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KINETICS AND MECHANISM OF
THE PROTONOLYSIS OF CERTAIN ALLYLTINS

BY

JOSEPH ANTHONY VERDONE

B.S., Lebanon Valley College, 1958

A THESIS

Submitted to the University of New Hampshire
In Partial Fulfillment of
The Requirements for the Degree of
Doctor of Philosophy

Graduate School
Department of Chemistry
November 1963

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ACKNOWLEDGEMENTS

The author wishes to thank Dr. Henry G. Kuivila for his guidance and patience throughout the course of this work.

Financial support from the Air Force Office of Scientific Research for part of this work is gratefully acknowledged.

Joseph A. Verdone

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SECTION I

INTRODUCTION

Electrophilic substitution which involves cleavage of a carbon-metal bond has commanded increasing attention in recent years. The Group IV metals have been examined in particular detail; the general reactions of the tetra-substituted Group IV metals with two commonly employed electrophiles, halogen and halogen acid, may be expressed as:

$$(1) \quad R_4M + HX \longrightarrow R_3MX + RH$$

$$(2) \quad R_4M + X_2 \longrightarrow R_3MX + RX$$

where R = alkyl or aryl

M = silicon[1], germanium, tin, or lead[2]

Extensive investigation of the mechanism of this reaction where an aryl-metal bond is cleaved has been reported by Eaborn and coworkers[3]. The rates of cleavage of substituted arylgermanium, -silicon, and -tin derivatives by both acids and halogens have been measured, and substituent effects discussed in detail. Aryl-tin cleavage proceeds most readily, and is found to be much less sensitive to the resonance effects of substituents than either aryl-silicon or aryl-germanium cleavage. The second order rate constant for the cleavage of phenyltrimethyltin by perchloric acid in 4% water-ethanol at 50° is found to be $5.2 \times 10^{-4}\ M^{-1}sec.^{-1}$

Organomercurials, although not members of the Group IV series, display similar behavior when subjected to electrophilic attack. Dessy and coworkers[4] have measured the rates of cleavage of certain dialkyl mercury compounds by acids in water-dioxane solvent. A four-center mechanism, which features attack by molecular acid or acid existing as ion pairs on the mercury-carbon σ bond, was proposed. Water added to the solvent system was found to decrease the rate, and chloride ion found to increase the rate markedly although ionic strength effects were found to be small.

In a more recent paper, Dessy and Paulik[5] have focused attention on the "assistor" role of chloride ion. The acid decomposition of certain carbomethoxymercurials in dimethyl sulfoxide in the presence of chloride ion gave an empirical rate expression first order in organomercurial, in acid, and in chloride ion. The stoichemetric expression may be written as:

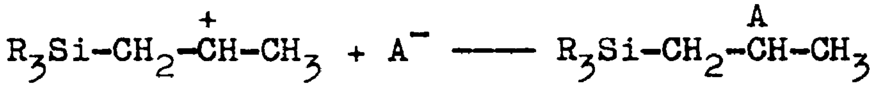
$$(3) \quad ClHgCOOCH_3 + 3Cl^- \xrightarrow[DMSO]{CF_3COOH} HgCl_4^{-2} + CO + CH_3OH$$

Two chloride ions are involved in a post-rate determining step. The role of chloride is envisioned as a coordination of chloride ion with the mercury atom in a step which precedes the attack of acid, which is regarded as the rate determining step. Nucleophilic assistance of this kind, Dessy states, will be observable whenever the solvent is relatively ineffective both as a nucleophile and in its ability to solvate ions. Thus protic solvents, which strongly solvate anions and may themselves be effective nucleophiles, will render the "assistance" phenomenon difficult to observe, while aprotic solvents such as dimethyl sulfoxide will enhance observation of the effect.

When an allyl group is attached to the metal atom, cleavage by electrophilic reagents proceeds most readily. Thus the allyl group cleaves in preference to vinyl or phenyl when it is attached to silicon[6,7], germanium[8], tin[9], lead[10,11], or mercury[12].

The general aim of this study was the elucidation of the mechanism of cleavage of allyltin derivatives by acids, using primarily kinetic studies to infer the structure of the transition state. At the time these studies were begun, no formal study of mechanism had been reported on allyl-metal cleavage of the Group IV series, although Whitmore and coworkers[6], in order to account for products of the reaction of allylsilanes with acids, had described the course of cleavage of allylsilanes as a two-step process in which protonation occurs at the terminal allylic carbon to give a carbonium ion in the first step. Attack by nucleophile in a second step completes the cleavage. Alternatively, the nucleophile may add to the carbonium ion as shown in step (5).

$$(4) \quad R_3Si - CH_2 - CH = CH_2 \xrightarrow{H^+A^-} R_3Si - CH_2 - \overset{+}{C}H - CH_3$$

(5) 

$$R_3Si-CH_2-\overset{+}{C}H-CH_3 + A^- \text{——} R_3Si-CH_2-\overset{A}{C}H-CH_3$$

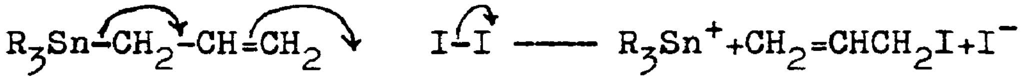
(Addition)

(6) $$R_3Si-CH_2-\overset{+}{C}H-CH_3 + A^- \text{——} R_3SiA+CH_2=CH-CH_3$$

(Cleavage)

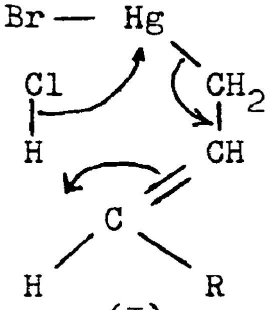
Hydrogen chloride and sulfuric acid gave only cleavage products, while hydrogen bromide gave both cleavage and addition products.

During the course of our investigation, Gielen and Nasielski[13] reported rates of cleavage of tetrallyltin by iodine in acetone solvent, and advanced an SE2' mechanism to account for the fact that tetrallyltin is cleaved about eight powers of ten more rapidly than tetra-n-propyltin. They represented the mechanism as:

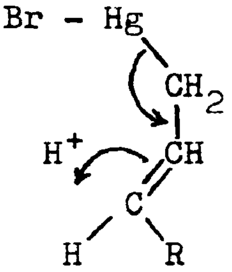
(7) 

$$R_3Sn-CH_2-CH=CH_2 \quad I-I \text{——} R_3Sn^+ + CH_2=CHCH_2I + I^-$$

A recent communication by Sleezer, Winstein, and Young[12] provided direct evidence for the SE' mechanism in allyl-metal cleavage. Both hydrochloric acid and perchloric acid cleaved crotyl- and cinnamyl-mercuric derivatives to give 1-butene and allylbenzene, respectively, as nearly exclusive cleavage products. With hydrogen chloride in diethyl ether, the SEi' description (I) is advanced. The SE2' path (II) seems consistent with perchloric acid in acetic acid as the electrophile. Either structure will collapse to give 1-butene (when R is methyl) or allylbenzene (when R is phenyl).



(I)



(II)

Crotylmercuric bromide was reported to react more rapidly than the n-butyl analog by a factor of 10^7.

The present study includes measurements of the rates of acid cleavage of allyltin derivatives in methanol and in water-methanol solvents. Salt effects, including the complex dependence of the rate on concentration of added chloride ion, are discussed. A study of the products of cleavage of crotyltin derivatives is presented; the results are parallel to those reported by Winstein and coworkers[12] for the crotylmercury derivatives. The mechanism is discussed in the final section, where experimental findings are reviewed in summary form, and correlations of the effect of structure on rate are advanced.

SECTION II

RESULTS AND DISCUSSION

Preliminary Investigations

Conductimetric Method for Following Rate of Cleavage

The reaction of allyltrialkyltin with hydrochloric acid to give trialkyltin chloride and propylene is quantitative, and proceeds with a net decrease in conductance in a polar solvent system. Accordingly, a conductimetric method was first investigated as a means of measuring the rate of cleavage. Diallyldibutyltin was investigated briefly but discarded because of its instability. Allyltributyltin was investigated in solvents which included dioxane, dioxane-dimethyl sulfoxide in varying proportions, and dioxane-water mixtures. The conductimetric method, described in the Appendix, did not yield useful results with either tin substrate in any of the solvent systems employed.

All systems investigated obeyed second order kinetics -- first order in acid and first order in allytin substrate -- over a limited extent of the reaction. The kinetic treatment used has been described in detail by Dessy,[4] and is applicable when the concentration of one reactant is directly proportional to conductance. Dessy had already shown that hydrochloric acid fulfills this condition in the solvent systems employed; this was confirmed by appropriate measurements. Consequently, when the rate plots proved to be non-linear, the contribution of the product trialkyltin chloride to the total conductance was measured. This did not account for the observed curvature, although it was subsequently shown that the rate of cleavage of allyltrimethyltin by hydrochloric acid in methanol could be followed conductimetrically if one applied a correction for the conductance due to solvent, and measured initial rates.

Selection of Substrate and Acid

Early in the investigation it was discovered that water reacts very quickly with diallyldibutyltin to give a white solid. This tin substrate could not be employed in aqueous media, and attention was focused on allyltributyltin, which could be synthesized readily, and possessed desirable handling properties. Purification of this substrate was accomplished by fractionation.

Hydrogen chloride was chosen as the electrophile since it is moderately dissociated in solvents of low polarity[14] and its reactions with tetrasubstituted organatins have been investigated in some detail by van der Kerk[15] and others.[16]

Spectrophotometric Method and Selection of Solvent

An examination of the ultraviolet spectrum of allyltributyltin in methanol revealed an unexpectedly strong end absorption with a maximum occurring at 215 mμ. Extinctions measured at this wavelength would have a large uncertainty in methanol solvent, therefore measurements were made at 230 mμ, a part of the curve which is smoothly descending. Solutions of allyltributyltin obeyed Beer's law in the concentration range 3.4×10^{-5} M to 254×10^{-5} M. The extinction coefficient at 230 mμ is 6.65×10^{3} and the products of cleavage do not absorb at this wavelength.

Methanol possesses the necessary transparency in this region of the spectrum, and the necessary dissolving power for polar and non-polar substances. It was therefore chosen for studying the kinetics.

Products of Cleavage

Allyltributyltin was allowed to react with hydrochloric acid in dioxane-water in such quantities that the products could be isolated. Both tributyltin chloride and propylene were characterized by their infra-red spectra. The procedure is described in the Experimental section .

Reaction of Allyltributyltin and Hydrochloric Acid

The ultraviolet absorption made it possible to develop a spectrophotometric technique for following rates of reaction, and further attempts to develop the conductimetric technique, which has only narrow applicability in such a study, were not made.

Kinetic Treatment - Spectrophotometric Method

The kinetic procedure adopted for these runs involved removal of an aliquot from the reaction mixture, which was maintained at 25.00°C in a constant temperature bath, addition of the aliquot to a basic quenching solution which neutralized unreacted acid, and measurement of the optical density of the mixture. For most runs it was convenient to add a 5 ml. aliquot to 2 ml. of quenching solution. Details are related in the Experimental Section.

For a second order reaction with equal initial concentrations of both reactants:

$$(8)\quad \frac{1}{C_t} - \frac{1}{C_o} = k_2 t$$

where C_o = concentration of both reactants at zero time.

C_t = concentration of both reactants at time t.

For the spectroscopic method the following relationship applies:

$$(9)\quad E = \varepsilon c \ell$$

where E = optical density or extinction

c = concentration (moles/liter)

ε = extinction coefficient

ℓ = pathlength in cms ($\ell = 1$ throughout these studies)

The concentration of allyltin in a given aliquot of reaction mixture which has been quenched, C_{sample}, is given by:

$$(10)\quad C_{\text{sample}} = \frac{E_{\text{sample}}}{\varepsilon}$$

Since the aliquot has been diluted by the quenching process, the concentration in the reaction mixture, $C_{\text{rxn.mix.}}$, is:

$$(11)\quad C_{\text{rxn.mix.}} = \frac{7}{5}\, C_{\text{sample}} = \frac{7}{5}\, \frac{E_{\text{sample}}}{\varepsilon}$$

When the optical density at infinite time has a value other than zero, a correction must be made.

$$(12)\quad E_{\text{sample}} = (\, E_{\text{observed}} - E_{\infty}\,)$$

And one obtains:

$$(13)\quad \frac{1}{C_{\text{rxn.mix.}}} = \frac{5}{7}\, \frac{\varepsilon}{(E_{\text{obs.}} - E_{\infty})}$$

The second order expression becomes;

$$(14)\quad \frac{5}{7}\, \frac{\varepsilon}{(E_{\text{obs.}} - E_{\infty})_t} - \frac{5}{7}\, \frac{\varepsilon}{(E_{\text{obs.}} - E_{\infty})_o} = k_2 t$$

or

$$\frac{1}{(E_{\text{obs.}} - E_{\infty})_t} - \frac{1}{(E_{\text{obs.}} - E_{\infty})_o} = \frac{7\, k_2 t}{5\, \varepsilon}$$

A plot of $\frac{1}{(E_{obs.}-E_{\infty})_t}$ vs. t is linear with slope $\frac{7\ k_2t}{5\ \varepsilon}$ and intercept $\frac{1}{(E_{obs.}-E_{\infty})_o}$.

When initial concentrations of reactants were not equal, the following expression was used:

$$(15)\quad \frac{2.303}{(a-b)} \log \frac{b(a-x)}{a(b-x)} = k_2t$$

where a = initial concentration of reactant present in excess.

b = initial concentration of reactant present in limiting amount.

x = concentration of both a and b reacted at time t.

Optical density could be converted to concentration by the relationship:

$$(16)\quad x = C_{o_{rxn.mix.}} - C_{t_{rxn.mix.}} = \frac{7}{5}\ \frac{E_{o_{sample}} - E_{t_{sample}}}{\varepsilon}$$

A plot of log $\frac{a-x}{b-x}$ vs. t is linear with slope $\frac{k_2(a-b)}{2.303}$ and intercept log $\frac{a}{b}$.

When pseudo-first order conditions are employed

$$(17)\quad 2.303 \log (a-x) = k_1t$$

which, from equations (11) and (12) becomes:

$$(18)\quad 2.303 \log (E_{obs} - E_{\infty})_t = k_1t$$

In later kinetic studies, the quenching procedure was not employed. When $E \cong 0$, the expression used was:

$$(19) \quad 2.303 \log E_t = k_1 t$$

Typical rate plots are reproduced in Figures 1, 2, and 3.

Rates of Cleavage in Anhydrous Methanol

Attempts to measure the rate of cleavage of allyl - tributyltin are recorded in Table I. In all of these runs, good second order kinetics were obtained to 80% reaction when equal initial concentrations of allyltin and acid were present or when acid was present in excess. When hydrochloric acid was present in limiting amount, the rate plot was not linear. None of these runs are included in Table I. Notice that rate constants could not be reproduced satisfactorily even though the rate plots were linear over a large extent of any given reaction.

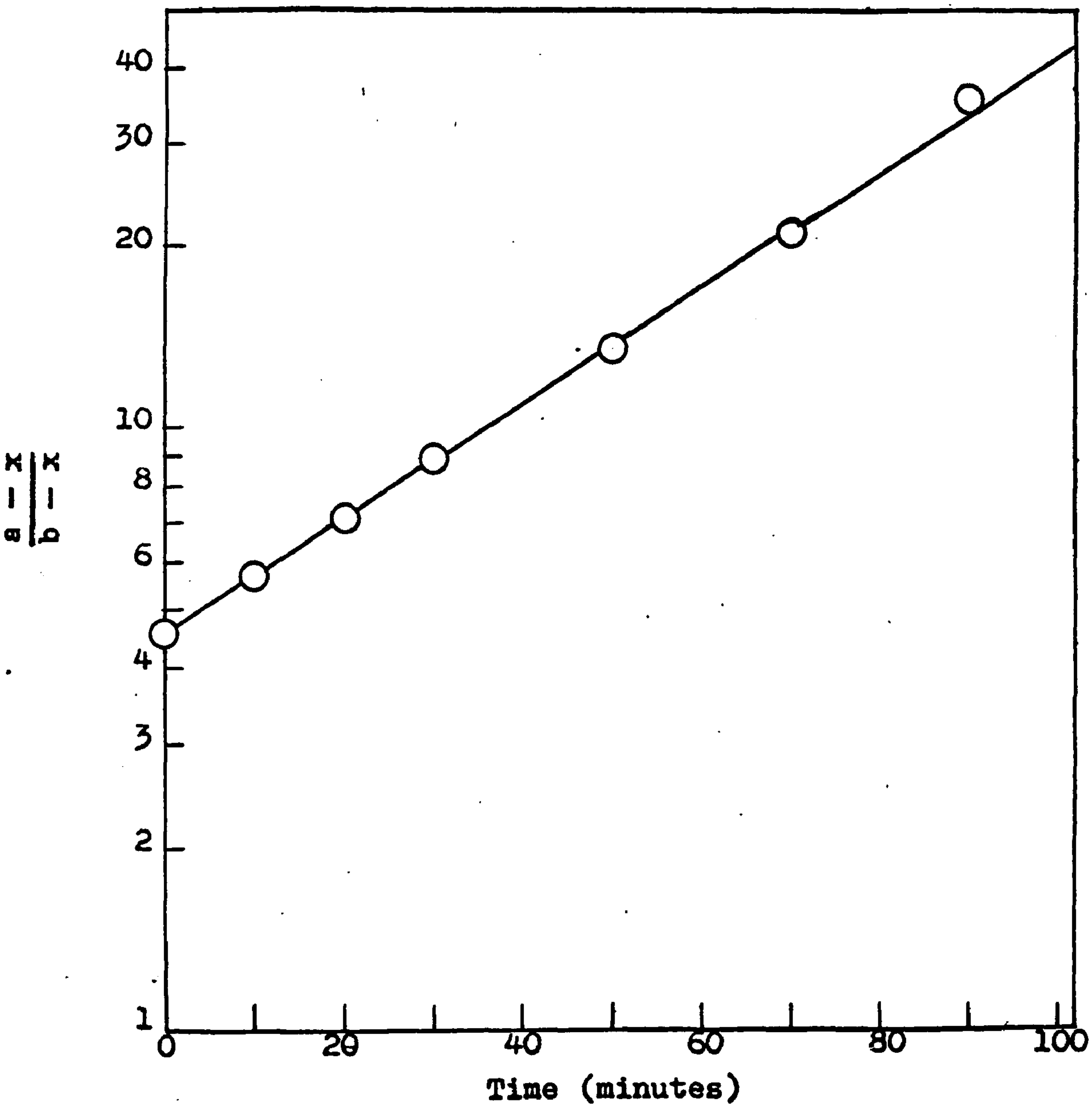


Figure 1. Second Order Rate Plot Obtained by the Aliquot Method for the Protonolysis of Allyltrimethyltin in 4% Water-Methanol. Run 110.

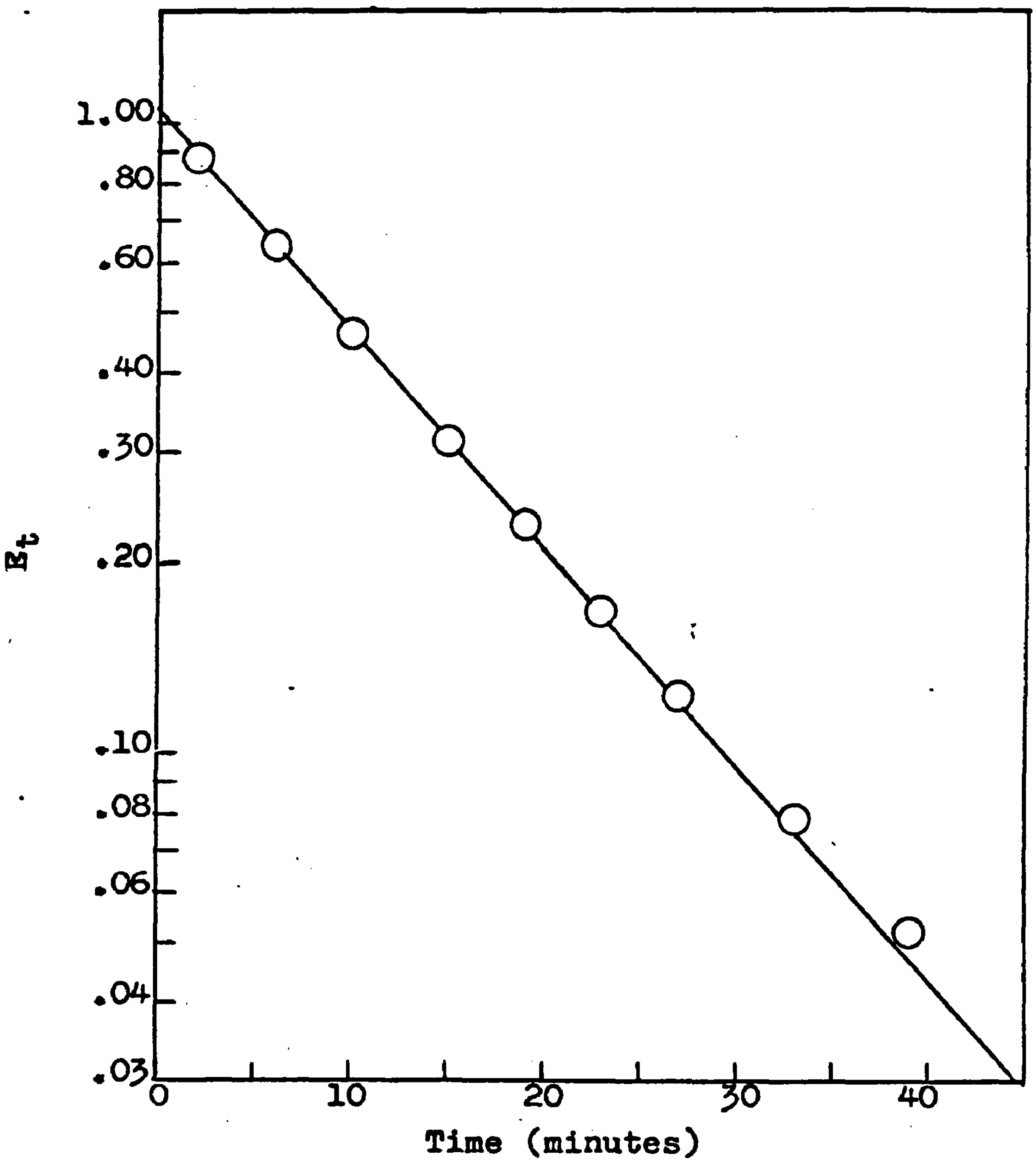


Figure 2. Pseudo-First Order Rate Plot Obtained by the Direct Method for the Protonolysis of Allyltrimethyltin in 4% Water-Methanol. Run 198.

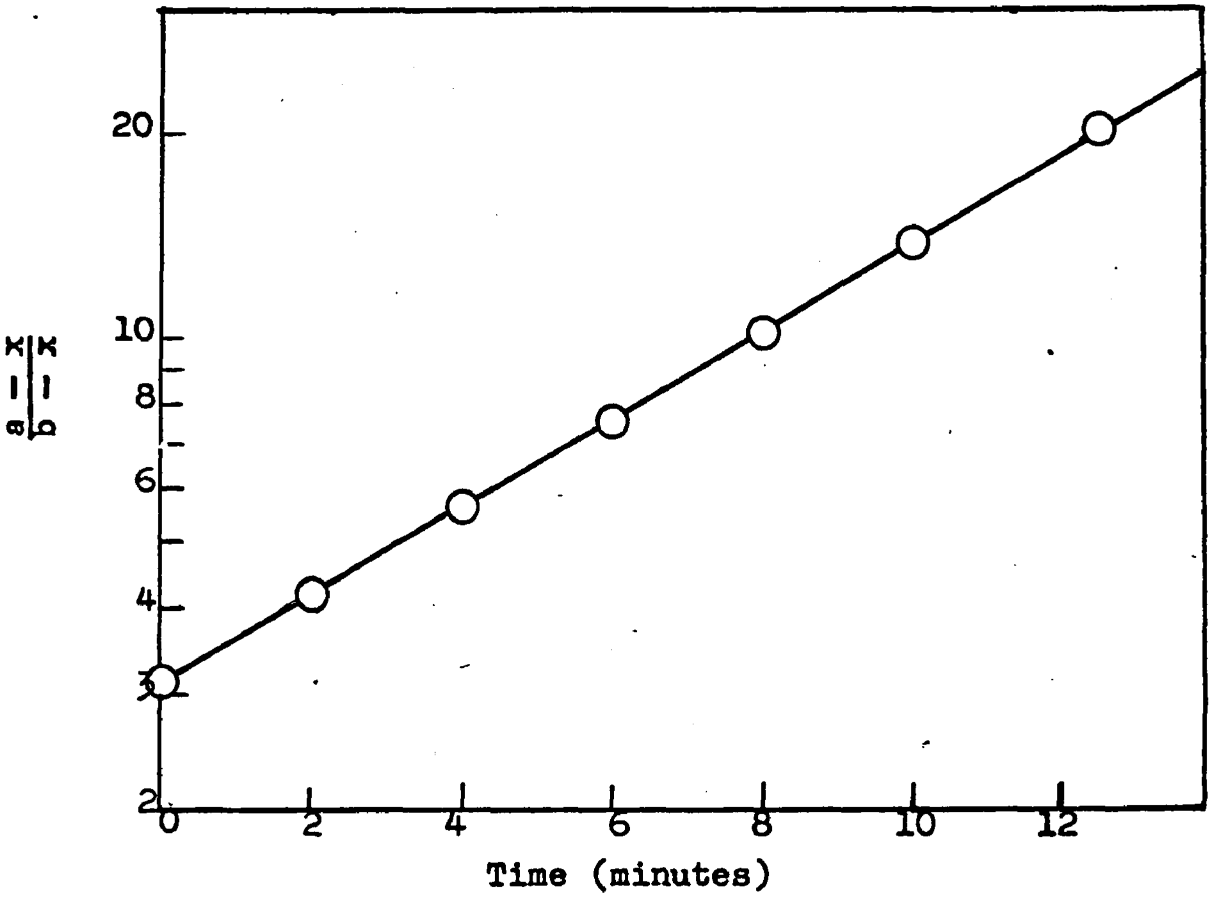


Figure 3. Second Order Rate Plot Obtained by the Direct Method for the Protonolysis of γ-Methylallyltrimethyltin in 4% Water-Methanol. Run 223.

Table I

Rate of Cleavage of Allyltributyltin by HCl in Anhydrous Methanol

Run	$(Bu_3SnAl)_o \times 10^4$ M	$(HCl)_o \times 10^4$ M	k_2 M^{-1} $sec.^{-1}$
1	2.89	2.89	4.88
2	2.31	2.31	5.74
3	2.31	2.31	5.15
5	2.31	4.01	4.88
6	2.89	4.01	3.72
13	2.21	4.39	4.00
14	2.21	4.39	4.71
15	3.46	4.39	3.58
16	2.76	4.39	4.57
17	2.89	4.39	5.04

Allyltrimethyltin Cleavage

Allyltributyltin undergoes decomposition, even when stored in ampules under vacuum. An attempt was made to purify this compound by reacting the material with potassium fluoride in methanol. This operation is designed to remove any trimethyltin chloride contaminant as the insoluble fluoride. However, allyltributyltin was destroyed under these conditions, and none could be recovered from the mixture.

The work of Gielen and Nasielski[13] suggests that a steric effect is operative. It seemed reasonable to focus attention on the sterically less hindered trimethyl analog, and attempts were made to synthesize allyltrimethyltin instead of making a new batch of allyltributyltin. The reaction of allylmagnesium chloride and trimethyltin chloride in diethyl ether ultimately produced a good yield of this substrate in high purity. The absorbance in the ultraviolet region was measured, and the rates of reaction followed by the methods outlined in the previous section.

Rates of Hydrochloric Acid Cleavage in Anhydrous Methanol

The rates of cleavage at 25.00°, measured spectrophotometrically, are outlined in Table II. The results are parallel to those observed in allyltributyltin cleavage. The reaction is first order in allyltrimethyltin and first order in acid, and the rate of reaction is comparable to that of allyltributyltin. The rate plots are linear to approximately 90% reaction, but reproducibility is poor, and several runs had to be discarded.

Table II
Rate of Cleavage of Allyltrimethyltin by HCl
in Anhydrous Methanol

Run	$(Me_3SnAl) \times 10^4$ M	$(HCl) \times 10^4$ M	k_2 M^{-1} $sec.^{-1}$
24	1.85	2.81	5.80
25	1.85	1.41	6.17
26	0.928	2.81	5.93
27	0.928	1.41	5.98
48	0.928	0.638	5.13
49	0.928	1.28	5.57
50	0.928	2.56	5.98
51	0.928	2.35	6.45
52[a]	0.928	2.56	5.88
		average	5.88

[a] Me_3SnCl added to reaction mixture (2.58×10^{-4} M)

Table III indicates a second series of runs in which a different lot of methanol was used, and a different ampule of allyltrimethyltin employed. In two of these runs, additional water was added to the solvent, increasing its water content from 0.01 - 0.02 % to 0.50 %. Notice the marked decrease in the rate constant when one compares Run 65 to 66 and Run 69 to 70. Runs 65 and 66 were carried out at the same time; the only variable in this pair is the solvent composition. Runs 69 and 70 were made at a later date;

again only the solvent is varied. Yet there is no agreement between the pairs of runs, again illustrating the poor reproducibility encountered.

Table III

Rate of Cleavage of Allyltrimethyltin by HCl in Anhydrous Methanol

Run	$(Me_3SnAl) \times 10^4$ M	$(HCl) \times 10^4$ M	k_2 M^{-1} $sec.^{-1}$
63	1.226	2.500	4.55
64	1.226	2.500	5.08
65	1.226	2.500	7.12
66[a]	1.226	2.500	4.57
67	1.226	2.500	5.27
68	1.226	2.500	5.52
69	1.226	2.500	5.12
70[a]	1.226	2.500	2.17

[a] Solvent contains 0.55% water.

It must be emphasized that the data on Tables II and III yield only <u>approximate</u> values for the rate constant for hydrochloric acid cleavage. Runs 66 and 70 indicate that the rate is extremely sensitive to small changes in water content of the solvent system. The difference between the values of k_2 in Table II and Table III is obvious, and may be due to this factor.

Another factor which introduced error, undiscovered at the time these runs were made, is the sensitivity of the reaction to trace amounts of metal ions. Therefore, while it seems certain that the values for k_2 are of the proper magnitude, the accuracy of these values is poor.

Effect of Added Salts - Anhydrous Methanol Solvent

Addition of sodium perchlorate to the reaction mixture had little effect upon rate of reaction. Addition of sodium chloride produced a significant increase in the observed rate, and the extent of acceleration appeared to depend inversely upon the initial concentration of hydrochloric acid. Possibly there also exists a dependence upon initial allyltrimethyltin concentration as well, but the pronounced scatter of the k_2 values makes this point uncertain. Table IV lists these data.

Again, the results on Table IV must be interpreted qualitatively. The reproducibility is poor, and there is too much scatter, even in duplicate pairs of runs, to allow quantitative correlation of any kind.

Table IV

Effect of Added Salt On the Rate of Allyltrimethyltin Cleavage in Anhydrous Methanol

Run	(Me$_3$SnAl) x 10^4 M	(HCl)x 10^4 M	Salt	Conc.of Salt M.	k$_2$ M^{-1}sec.$^{-1}$
33	0.639	1.896	NaClO$_4$	0.0455	7.02
34	0.639	1.896	"	0.0288	6.00
35	0.639	1.896	"	0.0114	6.08
36	0.639	0.946	NaCl	0.0455	25.5
37	0.639	0.946	"	0.0288	22.0
38	0.639	0.946	"	0.0144	21.3
43	0.639	0.468	"	0.0288	29.4
44	0.928	0.646	"	0.0250	16.9
45	0.928	0.646	"	0.0250	16.6
46	0.928	0.646	"	0.0250	17.5
53[a]	0.928	2.559	"	0.0125	8.03
54[a]	0.928	2.559	"	0.0125	7.87
55	0.928	2.474	"	0.0125	7.97
56	0.928	2.474	"	0.0250	9.68
58	0.928	2.474	"	0.0188	8.37
59	0.928	2.474	"	0.0375	12.3
61	1.226	2.500	"	0.0188	6.63
62	1.226	2.500	"	0.0375	8.99

[a] Me$_3$SnCl added to reaction mixture 2.575 x 10^{-4} M

Effect of Trace Amounts of Metal Ions

Data included in the previous section suggest that small amounts of water added to the solvent depresses the rate markedly, so that variable water content in the solvent might help account for poor reproducibility. Shortly after this effect was discovered, it was found that the reaction was accelerated by small amounts of impurities left behind after the distilled water, used as a final rinse for the reaction flasks, evaporated. The offending impurities, presumably metal ions, could be removed satisfactorily by a final careful methanol rinse. This washing technique, described in the Experimental section, noticeably improves the reproducibility of the measurements. In this connection, it was found that small amounts of cadmium II ion accelerated the rate of reaction. (See Run 99, Table VI)

Effect of Water

The effect of addition of small increments of water to the methanol solvent was investigated. Table IV shows that the progressive addition of water to the solvent produces a precipitous decrease at first, but later additions (see Figure 4) produce smaller decreases in the rate. Thus, the difference in the rate constant in a solvent containing 0.01% water and one containing 0.02% water is approximately 16%, while the difference between 4.01% and 4.02% water is negligible. This effect may be due to the fact that small

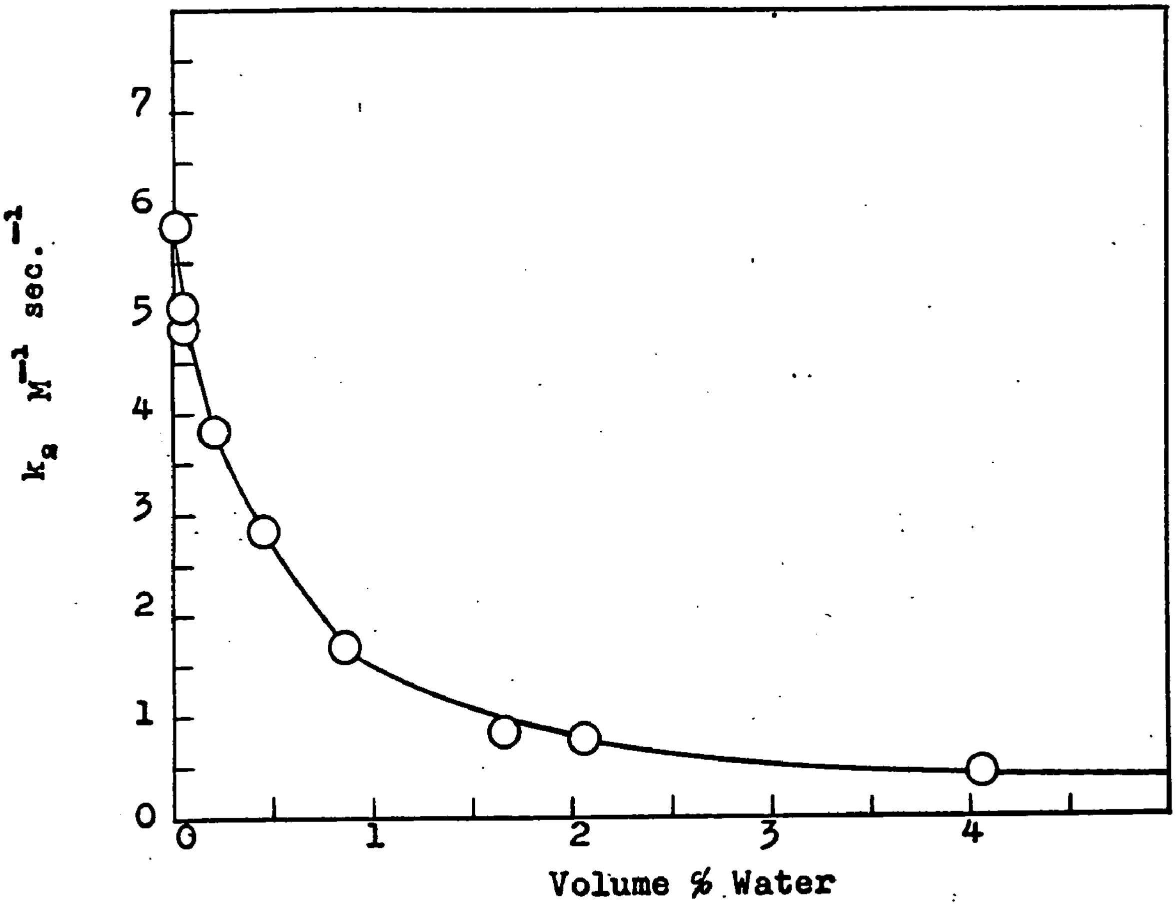


Figure 4. Dependence of Second Order Rate Constant on the Water Content of the Methanolic Solvent.

amounts of water added to hydrochloric acid in pure methanol will greatly decrease the acidity of the system.[17]

The shape of the curve of k_2 vs. % water would be expected to reflect the change in acidity function of the system hydrochloric acid in methanol - water solvent, but the necessary data are not available to test this correlation. This effect is discussed in detail in reference to the mechanism.

Table V

Effect of Added Water on Rate of Cleavage of Allyltrimethyltin

Run	H_2O vol.%	k_2 M^{-1} sec.$^{-1}$	average k_2
a	0.01	———	5.88
73	0.05	5.04	5.06
74	0.05	5.06	
75	0.05	5.08	
100	0.05	4.85	4.85
77	0.21	3.82	3.82
76	0.45	2.78	2.85
101	0.45	2.92	
78	0.85	1.51	1.70
102	0.85	1.89	
81	1.65	0.873	0.873
83	2.05	0.962	0.956
86	2.05	0.950	
82	2.05	0.782	0.790
87	2.05	0.798	
103	2.05	1.01	1.01
b	4.05	———	0.475

[a] Average of nine runs listed in Table II.

[b] Average of eleven runs listed in Table VI.

The deviations which are apparent in this table (for example, compare Runs 83 and 86 to Runs 82 and 87) may be accounted for by noting that the effect of impurities from distilled water was not discovered until Run 90. The low value for Run 81 cannot be explained.

Rate of Cleavage by Hydrochloric Acid in 4.05% Water-Methanol

Precision of the Kinetics. The results of Table IV indicate that greater accuracy would be attained if a solvent system was chosen which contained a higher percentage of water. This innovation, coupled with the improved washing procedure, gave rise to a higher degree of reproducibility, as illustrated by Table VI where the solvent is methanol containing 4.05% H_2O.

Table VI

Rate of Allyltrimethyltin Cleavage in 4.05% Water-Methanol

Run	HCl x 10^4 M	Me_3SnAl x 10^4 M	k_2 M^{-1} $sec.^{-1}$
93	4.980	1.753	0.473
94	4.980	1.753	0.480
96	4.980	1.753	0.495
97	4.980	1.753	0.470
98	4.980	1.753	0.470
99[a]	4.980	1.753	1.30
107	4.876	1.051	0.453
108	4.876	2.101	0.448
109	9.656	1.051	0.490
110	0.656	2.101	0.482
111	2.414	1.051	0.458
112	1.207	2.101	0.508
		average k_2 [b]	0.475 ± 0.014

[a] 2.097×10^{-4} $Cd(NO_3)_2$ added

[b] Run 99 not included in average

Alternate Method of Following the Reaction. The kinetic procedure which involved the taking of aliquots is unsuited for reactions much faster than those reported in Table VI. During the course of the research, it became possible to make use of a method which did not involve taking aliquots. This method, described in the Experimental section, consisted of running the reaction in the thermostatted cell compartment of a Beckmann DU, which allowed direct reading. It was possible to run the reaction at higher concentrations of hydrochloric acid. Results are listed in Table VII.

Table VII

Rate of Allyltrimethyltin Cleavage in 4.05% Water-Methanol Alternate Procedure

Run	$(HCl)_o \times 10^{-4}$ M	$(Me_3SnAl)_o \times 10^{-4}$ M	k_2 $M^{-1}sec.^{-1}$
196	25.05	1.519	0.538
198	25.05	1.519	0.528
199	25.05	1.519	0.527
200	25.05	1.519	0.543
201	10.02	0.659	0.548
202	10.02	0.659	0.548
203	125.2	0.659	0.470

Runs 200 and 201 should be compared with Runs 109 and 110 of Table VI. The results of Table VII yield a value for the rate constant approximately 10% higher than those values in Table VI. The reason for this discrepancy is not known. Run 203, with a much higher acid concentration, gives a value for the rate constant which is in good agreement with Table VI. It should be emphasized that hydrochloric acid, at concentration 1.25×10^{-2} M, is only 83% dissociated. (The dissociation constant for hydrochloric acid in 95.8% by weight methanol - 4.2% by weight water is 0.14 as determined by Shedlovsky and Kay.[14])

Effect of Added Sodium Perchlorate in 4% Aqueous Methanol. The addition of sodium perchlorate to the reaction mixture, using anhydrous methanol as a solvent, produced a small acceleration in the rate of reaction. In contrast, addition of the same salt to the reaction mixture in 4% aqueous methanol produced a marked increase in the rate. Table VIII summarizes the results. Attempts to correlate the data with the familiar Bronsted relationship[18]

$$\ln k = \ln k_o + 2\ Z_A\ Z_B \sqrt{\mu}$$

were unsuccessful. The failure of this relationship to correlate the data is expected, since one of the reactants, allyltrimethyltin, is a neutral molecule.

A second relationship, attributed to Debye[19], has proven useful in correlating a number of reactions involving two neutral molecules or a neutral molecule and an ion. This relationship, which may be written

$$\ln k = \ln k_o + (b_o + b_A - b_{\ddagger})\mu$$

predicts the logarithm of the rate constant to be a linear function of the first power of the ionic strength. The data did not obey this relationship. In both these attempted correlations, k is defined as the observed rate constant in the presence of added salt, while k_o is the rate constant in the absence of salt ($\mu \cong 1 \times 10^{-4}$). The value adopted for k_o is 0.475 M^{-1} sec.$^{-1}$, the average value from Table VI.

The secondary salt effect is not operative here.

At these concentrations, hydrochloric acid is completely dissociated in 4% aqueous methanol.[14]

It is pertinent that the value of the observed rate constant is independent, both of change in initial acid concentration and change in initial allyltrimethyltin concentration.

Table VIII

The Effect of Addition of $NaClO_4$ on the Rate of Cleavage

Run	$(Me_3SnAl)_o \times 10^4$ M	$(HCl)_o \times 10^4$ M	$NaClO_4$ M	k_2 $M^{-1}sec.^{-1}$
170	1.023	8.123	0.0125	0.560
171	1.023	8.123	0.0250	0.567
173	1.023	16.25	0.0250	0.555
178	0.948	4.062	0.0250	0.583
179	1.895	4.062	0.0250	0.577
117	1.176	4.828	0.0500	0.587
172	1.023	8.123	0.0500	0.593
174	1.023	16.25	0.0500	0.580
118	1.176	4.828	0.1000	0.698
119	1.176	4.828	0.2000	0.882

Effect of Added Sodium Chloride in 4% Aqueous Methanol. The dependence of rate of reaction upon added sodium chloride is much more complex. The following observations summarize the experimental results:

(1) In runs without added sodium chloride, initial hydrochloric acid concentration varied from 1.2×10^{-4} M to 9.7×10^{-4} M (Table VI) and from 10×10^{-4} M

to 25 x 10^{-4} M (Table VII). In these two series, the second order rate constant does not vary with change in acid concentration. Thus there is no variation with change in chloride ion at these concentration ranges, since hydrochloric acid is completely dissociated in this range.

(2) The addition of sodium chloride in moderate concentration accelerates the reaction, but the extent of acceleration is dependent upon initial hydrochloric acid concentration. The data of Table IX, reproduced in Figure 5, suggests that at constant sodium chloride concentration, the observed rate constant varies linearly with $\frac{1}{(\mathrm{HCl})}_{\mathrm{stoich}}$. The point derived from Runs 122 and 126 is almost certainly in error, yet no explanation could be advanced to reject them. This point is therefore included to illustrate the extent of scatter possible in these runs.

An analogous plot at 0.0500 M sodium chloride, Table X shows no such correlation. Perhaps there is too much scatter in this series.

(3) The foregoing point suggests that salt effect due to sodium chloride is most pronounced at low acid concentration. Table XI gives results which support this conclusion.

(4) Addition of sodium chloride to a solution of allyltrimethyltin in 4% water-methanol produces no change in ultraviolet absorbance in five hours.

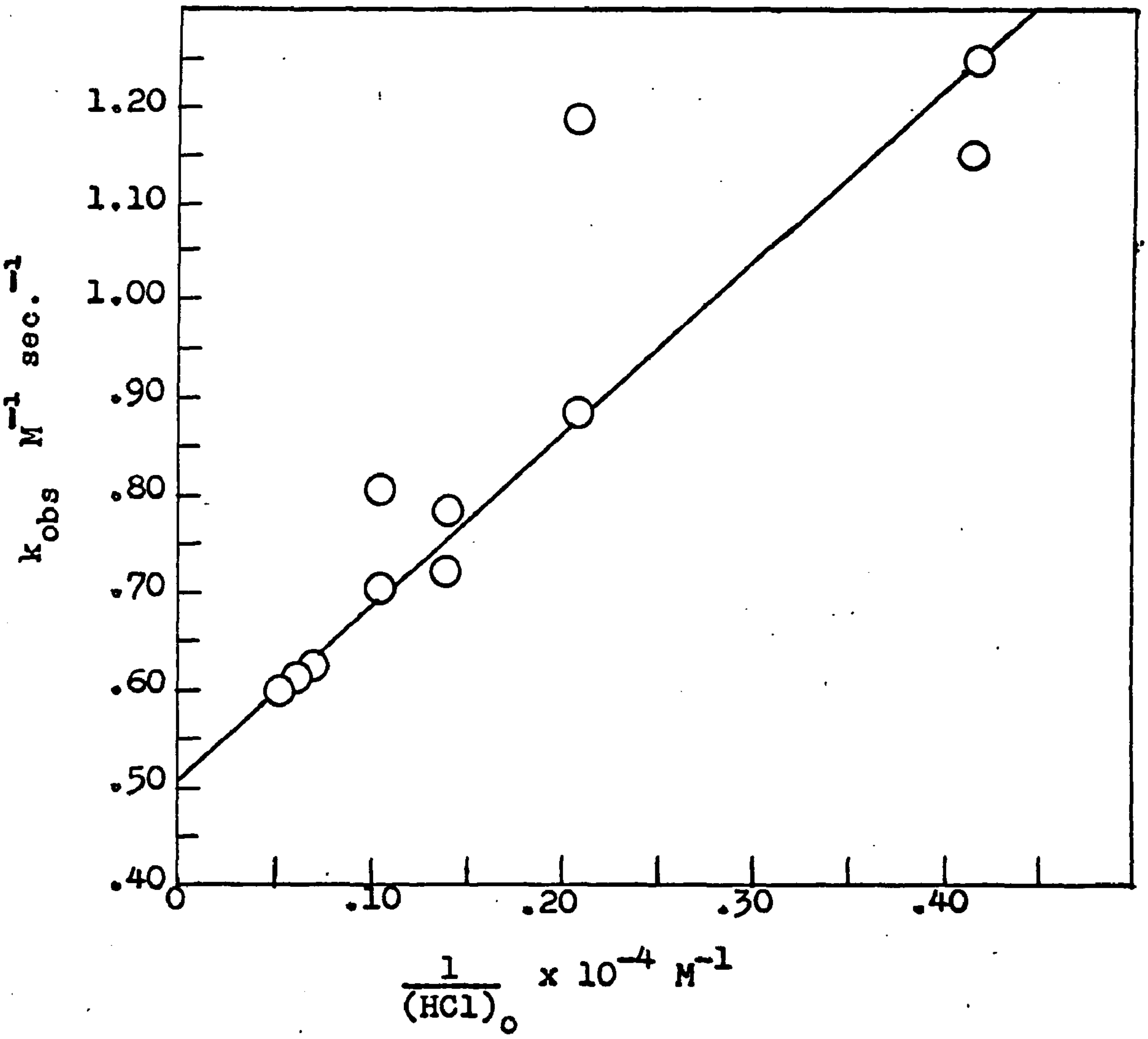


Figure 5. Dependence of the Observed Rate Constant on Initial Hydrochloric Acid Concentration in the Presence of 0.0250 M NaCl.

Table IX

Rates of Allyltrimethyltin Cleavage in the Presence of 0.0250 M NaCl

Run	HCl x 10^4 M	Me_3SnAl x 10^4 M	k_2 $M^{-1}sec^{-1}$	ave. k_2 $M^{-1}sec^{-1}$	$\frac{1}{HCl}$ x 10^{-4}
139	2.398	0.997	1.25	1.25	0.417
120	2.414	1.176	1.15	1.15	0.415
140	4.796	0.997	0.887	0.887	0.209
122	4.822	1.298	1.15	1.19	0.208
126	4.822	1.298	1.23		
136	7.194	0.997	0.724	0.724	0.139
165	8.123	1.041	0.787	0.787	0.139
130	9.592	1.077	0.688		
132	9.592	1.077	0.722	0.708	0.104
138	9.592	0.997	0.713		
128	9.644	1.263	0.807	0.807	0.104
135	14.38	0.997	0.627	0.627	0.0695
154	16.29	0.981	0.615	0.615	0.0615
137	19.18	0.997	0.602	0.602	0.0521

Table X

Rates of Allyltrimethyltin Cleavage in the Presence of 0.0500 M NaCl

Run	$(HCl)_o$ x 10^4 M	$(Me_3SnAl)_o$ x 10^4 M	k_2 $M^{-1}sec^{-1}$	ave k_2 $M^{-1}sec^{-1}$	$\frac{1}{(HCl)}$ x 10^{-}
121	2.414	1.176	0.952	0.952	0.415
123	4.822	1.298	1.30	1.24	0.208
127	4.822	1.298	1.18		
166	8.123	1.041	0.858	0.858	0.123
129	9.644	1.263	0.817	0.817	0.104
131	9.592	1.077	0.738	0.757	0.104
133	9.592	1.077	0.775		
155	16.29	0.981	0.655	0.655	0.0615

Table XI

Change in Rate of Allyltrimethyltin Cleavage With Change in Chloride Concentration

Run	$(HCl)_o \times 10^4$ M	$(Me_3SnAl)_o \times 10^4$ M	NaCl M	k_2 $M^{-1}sec^{-1}$
155	16.29	0.981	0.0500	0.655
154	16.29	0.981	0.0250	0.615
157	16.29	0.981	0.0125	0.572
156	16.29	0.981	0.0063	0.523
159	16.29	1.010	0.0031	0.489
158	16.29	1.010	0.0013	0.489
161	16.29	1.010	0.0006	0.459
160	16.29	1.010	0.0000	0.473
166	8.123	1.041	0.0500	0.858
165	8.123	1.041	0.0250	0.787
164	8.123	1.041	0.0125	0.710
169	8.123	1.041	0.0063	0.663
168	8.123	1.041	0.0031	0.617
167	8.123	1.041	0.0006	0.557

In any discussion of the rate increase due to the presence of sodium chloride, it must be recognized that a primary kinetic salt effect, similar in magnitude to that exerted by an equal concentration of sodium perchlorate, contributes to the acceleration. In addition, one must take into account the common ion effect, which decreases the dissociation of hydrochloric acid, and a secondary salt effect which increases the extent of dissociation. The net effect arising from these two considerations will vary as chloride and acid concentrations change. However, when chloride ion is greatly in excess of hydrogen ion, as in the runs of Table IX, per cent dissociation of the acid will remain constant as the initial concentration of acid is varied.

These three effects taken together will exert a constant contribution to the observed rate constant throughout Table IX, and these effects cannot be responsible for the change in k_{obs} with change in acid concentration.

One might postulate a chloride-allyltrimethyltin complex which would be more susceptible to electrophilic attack than allyltrimethyltin itself. An analagous effect in the cleavage of certain organometallic substrates has been proposed by Dessy.[5] If, however, this complex formed readily, the empirical rate expression would contain a term for chloride ion; i.e., in the present treatment the reaction would be first order in chloride ion. The data presented indicates that chloride ion enters the rate expression only when chloride ion is present in excess of acid concentration.

In view of the uncertainties present in the data, and the multitude of effects which are operative, an attempt to treat the data quantitatively would probably be fruitless. Possible explanations for this data will be advanced when the mechanism of cleavage is discussed.

Rate of Perchloric Acid Cleavage in Aqueous Methanol. When perchloric acid is used as the electrophile, the rate of cleavage is exactly the same as the rate of hydrochloric acid cleavage. Perchloric acid is a stronger acid than hydrochloric acid, and would also be completely dissociated at these concentrations. Since the rates are the same, it can be concluded that lyonium ion, rather than molecular acid or acid existing as ion pairs, is the attacking species. The rate does not depend on the species of anion present. (Notice the contrast between these results and those obtained with added salts where anion is greatly in excess of lyonium ion.)

Table XII

Rate of Cleavage of Allyltrimethyltin by Perchloric Acid in 4.05% Water-Methanol

Run	$(HClO_4) \times 10^4$ M	$(Me_3SnAl) \times 10^4$ M	k_2 $M^{-1}sec^{-1}$
185	2.096	2.067	0.521
184	4.920	1.034	0.490
182	8.384	2.058	0.483
183	8.384	2.067	0.488
180	16.77	1.029	0.478
181	16.77	1.029	0.475

Attempts were made to follow the rate of reaction of allyltrimethyltin with sulfuric acid. When the aliquots were quenched, however, a white insoluble substance was formed. Upon progressive addition of water this solid dissolved, but the tin compounds no longer stayed in solution. The solid was presumed to be sodium sulfate, which is less soluble in methanol than either sodium chloride or sodium perchlorate. Thus no rate data could be obtained for sulfuric acid.

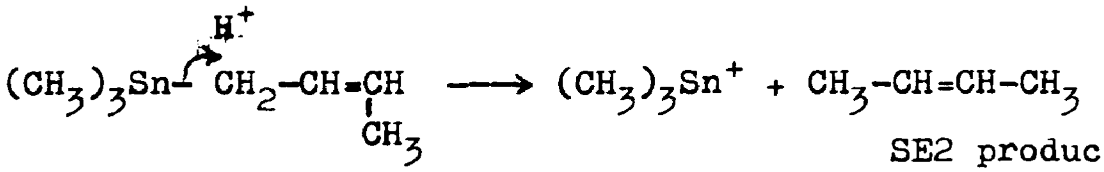
Kinetics by Conductimetric Technique. One run was followed simultaneously by spectrophotometric means and by conductance measurements. The conductimetric technique indicated a slower rate of reaction than that measured by the decrease in absorbance at 225 mμ. However, when the conductance of trimethyltin chloride is subtracted from the total conductance measured at any given time, the net conductance, presumed to be due to hydrochloric acid, yields a value for the concentration of hydrochloric acid which compares very accurately with that determined spectrophotometrically.

In principle it is entirely possible to obtain the same kinetics by following the disappearance of hydrochloric acid by a conductimetric technique. This data is presented in the Appendix.

Cleavage of cis and trans-γ-methylallyltrimethyltin

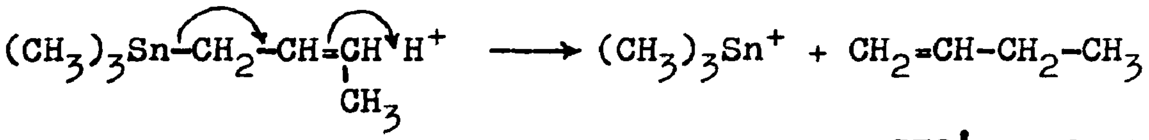
Objective of the Experiment

The site of lyonium ion attack may be investigated by examining the olefinic product of cleavage of appropriately substituted allylic groups attached to tin. An SE2 reaction might take place by attack of protonated species upon the carbon adjacent to the tin atom. Alternatively the attack might occur at the terminal carbon bearing the double bond, i.e. an SE2' mechanism might be operative. When allyltrimethyltin is the substrate, propylene will be formed by either mechanism. If γ-methylallyltrimethyltin is employed, two possibilities might be:



$$(CH_3)_3Sn-\overset{H^+}{CH_2}-CH=\underset{CH_3}{CH} \longrightarrow (CH_3)_3Sn^+ + CH_3-CH=CH-CH_3$$

SE2 product



$$(CH_3)_3Sn-CH_2-CH=\underset{CH_3}{CH}\ H^+ \longrightarrow (CH_3)_3Sn^+ + CH_2=CH-CH_2-CH_3$$

SE2' product

Analogously, one would expect α-methylallyltrimethyltin to yield 1-butene as an SE2 product, and 2-butene as an SE2' product.

It seemed reasonable that any synthetic technique employed to generate one of these isomers would generate the other as well. The surprising result of several syntheses by different methods showed that no α-methylallyltrimethyltin was formed but that cis and trans-γ-methylallyltrimethyltin could be synthesized in good yield. Determination of the olefinic cleavage product, as well as kinetics measurements, were carried out exclusively with the γ-methylallyl isomers.

Synthesis of γ-Methylallyltrimethyltin Isomers

Attempts were made to synthesize these substrates by the Grignard reaction between trimethyltin chloride and crotylmagnesium chloride in diethyl ether, and by the reaction of trimethyltinlithium and crotyl chloride in diethyl ether. The former method gave a modest yield of a 1:1 mixture of cis and trans-γ-methylallyltrimethyltin. The boiling range of the products proved to be 151-154°, while the boiling point of trimethyltin chloride has been reported as 154°. The Grignard reaction was incomplete, and unreacted trimethyltin chloride was present as an impurity. The organolithium reaction, attempted three times, produced only a trace of products.

The successful route of these isomers proved to be the reaction of trimethyltinsodium and either crotyl chloride or 3-chloro-1-butene in liquid ammonia, which gave a high yield of product with no unreacted trimethyltin chloride. remaining as a contaminant. Surprisingly, it was found that the primary chloride gave rise to a predominance of *trans*-γ-methylallyltrimethyltin while the secondary chloride, 3-chloro-1-butene, yielded chiefly *cis* isomer. The results are summarized in Table XIII.

Table XIII

γ-Methylallyltrimethyltin Isomer Distribution

Reaction	Starting Chloride	% trans	% cis	Yield
1[a]	3-chloro-1-butene	16	84	20%
2[a]	"	13	87	5%
3	"	30	70	not calculated
4	"	25	75	" "
5	"	25	75	80%
7	crotyl chloride	62	38	55%
8[b]	" "	74	23	78%
9[b]	3-chloro-1-butene	32	68	

[a] Ammonia solvent removed from solid trimethyltinsodium. Addition of chloride carried out in diethyl ether slurry.

[b] Products of reactions 8 and 9 were combined for distillation. The yield is the overall yield from both reactions.

The course of the reaction which dictates that the isomer distribution be dependent upon the identity of the starting chloride is not understood. The absence of α-methylallyltrimethyltin among the reaction products is noteworthy. It may be that this isomer is formed during the reaction but rapidly rearranges to the γ-methylallyl isomer. Thus the secondary chloride, 3-chloro-1-butene could give rise to the γ-methylallyl product by an SN2' reaction with trimethyltin anion; an SN2 reaction followed by rearrangement of the initially formed α-methylallyl isomer would also produce the γ-methylallyl compound. It is not at all obvious how either of these pathways should produce a product of predominantly cis configuration, but the experimental results clearly indicate that such must be the case. The product distribution in the case of the reaction of crotyl chloride (which exists predominantly in the trans configuration) with trimethyltin anion would be the trans-γ-methylallyl isomer if simple SN2 attack were taking place. Further, it has been observed that the cis and trans isomers readily undergo isomerization; further investigation of this interconversion is necessary to explain the course of the synthesis.

Structure Assignment of γ-Methylallyltrimethyltin Isomers

The structure of the two isomers was determined by a combination of carbon-hydrogen analysis, nuclear magnetic resonance spectra, and infra-red spectra. Pure samples of each isomer, obtained by vapor phase chromatography separation, were used for all determinations except the carbon-hydrogen analysis where a 1:1 isomer mixture was used.

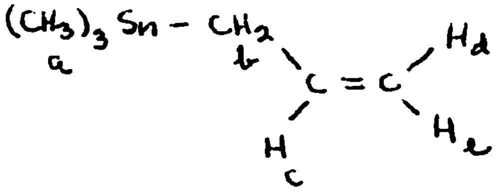
Carbon-hydrogen analysis indicates an empirical formula $C_7H_{16}Sn$. The integrated NMR spectra both show a ratio of five aliphatic protons to two vinyl protons in the methylallyl group; thus the α-methylallyl isomer is eliminated as a possible structure. This assignment was confirmed by the infra-red spectra, which were used to determine the configuration of each isomer.

Nuclear Magnetic Resonance Spectra. In principle the proton magnetic resonance spectra would enable one to distinguish the α-methylallyl isomer from the γ-methylallyl isomers, and in addition should give unambiguous results regarding the configuration of the γ-methylallyl isomers. The α-methylallyl isomer is eliminated by the results of the integrated spectrum. The assignment of configuration of the γ-methylallyl isomers is possible if the assignment of the coupling constants of the vinyl hydrogens can be made. However, the methylene signals occur almost at the same value as the signal from the methyl group attached to the double bond. Coupling constants for the vinyl protons cannot be assigned. The spectral data are summarized in Table XIV; the data for allyltrimethyltin are included for comparison.

Table XIV

N.M.R. Spectra

Spectrum No. 61 Allyltrimethyltin (neat)



Protons	Value	No. Peaks	Coupling Constants(C.P.S.
a	9.93	1	Jce = 9.9
b	8.29	2	Jbc = 8.6
c	4.11	10	Jcd =17.5
d	5.34	3 (plus second order splitting)	Jde = ?
e	5.29		

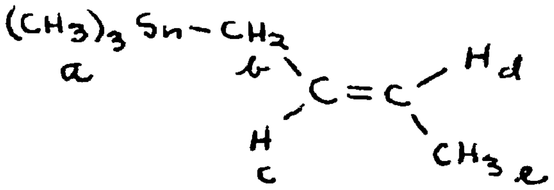
Integrated Spectrum

Protons	a	b	d,e	c
Calcd.	9	2	2	1
Found	9.2	2.1	2.0	1.0

Table XIV (Continued)

Spectrum No. 91 trans-γ-methylallyltrimethyltin

CCl_4 soln. 50% V.V



Protons	Value	No. Peaks
a	9.94	1
b	8.32	4
c	4.66	10
d	4.76	
e	8.36	2

Coupling Constants(C.P.S

Jde = 5.5
Jbc = 5.5(?)

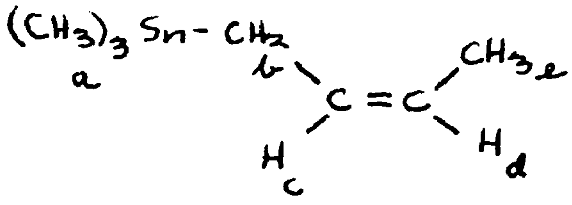
Integrated Peak Heights

Protons	a	b,e	c,d
Calcd.	9	5	2
Found	7.9	5.1	2.0

Table XIV (Continued)

Spectrum No. 90 cis-γ-methylallyltrimethyltin

CCl_4 soln. 50% V.V.



Coupling Constants - cannot be assigned

.P.S.)

Protons	Value	No. Peaks
a	9.93	1
b	8.30	?
c	4.25-5.12	16-18
d		
e	8.45	?

Integrated Peak Heights

Protons	a	b,e	c,d
Calcd.	9	5	2
Found	9	4.7	2.3

Infra-Red Spectra. The infra-red spectra of the γ-methylallyltrimethyltin isomers allow assignment of the configuration of the two isomers. The regions of the spectra most instructive are between 880-1000 cm^{-1}, the regions where vinyl hydrogens absorb, and the carbon-carbon double bond stretch, located near 1650 cm^{-1}. It has proven useful to compare these spectra with published spectra of olefins of similar structure. From these data, the higher boiling isomer was assigned the cis configuration; the lower boiling isomer the trans configuration. Table XV lists the bands found in these regions for both isomers as well as for allyltrimethyltin.

Table XV

Infra-Red Spectra

(1) Comparison of C=C Stretching Frequencies

Compound	Spectrum No.	ν cm^{-1}
1-pentene	API 275	1645 (s)[a]
cis-2-pentene	API 815	1658 (s)
trans-2-pentene	API 818	1670 (m)
allyltrimethyltin	1977	1630 (s)
cis-γ-methylallyltrimethyltin	1978, 243	1650 (s)
trans-γ-methylallyltrimethyltin	2002, 242	1655 (m)

[a] The relative intensities of the double bond stretch are 1-pentene > cis-2-pentene > trans-2-pentene. In the series of organatins, allyl > cis-γ-methylallyl > trans-γ-methylallyl.

Table XV (Continued)

(2) Comparison of C-H Out-of-Plane Deformation Frequencies

Compound	Spectrum No.	ν cm^{-1}
1-pentene	API 275	900 (s)
		990 (s)
cis-2-pentene	API 815	860 (w)
		933 (s)
		964 (m)
trans-2-pentene	API 818	943 (w)
		964 (s)
allyltrimethyltin	1977	890 (s)
		929 (m)
		982 (m-s)
		1020 (m)
cis-γ-methylallyltrimethyltin	1978, 243	720 (m)[a]
		895 (w)
		959 (w)
		990 (s)
trans-γ-methylallyltrimethyltin	2002, 242	884 (w)
		900 (m)
		957 (s)
		1030 (m)

[a] 720 cm^{-1} band resolved by use of KBr windows. *cis* vinyl hydrogens absorb near 690 cm^{-1}.[20]

The assignment of the 990 cm^{-1} peak in the <u>cis</u>-γ-methylallyl isomer is uncertain. This may be a carbon-carbon absorption corresponding to those at 1020 cm^{-1} and 1030 cm^{-1} found in the other two organatins. (A peak at 1000 cm^{-1} in tetraethyltin is attributed to a carbon-carbon mode.)[21] Otherwise, the comparison between the two series is reasonably close.

<u>Ultraviolet Spectra</u>. Spectra of the isomer were measured on a Model 2400 Beckman DU Spectrophotometer. No maximum was observed, although an inflection point at 215 mμ was observed. Much earlier the spectrum of allyltrimethyltin, measured on the Model 4000 Perkin-Elmer Spectracord had indicated a maximum at 215 mμ for this compound. In this region the methanol solvent has a high absorption; possibly the maximum cannot be seen because of this.

Extinction coefficients at 225 mμ are: <u>trans</u> isomer 6.83×10^3, <u>cis</u> isomer 5.71×10^3, allyltrimethyltin 7.12×10^3.

The extinction coefficient seems quite high for that of an isolated double bond. Perhaps the molecule exists in such conformation that overlap between the π electrons and the vacant d orbitals of tin gives rise to increased absorbance in the ultraviolet. There is, however, no proof for such an interaction.

<u>Hydroboration of Isomer Mixture</u>. Supplementary proof for the structure assignment was sought by subjecting

a mixture of the two isomers to hydroboration by disiamylborane. Brown and coworkers[22] have shown for a series of olefins that the <u>cis</u> disubstituted ethylenic double bond reacts more rapidly with this reagent (by a factor of 6 to 9) than the corresponding <u>trans</u> isomer. If one could follow the hydroboration of a 1:1 mixture of the γ-methylallyltrimethyltin isomers, that isomer which reacted faster toward disiamylborane would possess the <u>cis</u> configuration.

Accordingly, a 1:1 mixture of the isomers was added to a solution of disiamylborane in diglyme. At intervals aliquots were taken, added to water to decompose unreacted borane and to dissolve the salts present, and the organic layer remaining atop the water examined by vapor phase chromatography. The composition of the mixture of isomers remaining unreacted could be accurately determined in this manner.

Two methods of hydroboration were used. As in the method most commonly employed by Brown,[23] a solution of boron trifluoride etherate was added slowly to a solution of sodium borohydride and 2-methyl-2-butene in diglyme. Diborane was generated <u>in situ</u>, where it reacted smoothly with the olefin to yield disiamylborane. After this reaction had taken place, the γ-methylallyltrimethyltin isomers were added to the reaction mixture, and aliquots withdrawn at intervals.

The second method of hydroboration involved external generation of diborane, which passed from the generator and dissolved in dry tetrahydrofuran.[24] The concentration of the resulting diborane solution was assessed by hydrolyzing a sample of the solution and measuring the volume of hydrogen gas evolved. Two equivalents of 2-methyl-2-butene were added to a quantity of the solution known to contain one equivalent of diborane, and the mixture was stirred for several hours. Vapor phase chromatography analysis at this point showed only trace amounts of unreacted 2-methyl-2-butene, and the γ-methylallyltrimethyltin isomers were added to the mixture. The analysis for unreacted isomers was less accurate due to tailing of the solvent peak.

The results of one such experiment are summarized in Table XVI. In this run, the *in situ* method of hydroboration was used.

Table XVI

Reactivity of γ-Methylallyltrimethyltin Isomers
Toward Disiamylborane
(low) and (high) refer to low and high boiling isomers

Point	Sample Size(mμ)	Time(hr.)	Area(low)	Area(high)	$\frac{A(low)}{A(high)}$
1	10	0.10	9.19	7.71	1.19
2	10	1.16	7.56	4.44	1.70
3	10	2.25	6.29	3.84	1.64
4	20	3.75	14.09	7.80	1.18
5	19	6.25	11.93	6.95	1.72
6	20	11.75	11.49	9.93	1.16
7	20	40.75	8.86	9.21	0.98

Table XVI indicates that at first the high boiling isomer reacts faster than the low boiling isomer. This result would be anticipated from the assignment of structure made on the basis of the infra-red spectrum. This result is complicated, however, by the fact that the ratio reaches a maximum, then decreases with time until, at 41 hours, there is a larger proportion of low boiling isomer present than there was at the beginning of the reaction. This is interpreted as being due to isomerization of the isomers. Moreover, the chromatograms also display a peak which has the same retention time as 1-butene, the product of γ-methylallyltrimethyltin cleavage.

The results of experiments carried out using external generation of diborane are quite similar, but inaccuracies in calculating the areas are much greater, and the area ratios do not vary smoothly with time.

The hydroboration, if it takes place at all, is accompanied by cleavage, and also by isomerization. It appears that the investigation of this reaction by a more exacting technique, such as isolation of the resulting alcohols, might prove worthwhile, but the presence of competing reactions does not allow configurational assignment from these experiments. Of greater interest is the suggestion that the cleavage is effected by Lewis acids, possibly by disiamylborane itself, and the possibility that isomerization may take place under the conditions of these experiments.

Interconversion of γ-methylallyltrimethyltin Isomers

The possibility that the cis and trans isomers may be interconvertible has been advanced to account for the composition of products obtained in the synthesis of these isomers, and to explain the results of the hydroboration experiments. A more direct observation was made in connection with the measurement of the ultraviolet absorbances of these substrates. A fraction consisting of 90% cis, 10% trans isomer was dissolved in three parts methanol. This solution was analyzed by vapor phase chromatography at the end of two, five, eight, and sixteen hours, and the chromatograms indicated a gradual decrease of the cis isomer until, at 16 hours, the composition was 49% cis, 51% trans. Attempts to repeat this experiment, however, were unsuccessful. Isomerization did not occur during further attempts to measure the ultraviolet spectra.

Previously, it had been shown that no isomerization occurred when the isomer mixture was stored in ampoules, and also that no isomerization occurred in carbon tetrachloride solutions of comparable concentrations. Later, the rates of cleavage of these isomers were measured, and no indication of isomerization could be found in these studies. (The reaction time for the cleavage reaction was about thirty minutes. Isomerization might be very slow compared to this.) It was reluctantly concluded that a catalytic impurity was present in the experiment that indicated isomerization, and the problem was no longer pursued.

The results of this experiment, however obscure, strongly suggest that the matter be pursued more intently. Specifically, one should attempt to discover what kinds of reagents affect the interconversion. It is hard to imagine a cationic intermediate such as those proposed to account for isomerization of olefins. The results of the kinetics indicate that protonation is quickly followed by tin-carbon cleavage and the isomerization appears to be much slower than the cleavage reaction. One would have to postulate that deprotonation of the intermediate, as well as tin-carbon cleavage, could occur.

At the concentrations employed in the kinetic studies, however, it is doubtful that isomerization occurs to any appreciable extent.

Olefin Products of Cleavage

To determine the products of cleavage, an acid solution was added to a solution of a known isomeric mixture of the γ-methylallyltrimethyltin isomers dissolved in methanol and contained in a closed system. After sufficient time had elapsed to allow complete reaction, water was added to displace the butene product from solution, and the gaseous mixture was frozen out in a suitable trap. The mixture was then analyzed by vapor phase chromatography, using a column of dimethylsulfolane on firebrick. This column separated 1-butene, *trans*-2-butene, and *cis*-2-butene quite cleanly. Previous to carrying out the cleavage reaction, calibration curves were constructed so that the relationship between areas of the respective butenes and moles of each component is known precisely. This procedure is described in detail in the Experimental section.

All peaks in the vapor phase chromatogram could be accounted for. One unexpected peak appeared; this peak accounted for as much as 25% of the total area under the peaks depending on reaction conditions. This proved to be methyl chloride, formed by the reaction of hydrochloric acid and methanol. An authentic sample of methyl chloride had the same retention time as the unexpected peak, and the infra-red spectrum of the unknown was identical to that of a published spectrum of methyl chloride. The major peak in all these runs proved to be due to 1-butene. This also was confirmed by the infra-red spectrum.

The efficiency of the freezing traps used to condense the butenes was assessed by making several runs by the identical procedure described above, dissolving the frozen products in chloroform, and titrating with a solution of bromine in acetic acid of known concentration. In no case was a quantitative yield found; presumably some of the volatile butenes were not frozen out, but passed through the system. Yields of 81%, 79%, and 90% were realized on successive experiments where initial concentrations of γ-methylallyltrimethyltin and hydrochloric acid were approximately 0.2 M. At lower initial concentrations, on the order of 1×10^{-3} M, a 50% yield of butenes was found by bromine titration.

The results of the cleavage experiments are summarized in Table XVII. The main product in all cases is 1-butene. The relative percentages of butenes at a given initial concentration of reactants is constant regardless of the isomer composition. A surprising feature of these results is that cis isomer always predominates over trans, in contrast to the recently reported results of Winstein[12] on the cleavage of crotylmercury derivatives. The results of cleavage at low concentration are suspect. In order to displace butene from the methanol solution which has a volume of 2 liters, an equal volume of water must be added and the mixture refluxed for several hours. The butene mixture at this temperature can be expected to isomerize, and the appearance of a higher percentage of 2-butene may be due to this effect.

Table XVII

Products of Cleavage of
<u>cis</u> and <u>trans</u> γ-methylallyltrimethyltin

Composition of mixture	run 1	2	3	4
% trans: % cis	78:22	25:75	13:87	64:36
(Me_3SnCr) M	0.23	0.25	1.23×10^{-3}	1.37×10^{-3}
(HCl) M	0.28	0.28	1.51×10^{-3}	1.51×10^{-3}
1-butene (mole %)	98	98	86	87
cis-2-butene	1-2	1-2	13	12
trans-2-butene	trace	trace	1	1

These results suggest that an SE2' mechanism is operative. If the results of Runs 3 and 4 mean that a competitive mechanism is operative at lower concentrations, this would be reflected by a parallel change in the kinetics of the reaction as the initial concentrations were changed.

Kinetics of HCl Cleavage in 4% Water-Methanol

The kinetics of acid cleavage were measured by running the reaction in the thermostatted cell compartment of a Beckman DU, as described in the Experimental section. The absorbance of both <u>cis</u> and <u>trans</u> γ-methylallyltrimethyltin in the ultraviolet is not significantly different from that of allyltrimethyltin. The wavelength used for kinetic measurements was 225 $m\mu$, as with allyltrimethyltin, and both the cis and the trans substrate obey Beer's law throughout the concentration ranges employed.

Trans-γ-Methylallyltrimethyltin. The rate constant at 25.00° for the hydrochloric acid cleavage of the trans isomer in 4% water-methanol solvent is shown in Table XVIII.

Table XVIII

Rate of Cleavage of trans Isomer

Run	$(HCl)_o \times 10^4$ M	$(trans)_o \times 10^4$ M	k_2 M^{-1} sec^{-1}
192	5.01	1.64	0.0275
193	125.2	1.64	0.0271
194	125.2	3.28	0.0273
195	125.2	3.28	0.0276
		average k_2	0.0274

Cis-γ-methylallyltrimethyltin. The rate constant at 25.00° for the hydrochloric acid cleavage of the cis isomer in 4% water-methanol are outlined in Table XIX.

Table XIX

Rate of Cleavage of cis Isomer

Run	$(HCl)_o \times 10^4$ M	$(cis)_o \times 10^4$ M	k_2 M^{-1} sec^{-1}
204	125.2	3.018	0.0482
205	125.2	3.018	0.0518
206	250.4	1.508	0.0519
207	250.4	1.508	0.0513
		average k_2	0.0508 ± .

The *cis* isomer is demonstrated to react almost twice as fast as the *trans* isomer. Both substrates react much more slowly than allyltrimethyltin, for which $k_2 = 0.475$ M^{-1} $sec.^{-1}$

Kinetics of Cleavage of Other Substrates

Rate of Cleavage of Allyltriphenyltin

Allyltriphenyltin, obtained from M & T Chemicals, Inc., was recrystallized from methanol. The observed melting point was 73.5 - 74.0°, the reported melting point is 73.5 - 74.5°. Rate of cleavage at 25.00° by hydrochloric acid in 4% water-methanol was measured spectrophotometrically at 235 mμ. The ultraviolet spectrum of allyltriphenyltin shows, in addition to the fine structure of the phenyl group at 260 mμ, the same kind of end absorption found in allyltrimethyltin. Triphenyltin chloride, the product of cleavage, also exhibits end absorption, but this is much less intense. At 235 $m\mu$ the divergence in absorbance is greatest, hence this wavelength was chosen to measure the kinetics. Because of the absorbance of products, the rate plot is linear to only 50% reaction. The rate constants are reported in Table XX. A typical rate plot is shown on Figure 6.

Table XX

Rate of Cleavage of Allyltriphenyltin

Run	$(HCl)_o \times 10^4$	$(\text{Ø}_3\text{SnAl})_o \times 10^4$	$k_2\ M^{-1}\ sec^{-1}$
212	400.8	2.200	0.00423
213	400.8	1.100	0.00472
214	200.4	2.200	0.00427
		average k_2	0.00441

Rate of Cleavage of γ-Methylallyltriphenyltin

γ-Methylallyltriphenyltin was synthesized by D. Whittemore in these laboratories[25] by the reaction of trimethyltinsodium and crotyl chloride in ammonia solvent. The portion used for rate measurements was recrystallized twice from methanol; the observed melting point 51-52°. The ratio of trans to cis isomer is not known. Rate of cleavage at 25.00° by hydrochloric acid in 4% water-methanol was measured spectrophotometrically at 235 $m\mu$. Rate plot is linear to 35% in Runs 215 and 216. The beginning stages

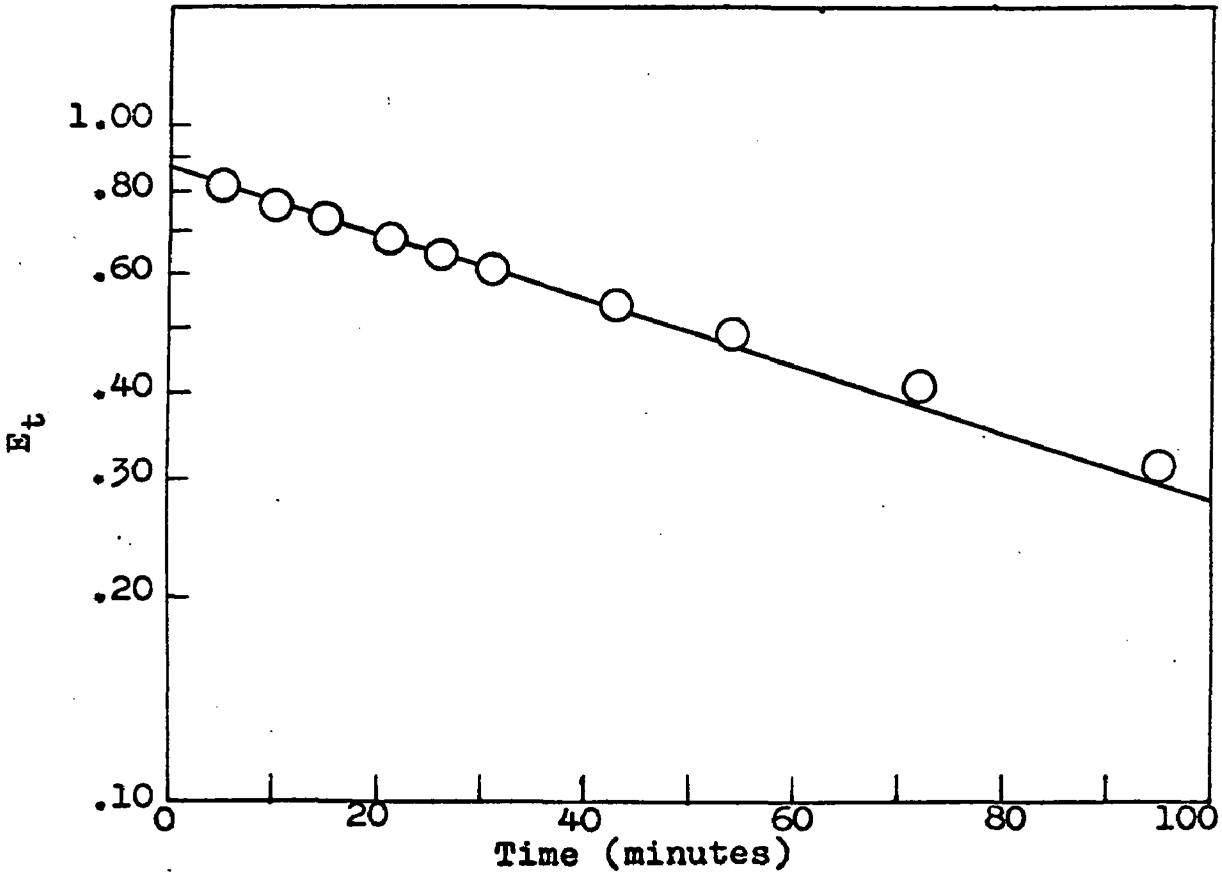


Figure 6. Pseudo-First Order Rate Plot Obtained by the Direct Method for the Protonolysis of Allyltriphenyltin in 4% Water-Methanol, Linear to 40% Reaction. Run 213.

of the reaction gave erratic points, which may be due to impurities present in the substrate. The results are summarized in Table XXI.

Table XXI

Rate of Cleavage of γ-methylallyltriphenyltin

Run	$(HCl)_0 \times 10^4$	$(\phi_3SnCr)_0 \times 10^4$	k_2 $M^{-1}sec^{-1}$
215	400.8	2.136	0.000335
216	400.8	1.068	0.000326
217	200.4	2.136	0.000298
		average k_2	0.000320

Rate of Cleavage of β-Methylallyltrimethyltin

β-methylallyltrimethyltin was synthesized in these laboratories by D. Whittemore[25] by the reaction of trimethyltinsodium and β-methylallyl chloride. The product boiled at 147°, and the carbon hydrogen analysis agrees with that predicted. The sample used for kinetics measurements was purified by vapor phase chromatography immediately before use, since this substrate proved more unstable in air and in the presence of moisture than any included in this study. Rate of cleavage at 25.00° by hydrochloric acid in 4% water-methanol was measured spectrophotometrically at 225 mμ. This substrate exhibits an ultraviolet absorbance in this region which approaches very closely that of allyltrimethyltin. Excellent kinetics were obtained, with second order rate plots linear to 90% reaction. Table XXII summarizes these runs.

Table XXII

Rate of Cleavage of β-Methylallyltrimethyltin

Run	$(HCl)_o \times 10^4$	$(Me_3SnBal)_o \times 10^4$	k_2 $M^{-1}sec^{-1}$
221	0.716	0.395	24.8
222	0.716	0.457	24.4
223	1.431	0.457	25.2
		average k_2	24.8

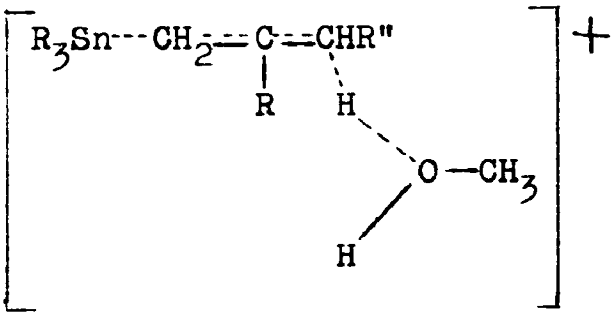
Mechanism of the Cleavage Reaction

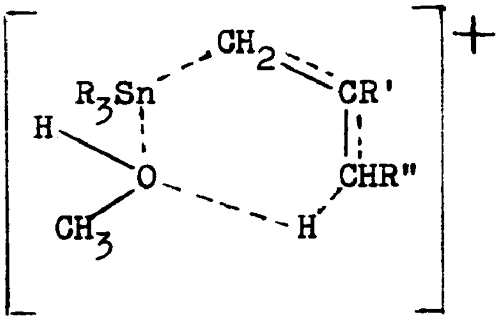
Nature of the Transition State

The kinetic order of the reaction in the absence of added salt indicates that the transition state contains one molecule of allyltin substrate and one molecule of acid. At the acid concentrations employed the acid is completely dissociated, hence the attacking reagent is lyonium ion rather than molecular acid or acid existing as a tight ion pair. Further support for lyonium ion attack is given by the observation that the rate of perchloric acid cleavage is the same as the rate of hydrochloric acid cleavage.

Since the product of cleavage of γ-methylallyl derivatives is almost exclusively 1-butene, the site of attack of lyonium ion is the terminal carbon atom of the allylic group. Thus attack is occurring at the carbon-carbon double bond two atoms removed from the large tin atom, and not at the tin-carbon σ bond as must occur with alkyl-tin cleavage. Gielen and Nasielski[13] have suggested the absence of steric interference in allyl-tin cleavage to be an important factor in the greater rate of cleavage of allyl - compared to alkyl-tin derivatives.

The transition state may be represented by either of two structures represented below. In both of these structures it is implied that formation of the substrate-lyonium ion bond is essentially complete, and the tin-carbon bond cleavage is well under way. Dotted lines represent partially formed or broken bonds.





I

II

Structure I represents an SE2' attack of lyonium ion. On completion of the formation of the new bonds, the emerging products are propylene and $R_3Sn^{\oplus}$ cation, with regeneration of a molecule of methanol. Structure II is an SE$'$ type in which lyonium ion attacks the double bond and the tin atom simultaneously. Tin-carbon cleavage is assisted by coordination of tin atom with the oxygen of the lyonium ion. This structure appears somewhat less likely than (I), particularly when one considers that solvent methanol could coordinate with the tin atom of (I) and furnish the same kind of assistance. The kinetics do not exclude this possibility, therefore it is included. Both $R_3Sn^{\oplus}$ and R_3SnOMe will react with chloride ion to generate R_3SnCl, which is the observed product of cleavage.

Effect of Water

The decrease in the observed rate constant upon addition of water is reported in Table V. This effect is attributed to the fact that addition of small amounts of water decreases the acidity of hydrochloric acid solutions in methanol. This effect was assessed by Braude and Stern,[17] who measured the acidity function, H, of hydrogen chloride in mixed aqueous and non-aqueous solvents. When ethanol, acetone, or dioxane was added to an aqueous solution of hydrochloric acid, the proton availability or acidity of the system decreased, passed through a minimum at 50 mole per cent organic solvent, and then increased, with a sharp increase occurring with ethanol and acetone in the region from 90 to 100 per cent organic solvent. In this range of solvent composition, addition of organic solvent steadily increases lyonium ion concentration while hydronium ion concentration decreases. The equilibrium (20) is displaced toward the left.

$$\mathrm{Et\overset{+}{O}H_2 + n\ H_2O \rightleftharpoons n\ H_2OH^+ + E{+}OH} \tag{20}$$

The reason for the dramatic increase in acidity as lyonium ion concentration increases can be ascribed to the fact that the equilibrium lies to the right (K=13), and the removal of hydronium ion constitutes removal of a species much less acidic than lyonium ion.

In 90% organic solvent, hydronium ion is thought to exist as the monomeric species (or n=1 in Equation (20)). This species acts as a much stronger base than water which is extensively solvated, as in pure water where n=4.

It should be noted that changes in dielectric constant, changes in per cent dissociation of the acid, and changes in activity coefficient are all operative as per cent organic solvent increases in this range. These changes are negligible, however, compared to the effect described above. Dielectric constant will decrease slightly in this range, and per cent dissociation will decrease roughly fourfold[14] as per cent methanol is increased from 90 to 100%. Both these factors would be expected to increase the rate of reaction as water content is increased, contrary to observation. It is suggested that these two effects are operative, but the greater effect of decreased acidity of the system is the overriding effect. Regarding the third effect, it is sufficient to note that the activity coefficient of hydrogen chloride itself changes by a factor of less than 5 on passing from pure water to pure ethanol.[17]

Effect of Inert Salt

The addition of sodium perchlorate produces a modest increase in the rate of reaction. The data fit neither the Bronsted relationship nor that proposed by Debye. It is difficult to attribute the acceleration to any particular facet of the mechanism.

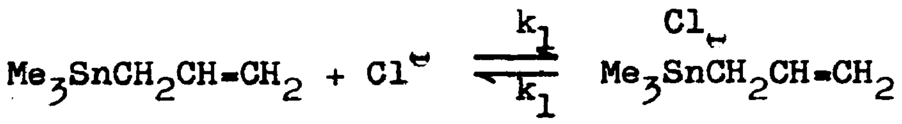
The magnitude of the salt effects indicate that the contribution of ionic strength effects to the observed rate over the range of acid concentrations employed is negligible.

Effect of Added Chloride Ion

The addition of chloride ion to the reaction mixture causes a sizable effect on the rate. The rate increases as chloride concentration increases; also, for a given chloride concentration, the rate increases as hydrogen ion concentration decreases. Thus a plot of k_{obs} vs. $\frac{1}{H^+}$ at constant sodium chloride concentration is linear.

One possibility to account for these observations is the formation of a chloride-tin substrate complex, analagous to that proposed by Dessy,[5] in a step preceding protonation. The resulting complex then undergoes cleavage faster than, but in competition with, cleavage of the tin substrate itself.

(21)



$$Me_3SnCH_2CH{=}CH_2 + Cl^{\ominus} \underset{k_1}{\overset{k_1}{\rightleftharpoons}} Me_3\overset{Cl^{\ominus}}{Sn}CH_2CH{=}CH_2$$

$$(22)\quad Me_3\overset{\overset{Cl^-}{\vdots}}{Sn}CH_2CH{=}CH_2 + H^+ \xrightarrow{k_2} \underset{\text{state}}{(\text{transition})} \xrightarrow[\text{fast}]{k_3} \text{Products}$$

$$(23)\quad Me_3SnCH_2CH{=}CH_2 + H^+ \xrightarrow{k_4} \underset{\text{state}}{(\text{transition})} \xrightarrow[\text{fast}]{k_5} \text{Products}$$

One might represent a methanol-tin substrate complex as well, certainly the present results do not exclude the possibility. There is no compelling evidence for this species, however, and the conclusions of the rate expression to follow are not altered by its absence. For simplicity the substrate is represented as not complexed with solvent.

$$(24)\quad \text{Rate} = \frac{d\ (\text{products})}{dt} = k_2\ (Me_3\overset{\overset{Cl^-}{\vdots}}{Sn}CH_2CH{=}CH_2)\ (H^+) + k_4\ (Me_3SnCH_2CH{=}CH_2)\ (H^+)$$

Assuming the steady state condition for $Me_3\overset{\overset{Cl^-}{}}{Sn}CH_2CH{=}CH_2$:

$$(25)\quad k_1\ (Me_3SnCH_2CH{=}CH_2)\ (Cl^-) = k_{-1}\ (Me_3\overset{\overset{Cl^-}{\vdots}}{Sn}CH_2CH{=}CH_2) + k_2\ (Me_3\overset{\overset{Cl^-}{\vdots}}{Sn}CH_2CH{=}CH_2)\ (H^+)$$

$$(26)\quad (Me_3\overset{\overset{Cl^-}{\vdots}}{Sn}CH_2CH{=}CH_2) = \frac{k_1\ (Me_3SnCH_2CH{=}CH_2)\ (Cl^-)}{k_{-1} + k_2\ (H^+)}$$

$$(27)\quad R = \frac{k_2k_1(Me_3SnCH_2CH{=}CH_2)\ (Cl^-)(H^+)}{k_{-1} + k_2\ (H^+)}$$

$$+ k_4\ (Me_3SnCH_2CH{=}CH_2)\ (H+)$$

$$(28)\quad R = (Me_3SnCH_2CH{=}CH_2)\ (H^+)\quad \frac{k_2k_1\ (Cl^-)}{\underline{k}_1 + k_2\ (H^+)} + k_4$$

If $k_2\ (H^+) \gg k_{-1}$:

$$(29)\quad R = (Me_3SnCH_2CH{=}CH_2)\ (H^+) \left\{ \frac{k_1\ (Cl^-)}{(H^+)} + k_4 \right\}$$

Thus $k_{obs} = \dfrac{k_1\ (Cl^-)}{(H^+)} + k_4.$

Qualitatively, this seems to agree with experimental results. The equation predicts that $k_{obs} = k_4$ in the absence of chloride ion (as when perchloric acid is the cleaving acid); when chloride concentration is equal to hydrogen ion concentration, however, $k_{obs} = k_1 + k_4$. Thus k_1 must be quite small compared to k_4 in order that the rate of cleavage in hydrochloric acid be the same as the rate of cleavage in perchloric acid.

The slope of a plot of k_{obs} vs. $\dfrac{1}{(H^+)}$ at constant chloride concentration should yield a slope of $k_1\ (Cl^-)$. From the data of Table IX reproduced in graphical form as Figure 5, the value of k_1 is calculated to be 7.04×10^{-3} $M^{-1}\ sec^{-1}$, much smaller than k_4. This means that chloride ion concentration must be 73 times larger than hydrogen ion concentration in order that the rate for Step I (equation 21) be equal to the rate of Step III (equation 23). Table IX indicates that the ratio of chloride to hydrogen ion is smaller than 73 for all but the first two runs. Thus formation of the complex would be slower than protonation of non-complexed tin substrate, and no increase in rate should be observed by this mechanism.

If the assumption is made that $k_{-1} \gg k_2\,(H^+)$, equation (28) becomes:

$$(30)\quad R = (Me_3SnCH_2CH{=}CH_2)\;(H^+)\;\left\{k_2\,K_{eq}\,(Cl^-) + k_4\right\}$$

and the term for dependence of k_{obs} on initial concentration of hydrogen ion vanishes.

Equation (28) would remain unchanged if $k_{-1} \cong k_2\,(H^+)$. The available data do not allow a test of this possibility.

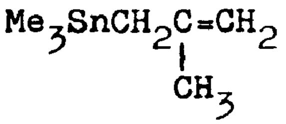
The data presented do not allow clearcut interpretation of the chloride ion effect. The pentacovalent chlorideallyltin substrate is not without precedent,[26] but the available data do not quantitatively support such an intermediate.

Reactivities of the Various Substrates

The second order rate constants for the various substituents are summarized in Table XXII. These are average values reported within the body of the thesis, and are estimated to be precise to ± 4%. Solvent is 4% water-methanol, acid is hydrochloric acid, temperature is 25.00° C.

Table XXIII

Reactivities of the Various Substrates

Compound	$k_2\ M^{-1}\ sec^{-1}$	Relative Rate
 $\mathrm{Me_3SnCH_2C(CH_3){=}CH_2}$	24.8	52.2
$\mathrm{Me_3SnCH_2CH{=}CH_2}$	0.475	1.00
cis $\mathrm{Me_3SnCH_2CH{=}CHCH_3}$	0.0508	0.107
trans $\mathrm{Me_3SnCH_2CH{=}CHCH_3}$	0.0274	0.0577
$\text{Ø}_3\mathrm{SnCH_2CH{=}CH_2}$	0.00441	0.00928
$\text{Ø}_3\mathrm{SnCH_2CH{=}CHCH_3}$[a]	0.000320	0.000674

[a] Isomeric composition unknown

Structure of the Leaving Group. From the table it is seen that allyltrimethyltin reacts 100 times faster than allyltriphenyltin. The tin-carbon bond in the ground state is polar, with the tin atom relatively positive. A methyl group attached to tin will further enhance the polarity by a positive inductive effect. In the transition state, heteralytic cleavage of this bond is well under way; a cationic tin species will result upon collapse of this structure. Thus, any substituent which can enhance polarity of this structure in the ground state or in the transition state should enhance the reactivity of a given allyltin substrate.

The phenyl group will reduce the polarity of the tin-carbon bond by its negative inductive effect.

If coordination of solvent molecule with the tin atom is a significant feature of the transition state, the phenyl groups might also decrease the rate by steric interference with coordinating solvent.

The great difference in rate of reaction between allyltrimethyltin and allyltriphenyltin is regarded as evidence that tin-carbon cleavage is underway in the transition state.

Substitution in the Allylic Group. Substitution of a methyl group for hydrogen at the β-carbon or at the γ-carbon of the allylic group gives rise to pronounced differences in reactivity. Comparison of these results with those obtained from investigations of addition of strong acids to various olefins is instructive. These studies have led to a reactivity series where:

$$(CH_3)_2C{=}CH_2 \sim (CH_3)_2C{=}CHCH_3 > CH_3CH{=}CH_2 > CH_2{=}CH_2$$

Thus ease of addition increases with increase in stability of the resulting carbonium ion.

β-Methylallyltrimethyltin reacts some 50 times faster than allyltrimethyltin. This order of reactivity would be expected if stability of the carbonium ion determines reactivity toward protonation. The former compound gives rise to a transition state with tertiary carbonium ion character; allyltrimethyltin gives a secondary carbonium ion.

The difference in reactivities between allyltrimethyltin and the <u>cis</u> and <u>trans</u>-γ-methylallyl isomers is unexpected. All attain secondary carbonium ion character in the transition state, and one might expect the methyl substituted isomers to form the more stable carbonium ion. However, allyltin reacts 9 times faster than the <u>cis</u> crotyl isomer and 17 times faster than the <u>trans</u> crotyl isomer.

A possible explanation for the difference in reactivity occurs in the studies of Taft and coworkers[27] on rates of hydration of isobutene and trimethylethylene. In this study it is found that isobutene reacts 1.3 times faster than trimethylethylene. The relatively small effect of change of structure on reactivities is thought to be due to compensating larger effects on the enthalpy and entropy of activation. Although the activation energy for hydration of dissolved trimethylethylene is greater than that for isobutene, the entropy of activation is more positive for the former reaction. It might be that the thermodynamic parameters do not compensate for the allyltins. Thus while the activation energies for allyltrimethyltin and γ-methylallyltrimethyltin might be similar, the former might exhibit a more positive entropy of activation. Since activation parameters were not measured in this study, data is not available to test this hypothesis.

In connection with discussion of the ultraviolet spectra, the possibility of a preferred conformation allowing maximum overlap of the π electrons of the double bond with the d orbitals of tin was advanced. If this conformation does in fact exist, one might expect the presence of a methyl group to introduce steric hindrance. As previously mentioned, overlap of this kind has not been established on a firm basis.

SECTION III

EXPERIMENTAL

Materials

Organotin Substrates

Allyltributyltin was obtained from M & T Chemicals Inc. and also was synthesized by the method of Jones and coworkers,[28] and was purified by treating an ethereal solution of the product with ammonia to remove unreacted tributyltin chloride, followed by distillation, b.p. 93-97°/0.65 mm.

Allyltrimethyltin, first reported by Petrov and coworkers,[29] was synthesized by an adaptation of the method of Jones and coworkers.[28] After allylmagnesium chloride and trimethyltin chloride had been refluxed together in diethyl ether, the reaction mixture was filtered, the solid was washed with ether and filtered again. After removal of most of the solvent on a Rinco evaporator the remaining liquid was fractionated at atmospheric pressure on a Todd column with spiral and rod packing, b.p. 126.5 - 127.5°. Since the compound decomposes when exposed to the atmosphere, it was stored in ampoules under reduced pressure. Yield: 64%. Analysis: Calculated for $C_6H_{14}Sn$: C, 35.17; H, 6.89. Found: C, 35.27; H, 6.85.

γ-Methylallyltrimethyltin was synthesized several times in the course of this study. Both cis and trans isomers were generated, and the dependence of isomer distribution on the structure of the starting chloride, as well as the yields obtained, are recorded in the Results and Discussion section. A typical preparation is outlined below.

Trimethyltinsodium was synthesized by an adaptation of the method of Kraus and Greer.[30] To a vigorously stirred suspension of 30 g. (0.15 mole) trimethyltin chloride in 100 ml. liquid ammonia was added small slices of sodium metal until the deep blue color characteristic of sodium dissolved in ammonia persisted for about ten minutes. A small quantity of trimethyltin chloride, sufficient to change the color of the mixture from deep blue to the dark yellow color characteristic of trimethyltinsodium in ammonia was then carefully added.

A solution of 15.8 g. (0.17 mole) crotyl chloride with 15 ml. diethyl ether was then added to the mixture, which discharged the yellow color immediately. Diethyl ether was added, the ammonia allowed to evaporate, and the mixture filtered. The solid was washed with ether and the washings added to filtrate, which was then stripped of solvent and fractionated on a Todd column. The product containing fractions boiled at $151.0 \pm 0.5^{\circ}$ (<u>trans</u> isomer) and $152.5 \pm 0.5^{\circ}$ (<u>cis</u> isomer). The isomer mixture was stored in ampoules under reduced pressure. Yield: 78%. Analysis: Calculated for $C_7H_{16}Sn$: C, 38.41; h, 7.37. Found: C, 38.23; H, 7.50.

The same procedure applied if 3-chloro-1-butene was the starting halide. Spectral data by which the structure of the isomers was assigned is reported in Results and Discussion.

Fractional distillation did not effect a complete separation of the isomers. When pure samples were required for spectral determination or kinetics measurements, the isomers were quantitatively separated by vapor phase chromatography on an 11 ft. column of General Electric XF 1150 silicone nitrile (17%) on 40-60 mesh Chromosorb P. Effluent was collected in two fractions, and reinjection of samples of each showed that each fraction was homogeneous.

Allyltriphenyltin, m.p. 73-74°, obtained from M & T Chemicals Inc., Lot 931-6A; after recrystallization from methanol it had m.p. 73.5 - 74.0°; Literature[31] m.p. 73.5-74.5°. Analysis (reported by M & T): Calculated for $C_{21}H_{20}Sn$: Sn, 30.35; Cl, 0.00. Found: Sn, 30.48; Cl, 0.00.

γ-Methylallyltriphenyltin was synthesized from triphenyltinsodium and crotyl chloride in liquid ammonia by D. Whittemore[33] in these laboratories. Infra-red spectrum of the product indicates both *cis* and *trans* isomer present; nuclear magnetic resonance suggests the *cis* isomer predominates. No separation of the isomers was achieved. Crude product was recrystallized from methanol, m.p. 51-52°. Analysis: Calculated for $C_{22}H_{22}Sn$: C, 65.22; H, 5.48. Found: C, 64.72; H, 5.30.

β-Methylallyltrimethyltin was synthesized from trimethyltinsodium and -methylallyl chloride in liquid ammonia by D. Whittemore[25] in these laboratories. Product was isolated by distillation on a Todd column, b.p. 147°. Impurities were still present, however, and final purification was effected on the silicone nitrile column immediately before rates of reaction were measured. This substrate is extremely sensitive to the atmosphere, and was stored in ampoules under reduced pressure. Analysis: Calculated for $C_7H_{16}Sn$: C, 38.41: H, 7.37. Found: C, 38.62; H, 7.34.

Hydrochloric Acid and Perchloric Acid

When anhydrous conditions were employed, hydrochloric acid solutions of known concentration were made by dissolving anhydrous hydrogen chloride (Matheson Co. 99.0% minimum purity) in anhydrous methanol and standardizing the resulting solution with sodium hydroxide to a phenolphthalein endpoint. Such solutions were unstable at room temperature and had to be restandardized before using. If the solution was stored in a refrigerator, the titer remained constant for 3-5 weeks.

When the kinetics solvent was 4.05% water-methanol, Fisher Reagent grade hydrochloric acid was diluted and standardized.

Perchloric acid used was Baker and Adamson Reagent grade diluted and standardized.

Salts

Sodium chloride was Fisher Reagent grade and was dried overnight at 110° before using.

Sodium perchlorate was Fisher Laboratory grade and was dried at 110° and pulverized repeatedly before using. It was weighed as the anhydrous salt.

Cadmium nitrate was Mallinckrodt Analytical Reagent grade and was dried overnight at 110° before using.

Trimethyltin chloride was crude material from M & T Chemicals Inc. and was purified by sublimation before using.

Solvents

Methanol was Fisher Certified Reagent grade, containing 0.01-0.05% water, depending on the lot, and was used without further purification.

Water was centrally distilled water redistilled through Pyrex apparatus used only for that purpose.

The greater number of reactions were run in "4% water-methanol" solvent. To make up this solvent, 4.00 ml. of water was placed in a 100 ml. volumetric flask, and methanol added to the calibration mark. The solvent therefore contained not only the 4 ml. of water, but the 0.01-0.05% water already present in the stock methanol. In the region of 4% water content of solvent, it can be seen that rate is insensitive to the small variation in water content which may arise in this way.

Kinetic Procedure

Aliquot Method

A typical run proceeded as follows: 20 ml. of a 10%

water-methanol solution and 25 ml. of stock solution of allyltrimethyltin in anhydrous methanol were pipetted into a 125 ml. Erlenmeyer flask with ground glass stopper, and placed in a constant temperature water bath maintained at 25.00 $\pm 0.01^{\circ}$. If salt was to be added, it was dissolved in the 10% water-methanol solvent. To start the reaction, 5 ml. of a stock solution of hydrochloric acid in anhydrous methanol was added to the mixture, and the stop watch started when the pipette was half empty. At intervals a 5 ml. aliquot was withdrawn and the reaction quenched by adding it to a solution of sodium methoxide in methanol of such concentration that more than enough was present to neutralize the acid.

Five or six such points were taken in a given reaction, and at the end of the reaction the optical density of these points were measured on a Beckman DU spectrophotometer, using as a reference a solution with the same water content, sodium methoxide concentration, and salt concentration as present in the quenched aliquot. In this connection it was found that sodium methoxide reacted slowly with allyltin substrate, so that the optical density of the quenched solution would show a slight decrease after 6-8 hours.

The optical density of the stock solution of allyltin substrate in methanol was measured daily, and a new stock solution made when a decrease in optical density was observed.

Direct Method

A more efficient method was devised when it became possible to control the temperature in the cell compartment of the DU by means of coils which fit snugly beside the cell compartment and through which water from the constant temperature bath could be circulated. Temperature could be controlled to 0.1^{o} by this arrangement. In the direct method, the reaction was run in the cell compartment of the DU, and the optical density read against an appropriate reference as the reaction progressed.

In a typical run, the reactants were all placed in a 50 ml. Erlenmeyer flask which has a concentric cylinder sealed to the bottom. Thus 5 ml. of hydrochloric acid solution were placed within the cylinder, and 5 ml. of allyltin stock solution plus 10 ml. 8% H_2O-methanol around the outside. The apparatus and reactants were brought to 25.00^{o}, and the reaction started by inverting the flask. An aliquot from the flask was quickly transferred to a DU cell, and the optical density read. This technique was particularly valuable for fast reactions, and allowed accurate rate measurements when the half life of the reaction was only 1.5 minutes.

Glassware Cleaning Procedure

Reaction vessels were filled with concentrated nitric acid and allowed to stand overnight. They were then washed with tap distilled water eight times, and finally rinsed with methanol three times and dried in an oven at 110°. The necessity of this final methanol rinse is demonstrated by the results shown on Table XXIII. When distilled water was used as the final rinse, catalytic impurities were left behind which accelerated the rate of reaction.

Table XXIV

Effect of Washing Procedure on the Observed Rate Constant

substrate: allyltrimethyltin
solvent: 4.05% water-methanol

Run	(HCl) x 10^4 M	(Me_3SnAl) x 10^4 M	k_2 $M^{-1}sec.^{-1}$	Final Rinse
90	4.980	1.850	0.530	dist. H_2O
91	2.490	1.850	0.701	" "
92	1.245	1.850	0.553	" "
93	4.980	1.753	0.473	methanol
94	4.980	1.753	0.480	"
95	4.980	1.753	0.633	dist. H_2O
97	4.980	1.753	0.470	methanol
98	4.980	1.753	0.470	"

Volumetric flasks which were to contain stock solutions were washed in the same manner as the reaction vessels. Those which were used to contain quenched aliquots were washed in detergent solution overnight, rinsed with tap distilled water, then with methanol, and dried in the oven. Pipettes were washed with concentrated nitric acid periodically, but were usually cleaned by rinsing several times with methanol, followed by drying on an aspirator.

Hydroboration

Disiamylborane was generated *in situ* by the method of Brown and coworkers[22]. To the resulting solution of 0.01 mole disiamylborane and 0.008 mole sodium borohydride in 19 ml. diglyme was added 3.5515 g. (0.016 mole) of a 1:1 mixture of *cis* and *trans*-γ-methylallyltrimethyltin. At intervals, 0.4 ml. of the reaction mixture was withdrawn and mixed with an equal volume of water. When the two layers separated, a sample of the organic layer was analyzed for unreacted isomers by vapor phase chromatography on the 11 ft. silicone nitrile column previously described.

A second method employed involved external generation of diborane. A solution of 0.844 g. (0.026 mole) of sodium borohydride in 12 ml. diglyme was added dropwise to 4.26 g. (0.030 mole) boron trifluoride etherate. The evolved diborane was passed through a small trap cooled by a Dry Ice - acetone mixture, then through a fritted glass tube into tetrahydrofuran purified in the manner prescribed by Fieser.[34] When the addition of borohydride was complete, a sample of the diborane solution was withdrawn by syringe and hydrolyzed on the Grignard machine to determine the concentration of the solution, which was such that 10 ml. of the solution contained 0.0062 mole diborane. A stoichemetric amount, 1.738 g. (0.0248 mole) 2-methyl-2-butene in 6 ml.

tetrahydrofuran was added to 10 ml. diborane solution. Three hours later, when the generation of disiamylborane was presumed to be complete, 2.72 g. (0.0124 mole) of a 1:1 mixture of cis and trans-γ-methylallyltrimethyltin was added, and sampling and analysis proceeded as previously described.

The results of these hydroborations are related in the Results and Discussion section.

Products of Cleavage

Allyltributyltin and hydrochloric acid

The reaction products of the cleavage of allyltributyltin by hydrochloric acid in dioxane solvent were identified by allowing 1.0 g. (.003 mole) allyltributyltin to react with 0.02 mole hydrochloric acid in 20 ml. dioxane on the Grignard apparatus. At first the mixture was heterogeneous, since the solubility of the allyltin substrate is limited, but the solution became homogeneous as the reaction progressed. The evolved gas was collected in the gas burette, transferred to a gas cell with sodium chloride windows, and the infra-red spectrum measured. The spectrum of this sample proved to be identical to a published spectrum of propylene.[33] The solvent was removed from the material in the reaction flask, and an infra-red spectrum of the remaining material was identical to that of an authentic sample of tributyltin chloride.

γ-Methylallyltrimethyltin and Hydrochloric Acid

The reaction products of cleavage of cis and trans-γ-methylallyltrimethyltin were identified by injecting 0.713 g. (0.00325 moles) of the isomer mixture through a serum cap into a flask containing 0.00466 moles hydrochloric acid in 12 ml. methanol. The outlet from the flask led to a trap made from a sidearm test tube which was immersed in liquid nitrogen. After the reaction was complete, water was added through the serum cap, and the displaced butenes frozen in the trap.

This procedure was shown to successfully trap up to 90% of the expected yield of butenes, as determined by bromine titration. To carry out the titration, pre-cooled chloroform was added to the frozen butenes in the trap, and a 0.432 M solution of bromine in acetic acid added by burette until the color of bromine persisted.

The material frozen in the traps was identified as consisting of predominantly 1-butene, with small amounts of cis and trans-2-butene, and a somewhat larger quantity of methyl chloride. Both 1-butene and methyl chloride were identified by comparison of infra-red spectra with spectra of authentic samples. Both 2-butenes were present in such small amounts that their presence could be inferred only by their retention times compared to the retention times of authentic samples, as measured by vapor phase chromatography on a 15 ft. column of 28% dimethylsulfolane on 40-60 mesh C-22 firebrick.

This column was able to completely separate the three butenes, and it was possible to calibrate the column so that the ratios of areas of the peaks could be converted to molar ratios. Table XVII in the Results and Discussion section illustrates the product composition arising from these experiments.

An attempt was made to determine the composition of the butene products at lower concentrations. In a typical run, 0.5329 g. (0.00244 moles) isomer mixture was added to a 1.51×10^{-3} M solution of hydrochloric acid in 2 l. 4% water-methanol. After three hours reaction time, 3 l. of water was added, and the mixture refluxed for 7 hours. Two traps, one cooled with Dry Ice-acetone and the other with liquid nitrogen, were used to try to stop the butenes, but the best yield of butenes attained was 50%. This long reflux period may have caused isomerization of the butenes so that the results listed in Table XVII are different at the two concentrations.

SECTION IV

TABLES

Key to Tables of Kinetics

Equations

1. Aliquot method

   a. Equal initial concentrations of substrate and acid.

$$\frac{1}{(E_{obs}-E_{\infty})_t} - \frac{1}{(E_{obs}-E_{\infty})_o} = \frac{7\ k_2\ t}{5\ \varepsilon}$$

Rate plot: $\frac{1}{(E_{obs}-E_{\infty})_t}$ vs. t

Slope = $\frac{7\ k_2}{5\ \varepsilon}$

   b. Unequal initial concentrations of substrate and acid.

$$\frac{2.303}{a-b} \log \frac{b(a-x)}{a\ (b-x)} = k_2 t$$

where a = initial concentration of reactant present in excess

b = initial concentration of reactant present in limiting amount.

x = concentration of both a and b which has reacted at time t.

$$x = C_{o_{\text{rxn. mixture}}} - C_{t_{\text{rxn. mixture}}} = \frac{7}{5}\,\frac{E_o - E_t}{\varepsilon}$$

Rate plot: $\log \frac{a-x}{b-x}$ *vs.* t

$$\text{Slope} = \frac{k_2\,(a-b)}{2.303}$$

c. Pseudo-first order conditions

$$\log\,(a-x) = k_1 t$$

$$x = \frac{7}{5}\,\frac{E_o - E_t}{\varepsilon}$$

Rate plot: $\log\,(a-x)$ *vs.* t

$$\text{Slope} = k_1 \quad ; \quad k_2 = \frac{k_1}{(HCl)_o}$$

2. Direct method (no dilution term)

a. Equal initial concentrations of substrate and acid.

Rate plot: $\frac{1}{(E_{obs} - E_{\infty})_t}$ *vs.* t

$$\text{Slope} = \frac{k_2}{\varepsilon}$$

b. Unequal initial concentrations of substrate and acid.

All quantities same except:

$$x = \frac{E_o - E_t}{\varepsilon}$$

c. Pseudo-first order conditions

$$\log E_t = k_1 t$$

$$\text{Slope} = k_1 \quad ; \quad \frac{k_1}{(\text{HCl})_o} = k_2.$$

Units and Abbreviations

In all tables, time is recorded in minutes.

The quantities x, (a-x), and (b-x) are abbreviations for x x 10^4 M, (a-x) x 10^4 M, and (b-x) x 10^4 M.

Abbreviations for substrates:

Bu_3SnAl = allyltributyltin

Me_3SnAl = allyltrimethyltin

cis = cis-γ-methylallyltrimethyltin

trans = trans-γ-methylallyltrimethyltin

Me_3SnBal = β-methylallyltrimethyltin

$\emptyset_3SnAl$ = Allyltriphenyltin

$\emptyset_3SnCr$ = γ-methylallyltriphenyltin

Solvent notations:

Anhydrous methanol - reagent grade methanol containing 0.01 - 0.02% water.

% H_2O designated - volume per cent water in the methanol solvent.

No designation - 4.05% by volume water in the methanol solvent.

Run 1 $a = b$

$HCl = Bu_3SnAl = 2.89 \times 10^{-4}M$ $E_\infty = 0.042$

anhydrous methanol

Time	$E_t - E_\infty$	$\frac{1}{E_t - E_\infty}$
5	0.940	1.06
10	0.728	1.37
20	0.503	1.99
40	0.315	3.17
70	0.198	5.05

$k_2 = 4.88M^{-1}$ sec.$^{-1}$

Run 2 $a = b$

$HCl = Bu_3SnAl = 2.31 \times 10^{-4}$ M $E_\infty = 0.044$

anhydrous methanol

Time	$E_t - E_\infty$	$\frac{1}{E_t - E_\infty}$
3	0.847	1.17
6	0.717	1.39
12	0.573	1.75
20	0.430	2.32
30	0.328	3.05
46	0.230	4.35
60	0.189	5.29
80	0.147	6.80

$k_2 = 5.74$ M^{-1} sec.$^{-1}$

Run 3 $a = b$

$HCl = Bu_3SnAl = 2.31 \times 10^{-4}$ M $E = 0.031$

anhydrous methanol

Time	$E_t - E$	$\frac{1}{E_t - E}$
2	0.905	1.11
4	0.825	1.21
9	0.653	1.53
13	0.584	1.71
20	0.432	2.32
46	0.253	3.95
60	0.206	4.85

$k_2 = 5.15\ M^{-1}\ sec.^{-1}$

Run 5 $a = HCl = 4.01 \times 10^{-4}$ M $\frac{a}{b} = 1.74$

$b = Bu_3SnAl = 2.31 \times 10^{-4}$ M

anhydrous methanol $E = 1.100$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.683	0.417	0.879	3.13	1.43	2.19
10	0.444	0.656	1.38	2.63	0.93	2.82
17	0.270	0.830	1.75	2.26	0.56	4.04
20	0.230	0.870	1.83	2.18	0.48	4.54
25	0.160	0.940	1.98	2.03	0.33	6.15
30	0.127	0.973	2.05	1.96	0.26	7.54

$k_2 = 4.88\ M^{-1}\ sec.^{-1}$

Run 6 $a = HCl = 4.01 \times 10^{-4}$ M $\frac{a}{b} = 1.39$

$b = Bu_3\ Sn\ Al = 2.89 \times 10^{-4}$ M

anhydrous methanol $E_o = 1.373$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
2	1.100	0.273	0.575	3.43	2.31	1.48
6	0.835	0.538	1.13	2.88	1.76	1.64
10	0.674	0.699	1.47	2.54	1.42	1.79
15	0.521	0.853	1.80	2.21	1.09	2.03
25	0.360	1.013	2.18	1.83	0.71	2.68
35	0.218	1.155	2.44	1.57	0.45	3.49
50	0.161	1.212	2.56	1.45	0.33	4.39

$k_2 = 3.72\ M^{-1}\ sec.^{-1}$

Run 11 $a = Bu_3SnAl = 2.31 \times 10^{-4}$ M $\frac{a}{b} = 1.54$

$b = HCl = 1.50 \times 10^{-4}$ M

anhydrous methanol $E_o = 1.100$

NaCl = 0.0440 M

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
2	0.828	0.272	0.57	1.74	0.93	1.87
5	0.767	0.333	0.70	1.61	0.80	2.02
10	0.676	0.424	0.89	1.42	0.61	2.33
15	0.616	0.484	1.02	1.29	0.48	2.69
20	0.547	0.553	1.16	1.15	0.34	3.38
30	0.491	0.609	1.28	1.03	0.22	4.68
40	0.476	0.624	1.31	1.00	0.19	5.26

$k_2 = 7.63\ M^{-1}\ sec.^{-1} = 7.63\ M^{-1}\ sec.^{-1}$

Run 13

$a = HCl = 4.39 \times 10^{-4}$ M
$b = Bu_3SnAl = 2.21 \times 10^{-4}$ M
anhydrous methanol

$\frac{a}{b} = 1.99$

$E_o = 1.050$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
4	0.499	0.551	0.70	3.69	1.51	2.44
9	0.323	0.727	1.23	3.16	0.98	3.22
15	0.212	0.838	1.57	2.82	0.64	4.41
20	0.157	0.893	1.73	2.66	0.48	5.55
25	0.122	0.928	1.84	2.55	0.37	6.90
30	0.088	0.962	1.94	2.45	0.27	9.08

$k_2 = 4.00\ M^{-1}\ sec.^{-1}$

Run 14

$a = HCl = 4.39 \times 10^{-4}$ M
$b = Bu_3SnAl = 2.21 \times 10^{-4}$ M
anhydrous methanol

$\frac{a}{b} = 1.99$

$E_o = 1.472$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
3	1.100	0.372	0.56	3.83	1.65	2.32
5	0.893	0.579	0.87	3.52	1.34	2.63
7	0.741	0.731	1.10	3.29	1.11	2.96
9	0.620	0.852	1.28	3.10	0.93	3.34
12	0.480	0.992	1.49	2.90	0.72	4.03
15	0.379	1.093	1.64	2.75	0.57	4.83
18	0.302	1.170	1.76	2.63	0.45	5.85
21	0.242	1.230	1.45	2.54	0.36	7.05
26	0.171	1.301	1.95	2.44	0.26	9.38
30	0.130	1.342	2.02	2.37	0.19	12.5
35	0.094	1.378	2.07	2.32	0.14	16.6

$k_2 = 4.71\ M^{-1}\ sec.^{-1}$

Run 15

a = HCl = 4.39 x 10^{-4} M
b = Bu_3SnAl = 3.46 x 10^{-4} M
anhydrous methanol

$\frac{a}{b}$ = 1.27

E_o = 2.280

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
3.5	1.72	0.560	0.841	3.55	2.62	1.35
4	1.68	0.600	0.903	3.49	2.56	1.36
6	1.45	0.830	1.25	3.14	2.21	1.42
8	1.28	1.000	1.50	2.89	1.96	1.48
12	1.08	1.200	1.81	2.58	1.65	1.56
15	0.875	1.405	2.11	2.28	1.35	1.69
20	0.694	1.586	2.38	2.01	1.08	1.86
22	0.638	1.642	2.47	1.92	0.99	1.94
25	0.568	1.712	2.58	1.81	0.88	2.06
28	0.510	1.770	2.66	1.73	0.80	2.16
30	0.474	1.806	2.72	1.67	0.74	2.26
35	0.402	1.878	2.82	1.57	0.64	2.46

k_2 = 3.44 M^{-1} $sec.^{-1}$

Run 16

$a = HCl = 4.39 \times 10^{-4}$ M
$b = Bu_3SnAl = 2.76 \times 10^{-4}$ M
anhydrous methanol

$\frac{a}{b} = 1.59$

$E_0 = 1.831$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
3	1.37	0.461	0.693	3.70	2.07	1.79
5	1.13	0.701	1.05	3.34	1.71	1.95
8	0.873	0.958	1.44	2.95	1.32	2.24
12	0.642	1.189	1.79	2.60	0.97	2.68
16	0.489	1.342	2.02	2.37	0.74	3.20
20	0.379	1.452	2.18	2.21	0.58	3.81
25	0.277	1.554	2.34	2.05	0.42	4.88
30	0.209	1.622	2.44	1.95	0.32	6.09
35	0.161	1.670	2.51	1.88	0.25	7.52

$k_2 = 4.57$ M^{-1} $sec.^{-1}$

Run 17

$a = HCl = 4.39 \times 10^{-4}$ M

$b = Bu_3SnAl = 2.89 \times 10^{-4}$ M

anhydrous methanol

$\frac{a}{b} = 1.52$

$E_o = 1.918$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
6	1.00	0.918	1.38	3.01	1.51	1.99
10	0.733	1.185	1.79	2.60	1.10	2.36
15	0.524	1.394	2.10	2.29	0.79	2.90
20	0.370	1.548	2.33	2.06	0.56	3.68
25	0.275	1.643	2.48	1.91	0.41	4.66
30	0.208	1.710	2.58	1.81	0.31	5.84

$k_2 = 5.04$ M^{-1} $sec.^{-1}$

Run 24

$a = HCl = 2.81 \times 10^{-4}$ M

$b = Me_3SnAl = 1.85 \times 10^{-4}$ M

anhydrous methanol

$\frac{a}{b} = 1.52$

$E_o = 0.603$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.398	0.205	0.64	2.17	1.21	1.79
10	0.279	0.324	1.01	1.80	0.84	2.14
15	0.210	0.393	1.23	1.58	0.62	2.55
25	0.120	0.483	1.51	1.30	0.34	3.82

$k_2 = 5.80$ M^{-1} $sec.^{-1}$

Run 26

$a = HCl = 2.81 \times 10^{-4}$ M

$b = Me_3SnAl = 0.93 \times 10^{-4}$ M

anhydrous methanol

$\frac{a}{b} = 3.02$

$E_o = 0.427$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
6	0.224	0.203	0.44	2.37	0.49	4.84
11	0.153	0.277	0.61	2.20	0.32	6.87
20	0.090	0.340	0.74	2.07	0.19	10.9
30	0.036	0.394	0.86	1.95	0.07	27.9

$k_2 = 5.90\ M^{-1}\ sec.^{-1}$

Run 27

$a = HCl = 1.41 \times 10^{-4}$ M

$b = Me_3SnAl = 0.93 \times 10^{-4}$ M

anhydrous methanol

$\frac{a}{b} = 1.52$

$E_o = 0.427$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.294	0.133	0.29	1.12	0.64	1.75
10	0.245	0.182	0.40	1.01	0.53	1.91
20	0.189	0.238	0.52	0.89	0.41	2.17
30	0.142	0.285	0.62	0.79	0.31	2.55
45	0.088	0.339	0.75	0.67	0.19	3.53

$k_2 = 6.00\ M^{-1}\ sec.^{-1}$

Run 33

$a = HCl = 1.90 \times 10^{-4}$ M

$b = Me_3SnAl = 0.639 \times 10^{-4}$ M

anhydrous methanol

$NaClO_4 = 0.0455$ M

$\frac{a}{b} = 2.98$

$E_o = 0.302$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.201	0.101	0.213	1.687	0.426	3.96
11	0.134	0.168	0.355	1.545	0.284	5.44
15	0.106	0.196	0.414	1.486	0.225	6.60
25	0.062	0.240	0.507	1.393	0.132	10.55
35	0.046	0.256	0.540	1.360	0.099	13.75

$k_2 = 7.02\ M^{-1}\ sec.^{-1}$

Run 34

$a = HCl = 1.90 \times 10^{-4}$ M

$b = Me_3SnAl = 0.639 \times 10^{-4}$ M

anhydrous methanol

$NaClO_4 = 0.0228$ M

$\frac{a}{b} = 2.98$

$E_o = 0.302$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.214	0.088	0.185	1.715	0.454	3.78
11	0.160	0.142	0.300	1.600	0.339	4.72
15	0.123	0.179	0.378	1.522	0.261	5.83
25	0.071	0.231	0.488	1.412	0.151	8.99
35	0.042	0.260	0.549	1.351	0.090	15.00

$k_2 = 6.00\ M^{-1}\ sec.^{-1}$

Run 35

a = HCl = 1.90 x 10^{-4} M

b = Me_3SnAl = 0.639 x 10^{-4}M

anhydrous methanol

$NaClO_4$ = 0.0114 M

$\frac{a}{b}$ = 2.98

E_o = 0.302

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.217	0.085	0.179	1.721	0.460	3.74
10	0.166	0.136	0.287	1.613	0.352	4.58
15	0.121	0.181	0.382	1.518	0.257	5.90
25	0.069	0.233	0.492	1.408	0.147	9.56
35	0.037	0.265	0.559	1.341	0.080	16.80

k_2 = 6.08 M^{-1} sec.$^{-1}$

Run 36

a = HCL = 0.946 x 10^{-4} M

b = Me_3SnAl = 0.639 x 10^{-4} M

anhydrous methanol

NaCl = 0.0455 M

$\frac{a}{b}$ = 1.48

E_o = 0.302

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
2	0.189	0.113	0.238	0.708	0.401	1.76
5	0.152	0.150	0.316	0.630	0.323	1.95
8	0.125	0.177	0.373	0.573	0.266	2.15
12	0.089	0.213	0.449	0.497	0.190	2.62
18	0.058	0.244	0.514	0.432	0.125	3.46

k_2 = 25.5 M^{-1} sec.$^{-1}$

Run 37

a = HCl = 0.946 x 10^{-4} M

b = Me_3SnAl = 0.639 x 10^{-4} M

anhydrous methanol

NaCl = 0.0227 M

$\frac{a}{b}$ = 1.48

E_o = 0.302

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
2	0.202	0.100	0.211	0.735	0.428	1.72
6	0.211	0.091	0.192	0.754	0.447	1.69
10	0.120	0.182	0.384	0.562	0.255	2.20
14.5	0.088	0.214	0.452	0.494	0.187	2.64
18	0.067	0.235	0.496	0.450	0.143	3.15

k_2 = 22.0 M^{-1} $sec.^{-1}$

Run 38

a = HCl = 0.946 x 10^{-4} M

b = Me_3SnAl = 0.639 x 10^{-4} M

anhydrous methanol

NaCl = 0.0114 M

$\frac{a}{b}$ = 1.48

E_o = 0.302

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
2.5	0.205	0.097	0.205	0.741	0.434	1.71
6	0.158	0.144	0.304	0.642	0.335	1.92
10	0.127	0.175	0.369	0.577	0.270	2.14
14	0.094	0.208	0.439	0.507	0.200	2.54
18	0.071	0.231	0.488	0.458	0.151	3.03

k_2 = 21.3 M^{-1} $sec.^{-1}$

Run 43

$b = HCl = 0.468 \times 10^{-4}$ M

$a = Me_3SnAl = 0.639 \times 10^{-4}$ M

anhydrous methanol

NaCl = 0.0228 M

$\frac{a}{b} = 1.37$

$E_o = 0.320$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
2	0.277	0.043	0.091	0.548	0.377	1.45
5	0.236	0.084	0.177	0.462	0.291	1.59
10	0.189	0.131	0.276	0.363	0.192	1.89
15	0.151	0.169	0.355	0.284	0.113	2.51
20	0.125	0.195	0.412	0.227	0.056	4.05

$k_2 = 29.4\ M^{-1}\ sec.^{-1}$

Run 44

$b = HCl = 0.646 \times 10^{-4}$ M

$a = Me_3SnAl = 0.928 \times 10^{-4}$ M

anhydrous methanol

NaCl = 0.0250 M

$\frac{a}{b} = 1.435$

$E_o = 0.458$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
2	0.416	0.042	0.089	0.839	0.557	1.51
4	0.374	0.084	0.177	0.751	0.469	1.60
8	0.323	0.135	0.284	0.644	0.362	1.78
12	0.282	0.176	0.372	0.556	0.274	2.03
16	0.328	0.130	0.264	0.664	0.382	1.74
24	0.187	0.271	0.572	0.356	0.074	4.81

$k_2 = 16.9\ M^{-1}\ sec.^{-1}$

Run 45

$b = HCl = 0.646 \times 10^{-4}$ M

$a = Me_3SnAl = 0.928 \times 10^{-4}$ M

anhydrous methanol

NaCl = 0.0250 M

$\frac{a}{b} = 1.435$

$E_o = 0.456$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
2	0.413	0.043	0.091	0.837	0.555	1.51
4	0.374	0.082	0.173	0.755	0.473	1.60
8	0.323	0.133	0.281	0.647	0.365	1.77
12	0.269	0.187	0.395	0.533	0.251	2.12
16	0.253	0.203	0.429	0.499	0.217	2.30
24	0.193	0.263	0.555	0.373	0.091	4.10

$k_2 = 16.6\ M^{-1}\ sec.^{-1}$

Run 46

$b = HCl = 0.646 \times 10^{-4}$ M

$a = Me_3SnAl = 0.928 \times 10^{-4}$ M

anhydrous methanol

NaCl = 0.0250 M

$\frac{a}{b} = 1.435$

$E_o = 0.457$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
2	0.398	0.059	0.130	0.798	0.516	1.55
4	0.369	0.088	0.194	0.734	0.452	1.62
8	0.317	0.140	0.296	0.632	0.350	1.80
12	0.296	0.161	0.340	0.588	0.306	1.92
17	0.230	0.227	0.479	0.449	0.167	2.69
25	0.169	0.288	0.608	0.320	0.038	8.42

$k_2 = 17.5\ M^{-1}\ sec.^{-1}$

Run 48 $b = HCl = 0.638 \times 10^{-4}$ M $\frac{a}{b} = 1.45$

$a = Me_3SnAl = 0.928 \times 10^{-4}$ M

anhydrous methanol $E_o = 0.457$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.428	0.029	0.061	0.865	0.577	1.50
10	0.392	0.065	0.133	0.795	0.505	1.58
15	0.368	0.089	0.188	0.740	0.450	1.64
25	0.321	0.136	0.287	0.641	0.351	1.83
35	0.295	0.162	0.342	0.586	0.296	1.98
50	0.266	0.191	0.402	0.526	0.236	2.23

$k_2 = 5.13\ M^{-1}\ sec.^{-1}$

Run 49 $a = HCl = 1.276 \times 10^{-4}$ M $\frac{a}{b} = 1.38$

$b = Me_3SnAl = 0.928 \times 10^{-4}$ M

anhydrous methanol $E_o = 0.457$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.379	0.078	0.165	1.111	0.763	1.46
10	0.322	0.135	0.285	0.991	0.643	1.54
15	0.277	0.180	0.380	0.896	0.540	1.66
25	0.229	0.228	0.481	0.795	0.447	1.78
35	0.186	0.271	0.572	0.704	0.356	1.98
50	0.131	0.326	0.688	0.588	0.240	2.45

$k_2 = 5.57\ M^{-1}\ sec.^{-1}$

Run 50 a = HCl = 2.564×10^{-4} M $\frac{a}{b}$ = 2.76
b = Me_3SnAl = 0.928×10^{-4} M
anhydrous methanol E_o = 0.466

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.315	0.151	0.319	2.245	0.609	3.69
10	0.223	0.243	0.513	2.051	0.415	4.94
20	0.127	0.339	0.715	1.849	0.213	8.68
30	0.077	0.389	0.820	1.744	0.108	16.15
50	0.038	0.428	0.904	1.661	0.025	66.5

k_2 = 5.98 M^{-1} $sec.^{-1}$

Run 51 a = HCl = 2.346×10^{-4} M $\frac{a}{b}$ = 2.53
b = Me_3SnAl = 0.928×10^{-4} M
anhydrous methanol E_o = 0.466

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.324	0.142	0.300	2.043	0.628	3.25
10	0.227	0.239	0.505	1.838	0.423	4.35
20	0.150	0.316	0.667	1.676	0.261	6.42
31	0.079	0.387	0.817	1.526	0.111	13.8
50	0.040	0.426	0.900	1.443	0.028	51.6

k_2 = 6.45 M^{-1} $sec.^{-1}$

Run 52 $a = HCl = 2.564 \times 10^{-4}$ M $\frac{a}{b} = 2.76$

$b = Me_3SnAl = 0.928 \times 10^{-4}$ M

anhydrous methanol $E_o = 0.466$

$Me_3SnCl = 2.575 \times 10^{-4}$ M

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.316	0.150	0.317	2.247	0.611	3.68
10	0.225	0.241	0.509	2.055	0.419	4.90
16	0.160	0.306	0.646	1.918	0.282	6.80
20	0.128	0.338	0.714	1.850	0.214	8.65
30	0.085	0.381	0.804	1.760	0.124	14.2

$k_2 = 5.88\ M^{-1}\ sec.^{-1}$

Run 53 $a = HCl = 2.559 \times 10^{-4}$ M $\frac{a}{b} = 2.75$

$b = Me_3SnAl = 0.928 \times 10^{-4}$ M

anhydrous methanol $E_o = 0.430$

NaCl = 0.0125 M

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
2	0.337	0.093	0.196	2.363	0.732	3.23
5	0.245	0.185	0.390	2.169	0.538	4.03
10	0.145	0.285	0.601	1.958	0.327	5.99
16	0.072	0.358	0.755	1.804	0.173	10.4
25	0.036	0.394	0.831	1.728	0.097	17.8
35	0.008	0.426	0.898	1.661	0.030	55.4

$k_2 = 8.03\ M^{-1}\ sec.^{-1}$

Run 54

a = HCl = 2.559 x 10^{-4} M

b = Me_3SnAl = 0.928 x 10^{-4} M

anhydrous methanol

NaCl = 0.0125 M

Me_3SnCl = 2.575 x 10^{-4} M

$\frac{a}{b}$ = 2.75

E_o = 0.430

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
2	0.329	0.101	0.213	2.346	0.715	3.28
5	0.247	0.183	0.386	2.173	0.542	4.00
10	0.146	0.284	0.599	1.960	0.329	5.96
15	0.102	0.328	0.692	1.867	0.236	7.90
20	0.066	0.364	0.768	1.791	0.160	11.2
25	0.030	0.400	0.843	1.716	0.085	20.2

k_2 = 7.87 M^{-1} $sec.^{-1}$

Run 55

a = HCl = 2.474 x 10^{-4} M

b = Me_3SnAl = 0.928 x 10^{-4} M

anhydrous methanol

NaCl = 0.0125

$\frac{a}{b}$ = 2.67

E_o = 0.457

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
2	0.361	0.096	0.202	2.272	0.726	3.13
5	0.310	0.147	0.310	2.164	0.618	3.50
10	0.181	0.276	0.583	1.891	0.345	5.49
15	0.121	0.336	0.710	1.764	0.218	8.10
20	0.095	0.362	0.764	1.710	0.164	10.4

k_2 = 7.97 M^{-1} $sec.^{-1}$

Run 56

$a = HCl = 2.474 \times 10^{-4}$ M
$b = Me_3SnAl = 0.928 \times 10^{-4}$ M
anhydrous methanol
NaCl = 0.0250 M

$\frac{a}{b} = 2.67$

$E_o = 0.457$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
2	0.346	0.111	0.234	2.240	0.694	3.23
5	0.251	0.206	0.425	2.049	0.503	4.08
10	0.152	0.305	0.644	1.830	0.284	6.45
13	0.128	0.329	0.695	1.779	0.233	7.63
18	0.073	0.384	0.810	1.664	0.118	14.1

$k_2 = 9.68$ M^{-1} $sec.^{-1}$

Run 58

$a = HCl = 2.474 \times 10^{-4}$ M
$b = Me_3SnAl = 0.928 \times 10^{-4}$ M
anhydrous methanol
NaCl = 0.01875 M

$\frac{a}{b} = 2.67$

$E_o = 0.457$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
2	0.347	0.110	0.232	2.242	0.696	3.22
4.5	0.281	0.176	0.372	2.102	0.556	3.78
8	0.214	0.243	0.513	1.961	0.415	4.73
12	0.144	0.313	0.661	1.813	0.267	6.80
18	0.099	0.358	0.755	1.719	0.173	9.94

$k_2 = 8.37$ M^{-1} $sec.^{-1}$

Run 59 a = HCl = 2.474×10^{-4} M $\frac{a}{b}$ = 2.67

b = Me_3SnAl = 0.928×10^{-4}

anhydrous methanol E_o = 0.457

NaCl = 0.03750 M

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
2	0.289	0.168	0.354	2.120	0.574	3.69
4	0.228	0.229	0.483	1.991	0.445	4.48
8	0.146	0.311	0.656	1.818	0.272	6.68
12	0.096	0.361	0.761	1.713	0.167	10.3
16	0.064	0.393	0.829	1.645	0.099	16.6

k_2 = 12.3 M^{-1} $sec.^{-1}$

Run 61 a = HCl = 2.500×10^{-4} M $\frac{a}{b}$ = 2.04

b = Me_3SnAl = 1.226×10^{-4} M

anhydrous methanol E_o = 0.573

NaCl = 0.01875 M

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
2.5	0.450	0.123	0.259	2.241	0.967	2.32
4	0.401	0.172	0.362	2.138	0.864	2.48
7	0.307	0.266	0.561	1.939	0.665	2.92
10	0.256	0.317	0.668	1.832	0.558	3.28
14	0.184	0.389	0.820	1.680	0.406	4.14
18	0.137	0.436	0.919	1.581	0.307	5.15

k_2 = 6.63 M^{-1} $sec.^{-1}$

Run 62

a = HCl = 2.500×10^{-4} M

b = Me_3SnAl = 1.226×10^{-4} M

anhydrous methanol

NaCl = 0.0375 M

$\frac{a}{b} = 2.04$

$E_o = 0.573$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
2	0.432	0.141	0.298	2.202	0.928	2.38
4	0.352	0.221	0.466	2.034	0.760	2.68
6.83	0.263	0.310	0.654	1.846	0.572	3.22
10	0.191	0.382	0.806	1.694	0.420	4.04
15	0.113	0.460	0.970	1.530	0.256	5.97
18	0.091	0.482	1.018	1.482	0.208	7.12

$k_2 = 8.99\ M^{-1}\ sec.^{-1}$

Run 63

a = HCl = 2.500×10^{-4} M

b = Me_3SnAl = 1.226×10^{-4} M

anhydrous methanol

$\frac{a}{b} = 2.04$

$E_o = 0.573$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
3	0.474	0.099	0.209	2.291	1.017	2.25
6	0.391	0.182	0.384	2.116	0.842	2.51
11	0.289	0.284	0.599	1.901	0.627	3.03
15	0.243	0.330	0.695	1.805	0.531	3.40
21	0.184	0.389	0.820	1.680	0.406	4.14
25	0.145	0.428	0.902	1.598	0.324	4.93

$k_2 = 4.55\ M^{-1}\ sec.^{-1}$

Run 64

a = HCl = 2.500 x 10^{-4} M

b = Me_3SnAl = 1.226 x 10^{-4} M

anhydrous methanol

$\frac{a}{b}$ = 2.04

E_o = 0.573

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
3	0.452	0.121	0.255	2.245	0.971	2.31
6	0.375	0.198	0.418	2.082	0.808	2.58
11	0.279	0.294	0.620	1.880	0.606	3.10
15	0.214	0.359	0.757	1.743	0.469	3.72
21	0.157	0.416	0.877	1.623	0.349	4.65
25	0.132	0.441	0.930	1.570	0.296	5.30

k_2 = 5.06 M^{-1} $sec.^{-1}$

Run 65

a = HCl = 2.500 x 10^{-4} M

b = Me_3SnAl = 1.226 x 10^{-4} M

anhydrous methanol

$\frac{a}{b}$ = 2.04

E_o = 0.590

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
6	0.342	0.248	0.523	1.977	0.703	2.81
10	0.262	0.328	0.692	1.808	0.534	3.39
15	0.179	0.411	0.866	1.634	0.360	4.54
20	0.126	0.464	0.979	1.521	0.247	6.16
25	0.095	0.495	1.043	1.457	0.183	7.96

k_2 = 7.12 M^{-1} $sec.^{-1}$

Run 66

$a = HCl = 2.500 \times 10^{-4}$ M

$b = Me_3SnAl = 1.226 \times 10^{-4}$ M

0.55% H_2O

$\frac{a}{b} = 2.04$

$E_o = 0.590$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.431	0.159	0.336	2.164	0.890	2.43
10	0.330	0.260	0.549	1.951	0.677	2.88
15	0.252	0.338	0.713	1.787	0.513	3.48
20	0.205	0.385	0.813	1.687	0.413	4.08
25	0.165	0.425	0.897	1.603	0.329	4.87

$k_2 = 4.57\ M^{-1}\ sec.^{-1}$

Run 67

$a = HCl = 2.500 \times 10^{-4}$ M

$b = Me_3SnAl = 1.256 \times 10^{-4}$ M

anhydrous methanol

$\frac{a}{b} = 2.04$

$E_o = 0.583$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
5.5	0.370	0.213	0.449	2.051	0.776	2.64
10	0.308	0.275	0.580	1.920	0.646	2.98
15	0.233	0.350	0.739	1.761	0.487	3.62
20	0.172	0.411	0.866	1.634	0.360	4.54
30	0.105	0.478	1.009	1.491	0.217	6.88

$k_2 = 5.27\ M^{-1}\ sec.^{-1}$

Run 68 a = HCl = 2.5000 x 10^{-4} M $\frac{a}{b}$ = 2.04

b = Me_3SnAl = 1.226 x 10^{-4} M

anhydrous methanol E_o = 0.583

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.411	0.172	0.363	2.137	0.863	2.48
10	0.291	0.292	0.616	1.884	0.610	3.09
15	0.220	0.363	0.765	1.735	0.461	3.77
20	0.166	0.417	0.880	1.620	0.346	4.68
30	0.099	0.484	1.020	1.480	0.206	7.19

k_2 = 5.52 M^{-1} $sec.^{-1}$

Run 69 a = HCl = 2.500 x 10^{-4} M $\frac{a}{b}$ = 2.04

b = Me_3SnAl = 1.226 x 10^{-4} M

anhydrous methanol E_o = 0.596

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.422	0.174	0.367	2.133	0.859	2.48
10	0.315	0.281	0.593	1.907	0.633	3.02
15	0.246	0.350	0.738	1.762	0.488	3.61
20	0.187	0.409	0.862	1.638	0.364	4.50
25	0.151	0.445	0.939	1.561	0.287	5.45
30	0.122	0.474	1.000	1.500	0.226	6.64

k_2 = 5.12 M^{-1} $sec.^{-1}$

Run 70

a = HCl = 2.500×10^{-4} M

b = Me_3SnAl = 1.226×10^{-4} M

0.55% H_2O

0.5% H_2O by vol.

$\frac{a}{b} = 2.04$

$E_o = 0.596$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.508	0.088	0.186	2.314	1.040	2.22
10	0.439	0.157	0.331	2.169	0.895	2.42
15	0.378	0.218	0.460	2.040	0.766	2.66
20	0.347	0.249	0.525	1.975	0.701	2.82
30	0.263	0.333	0.703	1.797	0.523	3.44

Run 73

a = HCl = 1.264×10^{-4} M

b = Me_3SnAl = 0.903×10^{-4} M

0.05% H_2O

$\frac{a}{b} = 1.40$

$E_o = 0.460$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.380	0.080	0.158	1.106	0.745	1.48
10	0.329	0.131	0.258	1.006	0.645	1.56
15	0.288	0.172	0.338	0.926	0.565	1.64
25	0.226	0.234	0.460	0.804	0.443	1.82
40	0.163	0.297	0.585	0.679	0.318	2.14
63	0.105	0.355	0.699	0.565	0.204	2.77

$k_2 = 5.04$ M^{-1} sec.$^{-1}$

Run 74

$a = HCl = 1.264 \times 10^{-4}$ M

$b = Me_3SnAl = 0.903 \times 10^{-4}$ M

0.05% H_2O

$\frac{a}{b} = 1.40$

$E_o = 0.460$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.375	0.085	0.167	1.097	0.736	1.49
10	0.334	0.126	0.248	1.016	0.655	1.55
15	0.282	0.178	0.350	0.914	0.553	1.65
25	0.220	0.240	0.473	0.791	0.430	1.84
40	0.169	0.291	0.573	0.691	0.330	2.10

$k_2 = 5.06$ M^{-1} $sec.^{-1}$

Run 75

$a = HCl = 1.580 \times 10^{-4}$ M

$b = Me_3SnAl = 0.903 \times 10^{-4}$ M

0.05% H_2O

$\frac{a}{b} = 1.75$

$E_o = 0.460$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.350	0.110	0.216	1.364	0.687	1.99
10	0.300	0.160	0.315	1.265	0.588	2.15
15	0.246	0.214	0.421	1.159	0.482	2.40
25	0.181	0.279	0.550	1.030	0.353	2.92
35	0.136	0.324	0.639	0.941	0.264	3.57

$k_2 = 5.08$ M^{-1} $sec.^{-1}$

Run 76

$a = HCl = 1.580 \times 10^{-4}$ M

$b = Me_3SnAl = 0.903 \times 10^{-4}$ M

0.45% H_2O

$\frac{a}{b} = 1.75$

$E_o = 0.460$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.392	0.068	0.134	1.446	0.769	1.88
10	0.351	0.109	0.215	1.365	0.688	1.98
15	0.319	0.141	0.278	1.302	0.625	2.08
25	0.261	0.199	0.392	1.188	0.511	2.32
35	0.215	0.245	0.482	1.098	0.421	2.61

$k_2 = 2.78\ M^{-1}\ sec.^{-1}$

Run 77

$a = HCl = 1.580 \times 10^{-4}$ M

$b = Me_3SnAl = 0.903 \times 10^{-4}$ M

0.21% H_2O

$\frac{a}{b} = 1.75$

$E_o = 0.460$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.381	0.079	0.156	1.424	0.747	1.91
10	0.330	0.130	0.256	1.324	0.647	2.05
16	0.275	0.185	0.360	1.220	0.543	2.25
25	0.225	0.235	0.463	1.117	0.440	2.54
35	0.179	0.285	0.562	1.018	0.341	2.99

$k_2 = 3.82\ M^{-1}\ sec.^{-1}$

Run 78

$a = HCl = 1.580 \times 10^{-4}$ M

$b = Me_3SnAl = 0.903 \times 10^{-4}$ M

0.85% H_2O

$\frac{a}{b} = 1.75$

$E_o = 0.460$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
10	0.397	0.063	0.124	1.456	0.779	1.87
20	0.346	0.114	0.225	1.355	0.678	2.00
31	0.301	0.159	0.313	1.267	0.590	2.13
51	0.235	0.225	0.443	1.137	0.460	2.47
70	0.204	0.256	0.505	1.075	0.398	2.70

$k_2 = 1.51$ M^{-1} $sec.^{-1}$

Run 81

$a = HCl = 1.580 \times 10^{-4}$ M

$b = Me_3SnAl = 0.903 \times 10^{-4}$ M

1.65% H_2O

$\frac{a}{b} = 1.75$

$E_o = 0.460$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
30	0.360	0.100	0.197	1.383	0.706	1.96
60	0.300	0.160	0.315	1.265	0.588	2.15
150	0.174	0.286	0.564	1.016	0.339	3.00
210	0.132	0.328	0.646	0.934	0.257	3.63
306	0.097	0.363	0.715	0.865	0.188	4.60

$k_2 = 0.87$ M^{-1} $sec.^{-1}$

Run 82

$a = HCl = 1.580 \times 10^{-4}$ M

$b = Me_3SnAl = 0.903 \times 10^{-4}$ M

2.05% H_2O

$\frac{a}{b} = 1.75$

$E_o = 0.460$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
30	0.374	0.086	0.169	1.411	0.734	1.93
60	0.309	0.151	0.297	1.283	0.606	2.12
150	0.195	0.265	0.522	1.058	0.381	2.78
210	0.145	0.315	0.620	0.960	0.283	3.40
306	0.106	0.354	0.697	0.883	0.206	4.28

$k_2 = 0.78\ M^{-1}\ sec.^{-1}$

Run 83

$a = HCl = 2.506 \times 10^{-4}$ M

$b = Me_3SnAl = 1.280 \times 10^{-4}$ M

2.05% H_2O

$\frac{a}{b} = 1.96$

$E_o = 0.650$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
10	0.559	0.091	0.179	2.327	1.101	2.11
20	0.487	0.163	0.321	2.185	0.959	2.28
40	0.389	0.261	0.514	1.992	0.766	2.60
70.5	0.305	0.345	0.680	1.826	0.600	3.04
130	0.180	0.470	0.926	1.580	0.354	4.46

$k_2 = 0.962\ M^{-1}\ sec.^{-1}$

Run 86

a = HCl = 2.506 x 10^{-4} M $\frac{a}{b}$ = 1.96
b = Me_3SnAl = 1.280 x 10^{-4} M
2.05% H_2O E_o = 0.620

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
21	0.470	0.150	0.296	2.210	0.984	2.25
40	0.361	0.259	0.511	1.995	0.769	2.60
70	0.248	0.372	0.734	1.762	0.546	3.23
120	0.153	0.467	0.921	1.585	0.359	4.41
150	0.107	0.513	1.010	1.496	0.270	5.55
270	0.031	0.589	1.160	1.346	0.120	11.20

k_2 = 0.950 M^{-1} sec.$^{-1}$

Run 87

a = HCl = 1.580 x 10^{-4} M $\frac{a}{b}$ = 1.23
b = Me_3SnAl = 1.280 x 10^{-4} M
2.05% H_2O E_o = 0.620

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
20	0.539	0.081	0.160	1.420	1.120	1.27
40	0.478	0.142	0.280	1.300	1.000	1.30
70	0.392	0.228	0.449	1.131	0.831	1.36
120	0.301	0.319	0.628	0.952	0.652	1.46
150	0.275	0.345	0.675	0.905	0.605	1.50
270	0.160	0.460	0.906	0.674	0.374	1.80
330	0.146	0.474	0.935	0.645	0.345	1.87

k_2 = 0.80 M^{-1} sec.$^{-1}$

Run 93

$a = HCl = 4.980 \times 10^{-4}$ M

$b = Me_3SnAl = 1.753 \times 10^{-4}$ M

$\frac{a}{b} = 2.84$

$E_o = 0.888$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
20	0.672	0.216	0.426	4.554	1.327	3.44
40	0.525	0.363	0.715	4.265	1.038	4.10
80	0.338	0.550	1.082	3.898	0.671	5.81
120	0.214	0.674	1.328	3.652	0.425	8.60
180	0.117	0.771	1.520	3.460	0.233	14.89

$k_2 = 0.473$ M^{-1} sec.$^{-1}$

Run 94

$a = HCl = 4.980 \times 10^{-4}$ M

$b = Me_3SnAl = 1.753 \times 10^{-4}$ M

$\frac{a}{b} = 2.84$

$E_o = 0.888$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
20	0.680	0.208	0.410	4.570	1.343	3.40
40	0.523	0.365	0.719	4.261	1.034	4.12
80	0.326	0.562	1.109	3.871	0.644	6.01
120	0.215	0.673	1.326	3.654	0.427	8.55
180	0.119	0.769	1.515	3.465	0.238	14.6

$k_2 = 0.480$ M^{-1} sec.$^{-1}$

Run 96

$a = HCl = 4.980 \times 10^{-4}$ M

$b = Me_3SnAl = 1.753 \times 10^{-4}$ M

$\frac{a}{b} = 2.84$

$E_o = 0.888$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
28	0.600	0.288	0.567	4.413	1.186	3.72
40	0.524	0.364	0.717	4.263	1.036	4.11
70	0.356	0.532	1.049	3.931	0.704	5.59
120	0.204	0.684	1.349	3.631	0.404	9.00

$k_2 = 0.495$ M^{-1} $sec.^{-1}$

Run 97

$a = HCl = 4.980 \times 10^{-4}$ M

$b = Me_3SnAl = 1.753 \times 10^{-4}$ M

$\frac{a}{b} = 2.84$

$E_o = 0.888$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
20	0.674	0.214	0.422	4.558	1.331	3.43
40	0.530	0.358	0.705	4.275	1.048	4.08
70	0.381	0.507	0.999	3.990	0.763	5.23
120	0.219	0.669	1.319	3.661	0.434	8.45

$k_2 = 0.470$ M^{-1} $sec.^{-1}$

Run 98 $a = HCl = 4.980 \times 10^{-4}$ M $\frac{a}{b} = 2.84$

$b = Me_3SnAl = 1.753 \times 10^{-4}$ M

$E_o = 0.888$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
20	0.678	0.210	0.414	4.566	1.339	3.41
40	0.537	0.351	0.691	4.289	1.062	4.04
70	0.374	0.514	1.011	3.969	0.742	5.35
120	0.213	0.675	1.330	3.650	0.423	8.64

$k_2 = 0.470$ M^{-1} $sec.^{-1}$

Run 99 $a = HCl = 4.980 \times 10^{-4}$ M $\frac{a}{b} = 2.84$

$b = Me_3SnAl = 1.753 \times 10^{-4}$ M

$Cd(NO_3)_2 = 2.097 \times 10^{-4}$ M $E_o = 0.888$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
20	0.390	0.498	0.981	3.999	0.772	5.18
40	0.249	0.639	1.259	3.721	0.494	7.55
70	0.107	0.781	1.539	3.441	0.214	16.1

$k_2 = 1.30$ M^{-1} $sec.^{-1}$

Run 100 $a = HCl = 2.438 \times 10^{-4}$ M $\frac{a}{b} = 2.58$

$b = Me_3SnAl = 0.945 \times 10^{-4}$ M

0.05% H_2O $E_o = 0.481$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.346	0.135	0.266	2.172	0.679	3.20
10	0.252	0.229	0.451	1.987	0.494	4.02
15	0.194	0.287	0.566	1.872	0.379	4.95
20.5	0.149	0.332	0.655	1.783	0.290	6.15
30	0.090	0.391	0.770	1.668	0.175	9.53

$k_2 = 4.85\ M^{-1}\ sec.^{-1}$

Run 101 $a = HCl = 2.438 \times 10^{-4}$ M $\frac{a}{b} = 2.58$

$b = Me_3SnAl = 0.945 \times 10^{-4}$ M

0.45% H_2O $E_o = 0.481$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.387	0.094	0.185	2.253	0.760	2.96
10	0.322	0.159	0.313	2.125	0.632	3.36
15	0.274	0.207	0.408	2.030	0.537	3.78
30	0.182	0.299	0.589	1.849	0.356	5.20
50	0.093	0.388	0.765	1.673	0.180	9.30

$k_2 = 2.92\ M^{-1}\ sec.^{-1}$

Run 102

$a = HCl = 2.438 \times 10^{-4}$ M

$b = Me_3SnAl = 0.945 \times 10^{-4}$ M

0.85% H_2O

$\frac{a}{b} = 2.58$

$E_o = 0.481$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.409	0.072	0.142	2.296	0.803	2.86
20	0.286	0.195	0.384	2.054	0.561	3.65
30	0.229	0.252	0.496	1.942	0.449	4.33
60	0.136	0.345	0.680	1.758	0.265	6.63
85	0.081	0.400	0.788	1.650	0.157	10.5

$k_2 = 1.89$ M^{-1} $sec.^{-1}$

Run 103

$a = HCl = 2.438 \times 10^{-4}$ M

$b = Me_3SnAl = 0.945 \times 10^{-4}$ M

2.05% H_2O

$\frac{a}{b} = 2.58$

$E_o = 0.481$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
20	0.351	0.130	0.256	2.182	0.689	3.17
40	0.280	0.201	0.396	2.042	0.549	3.72
70	0.181	0.300	0.591	1.847	0.354	5.22
110	0.128	0.353	0.695	1.743	0.250	6.97
160	0.080	0.401	0.790	1.648	0.155	10.61

$k_2 = 1.01$ M^{-1} $sec.^{-1}$

Run 107 $a = HCl = 4.876 \times 10^{-4}$ M $\frac{a}{b} = 4.63$

$b = Me_3SnAl = 1.051 \times 10^{-4}$ M

$E_o = 0.540$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
20	0.415	0.125	0.246	4.630	0.805	5.75
40	0.331	0.209	0.412	4.464	0.639	7.00
60	0.260	0.280	0.551	4.325	0.500	8.65
120	0.124	0.416	0.824	4.056	0.231	17.6
150	0.102	0.438	0.862	4.014	0.189	21.2
175	0.080	0.460	0.906	3.970	0.145	27.4

$k_2 = 0.448\ M^{-1}\ sec.^{-1}$

Run 108 $a = HCl = 4.876 \times 10^{-4}$ M $\frac{a}{b} = 2.32$

$b = Me_3SnAl = 2.101 \times 10^{-4}$ M

$E_o = 1.080$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
20	0.836	0.244	0.480	4.396	1.621	2.71
40	0.655	0.425	0.836	4.040	1.265	3.19
60	0.540	0.540	1.062	3.814	1.039	3.67
120	0.301	0.779	1.535	3.341	0.566	5.90
150	0.225	0.855	1.685	3.191	0.416	7.68
175	0.205	0.875	1.723	3.153	0.378	8.35

$k_2 = 0.453\ M^{-1}\ sec.^{-1}$

Run 109 $a = HCl = 9.656 \times 10^{-4}$ M $\frac{a}{b} = 9.18$

$b = Me_3SnAl = 1.051 \times 10^{-4}$ M

$E_o = 0.540$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
10	0.407	0.133	0.262	9.394	0.789	11.9
25	0.275	0.265	0.523	9.133	0.528	17.3
30	0.233	0.307	0.605	9.051	0.446	20.3
50	0.154	0.386	0.761	8.895	0.290	30.6
70	0.092	0.448	0.883	8.773	0.168	52.2
90	0.053	0.487	0.959	8.697	0.092	94.5

$k_2 = 0.490\ M^{-1}\ sec.^{-1}$

Run 110 $a = HCl = 9.656 \times 10^{-4}$ M $\frac{a}{b} = 4.60$

$b = Me_3SnAl = 2.101 \times 10^{-4}$ M

$E_o = 1.080$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
10	0.825	0.255	0.503	9.153	1.598	5.73
20	0.640	0.440	0.867	8.789	1.234	7.11
30	0.498	0.582	1.148	8.508	0.953	8.93
50	0.319	0.761	1.500	8.156	0.601	13.6
70	0.204	0.876	1.728	7.928	0.373	21.2
90	0.125	0.955	1.882	7.774	0.219	35.5

$k_2 = 0.482\ M^{-1}\ sec.^{-1}$

Run 111 $a = HCl = 2.414 \times 10^{-4}$ M $\frac{a}{b} = 2.30$
$b = Me_3SnAl = 1.051 \times 10^{-4}$ M $E_o = 0.530$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
50	0.387	0.143	0.282	2.132	0.769	2.77
105	0.283	0.247	0.486	1.928	0.565	3.42
150	0.221	0.309	0.609	1.805	0.442	4.08
200	0.178	0.352	0.694	1.720	0.357	4.82
270	0.125	0.405	0.798	1.616	0.253	6.39
350	0.093	0.437	0.861	1.553	0.190	8.18

$k_2 = 0.458$ M^{-1} sec.$^{-1}$

Run 112 $a = Me_3SnAl = 2.101 \times 10^{-4}$ M $\frac{a}{b} = 1.74$
$b = HCl = 1.207 \times 10^{-4}$ M $E_o = 1.060$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
50	0.904	0.156	0.307	1.795	0.900	2.00
105	0.802	0.258	0.508	1.593	0.699	2.28
150	0.727	0.333	0.656	1.445	0.551	2.62
200	0.673	0.387	0.762	1.339	0.445	3.01
270	0.610	0.450	0.886	1.215	0.321	3.79
350	0.575	0.485	0.955	1.106	0.212	5.22

$k_2 = 0.508$ M^{-1} sec.$^{-1}$

Run 117

$a = HCl = 4.828 \times 10^{-4}$ M

$b = Me_3SnAl = 1.176 \times 10^{-4}$ M

$NaClO_4 = 0.0500$ M

$\frac{a}{b} = 4.11$

$E_o = 0.599$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
20	0.431	0.168	0.331	4.497	0.845	5.32
40	0.308	0.291	0.574	4.254	0.602	7.07
60	0.237	0.362	0.714	4.114	0.462	8.89
80	0.180	0.419	0.825	4.003	0.351	11.4
100	0.135	0.464	0.914	3.914	0.262	14.9

$k_2 = 0.587$ M^{-1} $sec.^{-1}$

Run 118

$a = HCl = 4.828 \times 10^{-4}$ M

$b = Me_3SnAl = 1.176 \times 10^{-4}$ M

$NaClO_4 = 0.100$ M

$\frac{a}{b} = 4.11$

$E_o = 0.599$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
20	0.414	0.185	0.364	4.464	0.812	5.50
40	0.292	0.307	0.605	4.223	0.571	7.40
60	0.202	0.397	0.782	4.046	0.394	10.3
80	0.146	0.453	0.892	3.936	0.284	13.9
100	0.113	0.486	0.958	3.876	0.224	17.3

$k_2 = 0.698$ M^{-1} $sec.^{-1}$

Run 119

$a = HCl = 4.828 \times 10^{-4}$ M

$b = Me_3SnAl = 1.176 \times 10^{-4}$ M

$NaClO_4 = 0.200$ M

$\frac{a}{b} = 4.11$

$E_o = 0.599$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
20	0.371	0.228	0.449	4.479	0.727	6.16
40	0.239	0.360	0.709	4.120	0.467	8.84
60	0.156	0.443	0.872	3.957	0.304	13.0
80	0.112	0.487	0.960	3.869	0.216	17.9
100	0.074	0.525	1.034	3.795	0.142	26.7

$k_2 = 0.882$ M^{-1} sec.$^{-1}$

Run 120

$a = HCl = 2.414 \times 10^{-4}$ M

$b = Me_3SnAl = 1.176 \times 10^{-4}$ M

NaCl = 0.025 M

$\frac{a}{b} = 2.06$

$E_o = 0.599$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
10	0.520	0.079	0.156	2.258	1.020	2.21
20	0.451	0.148	0.292	2.122	0.884	2.40
30	0.386	0.213	0.420	1.994	0.756	2.64
40	0.337	0.262	0.516	1.898	0.660	2.88
50	0.295	0.304	0.599	1.815	0.577	3.14

$k_2 = 1.15$ M^{-1} sec.$^{-1}$

Run 121

$a = HCl = 2.414 \times 10^{-4}$ M

$b = Me_3SnAl = 1.176 \times 10^{-4}$ M

NaCl = 0.0500 M

$\frac{a}{b} = 2.06$

$E_o = 0.599$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
10	0.521	0.078	0.154	2.260	1.022	2.21
20	0.463	0.136	0.268	2.146	0.908	2.37
30	0.431	0.168	0.331	2.083	0.845	2.46
40	0.364	0.235	0.463	1.951	0.713	2.74
50	0.331	0.268	0.528	1.886	0.648	2.91

$k_2 = 0.952$ M^{-1} sec.$^{-1}$

Run 122

$a = HCl = 4.822 \times 10^{-4}$ M

$b = Me_3SnAl = 1.298 \times 10^{-4}$ M

NaCl = 0.0250 M

$\frac{a}{b} = 3.72$

$E_o = 0.660$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
20	0.350	0.310	0.611	4.211	0.687	6.12
30	0.277	0.383	0.755	4.067	0.543	7.51
40	0.213	0.447	0.880	3.942	0.418	9.44
50	0.154	0.506	0.997	3.825	0.301	12.7
60	0.122	0.538	1.060	3.762	0.238	15.8
70	0.092	0.568	1.119	3.703	0.179	20.7

$k_2 = 1.15$ M^{-1} sec.$^{-1}$

Run 123

a = HCl = 4.822 x 10^{-4} M

b = Me_3SnAl = 1.298 x 10^{-4} M

NaCl = 0.0500 M

$\frac{a}{b}$ = 3.72

E_o = 0.660

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
20	0.300	0.360	0.709	4.113	0.589	6.98
30	0.246	0.414	0.815	4.007	0.483	8.30
40	0.184	0.476	0.938	3.884	0.360	10.8
50	0.133	0.527	1.039	3.783	0.259	14.6
60	0.096	0.564	1.111	3.711	0.187	19.8
70	0.066	0.594	1.171	3.651	0.127	28.7

k_2 = 1.30 M^{-1} $sec.^{-1}$

Run 126

a = HCl = 4.822 x 10^{-4} M

b = Me_3SnAl = 1.298 x 10^{-4} M

NaCl = 0.0250 M

$\frac{a}{b}$ = 3.72

E_o = 0.660

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
10	0.454	0.206	0.406	4.416	0.892	4.95
20	0.339	0.321	0.633	4.189	0.665	6.30
30	0.265	0.395	0.778	4.044	0.520	7.78
41	0.189	0.471	0.928	3.894	0.370	10.5
50	0.148	0.512	1.010	3.812	0.288	13.2
60	0.107	0.553	1.090	3.732	0.208	17.9

k_2 = 1.23 M^{-1} $sec.^{-1}$

Run 127

a = HCl = 4.822×10^{-4} M

b = Me_3SnAl = 1.298×10^{-4} M

NaCl = 0.0500 M

$\frac{a}{b}$ = 3.72

E_o = 0.660

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
10	0.389	0.271	0.534	4.288	0.764	5.62
20	0.352	0.308	0.706	4.215	0.691	6.10
30	0.259	0.401	0.790	4.032	0.508	7.95
41	0.192	0.468	0.922	3.900	0.376	10.4
50	0.150	0.510	1.005	3.817	0.293	13.0
62	0.110	0.550	1.083	3.739	0.215	17.4

k_2 = 1.18 M^{-1} sec.$^{-1}$

Run 128

a = HCl = 9.644×10^{-4} M

b = Me_3SnAl = 1.263×10^{-4} M

NaCl = 0.0250 M

$\frac{a}{b}$ = 7.63

E_o = 0.643

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.526	0.117	0.230	9.414	1.033	9.10
10	0.406	0.237	0.467	9.177	0.796	11.5
15	0.342	0.301	0.593	9.051	0.670	13.5
20	0.265	0.378	0.745	8.899	0.518	17.2
25	0.213	0.430	0.847	8.797	0.416	21.1
35	0.142	0.501	0.988	8.656	0.275	31.5

k_2 = 0.807 M^{-1} sec.$^{-1}$

Run 129

$a = HCl = 9.644 \times 10^{-4}$ M

$b = Me_3SnAl = 1.263 \times 10^{-4}$ M

NaCl = 0.0500 M

$\frac{a}{b} = 7.63$

$E_o = 0.643$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.499	0.144	0.284	9.360	0.979	9.58
10	0.421	0.222	0.417	9.227	0.846	10.9
15	0.334	0.309	0.609	9.035	0.654	13.8
20	0.265	0.378	0.745	8.899	0.518	17.4
25	0.214	0.429	0.845	8.799	0.418	21.1
35	0.144	0.499	0.984	8.660	0.279	31.0

$k_2 = 0.817 \ M^{-1} \ sec.^{-1}$

Run 130

$a = HCl = 9.592 \times 10^{-4}$ M

$b = Me_3SnAl = 1.077 \times 10^{-4}$ M

NaCl = 0.0250 M

$\frac{a}{b} = 8.90$

$E_o = 0.548$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
6	0.427	0.121	0.238	9.354	0.839	11.1
10	0.373	0.175	0.345	9.247	0.732	12.6
15	0.317	0.231	0.455	9.137	0.622	14.7
20	0.257	0.291	0.574	9.018	0.503	17.9
25	0.215	0.333	0.656	8.936	0.421	21.2
35	0.161	0.387	0.763	8.829	0.314	28.1

$k_2 = 0.688 \ M^{-1} \ sec.^{-1}$

Run 131 $a = HCl = 9.592 \times 10^{-4}$ M $\frac{a}{b} = 8.90$

$b = Me_3SnAl = 1.077 \times 10^{-4}$ M $E_o = 0.548$

NaCl = 0.0500 M

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.433	0.115	0.226	9.366	0.851	11.0
10	0.363	0.185	0.364	9.228	0.713	13.0
15	0.303	0.245	0.483	9.109	0.594	15.3
20	0.243	0.305	0.601	8.991	0.476	18.9

$k_2 = 0.738\ M^{-1}\ sec.^{-1}$

Run 132 $a = HCl = 9.592 \times 10^{-4}$ M $\frac{a}{b} = 8.90$

$b = Me_3SnAl = 1.077 \times 10^{-4}$ M $E_o = 0.548$

NaCl = 0.0250 M

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.438	0.110	0.217	9.375	0.860	10.9
10	0.361	0.187	0.368	9.224	0.709	13.0
15	0.312	0.236	0.465	9.127	0.612	14.9
20	0.246	0.302	0.595	8.997	0.482	18.7
25	0.204	0.344	0.678	8.914	0.389	22.3
35	0.144	0.404	0.796	8.796	0.281	31.3

$k_2 = 0.722\ M^{-1}\ sec.^{-1}$

Run 133 $a = HCl = 9.592 \times 10^{-4}$ M $\frac{a}{b} = 8.90$

$b = Me_3SnAl = 1.077 \times 10^{-4}$ M

NaCl = 0.0500 M

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.440	0.108	0.213	9.379	0.864	10.9
10	0.356	0.192	0.378	9.214	0.699	13.2
15	0.291	0.257	0.506	9.086	0.571	15.9
20	0.235	0.313	0.617	8.975	0.460	19.5
26	0.186	0.362	0.714	8.878	0.363	24.4
35	0.140	0.408	0.804	8.788	0.273	32.2

$k_2 = 0.775$ M^{-1} sec.$^{-1}$

Run 135 $b = HCl = 14.388 \times 10^{-4}$ M

$a = Me_3SnAl = 0.997 \times 10^{-4}$ M

NaCl = 0.0250 M $E_o = 0.508$

Time	E_t	$E_o - E_t$	x	a-x
5	0.385	0.123	0.242	0.755
10	0.296	0.212	0.418	0.579
15	0.220	0.288	0.568	0.429
20	0.174	0.334	0.659	0.338
25	0.132	0.376	0.741	0.256
30	0.103	0.405	0.798	0.199

$k_2 = 0.627$ M^{-1} sec.$^{-1}$

Run 136

$a = HCl = 7.194 \times 10^{-4}$ M

$b = Me_3SnAl = 0.997 \times 10^{-4}$ M

NaCl = 0.0250 M

$\frac{a}{b} = 7.22$

$E_o = 0.508$

Time	E_t	$E_o - E_t$	x	a−x	b−x	$\frac{a-x}{b-x}$
5	0.431	0.077	0.152	7.042	0.845	8.33
10	0.373	0.135	0.266	6.928	0.731	9.47
15	0.323	0.185	0.364	6.830	0.633	10.8
20	0.280	0.228	0.449	6.745	0.548	12.3
25	0.241	0.267	0.526	6.668	0.471	14.2
35	0.184	0.324	0.638	6.556	0.359	18.3

$k_2 = 0.724 \ M^{-1} \ sec.^{-1}$

Run 137

$HCl = 19.18 \times 10^{-4}$ M

$a = Me_3SnAl = 0.997 \times 10^{-4}$ M

NaCl = 0.0250 M

$E_o = 0.508$

Time	E_t	$E_o - E_t$	x	a−x
5	0.357	0.151	0.297	0.700
10	0.254	0.254	0.500	0.497
15	0.181	0.327	0.644	0.353
20	0.129	0.379	0.746	0.251
25	0.091	0.417	0.822	0.175
30	0.060	0.448	0.882	0.115

$k_2 = 0.602 \ M^{-1} \ sec.^{-1}$

Run 138

$a = HCl = 9.592 \times 10^{-4}$ M

$b = Me_3SnAl = 0.997 \times 10^{-4}$ M

NaCl = 0.0250 M

$\frac{a}{b} = 9.63$

$E_o = 0.508$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
5	0.409	0.099	0.195	9.397	0.802	11.7
10.5	0.330	0.178	0.350	9.242	0.647	14.3
15	0.277	0.231	0.455	9.137	0.542	16.8
20	0.230	0.278	0.547	9.045	0.450	20.1
25	0.197	0.311	0.613	8.979	0.384	23.4
30	0.158	0.350	0.689	8.903	0.308	28.9

$k_2 = 0.713\ M^{-1}\ sec.^{-1}$

Run 139

$a = HCl = 2.398 \times 10^{-4}$ M

$b = Me_3SnAl = 0.997 \times 10^{-4}$ M

NaCl = 0.0250 M

$\frac{a}{b} = 2.41$

$E_o = 0.508$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
10	0.428	0.080	0.158	2.240	0.839	2.67
20	0.362	0.146	0.288	2.110	0.709	2.98
30	0.307	0.201	0.396	2.002	0.601	3.33
40	0.264	0.244	0.481	1.917	0.516	3.72
50	0.224	0.284	0.560	1.838	0.437	4.20
60	0.192	0.316	0.622	1.776	0.375	4.74

$k_2 = 1.25\ M^{-1}\ sec.^{-1}$

Run 140

$a = HCl = 4.796 \times 10^{-4}$ M

$b = Me_3SnAl = 0.997 \times 10^{-4}$ M

NaCl = 0.0250 M

$\frac{a}{b} = 4.81$

$E_o = 0.508$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
10	0.389	0.119	0.234	4.562	0.763	5.98
20	0.321	0.187	0.368	4.428	0.629	7.04
30	0.252	0.256	0.504	4.292	0.493	8.71
40	0.204	0.304	0.599	4.197	0.398	10.5
50	0.160	0.348	0.685	4.111	0.312	13.2
60	0.131	0.377	0.743	4.053	0.252	16.1

$k_2 = 0.887$ M^{-1} sec.$^{-1}$

Run 154

$HCl = 16.290 \times 10^{-4}$ M

$a = Me_3SnAl = 0.981 \times 10^{-4}$

NaCl = 0.0250 M

$E_o = 0.500$

Time	E_t	$E_o - E_t$	x	a-x
5	0.366	0.134	0.264	0.717
10	0.274	0.226	0.445	0.536
15	0.205	0.295	0.581	0.400
20	0.151	0.349	0.687	0.294
25	0.113	0.387	0.763	0.218
30	0.091	0.409	0.806	0.175

$k_2 = 0.615$ M^{-1} sec.$^{-1}$

Run 155 HCl = 16.290×10^{-4} M E_o = 0.500

a = Me_3SnAl = 0.981×10^{-4} M

NaCl = 0.0500 M

Time	E_t	E_o-E_t	x	a-x
5	0.360	0.140	0.276	0.705
10	0.265	0.235	0.463	0.518
15	0.196	0.304	0.599	0.382
20	0.141	0.359	0.707	0.274
25	0.105	0.395	0.779	0.202
30	0.083	0.417	0.821	0.160

k_2 = 0.655 M^{-1} $sec.^{-1}$

Run 156 HCl = 16.29×10^{-4} M E_o = 0.500

a = Me_3SnAl = 0.981×10^{-4} M

NaCl = 6.25×10^{-3} M

Time	E_t	E_o-E_t	x	a-x
5	0.380	0.120	0.236	0.745
10	0.298	0.202	0.398	0.583
15	0.228	0.278	0.547	0.434
20	0.179	0.321	0.632	0.349
25	0.141	0.359	0.707	0.274
30	0.109	0.391	0.770	0.211

k_2 = 0.523 M^{-1} $sec.^{-1}$

Run 157 $HCl = 16.29 \times 10^{-4}$ M $E_o = 0.500$

$a = Me_3SnAl = 0.981 \times 10^{-4}$ M

$NaCl = 0.01250$ M

Time	E_t	$E_o - E_t$	x	a-x
5	0.376	0.124	0.244	0.732
10	0.282	0.218	0.429	0.552
15	0.213	0.287	0.565	0.416
20	0.167	0.333	0.656	0.325
25	0.131	0.369	0.727	0.274
30	0.097	0.403	0.794	0.187

$k_2 = 0.572\ M^{-1}\ sec.^{-1}$

Run 158 $HCl = 16.29 \times 10^{-4}$ M $E_o = 0.513$

$a = Me_3SnAl = 1.010 \times 10^{-4}$ M

$NaCl = 1.25 \times 10^{-3}$ M

Time	E_t	$E_o - E_t$	x	a-x
5.5	0.390	0.123	0.242	0.768
10.5	0.314	0.199	0.392	0.618
15	0.252	0.261	0.514	0.496
20	0.198	0.315	0.620	0.390
25	0.162	0.351	0.692	0.318
30	0.123	0.390	0.769	0.241

$k_2 = 0.489\ M^{-1}\ sec.^{-1}$

Run 159

$HCl = 16.29 \times 10^{-4}$ M

$a = Me_3SnAl = 1.010 \times 10^{-4}$ M

$NaCl = 3.13 \times 10^{-3}$ M

$E_o = 0.513$

Time	E_t	E_o-E_t	x	a-x
5	0.398	0.115	0.227	0.783
10	0.319	0.194	0.382	0.628
15	0.254	0.259	0.510	0.500
20	0.197	0.316	0.623	0.387
25	0.156	0.357	0.704	0.306
30	0.125	0.388	0.765	0.245

$k_2 = 0.489\ M^{-1}\ sec.^{-1}$

Run 160

$HCl = 16.29 \times 10^{-4}$ M

$a = Me_3SnAl = 1.010 \times 10^{-4}$ M

$E_o = 0.513$

Time	E_t	E_o-E_t	x	a-x
5	0.404	0.109	0.215	0.795
10	0.327	0.186	0.366	0.644
15	0.255	0.258	0.509	0.501
20	0.201	0.312	0.614	0.396
25	0.165	0.348	0.685	0.325
30.5	0.125	0.388	0.764	0.246

$k_2 = 0.473\ M^{-1}\ sec.^{-1}$

Run 161

HCl = 16.29×10^{-4} M

a = Me_3SnAl = 1.010×10^{-4} M

NaCl = 6.3×10^{-4} M

E_o = 0.513

Time	E_t	E_o-E_t	x	a-x
5	0.406	0.107	0.211	0.799
10	0.323	0.109	0.374	0.636
15.5	0.256	0.257	0.506	0.504
21	0.202	0.311	0.613	0.397
25	0.165	0.348	0.686	0.324
31.5	0.126	0.387	0.763	0.247

k_2 = 0.459 M^{-1} $sec.^{-1}$

Run 164

a = HCl = 8.123×10^{-4} M

b = Me_3SnAl = 1.04k x 10^{-4} M

NaCl = 0.0125 M

$\frac{a}{b}$ = 7.80

E_o = 0.530

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
11	0.363	0.167	0.329	7.794	0.712	10.9
21	0.263	0.267	0.526	7.597	0.515	14.8
30	0.197	0.333	0.657	7.466	0.390	19.2
40	0.143	0.387	0.764	7.359	0.277	26.6
50	0.110	0.420	0.829	7.294	0.212	34.4
60	0.087	0.443	0.873	7.253	0.168	43.2

k_2 = 0.710 M^{-1} $sec.^{-1}$

Run 165

$a = HCl = 8.123 \times 10^{-4}$ M

$b = Me_3SnAl = 1.041 \times 10^{-4}$ M

NaCl = 0.0250 M

$\frac{a}{b} = 7.80$

$E_o = 0.530$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
10	0.363	0.167	0.329	7.794	0.712	10.9
20	0.253	0.277	0.546	7.577	0.495	15.3
32	0.167	0.363	0.715	7.408	0.326	22.7
40	0.127	0.403	0.794	7.329	0.247	29.7
50	0.093	0.437	0.861	7.262	0.180	40.4
60	0.065	0.465	0.916	7.207	0.125	57.7

$k_2 = 0.787\ M^{-1}\ sec.^{-1}$

Run 166

$a = HCl = 8.123 \times 10^{-4}$ M

$b = Me_3SnAl = 1.041 \times 10^{-4}$ M

NaCl = 0.0500 M

$\frac{a}{b} = 7.80$

$E_o = 0.530$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
10	0.354	0.176	0.347	7.776	0.694	11.2
20	0.242	0.288	0.567	7.556	0.474	15.9
30	0.167	0.363	0.715	7.408	0.326	22.7
42	0.099	0.431	0.850	7.273	0.191	38.1
50	0.078	0.452	0.890	7.233	0.151	47.8
60	0.053	0.477	0.940	7.183	0.101	71.0

$k_2 = 0.858\ M^{-1}\ sec.^{-1}$

Run 167

$a = HCl = 8.123 \times 10^{-4}$ M

$b = Me_3SnAl = 1.041 \times 10^{-4}$ M

NaCl $= 6.3 \times 10^{-4}$ M

$\frac{a}{b} = 7.80$

$E_o = 0.530$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
10	0.394	0.136	0.268	7.855	0.773	10.2
20	0.307	0.223	0.440	7.683	0.601	12.8
30	0.240	0.290	0.571	7.552	0.471	16.0
41.5	0.184	0.346	0.682	7.441	0.359	20.7
50	0.150	0.380	0.749	7.374	0.292	25.2
60	0.118	0.412	0.811	7.312	0.230	31.8

$k_2 = 0.557$ M^{-1} $sec.^{-1}$

Run 168

$a = HCl = 8.123 \times 10^{-4}$ M

$b = Me_3SnAl = 1.041 \times 10^{-4}$ M

NaCl $= 3.13 \times 10^{-3}$ M

$\frac{a}{b} = 7.80$

$E_o = 0.530$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
10	0.390	0.140	0.276	7.847	0.765	10.3
20	0.300	0.230	0.453	7.670	0.588	13.1
30	0.224	0.306	0.603	7.520	0.438	17.2
40	0.175	0.355	0.700	7.423	0.341	21.8
50	0.132	0.398	0.784	7.339	0.257	28.5
60	0.104	0.426	0.839	7.284	0.202	36.0

$k_2 = 0.617$ M^{-1} $sec.^{-1}$

Run 169

a = HCl = 8.123×10^{-4} M

b = Me_3SnAl = 1.041×10^{-4} M

NaCl = 6.25×10^{-3} M

$\frac{a}{b}$ = 7.80

E_o = 0.530

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
10	0.375	0.155	0.305	7.818	0.736	10.6
20	0.283	0.247	0.487	7.636	0.554	13.8
30	0.210	0.320	0.630	7.493	0.411	18.2
40.5	0.154	0.376	0.740	7.383	0.301	24.5
50	0.125	0.405	0.797	7.326	0.244	30.0
60	0.090	0.440	0.866	7.257	0.175	41.5

k_2 = 0.663 M^{-1} $sec.^{-1}$

Run 170

a = HCl = 8.123×10^{-4} M

b = Me_3SnAl = 1.023×10^{-4} M

$NaClO_4$ = 0.01250 M

$\frac{a}{b}$ = 7.95

E_o = 0.520

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
10	0.400	0.120	0.236	7.887	0.787	10.0
20	0.313	0.207	0.408	7.715	0.615	12.5
30	0.247	0.283	0.557	7.566	0.466	16.2
40	0.192	0.338	0.655	7.468	0.368	20.3
50	0.153	0.377	0.742	7.281	0.281	26.2
60	0.129	0.401	0.790	7.333	0.233	31.4

k_2 = 0.560 M^{-1} $sec.^{-1}$

Run 171

$a = HCl = 8.123 \times 10^{-4}$ M

$b = Me_3SnAl = 1.023 \times 10^{-4}$ M

$NaClO_4 = 0.0250$ M

$\frac{a}{b} = 7.95$

$E_o = 0.520$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
10	0.394	0.126	0.248	7.875	0.775	10.2
20	0.304	0.218	0.425	7.698	0.598	12.9
30	0.238	0.282	0.555	7.568	0.468	16.5
40	0.185	0.335	0.660	7.463	0.363	20.6
50	0.149	0.371	0.731	7.392	0.292	25.3
60	0.121	0.399	0.786	7.337	0.237	31.0

$k_2 = 0.567\ M^{-1}\ sec.^{-1}$

Run 172

$a = HCl = 8.123 \times 10^{-4}$ M

$b = Me_3SnAl = 1.023 \times 10^{-4}$ M

$NaClO_4 = 0.0500$ M

$\frac{a}{b} = 7.95$

$E_o = 0.520$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
10	0.384	0.136	0.268	7.855	0.755	10.4
20	0.292	0.228	0.449	7.674	0.574	13.4
30	0.222	0.298	0.587	7.536	0.436	17.3
40	0.172	0.348	0.685	7.438	0.338	22.0
50	0.138	0.382	0.753	7.370	0.270	27.3
60	0.105	0.415	0.818	7.305	0.205	35.7

$k_2 = 0.593\ M^{-1}\ sec.^{-1}$

Run 173

HCl = 16.25×10^{-4} M

a = Me_3SnAl = 1.023×10^{-4} M

$NaClO_4$ = 0.0250 M

E_o = 0.520

Time	E_t	E_o-E_t	x	a-x
5	0.390	0.130	0.256	0.767
10	0.300	0.220	0.434	0.589
15	0.232	0.288	0.567	0.456
20	0.180	0.340	0.670	0.353
25	0.147	0.373	0.735	0.288
30	0.109	0.411	0.809	0.214

k_2 = 0.555 M^{-1} sec.$^{-1}$

Run 174

HCl = 16.25×10^{-4} M

a = Me_3SnAl = 1.023×10^{-4} M

$NaClO_4$ = 0.0500 M

E_o = 0.520

Time	E_t	E_o-E_t	x	a-x
5	0.386	0.134	0.264	0.759
10	0.292	0.228	0.449	0.574
15	0.225	0.295	0.581	0.442
20	0.169	0.351	0.691	0.332
25	0.132	0.388	0.765	0.258
30	0.102	0.418	0.823	0.200

k_2 = 0.580 M^{-1} sec.$^{-1}$

Run 178

$a = HCl = 4.062 \times 10^{-4}$ M

$b = Me_3SnAl = 0.948 \times 10^{-4}$ M

$NaClO_4 = 0.0250$ M

$\frac{a}{b} = 4.29$

$E_o = 0.482$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
15	0.382	0.100	0.197	3.865	0.751	5.15
30	0.318	0.164	0.323	3.739	0.625	5.99
45	0.261	0.221	0.435	3.627	0.513	7.08
60	0.220	0.262	0.516	3.546	0.432	8.21
75	0.187	0.295	0.581	3.481	0.367	9.49
90	0.151	0.331	0.652	3.410	0.296	11.5

$k_2 = 0.583\ M^{-1}\ sec.^{-1}$

Run 179

$a = HCl = 4.062 \times 10^{-4}$ M

$b = Me_3SnAl = 1.895 \times 10^{-4}$ M

$NaClO_4 = 0.0250$ M

$\frac{a}{b} = 2.14$

$E_o = 0.964$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
15	0.784	0.180	0.354	3.708	1.541	2.41
30	0.657	0.307	0.605	3.457	1.290	2.68
45	0.555	0.409	0.805	3.257	1.090	2.99
60	0.470	0.494	0.973	3.089	0.922	3.35
75	0.408	0.556	1.097	2.965	0.798	3.72
90	0.346	0.618	1.218	2.844	0.677	4.20

$k_2 = 0.577\ M^{-1}\ sec.^{-1}$

Run 180 $HClO_4 = 16.77 \times 10^{-4}$ M $E_o = 0.523$

$a = Me_3SnAl = 1.029 \times 10^{-4}$ M

Time	E_t	E_o-E_t	x	a-x
10	0.312	0.211	0.416	0.613
20	0.205	0.318	0.626	0.403
30	0.120	0.403	0.794	0.235
40	0.077	0.446	0.879	0.150
50	0.052	0.471	0.928	0.101
60	0.037	0.486	0.958	0.071

$k_2 = 0.478\ M^{-1}\ sec.^{-1}$

Run 181 $HClO_4 = 16.77 \times 10^{-4}$ M $E_o = 0.523$

$a = Me_3SnAl = 1.029 \times 10^{-4}$ M

Time	E_t	E_o-E_t	x	a-x
10.5	0.309	0.214	0.421	0.608
20	0.202	0.321	0.632	0.397
30	0.126	0.397	0.782	0.247
40	0.080	0.443	0.872	0.157
50	0.053	0.470	0.925	0.104
60	0.038	0.485	0.955	0.074

$k_2 = 0.475\ M^{-1}\ sec.^{-1}$

Run 182

$a = HCl = 8.384 \times 10^{-4}$ M

$b = Me_3SnAl = 2.058 \times 10^{-4}$ M

$\frac{a}{b} = 4.07$

$E_o = 1.046$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
11	0.792	0.254	0.500	7.884	1.558	5.06
20	0.653	0.393	0.774	7.610	1.284	5.93
30	0.538	0.508	1.000	7.384	1.058	6.98
40	0.429	0.617	1.217	7.167	0.841	8.51
50	0.351	0.695	1.370	7.014	0.688	10.2
60	0.286	0.760	1.497	6.887	0.561	12.3

$k_2 = 0.483\ M^{-1}\ sec.^{-1}$

Run 183

$a = HClO_4 = 8.384 \times 10^{-4}$ M

$b = Me_3SnAl = 2.067 \times 10^{-4}$ M

$\frac{a}{b} = 4.05$

$E_o = 1.052$

Time	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
10	0.805	0.247	0.487	7.897	1.580	5.00
20	0.651	0.401	0.790	7.594	1.277	5.95
30	0.534	0.518	1.020	7.364	1.047	7.04
40	0.431	0.621	1.223	7.161	0.844	8.50
50	0.351	0.701	1.381	7.003	0.686	10.2
60	0.290	0.762	1.501	6.883	0.566	12.1

$k_2 = 0.488\ M^{-1}\ sec.^{-1}$

Run 184

$a = HClO_4 = 4.192 \times 10^{-4}$ M

$b = Me_3SnAl = 1.034 \times 10^{-4}$ M

$\frac{a}{b} = 4.05$

$E_o = 0.526$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
20	0.400	0.126	0.248	3.944	0.786	5.02
40	0.324	0.202	0.398	3.794	0.636	5.96
60	0.269	0.257	0.506	3.686	0.528	6.99
80	0.210	0.316	0.623	3.569	0.411	8.68
100	0.173	0.353	0.695	3.497	0.339	10.3
120	0.147	0.379	0.746	3.446	0.288	12.0

$k_2 = 0.490\ M^{-1}\ sec.^{-1}$

Run 185

$a = HClO_4 = 2.096 \times 10^{-4}$ M

$b = Me_3SnAl = 2.067 \times 10^{-4}$ M

Calculated as a = b

$\frac{1}{a} = 0.484$

$E_o = 1.052$

Time	E_t	$E_o - E_t$	x	a-x	$\frac{1}{a-x}$
20	0.915	0.137	0.270	1.797	0.577
40	0.824	0.228	0.449	1.618	0.619
60	0.758	0.294	0.580	1.487	0.673
80	0.697	0.355	0.700	1.367	0.732
100	0.640	0.412	0.812	1.255	0.795
120	0.596	0.456	0.899	1.168	0.856

$k_2 = 0.521\ M^{-1}\ sec.^{-1}$

Run 192 $a = HCl = 5.01 \times 10^{-4}$ M $\frac{a}{b} = 3.06$
$b = \text{trans} = 1.64 \times 10^{-4}$ M

$E_o = 1.120$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
10	1.109	0.011	0.016	4.99	1.62	3.08
30	1.087	0.033	0.048	4.96	1.59	3.12
60	1.057	0.063	0.092	4.92	1.55	3.18
116	0.990	0.130	0.190	4.82	1.45	3.32
660	0.686	0.434	0.636	4.37	1.00	4.37
780	0.615	0.505	0.740	4.27	0.90	4.75
993	0.534	0.586	0.858	4.15	0.78	5.32

$k_2 = 0.0275\ M^{-1}\ \text{sec.}^{-1}$

Run 193 $HCl = .25.2 \times 10^{-4}$ M
$a = \text{trans} = 1.64 \times 10^{-4}$ M

Time	E_t	Time	E_t
2	1.082	40	0.500
3	1.058	50	0.408
4	1.038	60	0.330
6	1.000	70	0.268
9	0.940	72	0.257
12	0.884	78	0.226
16	0.818	84	0.197
20	0.753	96	0.156
24	0.695	102	0.136
30	0.612	108	0.118
35	0.554		

$k_2 = 0.0271\ M^{-1}\ \text{sec.}^{-1}$

Run 194 HCl = 125.2×10^{-4} M

a = trans = 3.28×10^{-4} M

Time	E_t	Time	E_t
2	2.111	48	0.805
4	2.020	51	0.775
6	1.965	53	0.743
10	1.802	60	0.645
13	1.675	64	0.597
14	1.661	68	0.551
18	1.529	72	0.509
21	1.440	79	0.441
26	1.298	85	0.392
32	1.147	95	0.322
39	0.994	104	0.271
44	0.900	113	0.229

$k_2 = 0.0273\ M^{-1}\ sec.^{-1}$

Run 195 HCl = 125.2×10^{-4} M

a = trans = 3.28×10^{-4} M

Time	E_t	Time	E_t
4	2.050	47	0.836
6	1.920	54	0.720
8	1.870	58	0.662
10	1.792	60	0.635
12	1.719	64	0.586
15	1.616	68	0.541
20	1.459	72	0.495
26	1.289	79	0.430
31	1.164	89	0.350
38	1.008	98	0.291
42	0.920	101	0.243
44	0.890		

$k_2 = 0.0276\ M^{-1}\ sec.^{-1}$

Run 196 $HCl = 2.505 \times 10^{-3}$ M

$a = Me_3SnAl = 1.519 \times 10^{-4}$ M

Time	E_t	Time	E_t
3	0.845	20	0.226
4	0.778	23	0.184
5	0.720	24	0.163
7	0.610	26	0.152
10	0.477	29	0.113
13	0.380	32	0.095
16	0.298	36	0.076

$k_2 = 0.538\ M^{-1}\ sec.^{-1}$

Run 198 $HCl = 2.505 \times 10^{-3}$ M

$a = Me_3SnAl = 1.519 \times 10^{-4}$ M

Time	E_t	Time	E_t
3	0.813	21	0.197
4	0.750	23	0.169
6	0.642	25	0.145
8	0.546	27	0.124
10	0.465	30	0.099
13	0.369	33	0.079
15	0.314	36	0.064
17	0.268	39	0.052
19	0.230		

$k_2 = 0.528\ M^{-1}\ sec.^{-1}$

Run 199

$HCl = 2.505 \times 10^{-3}$ M

$a = Me_3SnAl = 1.519 \times 10^{-4}$ M

Time	E_t	Time	E_t
3	0.585	14	0.246
4	0.547	19	0.165
6	0.465	22	0.131
8	0.397	27	0.090
10	0.338		

$k_2 = 0.527\ M^{-1}\ sec.^{-1}$

Run 200

$HCl = 2.505 \times 10^{-3}$ M

$a = Me_3SnAl = 1.519 \times 10^{-4}$ M

Time	E_t	Time	E_t
2	0.895	18	0.228
3	0.835	21	0.196
5	0.706	23	0.167
6	0.652	25	0.143
8	0.554	28	0.114
11	0.434	32	0.085
13	0.368	42	0.042
16	0.268	48	0.030

$k_2 = 0.543\ M^{-1}\ sec.^{-1}$

Run 201

$HCl = 1.002 \times 10^{-3}$ M

$a = Me_3SnAl = 0.659 \times 10^{-4}$ M

Time	E_t	Time	E_t
4	0.395	29	0.172
6	0.369	34	0.146
8	0.346	39	0.123
13	0.293	45	0.100
18	0.247	50	0.084
24	0.203	64	0.052

$k_2 = 0.548$ M^{-1} $sec.^{-1}$

Run 202

$HCl = 1.002 \times 10^{-3}$ M

$a = Me_3SnAl = 0.659 \times 10^{-4}$ M

Time	E_t	Time	E_t
5	0.386	30	0.169
7	0.362	35	0.144
10	0.328	40	0.119
14	0.287	46	0.098
19	0.243	51	0.083
25	0.200	66	0.052

$k_2 = 0.548$ M^{-1} $sec.^{-1}$

Run 203

$HCl = 1.252 \times 10^{-2}$ M

$a = Me_3SnAl = 0.659 \times 10^{-4}$ M

Time	E_t	Time	E_t
1.25	0.287	4.50	0.091
1.75	0.241	5.00	0.076
2.00	0.222	5.50	0.063
2.50	0.187	6.00	0.053
2.75	0.171	6.50	0.043
3.00	0.156	7.00	0.036
3.50	0.132	14.00	0.006
4.00	0.110	22.00	0.005

$k_2 = 0.470\ M^{-1}\ sec.^{-1}$

Run 204

$HCl = 1.252 \times 10^{-2}$ M

a = cis = 3.018×10^{-4} M

Time	E_t	Time	E_t
3	1.543	38	0.415
5	1.449	44	0.333
9	1.246	49	0.279
17	0.920	55	0.225
24	0.703	62	0.177
28	0.605	70	0.137
33	0.501		

$k_2 = 0.0482\ M^{-1}\ sec.^{-1}$

Run 205 $HCl = 1.252 \times 10^{-2}$ M

$a = cis = 3.018 \times 10^{-4}$ M

Time	E_t	Time	E_t
3	1.540	33	0.477
6	1.362	38	0.392
9	1.212	43	0.324
11	1.126	49	0.258
18	0.854	56	0.200
22	0.731	64	0.149
27	0.602	70	0.120

$k_2 = 0.0518\ M^{-1}\ sec.^{-1}$

Run 206 $HCl = 2.504 \times 10^{-2}$ M

$a = cis = 1.509 \times 10^{-4}$ M

Time	E_t	Time	E_t
2	0.762	21	0.179
6	0.559	24	0.145
9	0.441	28	0.112
12	0.349	30	0.100
15	0.277	34	0.080
18	0.221		

$k_2 = 0.0519\ M^{-1}\ sec.^{-1}$

Run 212 HCl = 4.008×10^{-2} M

a = Ø$_3$SnAl = 2.200×10^{-4} M

Time	E_t	Time	E_t
3	1.615	51	0.992
7	1.552	60	0.900
16	1.409	76	0.771
23	1.309	88	0.692
30	1.215	100	0.624
39	1.107	123	0.515

$k_2 = 0.00423\ M^{-1}\ sec.^{-1}$

Run 213 HCl = 4.008×10^{-2} M

a = Ø$_3$SnAl = 1.100×10^{-4} M

Time	E_t	Time	E_t
5	0.822	31	0.610
10	0.772	43	0.541
15	0.735	54	0.489
21	0.683	72	0.410
26	0.645	95	0.315

$k_2 = 0.00472\ M^{-1}\ sec.^{-1}$

Run 214 $HCl = 2.004 \times 10^{-2}$ M

$a = \emptyset_3SnAl = 2.200 \times 10^{-4}$ M

Time	E_t	Time	E_t
4	1.658	53	1.274
9	1.611	71	1.157
14	1.565	94	1.031
20	1.516	111	0.959
25	1.475	126	0.887
30	1.436	140	0.831
42	1.349		

$k_2 = 0.00427\ M^{-1}\ sec.^{-1}$

Run 215 $HCl = 4.008 \times 10^{-2}$ M

$a = \emptyset_3SnCr = 2.136 \times 10^{-4}$ M

Time	E_t	Time	E_t
15	1.940	300	1.555
30	1.928	360	1.472
60	1.902	540	1.295
120	1.754	1380	0.860
240	1.609	1440	0.896

$k_2 = 3.35 \times 10^{-4}\ M^{-1}\ sec.^{-1}$

Run 216

$HCl = 4.008 \times 10^{-2}$ M

$a = \text{Ø}_3SnCr = 1.068 \times 10^{-4}$ M

Time	E_t	Time	E_t
15	0.982	300	0.784
30	0.974	360	0.745
60	0.942	540	0.650
120	0.890	1380	0.433
240	0.816	1440	0.431

$k_2 = 3.26 \times 10^{-4}$ M^{-1} $sec.^{-1}$

Run 217

$a = HCl = 2.004 \times 10^{-2}$ M

$b = (\text{Ø}_3SnCH_2CH{=}CHCH_3) = 2.136 \times 10^{-4}$ M

Time	E_t	Time	E_t
120	1.870	420	1.675
180	1.860	1260	1.255
240	1.800	1875	1.075

$k_2 = 3.35 \times 10^{-4}$ M^{-1} $sec.^{-1}$

Run 221

$a = HCl = 0.716 \times 10^{-4}$ M

$b = Me_3SnBal = 0.395 \times 10^{-4}$ M

$\frac{a}{b} = 1.81$

$E_o = 0.288$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
1.17	0.251	0.037	0.051	0.665	0.344	1.93
1.83	0.232	0.056	0.077	0.639	0.318	2.01
2.50	0.218	0.070	0.096	0.620	0.299	2.08
3.25	0.204	0.084	0.115	0.601	0.280	2.15
3.58	0.198	0.090	0.124	0.592	0.271	2.18
4.17	0.187	0.101	0.139	0.577	0.256	2.25
5.00	0.175	0.114	0.156	0.560	0.239	2.34
5.25	0.171	0.117	0.161	0.555	0.234	2.37
6.50	0.154	0.134	0.184	0.532	0.211	2.53
7.00	0.149	0.139	0.191	0.525	0.204	2.58
7.50	0.143	0.145	0.199	0.517	0.196	2.64
8.50	0.132	0.156	0.214	0.502	0.181	2.78
9.00	0.127	0.161	0.221	0.495	0.174	2.84
10.00	0.119	0.169	0.232	0.484	0.163	2.97
11.00	0.112	0.176	0.242	0.474	0.153	3.10
12.00	0.104	0.184	0.253	0.463	0.142	3.26
13.00	0.097	0.191	0.262	0.454	0.133	3.42
15.00	0.085	0.203	0.279	0.437	0.116	3.77
17.00	0.075	0.213	0.293	0.423	0.102	4.15
20.00	0.062	0.226	0.310	0.406	0.085	4.77
24.00	0.049	0.239	0.328	0.388	0.067	5.79
30.00	0.036	0.252	0.346	0.370	0.049	7.55
37.00	0.025	0.263	0.361	0.355	0.034	10.45
42.00	0.018					

$k_2 = 24.8\ M^{-1}\ sec.^{-1}$

Run 222

$a = HCl = 0.716 \times 10^{-4}$ M

$b = Me_3SnBal = 0.457 \times 10^{-4}$ M

$\frac{a}{b} = 1.57$

$E_o = 0.353$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
1.50	0.304	0.049	0.063	0.653	0.394	1.66
2.00	0.289	0.064	0.083	0.633	0.374	1.69
3.75	0.250	0.103	0.133	0.583	0.324	1.80
5.75	0.211	0.142	0.184	0.532	0.273	1.95
9.00	0.161	0.192	0.248	0.468	0.209	2.24
13.00	0.128	0.225	0.291	0.425	0.166	2.56
18.00	0.095	0.258	0.334	0.382	0.123	3.10
26.00	0.063	0.290	0.376	0.340	0.081	4.20
35.00	0.042	0.311	0.403	0.313	0.054	5.80

$k_2 = 24.4 \text{ M}^{-1} \text{ sec.}^{-1}$

Run 223 $a = HCl = 1.431 \times 10^{-4}$ M $\frac{a}{b} = 3.13$

$b = Me_3SnBal = 0.457 \times 10^{-4}$ M $E_o = 0.353$

Time	E_t	$E_o - E_t$	x	a-x	b-x	$\frac{a-x}{b-x}$
1.08	0.282	0.071	0.092	1.339	0.365	3.67
1.50	0.260	0.093	0.120	1.311	0.337	3.89
1.75	0.246	0.107	0.139	1.292	0.318	4.06
2.00	0.235	0.118	0.153	1.278	0.304	4.20
2.50	0.215	0.138	0.179	1.252	0.278	4.50
3.00	0.196	0.157	0.203	1.228	0.254	4.83
3.50	0.179	0.174	0.225	1.206	0.232	5.19
4.00	0.163	0.190	0.246	1.185	0.211	5.62
4.50	0.149	0.204	0.264	1.167	0.193	6.04
5.00	0.137	0.216	0.280	1.151	0.177	6.51
6.00	0.115	0.238	0.308	1.123	0.149	7.54
7.00	0.097	0.256	0.332	1.099	0.125	8.78
8.00	0.082	0.271	0.351	1.080	0.106	10.19
10.00	0.059	0.294	0.381	1.050	0.076	13.83
12.50	0.039	0.314	0.406	1.025	0.051	20.10

$k_2 = 25.2$ M^{-1} $sec.^{-1}$

SECTION V

APPENDIX

CONDUCTIMETRIC TECHNIQUE FOR MEASURING RATES OF CLEAVAGE

Before the study of allyltin cleavage was undertaken, attempts were made to measure the rates of cleavage of vinyltin derivatives by acid. A conductimetric technique was employed as a means of following the rates, but extensive attempts to achieve reproducibility were unsuccessful. Attention was then directed toward the cleavage of allyltin derivatives, and the conductimetric technique evaluated for this substrate. The discovery of the unexpected absorbance by allyltin derivatives in the ultraviolet region diverted this further examination, but not before it was shown that, with certain limitations, the conductimetric technique can yield usable rate data. The purpose of this section is to outline this technique and point out its limitations.

Any reaction which is to be followed by this method must show a pronounced change in conductance over the course of the reaction. In cleavage of both allyl- and vinyltin derivatives, acid concentration decreased with time, and a decrease in conductance was observed in all cases. However, in the case of the reaction of tributylvinyltin with perchloric acid in methanol, the net decrease was very small, presumably because the product, tributyltin perchlorate, dissociates appreciably. Again, when allyltin cleavage was attempted in dioxane solvent, both initial and final conductances were very small. Conductimetric techniques cannot be used in either of such cases.

A second condition must be met. The relationship of conductance to concentration of the species whose disappearance or appearance is being measured must be known precisely. When only one species is responsible for the conductance in a given system, this can be measured accurately. In the simplest case, conductance varies linearly with concentration over a given range, and a set of empirical rate equations can be derived in a straightforward manner. Second-order rate equations of this kind have been outlined by Dessy.[4] One might imagine that if two species in the system conduct, but the conductance as a function of concentration were known for both, one could subtract the conductance of the second species from the total conductance, and apply such equations.

For both allyl- and vinyltin cleavage, however, the total conductance is a complex function of time, and neither condition of the preceding paragraph applies. It has proven impossible to analyze the data obtained for vinyltin cleavage, but, knowing the rate constant for allyltin cleavage from spectrophotometric measurements, it became feasible to evaluate the limited conductance data available.

Experimentally it was found that both anhydrous methanol and 4% water-methanol possessed suitable ionizing power to be used as solvents for these studies. It was further found that a plot of specific conductance of hydrochloric acid varies linearly with concentration over a range of 2×10^{-3} to 6×10^{-2} M in anhydrous methanol and from 4×10^{-5} to 12×10^{-4} M in 4% water-methanol. In the latter relationship, the conductance due to solvent was subtracted from each measured conductance. The dissociation constant of tributyltin chloride in anhydrous methanol was measured, and the value $K_{diss} = 6.9 \times 10^{-5}$ is in agreement with similar measurements by Prince.[34] The value of K_{diss} in 4% water-methanol might be expected to be about twice this value.

A comparison of spectrophotometric and conductometric data for a run followed simultaneously by both techniques follows.

Table XXV

Comparison of Spectrophotometric With Conductimetric Rate Data

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Run 141 $a = HCl = 8.145 \times 10^{-4}$ M $\frac{a}{b} = 3.35$

$b = Me_3SnAl = 2.426 \times 10^{-4}$ M

$(a-b) = 5.719 \times 10^{-4}$ M $E_o = 1.233$

Solvent: 4% water-methanol

Spectrophotometric Data

Time[a]	E_t	E_o-E_t	x	a-x	b-x	$\frac{a-x}{b-x}$
15	0.848	0.385	0.759	7.386	1.667	4.43
30	0.631	0.602	1.188	6.957	1.238	5.62
45	0.476	0.757	1.491	6.654	0.935	7.12
60	0.346	0.887	1.749	6.396	0.677	9.45
75	0.264	0.969	1.910	6.235	0.516	12.1
90	0.197	1.036	2.040	6.105	0.386	15.8

$k_2 = 0.505\ M^{-1}\ sec.^{-1}$

[a] For explanation of column headings, see introductory part of Tables of Data.

Table XXV (Continued)

Conductimetric Data

Time	$L \times 10^4$ [b]	$L_{corr} \times 10^4$ [c]	a-x [d]	x	b-x	$\frac{a-x}{b-x}$
7	2.04	2.00	7.782	0.363	2.063	3.78
12	2.00	1.96	7.626	0.519	1.907	4.01
19	1.97	1.93	7.510	0.635	1.791	4.20
31	1.93	1.89	7.354	0.791	1.635	4.50
42	1.92	1.88	7.315	0.836	1.596	4.58
52	1.90	1.86	7.237	0.908	1.518	4.77
68	1.88	1.84	7.160	0.985	1.441	4.97
97	1.86	1.82	7.082	1.063	1.363	5.20

[b] L = specific conductance in mhos

[c] L_{corr} = specific conductance, L, minus specific conductance of solvent.

[d] (a-x) is obtained by dividing L_{corr} by the slope of the plot of Specific Conductance vs. Concentration of HCl, where m = 0.247.

A comparison of the rate plots by both techniques is shown in Figure 7. The deviation from linearity for the conductance data is marked, but for the first 20% of the reaction, the slopes of the rate plots agree quite closely. An initial rate treatment might therefore yield reasonably precise values of the rate constant, particularly if allyltin concentrations were initially equal to or greater than the acid concentration. From the direction of the observed cur-

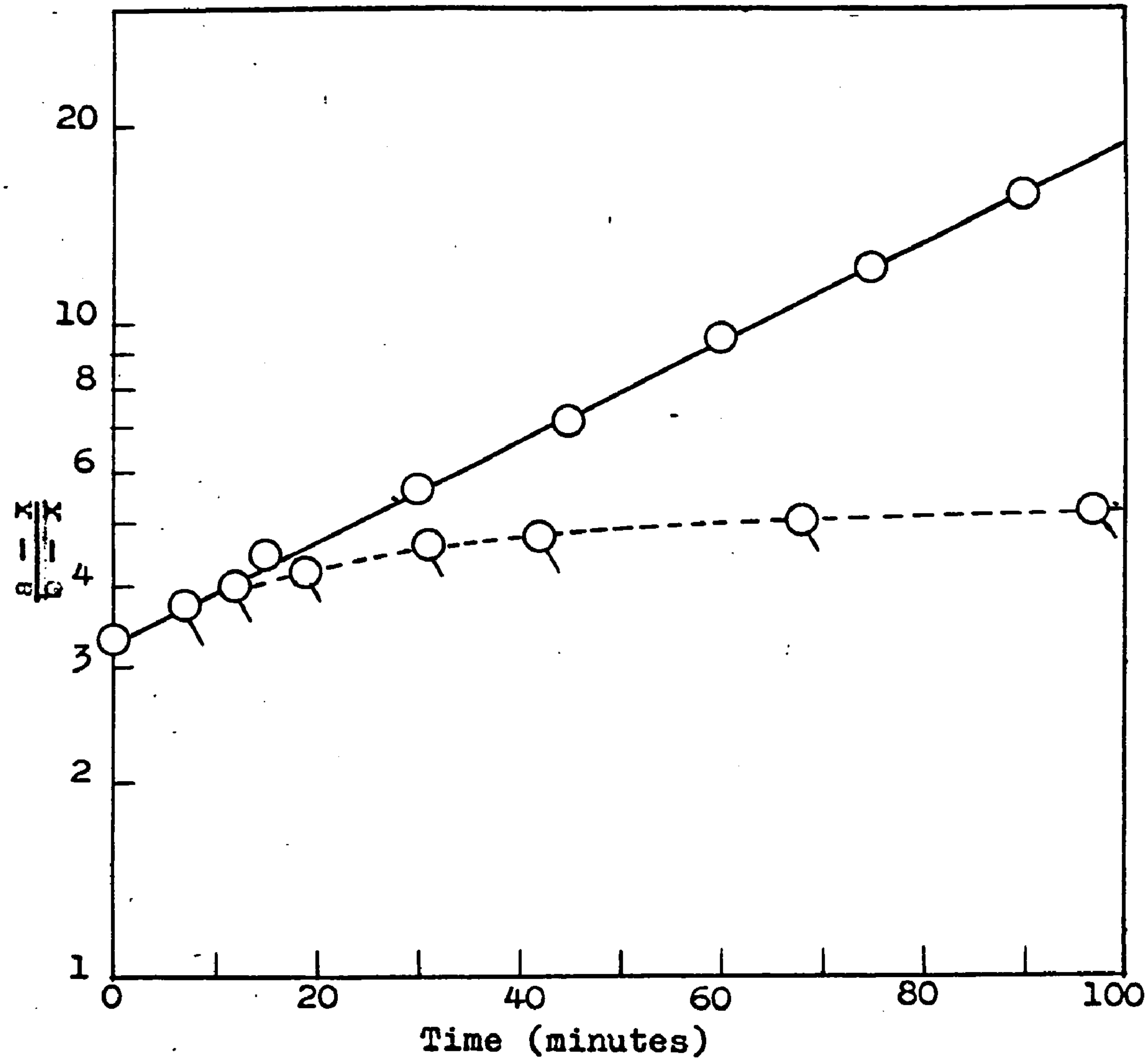

Figure 7. Comparison of Spectrophotometric and Conductimetric Techniques. Second Order Rate Plot for the Protonolysis of Allyltrimethyltin in 4% Water-Methanol. Run 141.

Solid line - Spectrophotometric Aliquot Method
Dotted curve - Conductimetric Method

vature, it is obvious that some species other than acid is contributing to the observed conductance.

In the conductimetric treatment used, a correction was applied for the conductance of the solvent, but no correction for the conductance of trimethyltin chloride was attempted. The reason for this is that the total conductance of the system is not simply the sum of the conductances of hydrochloric acid, methanol, and trimethyltin chloride. For example, the spectrophotometric method indicates that at 31 minutes half the allyltin has reacted, and the concentration of acid remaining is 6.932 x 10^{-4} M. The conductimetric method indicates an acid concentration of 7.354 x 10^{-4} M. If the former value is regarded as correct, the concentration of dissociated trimethyltin chloride in the presence of chloride ion from unreacted hydrochloric acid can be calculated from the expressions:

$$(1)\qquad \underset{(1.213 \times 10^{-4}) - x}{Me_3SnCl} \rightleftharpoons \underset{x}{Me_3Sn^+} + \underset{x + (6.932 \times 10^{-4})}{Cl^-}$$

$$(2)\qquad K_{diss} = \frac{(Me_3Sn^+)\,(Cl^-)}{(Me_3SnCl)} \cong 12 \times 10^{-5}$$

Solution of Equation (2) by the quadratic equation gives a value of 2 x 10^{-5} M dissociated trimethyltin chloride, or about 16% dissociation. Even if this concentration of the weak electrolyte had a specific conductance as high as that of the same concentration of hydrochloric acid, this would amount to only 5×10^{-6} mhos, and the corrected specific conductance at 31 minutes would be 1.84×10^{-4} mhos, which corresponds to a "corrected" acid concentration of 7.160×10^{-4} M, appreciably higher than that measured spectrophotometrically. Analagous observations were made in the allyltributyltin in anhydrous methanol system, although no accurate spectrophotometric data was available for comparison. Some unknown species apparently makes a contribution to the total conductance, and causes the observed curvature of the rate plot.

In Run 141 the reaction was followed spectrophotometrically by the Aliquot Method outlined in the Experimental section. Before the first point was taken, a portion of the reaction mixture was poured into a standard conductivity cell with fixed, platinum blacked plates and a cell constant of unity, and the conductivity measured on an Industrial Instruments Inc. Conductivity Bridge Model RC 16B1. In other attempts, acid was added by pipette into the cell which contained a solution of allyltin and methanalic solvent. The temperature of the reaction mixture was maintained at $25.00 \pm .01^{\circ}$, and all stock solutions were brought to this temperature before being transferred to reaction vessels.

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