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Protonolysis of the Tin–Hydrogen Bond. Kinetics and Mechanism[1a,1b]

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The kinetics of protonolysis of tri-n-butyltin hydride in acidic and basic methanol solutions have been studied. The acid reaction is subject to general acid catalysis with a Brönsted $\alpha = 0.58$. The data for both acid- and base-catalyzed reactions are consistent with a rate-determining proton and hydride transfer. The base-catalyzed reaction is believed to proceed through the pre-equilibrium formation of a pentacovalent organotin intermediate. The kinetics of the reaction of triphenyltin hydride with perchloric acid were also examined.

Introduction

Although it is quite generally known that metal hydrides will react with proton donors, the number of kinetic studies which have been made on such systems is limited. Reaction systems of this sort are unique in that they involve the three possible oxidation states of hydrogen in the hydride, acid, and product hydrogen. They are also interesting in that they can involve both hydride and proton transfers in the rate-determining step.

The first kinetic study of such a system was that initiated by Price[2] on the base-catalyzed hydrolysis of silanes. This reaction has since been studied in further detail by Gilman and Dunn,[3] Kaplan and Wilzbach,[4] and Steward and Pierce.[5] The results of these studies show the reaction to be first order in silane, hydroxide, and probably water, and will support a mechanism which involves either pre-equilibrium attack of hydroxide on the silane, followed by rate-determining hydrolysis, or a termolecular mechanism involving simultaneous attack of both hydroxide and water on the silane.

Among the recent studies of hydride transfers is the work of Hawthorne and Lewis[6] on the hydrolysis of pyridinediphenylborane. The authors concluded that this reaction was first order in both borane and water and that the reaction must proceed by a rate-controlling formation of a transition state which involves both B–H and O–H bond rupture. Swain and Davis, et $al.$,[7a,7b] and Dessy and Grannen[7c] have reported studies of borohydride solvolysis which are consistent with general acid catalysis involving rate-determining B–H and H–A bond breaking.

Recent work in these laboratories[8–10] on organotin compounds, as well as the current interest in isotope effects and acid catalysis, prompted a study of the kinetics of the tin hydride–acid reaction.

Krause and Greer[11] have reported that the reaction between trimethyltin hydride and hydrochloric acid

$$(CH_3)_3SnH + HCl \longrightarrow H_2 + (CH_3)_3SnCl \quad (1)$$

proceeds quantitatively at room temperature. Anderson[12] has reported that the reaction between triethyltin hydride and acetic acid proceeds quantitatively at reflux. An extensive study of organotin compounds by Noltes and van der Kerk[13] has verified the above results and indicates that the reaction between organotin monohydrides and acids is quite general.

In addition, Noltes and van der Kerk found that the base-catalyzed solvolysis of organotin hydrides (eq. 2) also proceeds rapidly at room temperature.

$$R_3SnH + CH_3O^- + CH_3OH \longrightarrow R_3SnOCH_3 + H_2 + CH_3O^- \quad (2)$$
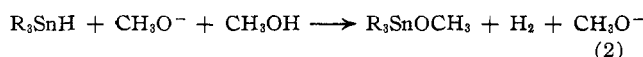
The solvolysis reactions of tin hydrides are of special interest then, since they may involve a hydride transfer in the rate-determining step as well as general acid and general base catalysis. This paper describes an investigation of the kinetics of these reactions.

Results and Discussion

It was convenient to study the course of the reaction manometrically, since the hydrogen-forming reaction between tin hydrides and proton donors is unaccompanied by side reactions. The technique was similar to that employed by DeTar[14] and is described in detail in the Experimental section. Tri-n-butyltin hydride was used in most of the investigation since its properties were desirable for storage and manipulation and it could be carefully purified by distillation. Since tetrahydrofuran (THF) is generally known to be a suitable solvent for hydride reactions, it was chosen as the initial solvent; later water was added to the THF to increase the rate; and finally methanol was chosen as the most satisfactory solvent for the present investigation.

Acid Catalysis.—Oxalic acid was the first acid chosen for study and gave acceptable results.[15] The kinetics of its reaction with tri-n-butyltin hydride were determined in 30% H_2O–THF (v./v.). Sufficient data were obtained with this system to demonstrate that the reaction obeyed second-order kinetics, first order in hydride and acid, over greater than 85% of the total reaction. It was necessary to employ an excess of acid in all of these studies since a very slow solvolysis of the product ester does occur under the conditions of the experiment and the regenerated acid may react with hydride if the latter is present in excess. In the initial stages of our experimentation rate increases become apparent at higher acid concentrations which were

(1) (a) Based on the doctoral dissertation of P. L. Levins, Sept., 1960; (b) This work was supported in part by the Office of Ordnance Research, United States Army, and the M & T Chemical Corp. Reproduction in whole or in part is permitted for any purpose of the United States Government; (c) Arthur D. Little, Inc., 15 Acorn Park, Cambridge 40, Mass.

(2) F. D. Price, $J. Am. Chem. Soc.$, **69**, 2600 (1947).

(3) H. Gilman and G. E. Dunn, $ibid.$, **73**, 3404 (1951).

(4) L. Kaplan and K. E. Wilzbach, $ibid.$, **77**, 1297 (1955).

(5) O. W. Steward and Q. R. Pierce, $ibid.$, **81**, 1983 (1959).

(6) M. F. Hawthorne and E. S. Lewis, $ibid.$, **80**, 4296 (1958).

(7) (a) R. E. Davis and C. G. Swain, $ibid.$, **82**, 5949 (1960); (b) R. E. Davis, C. L. Kirby, and C. G. Swain, $ibid.$, **82**, 5950 (1960); (c) R. E. Dessy and E. Grannen, Jr., $ibid.$, **83**, 3953 (1961).

(8) H. G. Kuivila and O. F. Beumel, Jr., $ibid.$, **83**, 1246 (1961).

(9) A. K. Sawyer and H. G. Kuivila, $ibid.$, **82**, 5958 (1960).

(10) H. G. Kuivila, L. W. Menapace, and C. R. Warner, $ibid.$, **84**, 3584 (1962).

(11) G. A. Krause and W. N. Greer, $ibid.$, **44**, 2629 (1922).

(12) H. H. Anderson, $ibid.$, **79**, 4913 (1957).

(13) J. G. Noltes and G. J. van der Kerk, "Functionally Substituted Organotin Compounds," Tin Research Institute, Greenford, Eng., 1958.

(14) D. F. DeTar, $J. Am. Chem. Soc.$, **78**, 3911 (1956).

(15) Halogenated carboxylic acids appeared to undergo an additional side reaction involving consumption of the tin hydride without hydrogen formation. Noltes and van der Kerk have reported that triphenyltin hydride reduces allyl chlorides forming triphenyltin chloride and the corresponding alkene (see ref. 13, p. 72). Recent publications[16,16] have demonstrated the use of tin hydrides as reducing agents for carbon–halogen bonds.

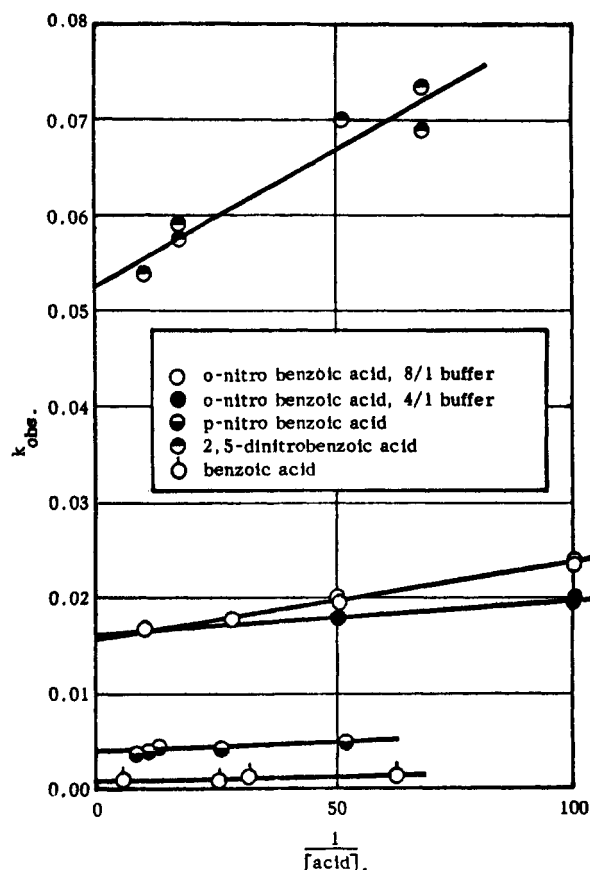(16) D. H. Lorenz and E. I. Becker, $J. Org. Chem.$, **27**, 3370 (1962).

Fig. 1.—Buffer treatment for benzoic acid reactions.

solely dependent on the acid concentration and not readily explained. As a result of these anomalies, the solvent was changed to anhydrous methanol and o-nitrobenzoic acid was chosen for study. Initial results with an unbuffered system were quite similar to those obtained with oxalic acid, so buffered systems were examined.

If the following reactions are important

$$Bu_3SnH + HA \xrightarrow{k_{HA}} products \quad (3)$$

$$Bu_3SnH + H^+ \xrightarrow{k_{H^+}} products \quad (4)$$
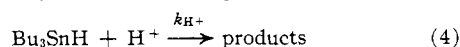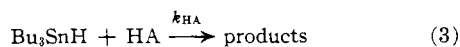
then, in a buffered system at constant ionic strength, the following rate expression should satisfactorily correlate the data, if the reaction is subject to general acid catalysis.

$$rate = k_{obsd}[Bu_3SnH][HA] = [Bu_3SnH]\{k_{HA}[HA] + k_{H^+}[H^+]\} \quad (5)$$

$$k_{obsd} = k_{HA} + k_{H^+}[H^+]/[HA] \quad (6)$$

A plot of k_{obsd} vs. $1/[HA]$ should give an intercept value of k_{HA} and a slope equal to $k_{H^+}[H^+]$. The rates of reaction of tri-n-butyltin hydride with 2,5-dinitrobenzoic, o-nitrobenzoic, p-nitrobenzoic, and benzoic acid buffers in methanol, adjusted to a total salt concentration of 0.1000 M by the addition of sodium perchlorate, were measured. Two different buffer ratios were used with o-nitrobenzoic acid in order to check further on the manner of treating the data. The data obeyed second-order kinetics over at least 80% of each reaction and the results obtained are listed in Table I. Initial concentrations of hydride were in the range of 0.005 to 0.01 M. The graphical treatment of the data by the method of least squares is shown in Fig. 1. The intercepts and slopes obtained from these lines are given in Table II.

TABLE I

OBSERVED RATE CONSTANTS FOR THE REACTION OF TRI-n-BUTYLTIN HYDRIDE WITH BENZOIC ACID BUFFERS

Run no.	1/[acid]	$k \times 10^2$, M^{-1} sec.$^{-1}$
o-Nitrobenzoic acid, [acid]/[base] = 4.00		
48	10.0	1.69
49	10.0	1.68
155	50.0	1.76
156	50.0	1.78
50	100.0	1.99
145	100.0	1.95
146	100.0	2.00
o-Nitrobenzoic acid, [acid]/[base] = 8.00		
61	10.2	1.68
62	25.6	1.78
149	50.0	1.95
150	50.0	2.01
151	100.0	2.40
152	100.0	2.36
2,5-Dinitrobenzoic acid, [acid]/[base] = 4.00		
68	10.2	5.39
163	17.1	5.75
164	17.1	5.90
70	51.2	7.00
167	68.4	7.34
168	68.4	6.90
p-Nitrobenzoic acid, [acid]/[base] = 4.00		
74	8.39	0.398
71	10.2	.399
75	12.6	.406
76	25.2	.434
73	51.1	.486
Benzoic acid, [acid]/[base] = 4.00		
79	5.02	0.113
80	5.02	.103
82	25.1	.0946
66	31.3	.121
67	62.6	.135

TABLE II

CORRELATION DATA FOR THE BUFFERED REACTION SYSTEMS

Benzoic acid	$k_{HA} \times 10^2$, M^{-1} sec.$^{-1}$	$[H^+]^a$	$k_{H^+}[H^+]$, sec.$^{-1}$	k_{H^+}, M^{-1} sec.$^{-1}$
o-Nitro (4/1)	1.63	7.1×10^{-7}	3.37×10^{-5}	47.4
o-Nitro (8/1)	1.59	1.55×10^{-6}	7.89×10^{-5}	50.9
2,5-Dinitro	5.24	4.8×10^{-7}	2.84×10^{-4}	59.0
p-Nitro	0.380	4.0×10^{-7}	2.09×10^{-4}	52.2
Benzoic	0.101	5.7×10^{-8}	4.77×10^{-6}	83.7

^{a} From pH measurements.

Using pH measurements as an indication of the lyonium ion concentration, one may obtain rate constants for the lyonium ion, k_{H^+}, by dividing the slopes of the plots $(k_{H^+}[H^+])$ by the corresponding lyonium ion concentrations. These results are also listed in Table II. The agreement among the k_{H^+} values is fair, with the only serious discrepancy being the value obtained from the benzoic acid data, for which the experimental errors were larger as a result of its slow reaction rate. The remainder of the k_{H^+} values are identical within the accuracy of the pH measurements.

The validity of the calculated k_{H^+} values may be tested by comparison with the observed rate constant obtained for the reaction with perchloric acid. Results obtained with perchloric acid are listed in Table III. The agreement between these observed values and the values calculated from the buffer data is quite satisfactory and further supports the reaction scheme and rate expression put forward above. It also indicates that the same lyonium species is involved in the buffer systems and in the perchloric acid reactions.

TABLE III

OBSERVED RATE CONSTANTS FOR THE PERCHLORIC ACID
REACTION

Run	$HClO_4 \times 10^4$	k_{obsd}, M^{-1} sec.$^{-1}$
100	7.25	50.6
101	7.25	52.4
103	4.36	54.5
104	4.36	50.5
106	3.64	50.4
		Av. 51.7 ± 1.4

The reaction of tri-n-butyltin hydride with solvent methanol was studied in order to increase the range of reactivities available for use with the hydrogen isotope study. The results obtained are given in Table IV. Since the reaction proceeds quite slowly, the final pressures used in the kinetic treatment of the data were those calculated on the basis of the initial amount of hydride. The reaction exhibited good first-order kinetics over the 20% reaction range usually studied. The second-order rate constants were obtained by dividing the observed first-order rate constants by the molar concentration of methanol.

TABLE IV

OBSERVED RATE CONSTANTS FOR METHANOL

Run	$k_{obsd} \times 10^6$, sec.$^{-1}$	$k \times 10^8$, M^{-1} sec.$^{-1a}$
196	1.48	6.04
197	1.14	4.65
198	1.36	5.55
199	1.47	6.00
		Av. 5.7 ± 0.3 × 10^{-8}

^{a} [CH$_3$OH] = 24.5 M.

The data obtained thus far were tested with the statistically corrected form of the Brönsted relation (eq. 7) in which k is the specific rate constant for a particular acid whose dissociation constant in methanol is

$$\log \frac{k}{p} = \alpha \log \left(\frac{q}{p} K_A \right) + \log G \qquad (7)$$

K_A, α and G are constants characteristic of the system, p is the number of equivalent protons in the acid, and q is the number of equivalent positions where a proton may be accepted in the conjugate base.[17] The data are listed in Table V. Figure 2 represents the least squares correlation of the data; the equation of the line is

$$\log \left(\frac{k}{p} \right) = 0.580 \log \left(\frac{q}{p} K \right) + 2.43 \qquad (8)$$

TABLE V

PERTINENT DATA FOR THE BRÖNSTED CORRELATION

Acid	k, M^{-1} sec.$^{-1}$	$-\log K$	p	q	$-\log (k/p)$	$-\log \left(\frac{q}{p} K \right)$
o-Nitrobenzoic	0.0161	7.580^a	1	2	1.793	7.279
Benzoic	.00101	9.422^a	1	2	2.996	9.121
2,5-Dinitrobenzoic	.0524	7.04^d	1	2	1.281	6.74
p-Nitrobenzoic	.00380	8.349^a	1	2	2.420	8.048
Methanol	5.7 × 10^{-8}	16.7^b	1	1	7.244	16.7
Perchloric	52	(1.80)^c	1	4	-1.716	(1.20)^c

^{a} J. H. Elliott and M. Kilpatrick, $J.$ $Phys.$ $Chem.$, **45**, 454 (1941). ^{b} R. W. Guerney, "Ionic Processes in Solution," McGraw-Hill Book Co., Inc., New York, N. Y., 1953, p. 236. ^{c} Extrapolated ^{d} Calculated on the assumption that the same proportional change occurs between benzoic acid and 2,5-dinitrobenzoic acid in methanol as in water.

Extrapolation of the line defined by the solvent and benzoic acids to the point corresponding to the perchloric acid reaction leads to a value of 0.016 for the dissociation constant of perchloric acid in methanol. Marshall and Grunwald[18] have reported ion-pair dis-

(17) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 209 ff.
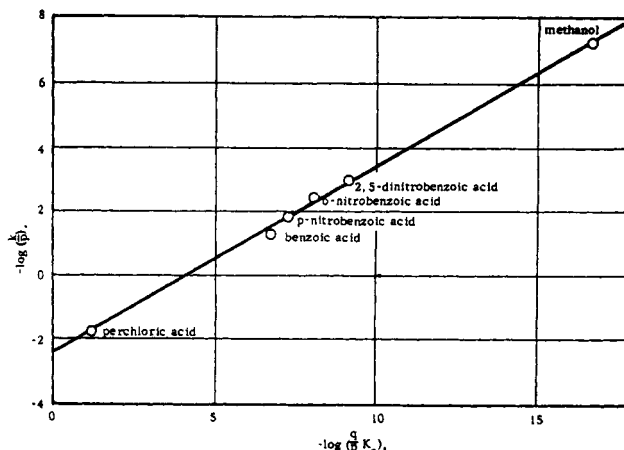

Fig. 2.—Brönsted correlation: $\log (k/p) = 0.580 \log (q/pK) + 2.43$.

sociation constants of hydrochloric acid in methanol ranging from 0.068 to 0.041. This similarity in magnitude of dissociation constants suggests that perchloric acid in methanol also exists largely in the form of ion-pairs.

Expanding the kinetic study to include triaryltin hydrides offered the potential of being able to study the effect of substituents on the aromatic nucleus in hopes of developing a better understanding of the transition state. When an attempt was made to study the reaction with o-nitrobenzoic acid, hydride was consumed without evolution of gas. Noltes and van der Kerk[13] have recently reported that triphenyltin hydride reacts with p-nitrostyrene forming hexaphenylditin. Presumably nitro group reduction occurs in each instance. The reaction of triphenyltin hydride with perchloric acid did proceed quantitatively and the rate data obtained are listed in Table VI. These results demonstrate that the tri-n-butyltin hydride reaction is 87 times faster than the analogous reaction with triphenyltin hydride. It is difficult to attach much significance to these results without further study, although the lower reactivity suggests that electron donation by the phenyl group, through d_π–p_π bonding, is not significant in the ground state. Fluorine n.m.r. studies[19] on m- and p-substituted trimethyl-(fluorophenyl)-tin give values of $\sigma_R = 0.02$ and $\sigma_I = 0.04$ for $(CH_3)_3Sn-$. The lower reactivity may be due solely to the inductive electron-withdrawing effect of the phenyl group.

TABLE VI

RATE CONSTANTS FOR THE PERCHLORIC ACID REACTION OF
TRIPHENYLTIN HYDRIDE

Run	$HClO_4$	k, M^{-1} sec.$^{-1}$
212	0.04732	0.501
213	.02366	.683
214	.02366	.690
		Av. 0.614

There are a number of mechanistic possibilities for the acid-catalyzed reaction which will satisfy the observations already presented.[20] The observation of general acid catalysis restricts the choice to a few possibilities. The reaction might proceed by a rate-determining proton transfer (eq. 9), in which case either the molecular acid or the kinetically indistinguishable anion–lyonium ion conjugate pair may be involved. The reaction
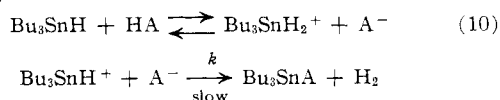
$$Bu_3SnH + HA \xrightarrow[\text{slow}]{k} Bu_3SnA + H_2 \qquad (9)$$
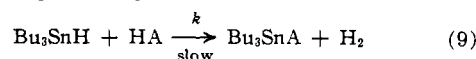
(18) H. P. Marshall and E. P. Grunwald, $J.$ $Chem.$ $Phys.$, **21**, 2143 (1953).
(19) R. W. Taft and P. L. Levins, unpublished results.
(20) An extensive discussion of the acid-catalyzed reactions may be found in ref. 17, p. 204 ff.

might also proceed by a pre-equilibrium proton transfer (eq. 10).

$$Bu_3SnH + HA \rightleftharpoons Bu_3SnH_2^+ + A^- \qquad (10)$$

$$Bu_3SnH^+ + A^- \xrightarrow[slow]{k} Bu_3SnA + H_2$$

Although these mechanistic possibilities are kinetically indistinguishable, they may be differentiated by measurement of the hydrogen isotope effect. A detailed discussion of the observed isotope effects will be presented at a later date. The observation of large normal isotope effects for the acids and the existence of a tin–hydride isotope effect support the former mechanism (eq. 9) which does not involve the symmetrical protonation required by eq. 10. The data are best explained by a mechanism involving rate-determining electrophilic attack of the Sn–H bond by molecular acid. By analogy with the discussion of Hawthorne and Lewis,[6] we prefer a three-center transition state which may be represented as

$$Bu_3Sn\text{----}H$$
$$\diagdown \diagup$$
$$H$$
$$|$$
$$A$$
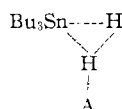
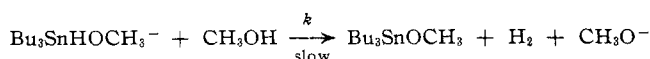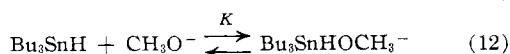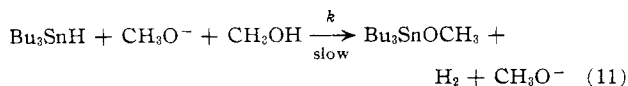where the broken lines refer to bonds of unspecified strength.

Base Catalysis.—The reaction between tri-n-butyltin hydride and sodium methoxide in methanol was studied in order to extend further the range of experiments available for a study of the solvent hydrogen isotope effect and to determine the mechanism of the reaction. The results obtained are shown in Table VII.

TABLE VII

RATE CONSTANTS FOR THE BASE-CATALYZED REACTION

Run	[CH₃ONa]	$k_{obsd} \times 10^3$, sec.$^{-1}$	$k \times 10^4$, M^{-2} sec.$^{-1}$
117	0.09916	2.05	8.10
118	.04958	1.05	8.14
176	.07500	1.65	8.98
177	.07500	1.60	8.74
178	.02500	0.530	8.67
179	.02500	0.512	8.38
256	.1000	1.73	7.95
263	.1000	2.03	8.30
264	.1000	2.09	8.55
		Av.	8.42 ± 0.28

The rate experiments obeyed first-order kinetics. Upon dividing the observed first-order rate constants by the concentration of base, a single value is obtained for the rate constant indicative of a pseudo-first-order reaction

$$Bu_3SnH + CH_3O^- + CH_2OH \xrightarrow[slow]{k} Bu_3SnOCH_3 +$$
$$H_2 + CH_3O^- \qquad (11)$$

$$Bu_3SnH + CH_3O^- \underset{}{\overset{K}{\rightleftharpoons}} Bu_3SnHOCH_3^- \qquad (12)$$

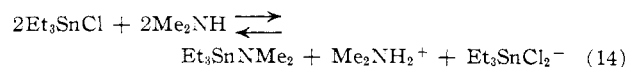$$Bu_3SnHOCH_3^- + CH_3OH \xrightarrow[slow]{k} Bu_3SnOCH_3 + H_2 + CH_3O^-$$

reaction. The reaction may therefore be represented by either eq. 11 or 12, each of which satisfies pseudo-first-order kinetics, since methanol, as solvent, is present in large excess and the methoxide ion is present in constant concentration, because it is regenerated. Although the rate data are correlated by eq. 13, the

$$rate = k_{obsd} C_{Bu_3SnH} C_{CH_3O}^- \qquad (13)$$

rate constants are listed in column 4 of Table VII as third-order rate constants by dividing the k_{obsd} by the concentration of both methoxide and methanol, since there must be at least one solvent molecule intimately

involved in the transition state as suggested by the hydrogen isotope effects which will be presented in detail at a later date. Although it is not possible to distinguish between mechanisms 11 and 12 from the data presented thus far, evidence available in the literature suggests that the latter may be more likely.

Eaborn, et al.,[21] have suggested that the large difference in reactivity is going from silicon and germanium to tin, in the perchloric acid cleavage of aryl compounds of the group IV elements, may be due to the ability of tin to utilize its vacant d-orbitals in further coordination. The relative acidities of the compounds p-R₃-MC₆H₄COOH, where M = C, Si, Ge, and Sn and R = CH₃ and C₂H₅, determined by Chatt and Williams,[22] suggest about equal degrees of $d_\pi-p_\pi$ bonding for Si, Ge, and Sn. Schmitz-DuMont and Bungard[23] suggest a pentacovalent tin atom in the product formed from reaction of triphenyltin chloride with sodium triethoxyaluminum hydride. Joshi and Wyatt[24] have presented strong evidence for the existence of a 1:1 complex between triethyltin chloride and 1°, 2°, and 3° amines. They suggest that eq. 14 and 15 represent the equilibria between triethyltin chloride and dimethylamine, dependent on the amounts of reactants used. Beattie, McQuillan, and Hulme[25] have recently demonstrated

$$2Et_3SnCl + 2Me_2NH \rightleftharpoons$$
$$Et_3SnNMe_2 + Me_2NH_2^+ + Et_3SnCl_2^- \qquad (14)$$

$$2Et_3SnCl + Me_2NH \rightleftharpoons Et_3SnNHMe_2^+ + Et_3SnCl_2^- \qquad (15)$$

that the trimethyltin chloride–pyridine adduct consists of monomeric covalent units with a trigonal bipyramidal coordination around the tin atom.

The results of studies on the base-catalyzed hydrolysis of silanes[1–4] show the reaction to be first order in silane and hydroxide and probably first order in water, which is usually present in large excess. The data will support either a pre-equilibrium mechanism similar to eq. 12 or a termolecular mechanism similar to eq. 11. Sommer, et al.,[26] have postulated a pentacovalent complex in the base-catalyzed hydrolysis of 1-methyl-1-silacyclobutane and suggest that such a complex is involved in the reaction with bridgehead and acyclic silanes as well.

Analogy with the evidence presented above, in addition to the fact that the rate plots for the present study always showed a slight decrease in rate after 85–90% reaction, possibly due to reaction between base and products (eq. 16), suggests that a likely course of reac-

$$Bu_3SnOCH_3 + CH_3O^- \rightleftharpoons Bu_3Sn(OCH_3)_2^- \qquad (16)$$

tion may be that represented by eq. 12.

The reaction between sodium methoxide and triphenyltin hydride was studied, but did not proceed as expected. Rather than a reaction similar to that for tri-n-butyltin hydride, decomposition occurred giving half a mole each of hydrogen and hexaphenylditin per mole of hydride (eq. 17).

$$2(C_6H_5)_3SnH \xrightarrow[CH_3OH]{NaOCH_3} H_2 + [(C_6H_5)_3Sn]_2 \qquad (17)$$
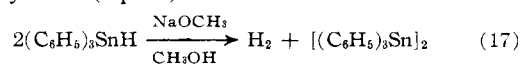
Experimental

Reagents. Tri-n-butyltin hydride was prepared according to the method of van der Kerk, et al.,[27] in 85% yield. The frac-

(21) (a) C. Eaborn and K. C. Pande, J. Chem. Soc., 1566 (1960); (b) C. Eaborn and J. A. Waters, ibid., 542 (1961).

(22) J. Chatt and A. A. Williams, ibid., 4403 (1954).

(23) O. Schmitz-DuMont and G. Bungard, Ber., 92, 2399 (1959).

(24) K. K. Joshi and P. A. H. Wyatt, J. Chem. Soc., 1566 (1959).

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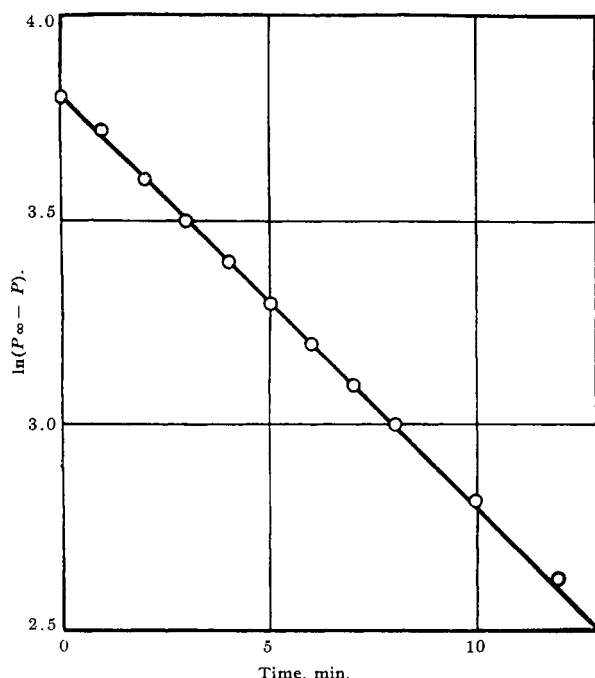(27) G. J. van der Kerk, J. G. Noltes, and J. G. A. Lutjen, J. Appl. Chem., 7, 366 (1957).

Fig. 3.—First-order rate plot for run 176: [Bu$_3$SnH] = 0.00664 M, [NaOCH$_3$] = 0.0750 M, k = 1.65 × 10^{-3} sec.$^{-1}$.

tion boiling at 80–83° (0.5 mm.) was collected and stored in scrupulously cleaned, evacuated ampoules (adventitious impurities in the ampoules caused hydride decomposition); infrared spectrum (smear) 1810 cm.$^{-1}$.

Triphenyltin hydride was prepared according to the above procedure from triphenyltin chloride and the fraction boiling at 196–200° (2.5 mm.) was collected; yield 59%.

Tetrahydrofuran was purified according to Fieser[28] and freshly distilled before use. Karl Fischer grade methanol (Matheson Coleman and Bell, 0.01% water) was used. All other materials were of the best grade commercially available.

pH Measurements.—Measurements were made using the technique of Grunwald and co-workers[29] employing the Cambridge Model R pH meter with glass and calomel electrodes. The glass electrode was pre-equilibrated in methanol for 1 week before use. The calomel electrode was filled with saturated methanolic potassium chloride solution and stored in the same solution. An o-nitrobenzoic acid buffer composed of 0.2000 N o-nitrobenzoic acid and 0.0500 N sodium o-nitrobenzoate was chosen as the standard at pH 6.253. Elliot and Kilpatrick[30] have reported pK_a = 6.855 at μ = 0.0500 for this acid in methanol. Measurements were accurate to ±0.05 pH unit.

Kinetic Methods.—The manometric technique of DeTar[14] was employed with a modification of the reaction flask.[31] The reaction flask contained a 5-ml. bucket mounted on a trapeeze which could be tipped at "zero" time by means of a glass rod rotated within a ground glass joint. This technique assured thorough mixing of the reactants and accurate temperature control as well as an extremely convenient means of controlling the starting time. The entire system, with the exception of the manometer, was maintained at 25.00 ± 0.02° as determined with a differential thermometer which had been

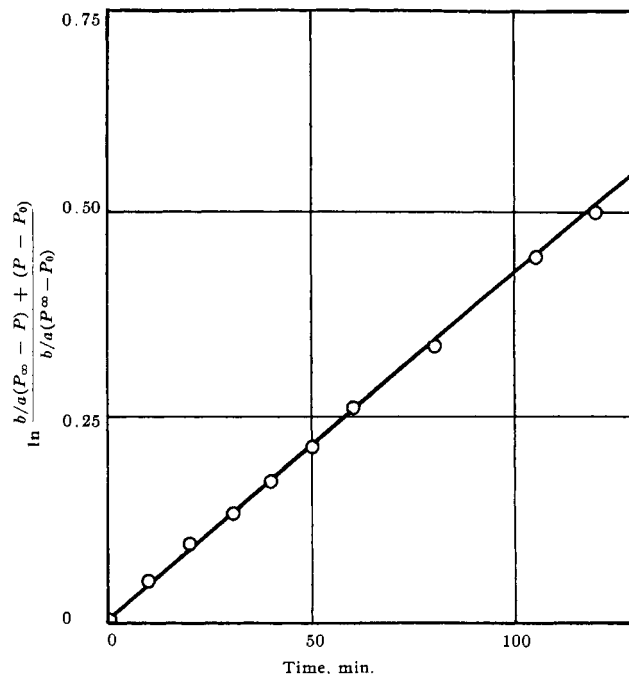(28) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 3rd Ed., 1955, p. 292.

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Fig. 4.—Second-order rate plot for run 146: a = [Bu$_3$SnH] = 0.00666 M, b = [o-NO$_2$C$_6$H$_4$COOH] = 0.0100 M, k = 1.65 × 10^{-3} sec.$^{-1}$.

calibrated against a thermometer calibrated at the National Bureau of Standards.

Buffer solutions were prepared from the appropriate amounts of acid and sodium methoxide. Perchloric acid solutions were prepared from 70% perchloric acid, since the water contamination at the desired concentrations was negligibly small. The normal protium acids were used for the runs in methanol-d, since exchange is rapid and the slight contamination by hydrogen is not important. Tin hydride solutions were prepared by diluting known weights of the hydride to the desired volume. A nitrogen atmosphere was used whenever hydride was present. Observed pressure changes were used as a measure of the initial hydride concentration. The actual concentrations were calculated by multiplying the theoretical concentrations by the per cent pressure change based on the weight of added hydride. The kinetic solutions were prepared by addition of the desired amounts of stock solutions to the reaction flask. The tin hydride solution was added to the bucket suspended in the reaction flask.

All of the rate experiments obeyed either first- or second-order kinetics, dependent on the system under investigation. Standard methods of treating the data were used; full development of the expressions is given by Frost and Pearson.[17] The observed first-order rate constants were obtained by use of the equation

$$\ln (P_\infty - P) = -kt$$

where P is the pressure at some time t and P_∞ is the final pressure reading, usually obtained after at least 6 half-lives. Figure 3 shows a representative first-order rate plot. Second-order rate constants were obtained from the equation

$$(b - a)kt = \ln \frac{b/a (P_\infty - P_0) - (P - P_0)}{a(P_\infty - P)}$$

where b and a represent the initial concentrations of acid and hydride, respectively, P_∞ is the final pressure, P_0 the initial pressure, P the pressure at time t, and k is the observed second-order rate constant. Figure 4 shows a representative second-order rate plot.