Preparation of Tetramethyl-1,3-diacetoxydistannoxane.—A mixture of dimethyltin oxide (4 g.) and acetic anhydride (25 g.) was refluxed for one hour, followed by distillation of the excess anhydride with 20-30 cc. of xylene. From the methanol solution of the product, which was evaporated on a hot plate, three portions of crystals amounting to 2 g., 1 g. and 1 g. were obtained. The first two portions of these crystals melted at 236-237°. The same substance was obtained when dimethyltin oxide was allowed to react with glacial acetic acid or 50% aqueous acetic acid. Recrystallization from methanol. by adding a small amount of acetic acid, gave crystals which melted at 240° and then frothed up to leave a waxy solid and a small amount of crystalline sublimate. The results of analyses of both preparations are given in Table I. Sublimation was not considered to be a suitable method to obtain a pure compound because of contamination with some decomposition products even under 1 mm. pressure.

Attempts to Obtain Dimethyldiacetoxystannane.—A reaction of dimethyltin dichloride and acetic acid with sodium acetate was carried out, but the product decomposed even when sublimation was carried out under 1 mm. pressure. A small amount of sublimate (m.p. 233°) seemed to be a dimeric compound which had a pungent acetic smell.

Tetramethyl-1,3-diacetoxydistannoxane (3.7 g.) was allowed to react with an excess of acetic anhydride. During the course of sublimation, a large wet crystalline sublimate (2.5 g.) was obtained. These crystals had a pungent acetic smell, turned white on exposure to air and melted at an indefinite temperature. Recrystallization from benzene gave a product composed mainly of the distannoxane. The reaction of dimethylchloroacetoxystannane with an excess of acetic anhydride did not give the desired compound.

Acknowledgments.—We are indebted to the Metal and Thermit Corporation for the gift of some dimethyltin dichloride. This work was supported in part by the Office of Naval Research.

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

The Infrared Spectra of the Methylacetoxysilanes and Some Methyltin Carboxylates. The Configuration of the Trimethyltin and the Dimethyltin Cations

BY ROKURO OKAWARA,[1] DAVID E. WEBSTER[2] AND EUGENE G. ROCHOW

RECEIVED SEPTEMBER 18, 1959

The infrared spectra of trimethylacetoxysilane, dimethyldiacetoxysilane, methyltriacetoxysilane and silicon tetraacetate have been examined over the range 1000-3500 cm.$^{-1}$. Trimethyltin acetate, formate, chloroacetates, propionate and halides, dimethyltin acetate, formate and halides and monomethyltin halides have also been studied over the range 400-3500 cm.$^{-1}$. The spectra of the silicon acetates are very similar to those of organic acetates, and it is concluded that the bonding is similar to that of an organic ester. The spectra of the tin acetate and other tin derivatives, on the other hand, show the presence of the carboxylate anion. Characteristic vibrations of the methyl-tin groups are found near 780 and 1200 cm.$^{-1}$. The trimethyltin cation is found to have a planar structure, and the dimethyltin cation is linear.

The methylacetoxysilanes have been known for some time, but only recently has a variety of methyltin esters been prepared.[3] As there is now an increasing interest in the organic derivatives of tin, we report the results of this comparative study of the infrared spectra of 24 compounds.

TABLE I

	M.p., °C.	Anal., calcd. Sn	C	H	Anal., found Sn	C	H
$(CH_3)_3SnOOCH$	151	56.84	23.01	4.83	56.88	23.37	4.83
$(CH_3)_3SnOOCCH_3$	197[a]	53.27	26.95	5.43	53.39	26.75	5.56
$(CH_3)_3SnOOCCH_2Cl$	148	46.13	23.34	4.31	46.21	23.79	4.71
$(CH_3)_3SnOOCCHCl_2$	135	40.69	20.58	3.46	40.87	20.84	3.75
$(CH_3)_3SnOOCCCl_3$	179	36.39	18.41	2.78	36.37	18.41	2.67
$(CH_3)_3SnOOCC_2H_5$	136		30.42	5.96		30.28	6.01
$(CH_3)_3SnF$		64.93	19.71	4.96	64.94	19.73	4.76

[a] Lit.[5] 196.5–197.5°.

Experimental

The methylacetoxysilanes and silicon tetraacetate were prepared by the reaction of the corresponding methylchlorosilane or silicon tetrachloride with acetic anhydride.[4]

Trimethyltin salts other than the fluoride were obtained by the reaction of trimethyltin hydroxide and the corresponding acid, followed by purification by sublimation. The fluoride was prepared by neutralization of trimethyltin hydroxide with 50% hydrofluoric acid and was recrystallized. Melting points and analyses are given in Table I.

The preparation of the dimethyltin derivatives has been reported.[3] Dimethyltin and methyltin halides were obtained by the reaction of the hydrohalogen acid with dimethyltin oxide or methylstannoic acid. All the halides, except the fluoride, were identified by their melting points.

The infrared absorption spectra were recorded using a Perkin-Elmer (Model 21) double-beam spectrophotometer equipped with NaCl or KBr[6] optics. Spectra were calibrated using known peaks of a polystyrene film or of 1,3,5-trichlorobenzene.

The spectra of the silicon acetates are those of solutions in carbon tetrachloride. In the NaCl region, the spectra of the methyltin halides, except the fluoride, are those of solutions in carbon tetrachloride and carbon disulfide. The other tin derivatives were insoluble, and the spectra were obtained using pressed KBr discs. In the KBr region, pure liquid, Nujol mull, and KBr discs were used.

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[1] Research Fellow in Chemistry at Harvard University, 1958-1959.

[2] Research Fellow in Chemistry at Harvard University, 1958-1959.

[3] R. Okawara and E. G. Rochow, THIS JOURNAL, **82**, 3285 (1960).

[4] "Inorganic Syntheses," Vol. IV, McGraw-Hill Book Co., New York, N. Y., 1953, p. 45.

[5] G. J. M. van der Kerk and J. G. A. Luitjen, *J. Appl. Chem.*, **6**, 49 (1956).

[6] We thank Dr. Nakamoto of Clark University, Worcester, Mass., for the use of his spectrophotometer equipped with KBr optics.

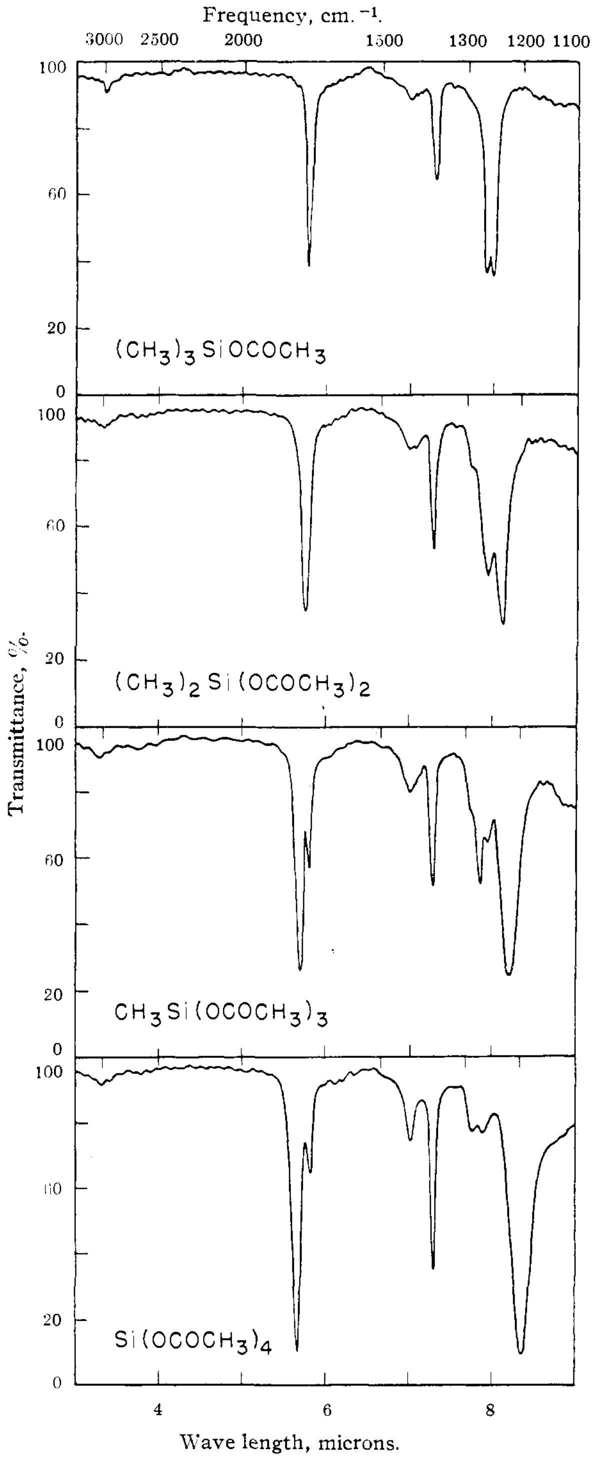

Fig. 1.—Infrared absorption spectra of methylacetoxysilanes.

The vibrational frequencies of trimethylacetoxysilane, dimethyldiacetoxysilane, methyltriacetoxysilane and silicon tetraacetate are listed in Table II, and the spectra in the region 1100–3500 cm.$^{-1}$ are shown in Fig. 1.

The compound dimethyltin diacetate could not be prepared, the products from dimethyltin dichloride being dimethylchlorotin acetate and tetramethyl-1,3-diacetoxydistannoxane.[3] The vibrational frequencies of these two compounds, together with those of trimethyltin acetate and of sodium acetate for comparison, are shown in Table III.

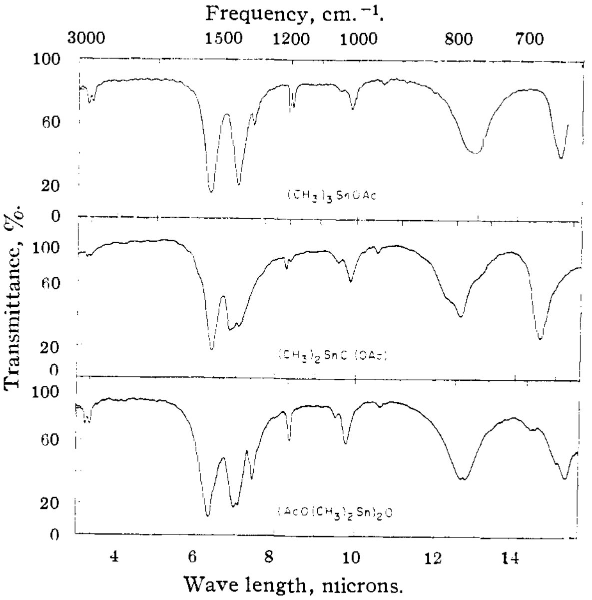

Fig. 2.—Infrared absorption spectra of methyltin acetates.

The spectra of the three tin acetates in the region 650–3500 cm.$^{-1}$ are given in Fig. 2.

TABLE II[a]

INFRARED VIBRATIONAL FREQUENCIES OF $(CH_3)_xSi(OOCCH_3)_{4-x}$: POSITIONS OF BANDS (IN CM.$^{-1}$)

$x = 3$	$x = 2$	$x = 1$	$x = 0$	Assignment
1018w	1018m	1019s	1022s	CH_3 rock.
..	1047w	1047w	1047w	
1257s	1262s	1279m	..	CH_3(–Si) sym. deform.
1267s	1235s	1220s	1200s	C–O(–Si) str.
..	1270sh	1262w	1270w	
(1291w)[b]	(1291w)	(1291w)	(1291w)	
1377m	1377m	1377s	1377s	CH_3 sym. deform.
1430w	1430w	1430w	1430w	CH_3 asym. deform.
	(1725sh)[b]	(1725w)	(1725w)	
1725s	1732s	1748s	1765s	C=O str.

[a] Frequencies over 2000 cm.$^{-1}$ are not shown in the tables. [b] The absorptions shown in the parentheses could be explained as those of acetic acid. The compounds shown in Table I are quite easily hydrolyzed to give acetic acid.

TABLE III

INFRARED VIBRATIONAL FREQUENCIES OF TRIMETHYLTIN AND DIMETHYLTIN ACETATES: POSITIONS OF BANDS (IN CM.$^{-1}$), R = $OOCH_3$

$(CH_3)_3$-SnR	$(CH_3)_2$-SnClR	$[R(CH_3)_2$-$Sn]_2O$	NaR[a]	Assignment
664s	685s	656s	647s	COO scissor.
		666sh		
		696w		
775s	795s	788s	..	CH_3(–Sn) rock.
	815sh			
940w	950w	940w	923m	C–C str.
1015m	1018m	1024m	1007m	CH_3 rock.
1048w	1047w	1053w	1045m	
1194m	1198w	1197m	..	CH_3(–Sn) sym. deform.
1206m	1215w	..	..	
1352m	..	1345m	1338w	CH_3 sym. deform.
1428s	1413s	1410s	1425m	COO sym. str.
..	1443sh	1430s	1440sh	CH_3 asym. deform.
..	1461s	..	1484sh	
1576s	1564s	1580s	1582s	COO antisym. str.

[a] K. Nakamura, *J. Chem. Soc. Japan*, **79**, 1411 (1958) (in Japanese). See also, L. H. Jones and E. McLaren, *J. Chem. Phys.*, **22**, 1796 (1954).

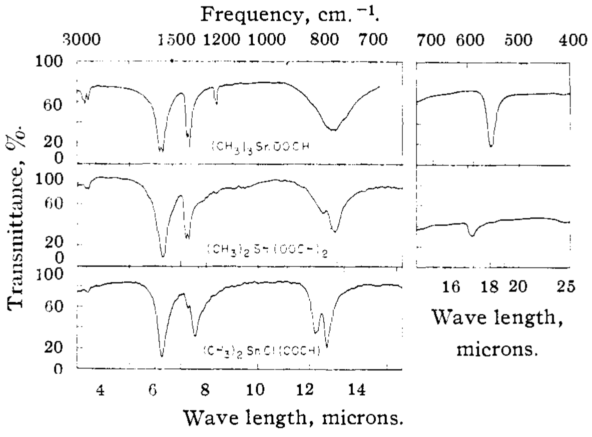

Fig. 3.—Infrared absorption spectra of methyltin formates.

The spectra of the trimethyltin and dimethyltin formates, chloroacetates and propionates are listed in Tables IV and V, and the spectra of the three tin formates are given in Fig. 3. To identify the bands associated with the methyl-tin groupings and to discuss their configurations, results from the study of certain methyltin halides are given in Table VI. In Fig. 4 are shown the spectra in the region 400-3500 cm.$^{-1}$ of the representative compounds in Table VI.

TABLE IV

INFRARED VIBRATIONAL FREQUENCIES OF TRIMETHYLTIN AND DIMETHYLTIN FORMATES: POSITIONS OF BANDS (IN CM.$^{-1}$), R = OOCH

$(CH_3)_3$-SnR[a]	$(CH_3)_2$-SnR_2[a]	$(CH_3)_2$-$SnClR$	NaR[b]	Assignment
770s	770s	789s	..	CH_3(–Sn) rock.
790sh	800m	818 ± 2s	784	COO deform.
..	..	..	1070	CH out-of-plane bend.
1195m	..	..	..	CH_3(–Sn) sym. deform.
1205m	1202w	1204w	..	
1363s	1373s	1325s	1365	CH in-plane bend.
1378s	1390s	1375m	1377	COO sym. str.
1590s 1615s	1588s	1595s	1620	COO antisym. str.

[a] In the KBr region, only one strong band is found at 552 cm.$^{-1}$ in the spectrum of $(CH_3)_3SnOOCH$ and at 592 cm.$^{-1}$ in $(CH_3)_2Sn(OOCH)_2$. [b] R. Newman, *J. Chem. Phys.*, **20**, 1663 (1952). See also, K. Ito and H. J. Bernstein, *Canad. J. Chem.*, **34**, 170 (1956).

TABLE V

METHYL(-TIN) VIBRATIONAL FREQUENCIES AND THE CO_2 STRETCHING FREQUENCIES OF THE CHLOROACETATES AND PROPIONATE IONS: POSITIONS OF BANDS (IN CM.$^{-1}$), $(CH_3)_3SnOOCR$

R = CH_2CH_3	CH_2Cl	$CHCl_2$	CCl_3	Assignment
775	765 or 783	765	772	CH_3(–Sn) rock.
1192	1196	1195	1195	CH_3(–Sn) sym. deform.
1202	..	1206	..	
1433	1418	1393	1352	COO str.
		1620		
1574	1640	1640	1656	
		1660		

Discussion

The Methylsilicon and Methyltin Carboxylic Acid Derivatives.—The spectra of the acetoxy derivatives of silicon (Table II) show the band associated with the carbonyl group[7] at 1725–1765 cm.$^{-1}$, the frequency increasing with an increasing number of acetate groups in the molecule. The band associated with the C–O(–Si) bond is found at 1200–1267 cm.$^{-1}$, the frequency decreasing with an increasing number of acetate groups in the molecule. These two bands are as found in organic acetates,[8] and it is concluded that in the acetoxysilanes the Si–O bond is covalent.

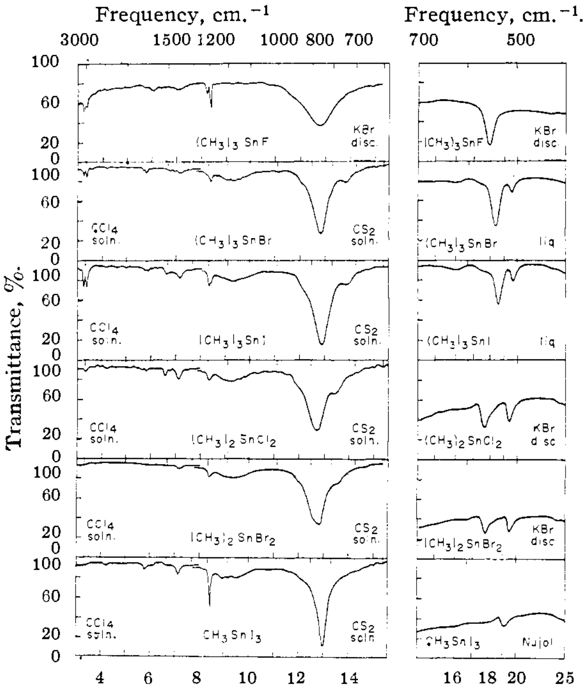

Fig. 4.—Infrared absorption spectra of methyltin halides.

The spectra of the acetoxy derivatives of tin (Table III) show completely different features from those of the methylacetoxysilanes. In all the tin compounds studied here, the spectra are interpreted as superpositions of the absorptions of the carboxylic acid anion and those of the methyltin cation. Freeman[7] has reported that di-*n*-butyltin acetate is an ionic compound.

Assignment of the characteristic bands of the acetate ion can be made with certainty. The remaining strong band near 780 cm.$^{-1}$ and the two sharp bands near 1200 cm.$^{-1}$ then can be assigned to the rocking and symmetric deformation vibrations of the methyl groups attached to tin. This assignment is supported by the spectra of the methyltin formates (Table IV). Most of the bands are readily assigned to the formate ion; only slight differences occur between the tin derivatives and sodium formate. The main differences are the appearance of a strong band near 780 cm.$^{-1}$ and one, or two, sharp bands near 1200 cm.$^{-1}$. These, as for the acetate, are assigned to methyl-tin vibrations. In the chloroacetates (Table V), the C–Cl bands are near the 780 cm.$^{-1}$ band but assignment is still possible.

Characteristic Vibrations of the Methyltin Compounds and the Configuration of the Trimethyltin and Dimethyltin Cations.—Since the rocking vibra-

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(7) J. P. Freeman, THIS JOURNAL, **80**, 5954 (1958), reports this band at 1715 cm.$^{-1}$ for the trimethyl compound.

(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen, London, 1958.

TABLE VI

INFRARED VIBRATIONAL FREQUENCIES OF METHYLTIN HALIDES IN THE REGION 400–1500 CM.$^{-1}$: POSITIONS OF BANDS (IN CM.$^{-1}$)

	$(CH_3)_3SnX$				$(CH_3)_2SnX_2$			CH_3SnX_3			$(CH_3)_4Sn$	
X =	F	Cl	Br	I	Cl	Br	I	Cl	Br	I		
	k[a]	n	l	l	k	k,n	n	k	k,n	k,n	[b]	[c]
	..	513m	512m	509m	515s	514s	511m					
								540s	539s	527s	524	528
	555s	545s	543s	540s	567s	563s	547m					
		722m	723w	720w	745w	743sh	735sh					
	782s	782s	781s	780s	786s	779s	772s	788s	780s	770s	764	770
						790sh	789sh					
	1194m	1200w	1198w	1194w	1204w	1198w	1198w	1204w	1197m	1188m	1190	1198
	1216w			1204w								
	1412w	1410w	1400w	1400w	1410w	1410w	1404w	1402w	1406w	1402w	1445	1443

[a] Nujol mull (n), KBr pressed disc (k) or a liquid film (l) was used in the KBr region. [b] W. F. Edgell and C. H. Ward, THIS JOURNAL, **77**, 6486 (1955). [c] E. R. Lippincott and M. C. Tobin, *ibid.*, **75**, 4141 (1953).

tion near 780 cm.$^{-1}$ is strong and can be found in all of the methyltin compounds, this vibration is considered characteristic of methyltin compounds. The symmetric deformation vibration of methyl groups attached to silicon and to germanium[9] produces sharp bands near 1260 and 1230 cm.$^{-1}$, respectively; the former band has been considered characteristic of all methylsilicon compounds. In the methyltin compounds the band is sometimes weak, but it is helpful for identification.

Another characteristic band, attributable to the asymmetric deformation vibration of the methyl group attached to tin, is hidden in the carboxylates but is found as a weak band, near 1400 cm.$^{-1}$, in the halides shown in Table VI. Two other weak bands associated with C–H stretching vibration of the $CH_3(-Sn)$ group are found near 3000 cm.$^{-1}$.

Valuable information is obtained from the spectra of the methyltin compounds in the KBr region. All the compounds shown in Table VI have one or two strong absorptions in the range 500–600 cm.$^{-1}$. In the trimethyltin and dimethyltin chlorides, bromides and iodides, which all have been known to have a tetrahedral structure,[10] the band near 512 cm.$^{-1}$ and the band at 540–570 cm.$^{-1}$ can be assigned as the Sn–C symmetric and asymmetric stretching vibrations, respectively.

Earlier we have shown from the spectra in the NaCl region that trimethyltin formate and dimethyltin diformate are ionic, the spectra being interpreted as due to the superposition of absorptions of the methyltin cation and the formate anion. Since the formate anion shows no bands below 700 cm.$^{-1}$, the band found in the spectra of the tin formates must be due to the methyltin cation. The spectra of these compounds have only one band in the KBr region, as shown in Fig. 3. If we assume the configuration of the trimethyltin cation to be planar and that of the dimethyltin cation to be linear, then the Sn–C symmetric stretching vibrations are infrared inactive, and we can expect only the Sn–C asymmetric stretching vibration in this region. This assumption is further supported by the frequency of the band.

For the trimethyltin acetate, chloroacetates and propionate the strong absorption found at 552 ± 3 cm.$^{-1}$ is also assigned to Sn–C vibration, and all other bands can be assigned to the COO deformation vibrations of the acid anion.

Trimethyltin fluoride is found to have only one band at 555 cm.$^{-1}$ in the KBr region, due to the planar trimethyltin cation. This confirms the conclusion from chemical evidence that this compound is ionic.

Acknowledgments.—We thank Dr. I. Nakagawa for many helpful discussions. This work was supported in part by the Office of Naval Research.

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[9] M. P. Brown, R. Okawara and E. G. Rochow, submitted to *Spectrochim. Acta.*

[10] H. A. Skinner and A. D. Sutton, *Trans. Faraday Soc.*, **40**, 164 (1944).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA]

Amine Boranes. I. Kinetics of Acid Hydrolysis of Trimethylamine Borane

BY GEORGE E. RYSCHKEWITSCH

RECEIVED NOVEMBER 30, 1959

The rates of the reaction of trimethylamineborane with aqueous HCl and with HCl in 20% dioxane-water mixtures have been studied at $0.1 < [H_3O^+] < 0.6$ and in the temperature range 35 to 44°. The reaction is first order with respect to amine borane and with respect to acid concentration and increases with the ionic strength of solution; the experimental results are very well represented by: $d[(CH_3)_3NBH_3]/dt = -k'[(CH_3)_3NBH_3]$; $k' = k[H_3O^+] \exp b[H_3O^+]$; $k = A \exp(-\Delta E/RT)$. The apparent activation energy in either solvent was 25.73 ± 0.13 kcal./mole.

In most compounds containing a boron–hydrogen bond, removal of hydrogen can be achieved by the attack of protonic reagents. The reactivity of such compounds in homogeneous media varies widely ranging, *e.g.*, from extremely rapid attack of alcohols on some boron hydrides to the extreme resistance of phosphinoboranes even to hot mineral acids. Even though a good deal of qualitative and