	NaI	.067	1.11×10^{-4}	1.67×10^{-3}
II-F	.067	.67	KSCN	.067	6.3×10^{-4}	9.6×10^{-3}
II-F	.067	.67	KSCN	.067	6.0×10^{-4}	9.0×10^{-3}
II-G	.067	.67	LiClO₄	.067	5.0×10^{-5}	7.5×10^{-4}
II-G	.067	.67	LiClO₄	.067	5.5×10^{-5}	8.2×10^{-4}
II-H	.067	.67	$(C_4H_9)_3SnOAc$	.067	3.6×10^{-5}	....
II-H	.067	.67	$(C_4H_9)_3SnOAc$	.067	3.7×10^{-5}	....
II-J	.067	.67	$(C_6H_5)_3P$	.067	4.2×10^{-5}	....
II-K	.067	.67	$(C_6H_5)_3P{\rightarrow}O$	.067	5.5×10^{-5}	....
	$((C_4H_9)_3SnD)$, M					
II-A-d	0.137	1.37	...	...	2.70×10^{-5}	
II-A-d	.137	1.37	...	...	2.74×10^{-5}	
II-B-d	.067	0.67	LiCl	0.067	1.06×10^{-2}	1.59×10^{-1}
II-B-d	.067	0.67	LiCl	0.067	1.03×10^{-2}	1.56×10^{-1}

ployed pseudo-first-order plots are linear indicates that the halogen ion is serving as a catalyst, apparently being regenerated after the rate-determining step or released during the rate-determining step. The assumption that the reaction, under these conditions, is now also first order in halogen ion leads to the calculated k_3 values shown. Runs I-C-1, 2, and 3 indicate that this assumption is valid.

There appears to be no cation effect, as a comparison of runs I-C and D indicates.

Finally, the addition of NaI or $(C_6H_5)_3P$ in stoichiometric amounts does not increase k_2 sufficiently to place them beyond the domain of the autocatalytic acetate term, and the effect of KSCN or $(C_6H_5)_3P{\rightarrow}O$ is weak indeed.

These facts, taken as a whole, suggest that nucleophilic assistance at tin is important in the acetolysis of tributyltin hydride in DMSO, an occurence which might be symbolized as

$$R_3SnH + X^- \underset{\text{fast}}{\overset{\text{fast}}{\rightleftharpoons}} \left(\begin{array}{c} H \\ R_3Sn \\ X \end{array}\right) \xrightarrow[\text{HOAc}]{\text{slow}} R_3SnOAc + H_2 + X^-$$
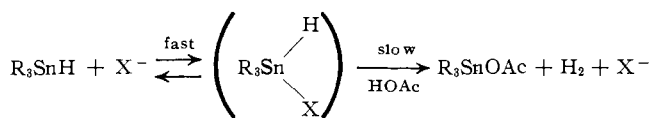
It is not known whether front or back side coordination by halide ion is involved.

The fact that the apparently unassisted reaction is first order in acetic acid suggests that: (a) no assistance is involved, (b) DMSO is serving as an assistor, or (c) the carbonyl oxygen of the acetic acid is assisting. Case b or c seems most probable.

Since the assisted (by halide ion) reaction involves charge dispersal in the transition state while the apparently unassisted case is associated with charge production, it seemed advisable to lower the dielectric constant of the system without altering its solvation properties by the addition of diglyme to increase the observed span of rate constants. This would have the added advantage of reducing the autocatalytic term if acetate ion were indeed responsible for it.

Table II shows the result of this study. Runs II-C-1, 2, and 3 indicate that the same kinetic pattern—first order in hydride and acetic acid and first order and catalytic in halide ion—is observable. Pseudo-first-order plots are linear for over 80% of the reaction course, when chloride ion or a bromide ion is involved. As expected, the rate of the unassisted reaction is lowered (comparison of runs I-A and II-A), and the rates of the assisted reactions are increased (comparison of runs I and II-B, C, D, E, and F). Even more satisfactory is the datum concerning the autocatalytic term, which is decidedly suppressed. The outcome of this accentuation of the assisted reactions, the suppression of the autocatalytic term, and the diminishing of the rate of the unassisted reaction is the clear indication that SCN^- and I^- are assistors in this system. $(C_6H_5)_3P$ and $(C_6H_5)_3P{\rightarrow}O$ do not show sufficient activity to warrant consideration of their participation in the reaction.

One interesting aspect of this increase in rate span is the fact that there is possible advantage in nucleophilic displacements in the utilization of mixed DMSO–diglyme solvents, rather than DMSO alone. The latter is known to aid nucleophilic displacements, presumably by its lack of ability to solvate the anions used. Its high dielectric is somewhat of a disadvantage, however, and it is suggested that lowering the bulk dielectric with diglyme or other similar materials will aid the synthetic chemist.

Some idea of the transition state details may be derived from deuterium isotope effects on the reaction. The replacement of H by D in the tributyltin hydride leads to the evolution of H–D in the reaction with HOAc–DMSO–diglyme or HOAC, Cl^-–DMSO-diglyme. The isotopic purity of this gas, better than 98% H–D, indicates that in neither case is exchange with the solvent pool important. In the unassisted case (runs II-A and II-A-d) the k_H/k_D ratio is 0.92. In the assisted case (Cl^-) the k_H/k_D ratio is 1.2.

Utilizing the stretching frequencies for Sn–H and Sn–D (1825 and 1290 cm.$^{-1}$) and H–H and H–D (4405

and 3817 cm.$^{-1}$),[10] it is possible to calculate k_H/k_D ratios for two extreme cases: (1) where the hydride ion from the tributyltin hydride is unbonded in the transition state, and (2) where the bond between the two participating hydrogens is complete in the transition state.[10] For case 1 $k_H/k_D = 4.1$, while for case 2 k_H/k_D is 0.9. The data would argue for a transition state then in which the bond between the participating hydrogens was almost completely formed, one in which the transition state resembled product. Dessy and Paulik have indicated that the function of assistor is to weaken the M–X bond, which in this case yields a more hydridic hydrogen. The observation that the assisted reaction has a higher k_H/k_D ratio is consistent with this argument, since the transition state would be expected to occur earlier along the reaction coordinate, where the bond between the proton and incipient hydride ion was not as complete.

Finally, the point should be made that such nucleo-philic assistance is not found in reactions run in protic solvent, where the halide ion is strongly hydrogen bonded.[17]

(17) H. G. Kuivila and P. L. Levins [*J. Am. Chem. Soc.*, **86**, 23 (1964)] have investigated the acid- and base-catalyzed solvolysis of tributyltin hydride in *methanol* and found that no assistance was provided by halide ion. This is completely consistent with the feeling that nucleophilic assistance in organometal reactions will be observable only when solvents which do not coordinate with, and therefore mitigate the effect of, anions are employed.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WILLIAM MARSH RICE UNIVERSITY, HOUSTON, TEXAS]

The Reactions of Diazonium Salts with Nucleophiles. X. A Tracer Demonstration of the Reversible Step in Diazonium Ion Hydrolysis[1]

BY EDWARD S. LEWIS AND JOAN M. INSOLE

The rearrangement $ArN^{+15}{\equiv}N \rightarrow ArN^{+}{\equiv}N^{15}$ is shown to accompany the hydrolysis of diazonium salts at a rate slower than the solvolysis by a factor of 0.014 for Ar = C_6H_5, and a factor of 0.029 for Ar = $p\text{-}CH_3C_6H_4$. A degradation to determine the position of N^{15} label in ArN_2^+ is described. It is shown that the extent of rearrangement is not simply correlated with the previously observed acceleration of the decomposition in the presence of thiocyanate. A relation between nitrogen fixation and this reaction is shown to be improbable.

Introduction

The solvolysis of aromatic diazonium salts was believed to pass through an intermediate aryl cation, which then reacts very rapidly with solvent or other nucleophiles; the evidence for this mechanism has been frequently presented.[2] Recently, the mechanism was modified by the inclusion of an initial reversible step to account for the small increase in rate on adding thiocyanate ion.[3] The structure of this reversibly-formed intermediate was the subject of speculation; the high reactivity suggests an intermediate of energy content close to that of the transition state for the slow step, and thus a structure resembling the phenyl cation.

In view of the fact that the carbon–nitrogen bond must therefore be nearly, if not completely, broken in this intermediate, there was a chance that when the diazonium salt was re-formed, the new bond might be formed to the other nitrogen atom. In other words, the isotopic rearrangement (1) might occur through the
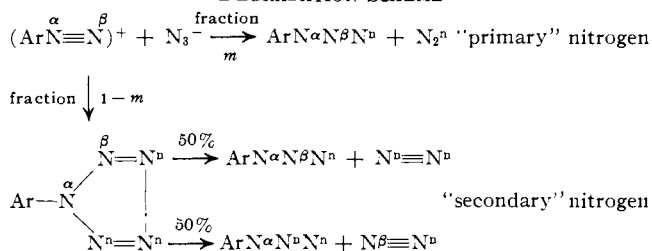
$$(ArN^*{\equiv}N)^+ \longrightarrow (ArN{\equiv}N^*)^+ \qquad (1)$$
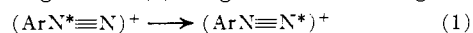
same intermediate responsible for the rate acceleration by thiocyanate. A search for this reaction in benzenediazonium and p-toluenediazonium salts is presented here.

Results and Discussion

Aniline-N^{15} was prepared from ammonium-N^{15} chloride *via* benzamide and the Hoffman reaction. On diazotization with normal nitrite, it yielded benzenediazonium-α-N^{15} ion, isolated as the fluoroborate. The degradation of the diazonium salt was based upon the reaction with azide ion, as elucidated by the work of Clusius[4] and Huisgen and Ugi.[5] It is shown in Chart I. Reaction at $-27°$ in aqueous ethanol solution between the diazonium salt and the azide gave "primary" nitrogen (derived from the azide ion only) of normal isotopic abundance. On warming, the "secondary" nitrogen (derived from the decomposition of phenylpentazole) was evolved and collected for analysis. The phenyl azide from both paths was reduced to aniline and nitrogen gas, which was also collected for analysis.

CHART I
DEGRADATION SCHEME

$$(Ar\overset{\alpha}{N}{\equiv}\overset{\beta}{N})^+ + N_3^- \xrightarrow[m]{\text{fraction}} ArN^\alpha N^\beta N^n + N_2^n \text{ "primary" nitrogen}$$

$$\text{fraction} \downarrow 1-m$$

$$Ar{-}N\overset{\beta}{\underset{\alpha}{\diagup}} \begin{cases} \overset{\beta}{N}{=}N^n \xrightarrow{50\%} ArN^\alpha N^\beta N^n + N^n{\equiv}N^n \\[2mm] {\searrow} \\ N^n{=}N^n \xrightarrow{50\%} ArN^\alpha N^n N^n + N^\beta{\equiv}N^n \end{cases}$$

"secondary" nitrogen

Let us define the terms

m, the fraction of "primary" nitrogen
f_S, the atom fraction of N^{15} in the "secondary" nitrogen
f_A, the atom fraction of N^{15} in nitrogen from reduction of aryl azide
f_D, the atom fraction of N^{15} in the α-position of the diazonium salt
f_N = natural abundance of N^{15}
p, the fraction of molecules of diazonium salt which have undergone the turnaround reaction 1

It is then easy to derive two equations, 2 and 3, assuming no isotope effect in the cleavage of the arylpentazole.

(1) A portion of this paper was published in preliminary form: J. M. Insole and E. S. Lewis, *J. Am. Chem. Soc.*, **85**, 122 (1963); part IX is ref. 3.
(2) For example, E. S. Lewis, *ibid.*, **80**, 1371 (1958).
(3) E. S. Lewis and J. E. Cooper, *ibid.*, **84**, 3847 (1962).
(4) K. Clusius and H. Hürzeler, *Helv. Chim. Acta*, **37**, 798 (1954).
(5) R. Huisgen and I. Ugi, *Chem. Ber.*, **90**, 2914 (1957).