tions required by the stoichiometries of reactions 1 and 4

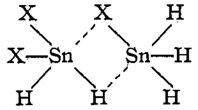
$$n_{\mathrm{HCl}} + n_{\mathrm{H_2}} = n_{\mathrm{SnCl_2}}$$
$$2n_{\mathrm{HCl}} + n_{\mathrm{H_2}} = n_{\mathrm{SnH_4}}$$

The symbol n represents the number of moles of each product.

The formation of hydrogen chloride suggests the intermediate formation of trichlorostannane (which would be expected to be unstable toward decomposition into tin(II) chloride and hydrogen chloride).[22] Trichlorostannane could reasonably form by a ligand-interchange reaction between chlorostannane and dichlorostannane. Thus we suggest that, in the case of SnH_3Cl, the following steps should be added to the general mechanism (reactions 2 and 3) given above

$$SnH_3Cl + SnH_2Cl_2 \longrightarrow SnHCl_3 + SnH_4 \quad (5)$$
$$SnHCl_3 \longrightarrow SnCl_2 + HCl \quad (6)$$

A plausible activated complex for reaction 5 is



(X = Cl, Br, I). As the halogen atoms, X, become both smaller and more electronegative, the coordination of five ligands around each of the tin atoms should be favored both for steric reasons and because of the development of a more positive charge on the tin atoms. The fact that hydrogen halide was formed only in the case of chlorostannane suggests that only in that case was reaction 5 fast enough to compete effectively with reaction 3.

Acknowledgment.—This work was supported by the U. S. Atomic Energy Commission. We wish to thank Professor Herbert Strauss and Dr. Soe Aung for their help with the Raman spectroscopy.

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[22] Trichlorogermane is reported to decompose to germanium(II) chloride and hydrogen chloride at temperatures as low as −30°: C. W. Moulton and J. G. Miller, *J. Amer. Chem. Soc.*, **78**, 2702 (1956).

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The Thermal Decomposition of Methyldisilane and 1,2-Dimethyldisilane

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The gas-phase pyrolyses of $CH_3Si_2H_5$ and 1,2-$(CH_3)_2Si_2H_4$ have been examined neat and in the presence of excess $C_2H_5SiD_3$. The results of these experiments demonstrate that 1,2-$(CH_3)_2Si_2H_4$ decomposes solely into CH_3SiH and CH_3SiH_3 while $CH_3Si_2H_5$ decomposes into CH_3SiH, SiH_2, CH_3SiH_3, and SiH_4. The results from the observed $[SiH_4]/[CH_3SiH_3]$ are discussed. Both methyldisilanes were found to decompose at a rate which is similar to that of disilane and much greater than that of hexamethyldisilane. This result can be attributed to the different modes of decompositions found between hexamethyldisilane and the other disilanes.

Introduction

Results from the flow pyrolysis of disilane led to the suggestion that disilane decomposed into SiH_4 and SiH_2 followed by the insertion of SiH_2 into Si_2H_6[1] (eq 1 and 2). This mechanism was verified independently by the

$$Si_2H_6 \longrightarrow SiH_4 + SiH_2 \quad (1)$$
$$SiH_2 + Si_2H_6 \longrightarrow Si_3H_8 \quad (2)$$

trapping of SiD_2 (from Si_2D_6) into CH_3SiH_3[2,3] forming $CH_3SiH_2SiD_2H$. It has been demonstrated that the pyrolysis of $(CH_3)_6Si_2$ occurs *via* the formation of $(CH_3)_3Si$ radicals[4] while the results from the pyrolysis of $(CH_3)_5Si_2H$ are best in accord with initial decomposition into $(CH_3)_3SiH$ and $(CH_3)_2Si$.[5] The thermolyses of methoxymethyldisilanes occur *via* the formation of a silane and a silylene *via* transfer of the methoxy group but not the methyl group.[6] It has been proposed that the activated complex leading to silylene formation contains a hydrogen[2] or a methoxy group[6] bridged between the two silicon atoms. All of the above data suggest that methyl groups do not enter the bridged position.

In this paper, we report our results on the pyrolysis of 1,2-$(CH_3)_2Si_2H_4$ and of $CH_3Si_2H_5$. The goals of this investigation were (1) to demonstrate that methyldisilanes do thermally decompose into a silane and a silylene *via* intramolecular hydrogen atom transfer, (2) to trap the silylene or silylenes formed, (3) to determine the directional effect of the methyl group in the hydrogen-transfer process, and (4) to examine the relative stabilities of the alkyldisilanes and compare these results to those of disilane[1] and the much more stable $(CH_3)_6Si_2$.[4] A correlation between mechanism and relative stability would be expected.

Results

The following results were obtained from experiments in flow systems with low-temperature trapping.

1. Pyrolysis of 1,2-$(CH_3)_2Si_2H_4$.—The thermal decomposition of 1,2-$(CH_3)_2Si_2H_4$ was examined at 400°, the products were methylsilane, a small quantity of hydrogen, and 1,2,3-$(CH_3)_3Si_3H_5$. The mass and nmr spectra of this compound demonstrated that it was a trimethyltrisilane and most likely 1,2,3-$(CH_3)_3Si_3H_5$.

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[1] E. M. Tebben and M. A. Ring, *Inorg. Chem.*, **8**, 1787 (1969).

[2] P. Estacio, M. D. Sefcik, E. K. Chan, and M. A. Ring, *ibid.*, **9**, 1068 (1970).

[3] M. Bowrey and J. H. Purnell, *J. Amer. Chem. Soc.*, **92**, 2594 (1970).

[4] I. M. T. Davidson and I. L. Stephenson, *J. Chem. Soc. A*, 282 (1968).

[5] H. Sakurai, A. Hosemi, and M. Kumada, *Chem. Commun.*, 4 (1969).

[6] W. H. Atwell and D. R. Weyenberg, *J. Amer. Chem. Soc.*, **90**, 3438 (1968).

This product was obtained from the insertion of CH_3SiH into 1,2-$(CH_3)_2Si_2H_4$

$$CH_3SiH_2SiH_2CH_3 \longrightarrow CH_3SiH + CH_3SiH_3 \quad (3)$$

$$CH_3SiH + CH_3SiH_2SiH_2CH_3 \longrightarrow 1,2,3\text{-}(CH_3)_3Si_3H_5 \quad (4)$$

In the Discussion we show that 1,2-$(CH_3)_2Si_2H_4$ decomposes *via* route 3 and it has been demonstrated that SiH_2 inserts into silicon–hydrogen bonds and not into silicon–carbon bonds.[2] The possibility of insertion into silicon–silicon bonds does exist, but in this case, the same product would be formed.

When 1,2-$(CH_3)_2Si_2H_4$ was pyrolyzed in the presence of a 20:1 excess of $C_2H_5SiD_3$ at 380°, the products were methylsilane (which contained no silicon–deuterium bonds) and $C_2H_5SiD_2SiD(H)(CH_3)$. The mass and nmr spectra demonstrated that this product was an isomer of $(C_2H_5)(CH_3)Si_2HD_3$. The insertion of CH_3SiH into a silicon–deuterium bond of $C_2H_5SiD_3$ would have produced $C_2H_5SiD_2SiD(H)(CH_3)$.

2. Pyrolysis of $CH_3Si_2H_5$.—The pyrolysis of $CH_3Si_2H_5$ was examined at 342 and 360° where the most volatile products were CH_3SiH_3 and SiH_4 in a ratio of 1.8:1. Small quantities of hydrogen were also obtained. The less volatile products were not isolated but appeared to be $CH_3Si_3H_7$ and $(CH_3)_2Si_3H_6$. An investigation of these products to determine the relative position of insertion by the silylene is under way.

The pyrolysis of $CH_3Si_2H_5$ was also examined in the presence of excess $C_2H_5SiD_3$ at 375°. The ratio of methylsilane to silane was 1.7 and both of these compounds contained no silicon–deuterium bonds. The less volatile products were $C_2H_5SiD_2SiH_2D$ and an isomer of $(C_2H_5)(CH_3)Si_2HD_3$ [probably $C_2H_5SiD_2SiD(H)(CH_3)$] in about a 2:1 ratio.

In a separate control experiment it was demonstrated that $C_2H_5SiH_3$ is stable to pyrolysis under the reaction conditions.

Discussion

The homogeneous gas-phase thermal decomposition of $CH_3Si_2H_5$ and 1,2-$(CH_3)_2Si_2H_4$ could in principle occur *via* several distinct modes: (1) rupture of the silicon–hydrogen or silicon–carbon bonds forming hydrogen atoms or methyl radicals along with disilanyl radicals; (2) cleavage of the silicon–silicon bond forming silyl radicals as in hexamethyldisilane;[4] (3) rearrangement of substituents and rupture of the silicon–silicon bond forming a silylene and a silane as in the pyrolysis of disilane.[2] The fact that essentially no hydrogen or methane was obtained during the pyrolysis of $CH_3Si_2H_5$ or 1,2-$(CH_3)_2Si_2H_4$ eliminates the first of these possibilities.

The main reactions between silyl radicals and silane are[7]

$$SiH_3 + SiH_4 \longrightarrow SiH_4 + SiH_3 \quad (5)$$

$$SiH_3 + SiH_4 \longrightarrow Si_2H_6 + H \quad (6)$$

If the pyrolysis of 1,2-$(CH_3)_2Si_2H_4$ proceeded *via* a silyl radical mechanism in the presence of excess $C_2H_5SiD_3$, the following reactions would have occurred

$$CH_3SiH_2SiH_2CH_3 \longrightarrow 2CH_3SiH_2 \quad (7)$$

$$CH_3SiH_2 + C_2H_5SiD_3 \longrightarrow \underline{CH_3SiH_2D} + C_2H_5SiD_2 \quad (8)$$

$$CH_3SiH_2 + C_2H_5SiD_3 \longrightarrow C_2H_5SiD_2SiD(H)(CH_3) + H \quad (9)$$

$$H(D) + C_2H_5SiD_3 \longrightarrow \underline{HD(D_2)} + C_2H_5SiD_2 \quad (10)$$

$$C_2H_5SiD_2 + C_2H_5SiD_3 \longrightarrow \underline{C_2H_5Si_2D_4C_2H_5} + D \quad (11)$$

The previously underlined compounds were not obtained and thus we can eliminate this mechanism. The pyrolysis of $CH_3Si_2H_5$ in the presence of excess $C_2H_5SiD_3$ could be treated as above. It is clear that CH_3SiH_2D, SiH_3D, $C_2H_5Si_2D_4C_2H_5$, and hydrogen $(HD + D_2)$, which were not produced, would have been obtained if $CH_3Si_2H_5$ had decomposed into SiH_3 and CH_3SiH_2 radicals.

The third mechanism, involving the formation of a silylene and a silane, is thus the only one which explains the observed results from the pyrolysis of both methyldisilanes studied.

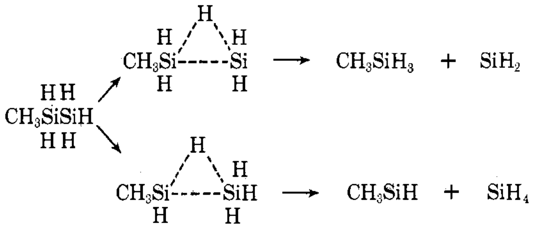
The formation of CH_3SiH from 1,2-$(CH_3)_2Si_2H_4$ and the formation of SiH_2 and CH_3SiH from $CH_3Si_2H_5$ was further confirmed by the isolation of compounds formed by the insertion of these silylenes into $C_2H_5SiD_3$.

The thermal decomposition of 1,2-$(CH_3)_2Si_2H_4$ generated CH_3SiH_3 and no $(CH_3)_2SiH_2$. Thus it appears that 1,2-$(CH_3)_2Si_2H_4$ decomposes solely into CH_3SiH and CH_3SiH_3 (eq 12) and that the silicon–carbon bond

$$CH_3SiH_2SiH_2CH_3 \longrightarrow CH_3SiH + CH_3SiH_3 \quad (12)$$

is inert during the pyrolysis. When these results are coupled with those from the pyrolysis of $(CH_3)_5Si_2H$[5] and the methoxymethyldisilanes,[6] it does appear that one can expect all methyldisilanes $[(CH_3)_{6-x}Si_2H_x, x = 1–6]$ and probably all such alkylpolysilanes to decompose thermally into a silylene and a silane *via* intramolecular hydrogen atom transfer at least in the gas phase. This same conclusion has very recently been made by Davidson[8] based on essentially thermodynamic arguments and the observed fact that silylenes do not insert into silicon–carbon bonds.

If we assume that $CH_3Si_2H_5$ decomposed by a hydrogen atom and not by a methyl group shift; we have, on statistical grounds, that [rate of (13)]/[rate of (14)] should be 1.5. If the initiation were due to a hydride attack on the opposite silicon followed by silicon–silicon bond fission, the ratio would be less than 1.5 since the hydrogen α to the methyl group would be the most hydridic and the β silicon the most positive.[9–13] The experimental value between 1.7 and 1.8 indicates that this mode is not the prime rate-controlling step. In a concerted mechanism, the more positive β silicon would at-



(13)

(14)

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(7) M. A. Ring, M. J. Puentes, and H. E. O'Neal, *J. Amer. Chem. Soc.*, **92**, 4845 (1970).

(8) I. M. T. Davidson, *J. Organometal. Chem.*, **24**, 97 (1970).

(9) An examination of Si–H electric moments has led to the suggestion that methyl groups release electrons to silicon when compared to hydrogen.[10] This suggestion is in agreement with the observation that the introduction of methyl groups in place of hydrogen[11] or chlorine[12] bound to silicon weakens the acidic acceptor power of the silicon atom. Since this decrease appears to prevail in going from hexachlorodisilane to methylpentachlorodisilane and on to more highly methylated chlorodisilanes,[13] the change in acceptor power is probably primarily inductive and not steric.

(10) V. N. Krishnamurthy and S. Soundararajan, *J. Inorg. Nucl. Chem.*, **27**, 2341 (1965).

(11) H. J. Campbell-Ferguson and E. A. V. Ebsworth, *J. Chem. Soc. A*, 1508 (1966).

(12) I. R. Beattie and G. J. Leigh, *J. Inorg. Nucl. Chem.*, **23**, 55 (1961).

(13) R. F. Trandell, reported by G. Urry, *Accounts Chem. Res.*, **3**, 306 (1970).

tract both the hydrogen being transferred and also the electrons released by the silicon–silicon bond rupture more than the α silicon. The former favors generation of CH_3SiH and SiH_4 while the latter promotes formation of SiH_2 and CH_3SiH_3. Apparently the energy difference between the two opposing factors is small since the experimental ratio is nearly statistical.

The thermal stability of both $CH_3Si_2H_5$ and 1,2-$(CH_3)_2Si_2H_4$ was found very similar to that of disilane[2] but much less than the thermal stability of $(CH_3)_6Si_2$.[4] This observation can be correlated with the fact that the former three compounds contain silicon–hydrogen bonds which take part in a hydrogen shift mechanism forming a silylene and a silane. This route has a lower activation energy than that of pure silicon–silicon bond rupture.[2] In $(CH_3)_6Si_2$, where the methyl group does not undergo a simple shift, the decomposition involves the rupture of the silicon–silicon bond.[4]

Experimental Section

All pyrolysis experiments were carried out in a flow system containing an automatic Toepler pump and a cold "U" trap which set the pressure of the reactants and trapped the less volatile products. the pyrolysis tube was 9-mm o.d. Vycor tubing which was coated on the inside by a silicon mirror[14] to ensure homogeneous decompositions.[1,14] the tube was heated by a heating tape in a 10-cm zone and well insulated with asbestos. Temperatures were measured by a thermometer inserted in a well between the heating tape and the heated zone. All separations were made by repeated trap to trap distillations at low temperatures in a high-vacuum system. Proton nmr spectra were obtained on neat samples with TMS at δ 0.00 as an external standard.

The products silane and methylsilane were identified as follows: (1) silane: the infrared spectrum was identical with that of silane[15] and the mass spectrum was formed only by heavy ions of the type SiH_x^+; (2) methylsilane: the infrared spectrum was identical with that of methylsilane[16] and the very strong 910-cm^{-1} band from silane was absent. The mass spectrum was formed only by heavy ions of the type $CSiH_x^+$, SiH_x^+, and CH_x^+.

1. Thermal Reactions of 1,2-$(CH_3)_2Si_2H_4$.—The 1,2-$(CH_3)_2Si_2H_4$ was prepared by the pyrolysis of CH_3SiH_3[17] (purity verified as described above). The purity of the 1,2-$(CH_3)_2Si_2H_4$ was verified as follows: (1) the infrared spectrum was identical with that of 1,2-$(CH_3)_2SiH_4$;[18] (2) the mass spectrum was formed only of ions expected from 1,2-$(CH_3)_2Si_2H_4$; (3) the vapor pressure was <1 mm at −78° (no lighter molecules present) and 105 mm at 0° (lit.[18] 107 mm); (4) the proton nmr spectrum demonstrated that 1,1-$(CH_3)_2Si_2H_4$[19] and $CH_3Si_2H_5$[20] were absent.

A. Pyrolysis of 1,2-$(CH_3)_2Si_2H_4$.—In a typical experiment, 0.45 mmol of 1,2-$(CH_3)_2Si_2H_4$ was pyrolyzed in our flow system at 400° for 6 hr with the cold trap set at −36°. The product passing a −196° trap was hydrogen (0.04 mmol) while the only product passing a −78° trap was methylsilane (0.24 mmol). The product stopping at −78° was 1,2,3-$(CH_3)_3Si_3H_5$ (about 0.2 mmol). This product was identified as follows: (1) The mass spectrum was formed only by heavy ions of the types (with relative envelope intensities) $C_3Si_3H_x^+$ (11.2), $C_2Si_3H_x^+$ (9.4), $CSi_3H_x^+$ (4.7), $C_2Si_2H_x^+ + Si_3H_x^+$ (100), $CSi_2H_x^+$ (22.7), ($Si_2H_x^+$ (12.0), and $CSiH_x^+$ (33.1). (2) The proton nmr spectrum consisted of a carbon–hydrogen resonance at δ 0.28 and a silicon–hydrogen resonance at δ 3.62 with relative integrated intensities of 1.9:1 (calcd 1.8). The carbon–hydrogen resonance consisted of a strong triplet centered at δ 0.28 (J = 4.3 Hz; this value is 4.2 Hz in $CH_3Si_2H_5$[20]) and a weak doublet centered at δ 0.30 (J = 4.2 Hz). The silicon–hydrogen resonance consisted of a complex multiplet with a half-width of only 0.22 ppm. In 1,2-$(CH_3)_2Si_2H_4$ we observed a half-width of 0.24 ppm in the silicon–hydrogen resonance. In 1,1-$(CH_3)_2Si_2H_4$[19] and $CH_3Si_2H_5$[20] the different silicon–hydrogen resonances are centered 0.38 and 0.50 ppm apart, respectively. Therefore it seems unlikely that the silicon–hydrogen resonances in the $(CH_3)_3Si_3H_5$ isomers other than the 1,2,3 isomer would have a half-width of less than 0.5 ppm. Thus the nmr spectrum is only consistent with the 1,2,3-trimethyl isomer.

The gas-phase infrared spectrum consisted of the following bands in cm^{-1}: 2980 (m), 2920 (w), 2145 (vs), 1665 (w), 1550 (w), 1445 (w), 1255 (m), 933 (s), 866 (vs), 791 (s), 714 (m), 688 (m), 660 (m), 580 (w). The very strong 844-cm^{-1} band of 1,2-$(CH_3)_2Si_2H_4$[18] was absent.

B. Pyrolysis of 1,2-$(CH_3)_2Si_2H_4$ in the Presence of Excess $C_2H_5SiD_3$.—The $C_2H_5SiD_3$ was prepared by the $LiAlD_4$ reduction of $C_2H_5SiCl_3$. The purity was demonstrated by a mass spectrum which was consistent for $C_2H_5SiD_3$ and an infrared spectrum which had only a very weak band at 2150 cm^{-1} (due to impurities from the $LiAlH_4$ impurity in $LiAlD_4$) and no absorptions at 681 cm^{-1} (no SiD_4),[15] at 802 cm^{-1} (no $(C_2H_5)_2SiD_2$), or at 790 cm^{-1} (no CH_3SiD_3). The CH_3SiD_3 and $(C_2H_5)_2SiD_2$ were obtained by reduction of CH_3SiCl_3 and $(C_2H_5)_2SiCl_2$. The spectrum of $C_2H_5SiD_3$ was similar to that of $C_2H_5SiH_3$[16] with the 2150-cm^{-1} band shifted to 1575 cm^{-1} (Si–H to Si–D) and the 938-cm^{-1} band shifted to 722 cm^{-1} (SiH_3 to SiD_3). In a typical experiment, a mixture containing 0.46 mmol of 1,2-$(CH_3)_2Si_2H_4$ and 1.93 mmol of $C_2H_5SiD_3$ was pyrolyzed for 19 hr at 380° with the cold trap set at −45°. The relative pressures in the reaction zone were about 20:1 in favor of $C_2H_5SiD_3$. Hydrogen (0.013 mmol) was obtained and Toepler pumped into a known volume. The condensate in the −196° trap was CH_3SiH_3 (0.12 mmol). The infrared spectrum contained no bands near 1600 cm^{-1} thus demonstrating that silicon–deuterium bonds were absent from this compound. The final condensate in the −145° trap was $C_2H_5SiD_3$ (1.66 mmol). Another small fraction contained some CH_3SiH_3 but was mostly $C_2H_5SiD_3$. The condensate in the −112° trap was 1,2-$(CH_3)_2Si_2H_4$ (0.27 mmol) while the condensate in the −95° trap was $C_2H_5SiD_2SiD(H)(CH_3)$ (0.12 mmol). This compound was identified as follows: (1) The mass spectrum was formed from heavy ions of the types (with relative envelope intensities) $C_3Si_2D_xH_y^+$ (40.7), $C_2Si_2D_xH_y^+$ (16.5), $CSi_2D_xH_y^+$ (100), $Si_2D_xH_y + C_2SiD_xH_y^+$ (90), and $CSiD_xH_y^+$ (40.2). The parent peak *m/e* 107 was large (relative intensities at *m/e* 109, 108, 107, 106, 105, 104: 10, 28, 100, 23, 18, 27). (2) The proton nmr spectrum contained four resonances at δ 3.55, 0.48, 0.27, and 0.08 ppm. The relative intensity of the C–H to Si–H resonances was 7.5:1 (calcd 8:1). (3) The infrared spectrum contained a stronger silicon–deuterium stretching band than a silicon–hydrogen stretching band and the strong 938-cm^{-1} absorption of 1,2-$(CH_3)_2Si_2H_4$ was absent.

C. The Pyrolysis of 1,2-$(CH_3)_2Si_2H_4$ in the Presence of Excess $C_2H_5SiH_3$.—In a procedure similar to 1B, 1,2-ethylmethyldisilane was obtained. The mass spectrum had a strong parent peak, *m/e* 104. The nmr spectrum had the expected CH_3 triplet at δ 0.78 ppm and the silicon–hydrogen resonance at δ 3.40 ppm.

D. Control Experiment.—In a control experiment it was demonstrated that $C_2H_5SiH_3$ is stable at 440° under the above conditions.

2. Thermal Reactions of $CH_3Si_2H_5$.—The $CH_3Si_2H_5$ was obtained from the flow pyrolysis of Si_2H_6 in the presence of excess CH_3SiH_3.[2] The purity was verified by an infrared spectrum, a mass spectrum, and a vapor pressure of 16 mm at −57° (lit.[20] 17 mm).

A. Pyrolysis of $CH_3Si_2H_5$ in the Presence of Excess $C_2H_5SiD_3$.—In a typical experiment 0.49 mmol of $CH_3Si_2H_5$ and 1.64 mmol of $C_2H_5SiD_3$ were pyrolyzed for 14.5 hr at 375° with the cold trap set at −57°. Only a very small amount of hydrogen was produced. The condensate in the −196° trap was SiH_4 (0.07 mmol) which had an infrared spectrum demonstrating that no deuteriosilanes were present. The condensate in the −145° trap was CH_3SiH_3 (0.12 mmol) with no deuterated methylsilanes present. The condensate in the −123° trap was 1.31 mmol of $C_2H_5SiD_3$. The condensate in the −119° trap (0.02 mmol) was a mixture of $C_2H_5SiD_3$ and $CH_3Si_2H_5$ while the condensate in the −112° trap was 0.21 mmol of $CH_3Si_2H_5$. The condensate in the −95° trap (0.06 mmol) was a mixture of $CH_3Si_2H_5$ and $C_2H_5SiD_2SiH_2D$. The condensate in the −83° trap was $C_2H_5SiD_2$-

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[14] J. H. Purnell and R. Walsh, *Proc. Roy. Soc., Ser. A*, **293**, 543 (1966).

[15] J. H. Meal and M. K. Wilson, *J. Chem. Phys.*, **24**, 385 (1956).

[16] S. Kaye and S. Tannenbaum, *J. Org. Chem.*, **18**, 1750 (1953).

[17] J. J. Kohanek, P. Estacio, and M. A. Ring, *Inorg. Chem.*, **8**, 2516 (1969).

[18] A. D. Craig and A. C. MacDiarmid, *J. Inorg. Nucl. Chem.*, **24**, 161 (1962).

[19] E. A. Groschwitz, W. M. Ingle, and M. A. Ring, *J. Organometal. Chem.*, **9**, 421 (1967).

[20] M. Abedini and A. G. MacDiarmid, *Inorg. Chem.*, **11**, 2040 (1966).

SiH_2D (0.1 mmol) while the condensate in the −78° trap was mostly $C_2H_5SiD_2SiD(H)(CH_3)$ (0.05 mmol).

The compound $C_2H_5SiD_2SiH_2D$ was identified by a mass spectrum formed only from heavy ions of the types (with relative envelope intensities) $C_2Si_2D_xH_y^+$ (29.4), $CSi_2D_xH_y^+$ (10.5), and $Si_2D_xH_y^+ + C_2SiD_xH_y^+$ (100). The parent peak *m/e* 93 was large and contained 31.6% of the intensity of the C_2Si_2 envelope. The peak at *m/e* 33 ($HSiD_2^+$) was small compared to the peak at *m/e* 32 $(H_2SiD)^+$ which is expected for $C_2H_5SiD_2SiH_2D$ but not for $C_2H_5SiH(D)SiHD_2$.

The condensate in the −78° trap had a mass spectrum that was very similar to that of the $C_2H_5SiD_2SiD(H)(CH_3)$ formed in experiment 1B at high masses (*m/e* 108–83) while the mass spectrum had slightly more intense peaks at lower masses suggesting the presence of small quantities of methyldisilane.

B. Pyrolysis of $CH_3Si_2H_5$.—The pyrolysis of $CH_3Si_2H_5$ was carried out in our flow system at 342 and 360° with the cold trap set at −45°. The ratio of $CH_3SiH_3:SiH_4$ produced was 1.8 at both temperatures. The less volatile products were not isolated in a pure state but the mass spectrum of our samples suggested they were mixtures of $CH_3Si_3H_7$ and $(CH_3)_2Si_3H_6$.

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The Raman Spectra of Molten Aluminum Trihalide–Alkali Halide Systems[1a]

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Raman spectra are presented for $AlBr_3$–NaBr and AlI_3–CsI melts in the region from 50:50 mol % to pure aluminum halide. These data are compared with previously published data for the $AlCl_3$–NaCl system. Raman frequencies are assigned for the $AlBr_4^-$, $Al_2Br_7^-$, AlI_4^-, and $Al_2I_7^-$ ions. Valence force constants have been calculated for the series of tetrahedral ions: $AlCl_4^-$, $AlBr_4^-$, AlI_4^-.

In a previous paper[2] we presented a study of the Raman spectra of molten mixtures of $AlCl_3$–NaCl in the concentration region from 50:50 mol % to pure $AlCl_3$. This paper reports a similar study of the systems $AlBr_3$–NaBr and AlI_3–CsI. Comparisons are made between the different halide systems and evidence for the ionic species present is examined.

Experimental Section

Aluminum bromide was prepared by the reaction of high-purity, zone-refined aluminum metal (99.9999%, Cominco Products, Inc.) with purified HBr in a manner previously described[3] for $AlCl_3$. Aluminum iodide was synthesized in a similar preparation by treating aluminum metal with iodine (99.99%, Alfa Inorganics, Inc.). Sodium bromide and CsI were purified by the high-temperature filtration and sparging method described[4] for LiCl–KCl eutectic preparation, except that for these higher melting compounds, the apparatus was constructed of quartz instead of borosilicate glass, and in the case of CsI the filtered material was sublimed under vacuum before use.

After preparation, all handling operations were conducted in a nitrogen-filled drybox with the H_2O content below 10 ppm. The mixtures were placed in quartz tubes (∼4-mm o.d.), evacuated to $\sim 10^{-3}$ Torr and sealed with a torch. The quartz tube containing the salt was mounted in the Raman spectrophotometer and the sample was melted by passing current through a platinum wire wrapped around the tube. The sample temperatures were in the range 200–260°.

In most cases a Spectra-Physics Model 141 argon ion laser was used to excite the Raman spectra. Observations were made with the 4880- and 5145-Å laser lines. In the case of the AlI_3–CsI 50:50 mol % sample, a Spectra-Physics Model-125 helium–neon laser emitting light at 6328 Å was used to excite the spectrum, since the melt was somewhat yellow. Power levels at the sample were approximately 100 mW for the 4880- and 5145-Å lines and 25 mW for the 6328-Å line. A Cary Model 81 monochromator, coupled with a cooled 9558 EMI photomultiplier tube and a photon counting system, was used to record the Raman spectra. Several confirmatory Raman spectra were also run on a Jarrell-Ash Model 25-300, Raman spectrophotometer using the 4880-Å argon ion laser line for excitation.

The samples were illuminated with the laser beam focused at right angles to the long axis of the sample tubes and at the center of the sample volume. Raman light was collected at right angles to the laser beam by a 75-mm, *f*/1.9 collimating lens and was focused on the spectrometer entrance slit by means of a 335-mm, *f*/6.5 lens. Qualitative polarization measurements were made by rotating the plane of polarization of the laser beam with a half-wave plate. Appropriate spike filters were employed in the laser beam to eliminate the background laser lines from the Raman spectra.

Results

Figure 1 shows the Raman spectra of several mixtures of molten $AlBr_3$–NaBr in the concentration region from 50:50 to 100:0 mol %. In the case of the $AlBr_3$–NaBr mixture, the NaBr-saturated melt which has a composition[5] very close to 50:50 mol % was used for the equimolar sample. The data are recorded in Table I. The Raman spectra for three concentrations of the AlI_3–CsI system are shown in Figure 2, and the data for these melts are given in Table II. We observed the AlI_3–CsI system rather than the AlI_3–NaI system because samples of the former materials were already available. In addition, for the cesium-containing system, it was possible to prepare the solid compound $CsAl_2I_7$ in crystalline form, indicating a greater stability for the $Al_2I_7^-$

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[2] G. Torsi, G. Mamantov, and G. M. Begun, *Inorg. Nucl. Chem. Lett.*, **6**, 553 (1970).

[3] N. J. Bjerrum, C. R. Boston, and G. P. Smith, *Inorg. Chem.*, **6**, 1162 (1967).

[4] C. R. Boston and G. P. Smith, *J. Phys. Chem.*, **62**, 409 (1958).

[5] J. Kendall, E. D. Crittenden, and H. K. Miller, *J. Amer. Chem. Soc.*, **45**, 963 (1923).