

hydrogens bound to the  $\text{N}_2\text{O}_3^{-2}$  ion at each point was calculated by the equation

$$\bar{n} = \frac{aC_N - [\text{H}^+]}{C_N} = a - [\text{H}^+]/C_N \quad (1)$$

where  $C_N$  is the analytical concentration of  $\alpha$ -oxyhyponitrite in all forms (after correction for dilution),  $a$  is the number of equivalents of hydrogen ion added per mole of  $\alpha$ -oxyhyponitrite,  $[\text{H}^+]$  is the concentration of free hydrogen ions in solution.  $C_N$  was calculated from the weight of sodium  $\alpha$ -oxyhyponitrite and the total volume and was verified by the volume of titrant needed to reach the end point,  $a$  was calculated from the titration volumes, and  $[\text{H}^+]$  was obtained from the pH and the activity coefficients of Harned and Hamer.<sup>4</sup> The values of  $K_1$  were calculated from the values of  $\bar{n}$  and  $K_2$  by use of eq. 3 which was derived from eq. 2 by substituting the mixed acid constant expressions for the concentrations of the various species.

$$\bar{n} = \frac{[\text{HN}_2\text{O}_2^-] + 2[\text{H}_2\text{N}_2\text{O}_3]}{[\text{N}_2\text{O}_3^{-2}] + [\text{HN}_2\text{O}_3^-] + [\text{H}_2\text{N}_2\text{O}_3]} \quad (2)$$

$$K_1 = \frac{[2 - \bar{n}](\text{H}^+)^2}{\bar{n}K_2 + [\bar{n} - 1](\text{H}^+)} \quad (3)$$

In eq. 3 molar concentrations are indicated by brackets, while activities are indicated by parentheses.

It was found that if the solution becomes more acidic than about pH 4.60,  $\alpha$ -oxyhyponitrite is unstable and decomposes to form NO gas, eq. 4 and 5, while the pH of the solution increases.

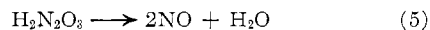


Figure 1 shows the increase of pH with time. It was concluded that significant experimental measurements could not be made below pH 4.60. Unfortunately, at this pH  $\bar{n}$  is approximately 1.005 rather than 1.50 where  $K_1$  could be evaluated most accurately.

The calculated values of the constants are summarized in Table I.

Ionic strength	TABLE I	
	$\text{p}K_1$	$\text{p}K_2$
1.02	$2.32 \pm 0.01$	$9.18 \pm 0.01$
0.38	$2.30 \pm 0.01$	$9.30 \pm 0.01$
0.12	$2.40 \pm 0.05$	$9.43 \pm 0.01$
0.02	$2.46 \pm 0.05$	$9.56 \pm 0.01$
0.00 extrapolated	2.51	9.70

All values except for  $\text{p}K_1$  at  $\mu = 0.38$  are the results of at least two separate experiments. The errors indicated for  $\text{p}K_1$  are the average deviations of the calculated  $\text{p}K_1$  values of all experimental points for the region  $\bar{n} = 1.001$  to  $\bar{n} = 1.005$ . The errors for  $\text{p}K_2$  represent the limits of the values obtained by interpolation of the titration curves.

### Discussion

In general when a molecule has two acid groups of the same type the two  $\text{p}K$  values become closer as the distance between the acid groups increases. This is seen in a comparison of the last two  $\text{p}K$  values of chain polyphosphates where (at  $\mu = 1$ ) these  $\text{p}K$  values for pyrophosphate are 8.93 and 6.13<sup>5</sup>; for tripolyphosphate, 8.81 and 5.83<sup>6</sup>; for tetrapolyphosphate, 8.38 and 6.59<sup>7</sup>; and for a long chain polyphosphate,  $\text{HO}_2\text{P}(\text{HPO}_3)_{58}(\text{av})\text{PO}_2\text{H}$ , they are 8.17 and 7.22.<sup>8</sup> The spacing between the groups in HO-NON-OH would be similar to that in pyrophosphate. Furthermore, in dicarboxylic acids

- (4) H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **55**, 2194 (1933).  
 (5) S. M. Lambert and J. I. Watters, *ibid.*, **79**, 4262 (1957).  
 (6) J. I. Watters, E. D. Loughran, and S. M. Lambert, *ibid.*, **78**, 4855 (1956).  
 (7) R. Simonaites, P. E. Sturrock, and J. I. Watters, *Inorg. Chem.*, in press.

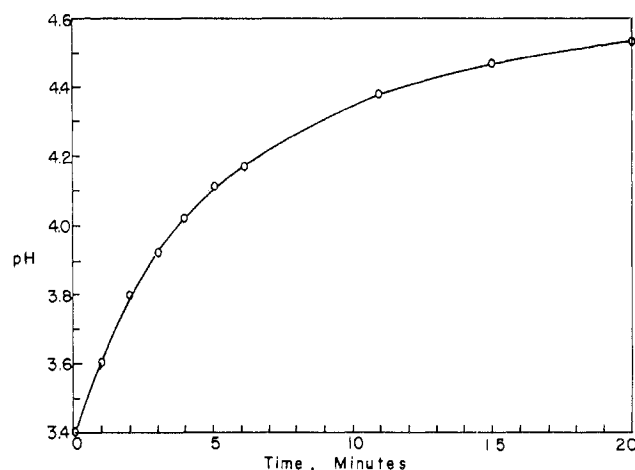
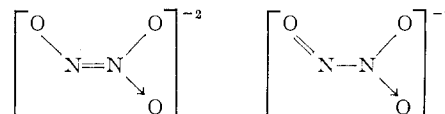


Fig. 1.—Change of pH as a function of time resulting from decomposition of  $\text{H}_2\text{N}_2\text{O}_3$ .

the two  $\text{p}K$  values are separated by about 3  $\text{p}K$  units or less except in cases like maleic acid where conjugated unsaturation may occur. From these analogies it is concluded that in the case of  $\alpha$ -oxyhyponitrous acid the structure HO-NON-OH is improbable since the two  $\text{p}K$  values are separated by 7.19 units.

Several structures have been suggested for  $\alpha$ -oxyhyponitrous acid.<sup>3</sup> The calorimetric experiments of Hunt, Cox, and Ray<sup>2</sup> have excluded the peroxide structure. The remaining structures all have in common a nitrogen to nitrogen bond with two oxygen atoms bonded to one nitrogen and the third oxygen to the other nitrogen. Thus the resonance structures



are possible for the  $\alpha$ -oxyhyponitrite ion. The remaining question, the location of the protons in the monohydrogen  $\alpha$ -oxyhyponitrite ion and the free acid, will be discussed in terms of Hammett  $\sigma\rho$  relationships in a future paper.

(8) R. R. Irani and C. F. Callis, *J. Phys. Chem.*, **65**, 934 (1961).

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### The Chemistry of Alane. I. Some Observations on the Effect of the Coördinating Base on the Aluminum-Hydrogen Absorption in the Infrared<sup>1</sup>

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The infrared spectra of solutions of various alane-

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TABLE I  
 INFRARED AND MOLECULAR WEIGHT DATA FOR ALANE-LEWIS BASE COMPLEXES

Lewis base	Alane:base ratio	Solvent	Al-H absorption, cm. <sup>-1</sup>	Mol. wt., found	Monomer mol. wt.	Degree of assocn.
Diethyl ether	...	Diethyl ether	1801	30.4 <sup>a</sup>	30	1.00
Diethyl ether	1:4	Benzene	1840, shoulder at 1800	126	104	1.21
THF	...	THF	1724	30 <sup>b</sup>	30	1.00
THF	1:1	Benzene	1786	158	102	1.55
THF-diethyl ether	1:1:1	Benzene	1710, shoulder at 1695	174	176	0.99
Trimethylamine	1:2	Diethyl ether	1695, shoulder at 1739	153	148	1.03
Trimethylamine	1:2	THF	1695	152	148	1.03
Trimethylamine	1:2	Benzene	1690	145 <sup>a</sup>	148	0.98
Trimethylamine	1:1	Diethyl ether	1770 (s) <sup>c</sup> 1724 (w) <sup>c</sup>	93 <sup>a</sup>	89	1.05
Trimethylamine	1:1	THF	1710, 1695, shoulder at 1770	90	89	1.01
Trimethylamine	1:1	Benzene	1786	128 <sup>a</sup> 124 <sup>d</sup>	89	1.42

<sup>a</sup> E. Wiberg, H. Graf, and R. Usón, *Z. anorg. allgem. Chem.*, **272**, 221 (1953). <sup>b</sup> E. Wiberg and W. Gösele, *Z. Naturforsch.*, **11b**, 485 (1956). <sup>c</sup> s, strong; w, weak. <sup>d</sup> J. K. Ruff and M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 2141 (1960).

Lewis base complexes have been reported recently by several workers,<sup>2-5</sup> all of whom observed a shift of the Al-H absorption in monotrimethylamine alane to a lower frequency when a second molecule of trimethylamine was added. Dautel and Zeil<sup>5</sup> prepared several mono- and bis-Lewis base-alane complexes, including several mixed bis-complexes with Lewis bases such as tetrahydrofuran, dioxane, and trimethylamine. A shift in the Al-H absorption of a mono-adduct on dissolving it in a second Lewis base was observed. The Al-H absorptions were correlated with the coordination number of aluminum in the complexes, the higher frequency being considered as characteristic of tetravalent aluminum, while the lower frequency was associated with the pentavalent state.

In the course of studies on alane chemistry in these Laboratories, several alane-Lewis base complexes were prepared in different solvents. We wish to report three instances of apparent deviation of the position of the Al-H absorption in the infrared spectrum of solutions of alane adducts from the assignments of Dautel and Zeil. Our results are listed in Table I, together with available molecular weight data. The three adducts giving anomalous results were diethyl ether alane in diethyl ether, a 4:1 diethyl ether-alane complex in benzene, and monotrimethylamine alane in diethyl ether. These show the Al-H absorption at the higher frequency assigned by Dautel and Zeil to the tetravalent state. On the other hand, the mixed bis-complex, tetrahydrofuran-diethyl ether alane, in benzene shows the Al-H absorption at the lower (pentavalent) frequency as expected. The remainder of our experimental work also supports the conclusions reached by Dautel and Zeil.

It seemed strange that alane solutions containing a considerable excess of diethyl ether did not show the shift in the Al-H absorption, whereas monotetrahydrofuran alane in benzene did give a shift on addition of just one equivalent of diethyl ether. It was also of interest that Dautel and Zeil reported a shift when monotrimethylamine alane was dissolved in tetrahydrofuran. Confirming this, we have found that monotrimethylamine alane in tetrahydrofuran shows its strongest Al-H absorptions at 1710 and 1695 cm.<sup>-1</sup> with a shoulder at 1770 cm.<sup>-1</sup> (the tetravalent frequency); in diethyl ether, however, it shows two Al-H absorptions, with the stronger one at the frequency associated with the tetravalent alane (1770 cm.<sup>-1</sup>).

We feel that these results can best be explained on the basis of steric considerations similar to those advanced by Brown<sup>6</sup> for the difference in stability of the trimethylboron complexes with triethylamine and quinuclidine. Diethyl ether has greater steric requirements than tetrahydrofuran, which results in greater F-strain in diethyl ether-alane complexes. This effect is especially apparent in the relative tendencies for formation of bis-complexes. Thus, bis-(diethyl ether) alane apparently does not form at all due to these steric factors, and similarly only a small amount of the mixed diethyl ether-trimethylamine alane is formed in benzene solution. On the other hand, the 1:1:1 diethyl ether-tetrahydrofuran-alane does form readily. If Dautel and Zeil's explanation for the position of the principal Al-H absorption bands is correct, our results support the explanation based on steric considerations. The observed molecular weight data also support this explanation. For example, when diethyl ether is added to monotetrahydrofuran alane in benzene, in addition to the shift of the Al-H absorption to the lower frequency, the molecular weight increases to

(2) W. Zeil, R. Dautel, and W. Honsberg, *Z. Elektrochem.*, **60**, 1131 (1956).

(3) E. G. Hoffmann and G. Schomburg, *ibid.*, **61**, 1101 (1957).

(4) G. Schomburg and E. G. Hoffmann, *ibid.*, **61**, 1110 (1957).

(5) R. Dautel and W. Zeil, *ibid.*, **64**, 1234 (1960).

(6) H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

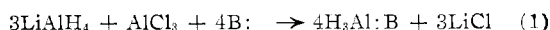
that of the mixed bis-adduct. On the other hand, when excess diethyl ether is added to a solution of mono-(diethyl ether) alane in benzene, the molecular weight only increases to 126, *vs.* a theoretical value of 178 for a bis-ether complex. This indicates that a second molecule of ether does not actually coordinate with the  $\text{AlH}_3$ . It also is interesting to note that in benzene monotetrahydrofuran alane shows a greater degree of association than diethyl ether alane, again indicating that the steric requirements of diethyl ether are greater than those of tetrahydrofuran and molecular association of diethyl ether alane is thereby inhibited.

The behavior of monotrimethylamine alane in ether and tetrahydrofuran also is best explained by these steric considerations. As previously noted, the spectrum of monotrimethylamine alane in diethyl ether shows two Al-H absorptions, with the stronger being at the higher frequency, indicating that a mixture of tetra- and pentacoordinate complexes has been formed in which the former is the major component. Trimethylamine alane in tetrahydrofuran, however, shows the Al-H absorption at the lower frequency, suggesting a small steric interference between tetrahydrofuran and trimethylamine.

These results show that the Lewis bases studied fall in the following order in their tendency to form bis-complexes with alane: tetrahydrofuran > trimethylamine > diethyl ether. This order is the reverse of that given by the steric requirements of these bases, using the degree of association of monotetrahydrofuran alane, monotrimethylamine alane, and diethyl ether alane in benzene (1.55, 1.42, and 1.21, respectively) as a criterion of the steric requirements. The order does not correspond to the expected order of basicity of the Lewis bases toward alane, *i.e.*, trimethylamine > tetrahydrofuran > diethyl ether. That tetrahydrofuran is actually a weaker base toward alane than trimethylamine is demonstrated by the fact that trimethylamine is not displaced from its 1:1 complex when the latter is dissolved in tetrahydrofuran. Data which would unequivocally relate the basicities of diethyl ether and tetrahydrofuran toward alane are presently incomplete, although the preponderant evidence shows that tetrahydrofuran is the stronger base. Molecular weight data could provide additional proof of the strength of a particular base which is used as the solvent. Thus, if a Lewis base (B) is displaced from its alane complex when it is dissolved in a second Lewis base (B'), the apparent molecular weight of the complex will approach one-half of the formula weight of the original alane-Lewis base complex.

#### Experimental

**Alane-Lewis Base Complexes.**—The alane complexes with the various Lewis bases were prepared in the appropriate solvent by the basic method of Finholt, *et al.*<sup>7</sup> (eq. 1). The lithium chlo-



(7) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).

ride was removed by filtration and the alane-Lewis base ratios were determined by quantitative hydrolyses and standard wet chemical analyses on the residues. Molecular weights were determined cryoscopically in benzene and ebullioscopically in the ethers. Infrared spectra were determined as differentials in solution using a Perkin-Elmer Model 21 infrared spectrophotometer with sodium chloride optics. In the case of diethyl ether alane in diethyl ether the infrared spectrum had to be determined immediately upon filtration, since the insoluble  $(\text{AlH}_3)_2 \cdot (\text{C}_2\text{H}_5)_2\text{O}$  generally started to precipitate within 20 min. after removal of the lithium chloride.

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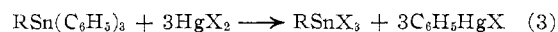
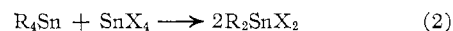
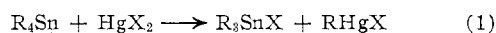
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### Cyclopropyltin Halides and Related Compounds

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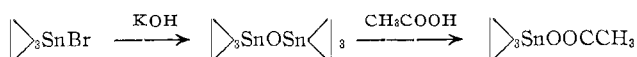
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Recently we have reported the synthesis of a number of cyclopropyltin compounds by the Grignard procedure.<sup>2</sup> Using these compounds as starting materials, we have prepared mono-, di-, and tricyclopropyltin chlorides and bromides by the reactions listed below (R = cyclopropyl, X = Cl and Br)



Reaction 1 appears to be a good route to cyclopropylmercuric chloride and bromide as well as to tricyclopropyltin halides. Reaction 3 suggests that the phenyl group is cleaved from tin much more readily than is the cyclopropyl group. This observation is of some interest when compared with the finding that hydrogen chloride in dimethyl sulfoxide solution cleaves a cyclopropyl group from dicyclopropylmercury at a rate ten times greater than the cleavage of a phenyl group from diphenylmercury.<sup>3</sup> In connection with reaction 2, which was carried out at *ca.* 220°, it was desirable to establish the thermal stability of tetracyclopropyltin. It was found that this compound was stable for at least 2 hr. at 230° in a nitrogen atmosphere.

Tricyclopropyltin iodide, dicyclopropyltin diiodide, tricyclopropyltin fluoride, and dicyclopropyltin dithiocyanate were prepared by standard methathetical reactions. Tricyclopropyltin acetate resulted from the sequence



(1) (a) Alfred P. Sloan Research Fellow; (b) Allied Chemical Corporation Fellow, 1960-1961.

(2) D. Seyferth and H. M. Cohen, *Inorg. Chem.*, **1**, 913 (1962).

(3) R. E. Dessy, G. F. Reynolds, and J.-Y. Kim, *J. Am. Chem. Soc.*, **81**, 2683 (1959).