simple isomerization, one can look for an analogy in the well known fluoroolefin dimerizations to cyclobutane derivatives, whereas the corresponding hydrocarbons do not dimerize. Principally one would cite the dimerizations of tetrafluoroethylene,[11] of chlorotrifluoroethylene,[12] and of hexafluoropropene.[13] Similarly, the saturation of C_2F_4[14] vs. C_2H_4[15] exhibits such an effect. Such stabilizations have been noted in the discussions of Patrick[14] and Peters.[16] Interestingly though, 3,3,4,4-tetrafluorocyclobutene was observed at 700° to react quantitatively to 1,1,4,4-tetrafluorobutadiene.[17] This may, of course, be the result of a small heat of reaction. Many explanations could be constructed for this effect. It is clear that what must be involved is either (a) an unusually large change in the carbon bonding in going from a C=C bond to a C—C bond in a fluorocarbon system (as compared to a hydrocarbon system) or (b) an unusually large difference in the stability of the C—F bonds being attached to an ethylenic rather than to a saturated carbon, or perhaps both. The first effect might be due to a change in the π-electron energy of the C=C bonds, or a difference in the new C—C bonds formed. The second effect could be due to a change in hybridization or charge on the carbon atom at which bonding occurs.[18]

Peters[16] argues that the ethylenes are essentially similar in their C=C strengths, whereas the fluorine acts on the sp³ electrons at the saturated carbons to lead to further stabilization for a fluorocarbon as against the hydrocarbon. Hence Peters assumes that the fluorine effect is entirely due to (b) above. One could also argue that fluorination leads to a change in bond order and hence an effect due to (a).

If this effect is due to a decreased stability of the double bond upon fluorine substitution (a), one might

(11) (a) B. Atkinson and A. B. Trenwith, *J. Chem. Soc.*, 2082 (1953); (b) B. F. Gray and H. O. Pritchard, *ibid.*, 1002 (1956); (c) B. Atkinson and V. A. Atkinson, *ibid.*, 2086 (1957); (d) J. N. Butler, *J. Am. Chem. Soc.*, **84**, 1393 (1962).

(12) B. Atkinson and M. Stedman, *J. Chem. Soc.*, 512 (1962).

(13) H. C. Brown, *J. Org. Chem.*, **22**, 1256 (1957).

(14) C. R. Patrick, "Advances in Fluorine Chemistry," Vol. 2, Academic Press, Inc., New York, N. Y., 1961, pp. 21, 22.

(15) (a) C. R. Patrick, ref. 14, p. 22; (b) Natl. Bur. Standards Circ. 461, 1946.

(16) D. Peters, *J. Chem. Phys.*, **38**, 561 (1963).

(17) J. L. Anderson, R. E. Putman, and W. H. Sharkey, *J. Am. Chem. Soc.*, **83**, 382 (1961).

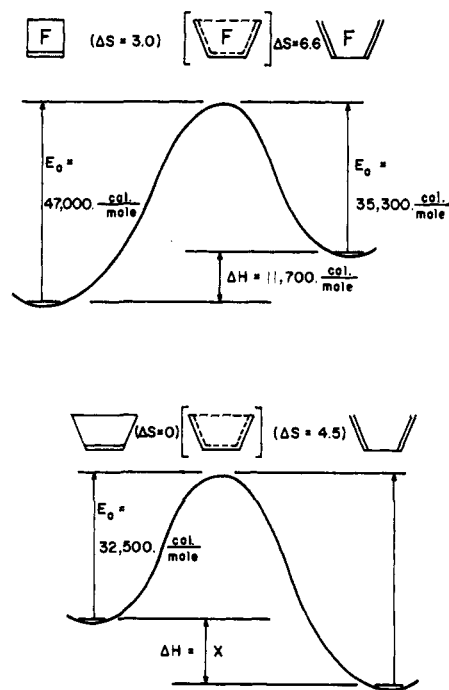(18) V. Gold, *Trans. Faraday Soc.*, **45**, 191 (1949).

Fig. 3.—Reaction diagram.

expect a considerable lowering of the activation energy for *cis–trans* isomerization in fluoroolefins, as compared to regular olefins. As an extreme this could produce as low a value as 40–45 kcal./mole (an investigation of this is underway). A large change in activation energy would then be a strong argument for (a) being important, since in the transition state there is probably very little interaction between the π-orbitals,[18] and hence one could look on this as a measure of a "π-uncoupling" energy. At the present moment one can only conclude that though this effect is quite general, data are not yet varied enough to allow for any unequivocal understanding of its origin.[19] Some quantitative studies of mixed fluorine–hydrogen isomers would obviously be of interest here.

(19) Since submission of this work, J. Hine, *J. Am. Chem. Soc.*, **85**, 3239 (1963), also has come to the conclusion that present data are inadequate to decide the origin of the effect.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF NEW YORK AT STONY BROOK, STONY BROOK, N. Y.]

Vibrational Spectra and Structures of Digermyl Ether and Digermyl Sulfide[1]

BY THEODORE D. GOLDFARB AND SEI SUJISHI

Digermyl sulfide has been found to react with mercuric oxide at low temperatures to give digermyl ether. The volatile ether and sulfide and their deuterated analogs have each been sufficiently purified to permit high resolution infrared investigations of the vapors as well as a Raman investigation of the liquid sulfide. Approximate molecular weight and vapor pressure determinations have also been performed. The spectroscopic evidence in terms of frequency assignments, selection rules, and band envelopes indicates a highly bent skeleton for the ether as well as the sulfide in contrast to the near-linear skeleton of disilyl ether (disiloxane). This result is interpreted in terms of the smaller tendency of germanium to participate in (p → d)π-bonding.

Introduction

The silicon analog of dimethyl ether has been the subject of several experimental investigations and

theoretical speculations focused on the determination of the Si–O–Si bond angle.[2–7] The results of these
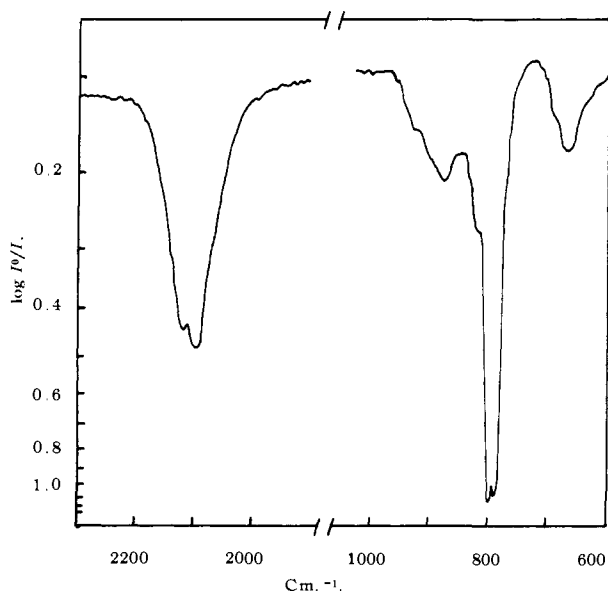
Fig. 1a.—Infrared spectrum of gaseous $(GeH_3)_2O$ at a pressure of 6 mm. and a path length of 10 cm.

Fig. 1b.—Infrared spectrum of gaseous $(GeD_3)_2O$; path length of 10 cm. and pressures of 3 mm. for 700–1650 cm.$^{-1}$ region and 6 mm. for 475–700 cm.$^{-1}$ region.

studies provide considerable evidence for an apex angle of $\sim150°$ in contrast to angles of 111, 105, and $\sim100°$ which have been determined for $(CH_3)_2O$,[8] $(CH_3)_2S$,[9] and $(SiH_3)_2S$,[10] respectively. The near linearity of the disilyl ether (disiloxane) skeleton has been attributed[11] to $(p \rightarrow d)\pi$-bonding which is not possible for the methyl compound and is likely to be of less importance for the sulfide.

The extension of these studies to include digermyl ether and sulfide has been hindered by difficulties encountered in synthesizing and purifying the ether. Its presence in the gas phase equilibrium has been

$$2GeH_3CN + H_2O = (GeH_3)_2O + 2HCN$$
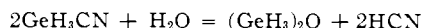
detected,[12] but all attempts at fractionation or other means of physical or chemical separation of that system met with failure. By the techniques described below we have now succeeded in preparing samples of both compounds that are pure enough for vibrational spectroscopic investigation.

Experimental

Preparation of Digermyl Sulfide.—Digermyl sulfide was prepared by the reaction of germyl iodide with mercuric sulfide.[13] The vapor pressure at 0° (5 mm.) agreed with the value observed previously.

Preparation of Digermyl Ether.—Digermyl ether was prepared by the reaction of digermyl sulfide with red mercuric oxide at −40°. Although germyl iodide was found to react with red mercuric oxide at −40° to yield digermyl ether, the higher

(2) R. C. Lord, D. W. Robinson, and W. C. Schumb, J. Am. Chem. Soc., **78**, 1327 (1956).

(3) R. F. Curl and K. S. Pitzer, ibid., **80**, 2371 (1958).

(4) D. C. McKean, Spectrochim. Acta, **13**, 38 (1958).

(5) D. C. McKean, Proc. Chem. Soc., 321 (1959).

(6) J. R. Aronson, R. C. Lord, and D. W. Robinson, J. Chem. Phys., **33**, 1004 (1960).

(7) D. W. Robinson, W. J. Lafferty, J. R. Aronson, J. R. Durig, and R. C. Lord, ibid., **35**, 2245 (1961).

(8) U. Blukis, P. H. Kasai, and R. J. Myers, ibid., **38**, 2753 (1963).

(9) L. O. Brockway and H. O. Jenkins, J. Am. Chem. Soc., **58**, 2036 (1936).

(10) H. R. Linton and E. R. Nixon, J. Chem. Phys., **29**, 921 (1958).

(11) E. A. V. Ebsworth, "Volatile Silicon Compounds," The Macmillan Co., New York, N. Y., 1963, Chapter 6.

(12) S. Sujishi and T. Goldfarb, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961, p. 35N.

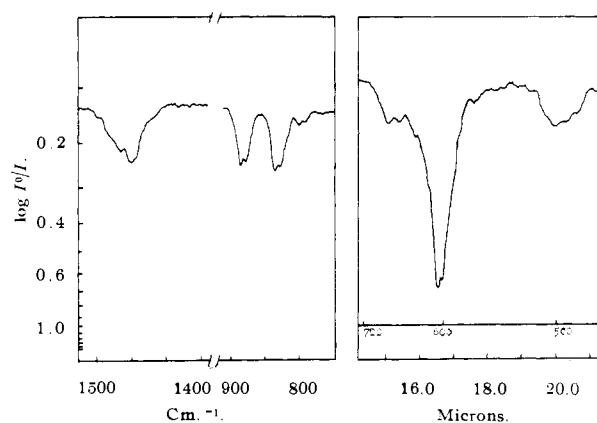(13) S. Sujishi, Abstracts of XVIIth Intern. Congr. of Pure and Appl. Chem., 1959, p. 53.

volatility of the germyl iodide (v.p. 20 mm. at 0°) led to greater difficulty in the separation of the desired product (v.p. 66 mm. at 0°) from the unconsumed germyl iodide.

About 1 mmole of digermyl sulfide was shaken with 32 g. of granular red mercuric oxide (Baker's Analyzed) at −40° for 40 min. (yellow and powdery red mercuric oxide were not satisfactory). The volatile products were distilled at −40° through traps at −78 and −112°. The condensate at −112° was essentially digermyl ether. The condensate at −78° contained digermyl sulfide.

The above procedure was repeated twice more with the −78° condensate and new batches of mercuric oxide, 23 and 21 g., respectively. The final yield of digermyl ether was 0.35 mmole. The molecular weight of the gas at 25° and 35 mm. was 165 ± 1 (calcd. for $(GeH_3)_2O$, 167). The infrared spectrum at 20°K. in a nitrogen matrix showed the presence of a trace of water. The vapor pressure of the liquid at 0° was initially 66 mm., but decreased slowly on standing. After 8 hr. the pressure was 46 mm. The nature of the decomposition, which may be catalyzed by the presence of water, is not clear, but it was established that germane was not formed.

Deuterated digermyl ether and digermyl sulfide were prepared by procedures analogous to those described above for the normal compound by using GeD_3I (98% D) as the starting material.

Spectroscopy.—Survey infrared spectra were recorded with a Perkin–Elmer Model 21 spectrophotometer equipped with NaCl and CsBr interchange units. High resolution spectra were recorded with a Beckman IR-7 with a NaCl prism-grating interchange. Gas cells were 10 cm. long with glass bodies and KBr or CsBr windows sealed on with Apiezon W wax. The matrix isolation technique developed by Pimentel and co-workers[14] was employed for spectroscopic measurements of samples suspended in solid nitrogen at 20°K. Raman measurements were made with a Cary Model 81 spectrophotometer using 2-mm o.d. sample cells.

Results

The absorption features observed in the low resolution vapor phase spectra of $(GeH_3)_2O$, $(GeD_3)_2O$, $(GeH_3)_2S$, and $(GeD_3)_2S$ over the 280–4000 cm.$^{-1}$ region are shown in Fig. 1a, 1b, 2a, and 2b. Since higher resolution spectra failed to reveal the number of contributing bands in the GeH_3 stretching, bending, and rocking regions, the infrared spectra over the 650–4000 cm.$^{-1}$ region of dilute (1:800) solutions of $(GeH_3)_2O$ and of $(GeH_3)_2S$ in solid nitrogen at liquid hydrogen temperature were obtained and are displayed in Fig. 3 and 4.

Table I lists all of the absorption peaks from Fig. 1 and 2 as well as those observed in the matrix spectra of $(GeH_3)_2S$. Samples of the other molecules large enough for Raman investigation have not been made.

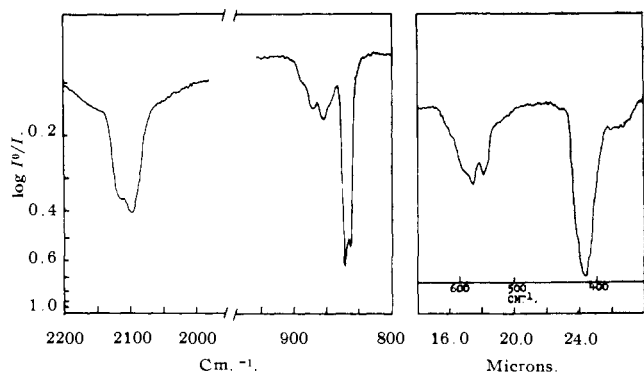(14) E. Whittle, D. A. Dows, and G. C. Pimentel, J. Chem. Phys., **22**, 1943 (1954).

Fig. 2a.—Infrared spectrum of gaseous (GeH₃)₂S; path length of 10 cm. and pressures of 6 mm. for 700–2200 cm.⁻¹ region and 14 mm. for 300–700 cm.⁻¹ region.
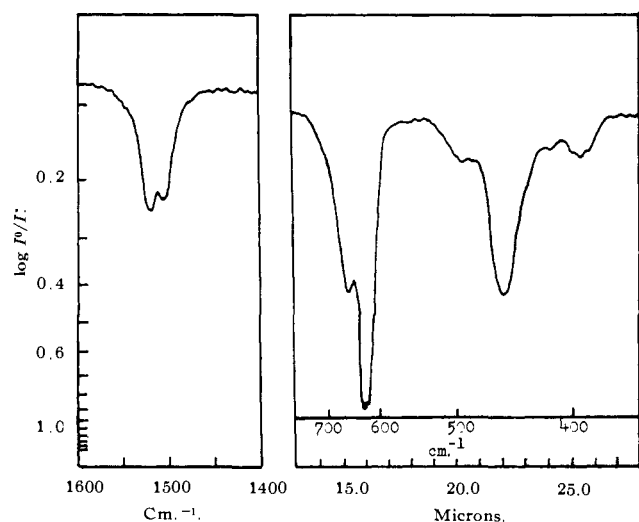

Fig. 2b.—Infrared spectrum of gaseous (GeD₃)₂S; path length 10 cm. and pressures 6 mm. for 1400–1600 cm.⁻¹ region and 13 mm. for 350–750 cm.⁻¹ region.

Fig. 3.—Infrared spectrum of (GeH₃)₂O in a nitrogen matrix at a dilution of 1:800.

Fig. 4.—Infrared spectrum of (GeH₃)₂S in a nitrogen matrix at a dilution of 1:800.

Discussion

The assignments indicated in Table I are based on band contours, deuterium frequency shifts, and results for similar molecules. Assignment of the asymmetric skeletal stretch of gaseous (GeD₃)₂S to a band that is 24 cm.⁻¹ higher than its (GeH₃)₂S counterpart could be due to mechanical interaction of this mode with the rocking frequencies which underlie the skeletal stretching region for the deuterated molecule. A similar but less pronounced isotope effect on the same vibrational mode has been observed for disilyl sulfide.[10]

The number of vibrational modes of each type that will be active in the infrared and Raman spectra of a (GeH₃)₂X molecule is given in Table II for the most probable point groups with linear or bent skeletal configurations. Failure to observe all of the predicted active modes is not good evidence for discarding structure due to the high probability of coincidence or near coincidence of two or more bands particularly in the GeH₃ vibrational regions. On the other hand, the appearance of features forbidden by a particular symmetry can be weighed heavily in arguing against that symmetry.

The skeletal stretching region of digermyl sulfide provides strong evidence against a D₃ₕ or D₃d configuration. There is a second, weak band on the low frequency side of the strong asymmetric skeletal stretching band in the infrared spectra of both the light and heavy molecules. Both bands show up
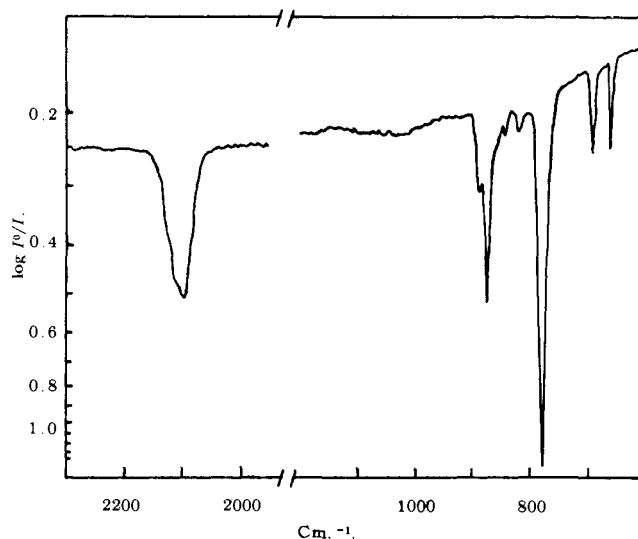
clearly in the Raman spectrum of (GeH₃)₂S with the lower frequency (370 cm.⁻¹) band appearing as a strong polarized Raman line. In the GeH₃ rocking region at least two overlapping bands appear both in the infrared and Raman spectra of (GeH₃)₂S in disagreement with the number of fundamentals permitted by D₃ₕ or D₃d selection rules. Further Raman evidence for a bent structure for (GeH₃)₂S is the appearance of a moderately strong line at 110 cm.⁻¹ clearly assignable to the bending mode which is forbidden by D₃d selection rules and should be very weak in the case of D₃ₕ symmetry. Supporting evidence is found in the infrared spectrum of (GeH₃)₂S in a nitrogen matrix which shows at least four bands in the GeH₃ deformation region whereas only two fundamentals are allowed by either point group for the linear skeletal geometry.

A comparison of the selection rules and infrared spectra of digermyl ether also indicates a Ge–O–Ge angle of less than 180°, although the evidence is less compelling. Unfortunately the symmetric skeletal stretch has not been detected in the (GeH₃)₂O spectrum but should be weak and may be hidden by the GeH deformation or rocking bands. A band appears at

TABLE I

VIBRATIONAL ABSORPTION BANDS OF $(GeH_3)_2O$, $(GeD_3)_2O$, $(GeH_3)_2S$, AND $(GeD_3)_2S$ (CM.$^{-1}$)[a]

Type of vibration	$(GeH_3)_2O$ Infrared (vapor)	$(GeH_3)_2O$ Infrared (matrix)	$(GeD_3)_2O$ Infrared (vapor)	$(GeH_3)_2S$ Infrared (vapor)	$(GeH_3)_2S$ Infrared (matrix)	$(GeH_3)_2S$ Raman (liq.)	$(GeD_3)_2S$ Infrared (vapor)
GeH_3 stretch	2130	2106	1475–1550	2110	2132	2071	1515
	2107‖		1499	2097‖	2107		1499
GeH_3 deform.	926	888	580–660	872	895	865	612
		842		849	869	842	
		(815)[b]			846		
	R798‖	783	R610‖	R823‖	816	800	R594‖
	P789‖		P601‖	P816‖			P587‖
GeH_3 rock	670	689	475–525	577		608	425–500
		657		556		585	
Ge–X–Ge stretch	878‖	872	R884‖	412‖		408	436
			P875‖				
			(829)[c]	382		370	380
Ge–X–Ge bend						110	
Overtones and combinations	1498			2940			
	1400			1505			
	1340			1155			
	1263						
	1058						

[a] The symbol ‖ denotes a parallel-type band envelope. [b] This weak band is probably due to a trace of $(GeH_3)_2S$. [c] This band is probably due to partially deuterated $(GeH_3)_2O$.

TABLE II

NUMBER OF INFRARED- AND RAMAN-ACTIVE VIBRATIONAL MODES FOR SEVERAL POSSIBLE POINT GROUPS OF A $(GeH_3)_2X$ MOLECULE[a]

Type of vibration	Linear skeleton D_{3h}	Linear skeleton D_{3d}	Bent skeleton C_{2v}	Bent skeleton C_{2s} or C_s
GeH_3 stretch	2I 3R	2I 2R	5I 6R	6I 6R
GeH_3 deform.	2I 3R	2I 2R	5I 6R	6I 6R
GeH_3 rock	1I 2R	1I 1R	3I 4R	4I 4R
Ge–X stretch	1I 1R	1I 1R	2I 2R	2I 2R
Ge–X–Ge deform.	1I 1R	1I ..	1I 1R	1I 1R
Torsion	...	...	1I 2R	2I 2R

[a] xI yR indicates x infrared-active and y Raman-active modes.

829 cm.$^{-1}$ in the $(GeD_3)_2O$ spectrum which might be assigned to the symmetric skeletal stretching mode; however, it is most likely due to the GeH_3 symmetric deformation of partially deuterated digermyl ether. The matrix spectrum of $(GeH_3)_2O$ clearly shows two

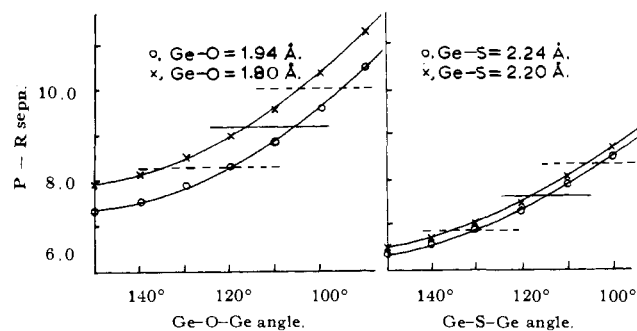Fig. 5.—Calculated P − R maxima separations vs. Ge–X–Ge angle for $(GeH_3)_2O$ and $(GeH_3)_2S$. Solid horizontal lines are the measured P − R separations and dotted lines allow for an error of ±10%.

infrared-active GeH_3 rocking bands. Four bands appear in the matrix spectrum in the GeH_3 deformation region, but two of these are weak shoulders on the skeletal stretching band and the third, at 815 cm.$^{-1}$, is probably an impurity band due to a trace of $(GeH_3)_2S$.

If a simple valence force field is assumed and the GeH_3 groups are treated as rigid units, the three skeletal frequencies can be used to calculate an approximate apex angle. The Raman spectrum of $(GeH_3)_2S$ pro-

vides all three frequencies and the calculation yields a Ge–S–Ge angle of 108°. A similar calculation for the ether is not possible because only one of the three skeletal modes has been observed.

Although no vibration–rotation structure was resolved for either the ether or the sulfide, the infrared spectra of both molecules under high resolution show clearly defined P and R branches for the out-of-phase symmetric GeH_3 deformation modes. It has recently been shown[15] that the formulas of Gerhard and Dennison[16] for calculating separations between P and R branch maxima when applied to symmetric or nearly symmetric top molecules yield results that agree to better than ±10% with experimental measurements on clearly defined parallel bands. Both digermyl ether and sulfide remain nearly symmetric tops for all assumed apex angles from 180 to 90°. Although the Ge–O and Ge–S distances are not known, they were estimated to be 1.87 ± 0.07 Å. and 2.22 ± 0.02 Å. from sums of covalent radii corrected for electronegativity differences. The Ge–H distance was taken to be 1.5 Å.; P − R separations were calculated as a function of apex angle for both molecules using the limiting values of the Ge–O and Ge–S distances. A comparison of the observed P − R separations of 9.2 ± 0.2 cm.$^{-1}$ for $(GeH_3)_2O$ and 7.6 ± 0.2 cm.$^{-1}$ for $(GeH_3)_2S$ with those calculated are given graphically in Fig. 5. The two curves for each molecule are the calculated separations for the two Ge–X distances; the intersecting solid line is the observed separation. The dotted lines allow for a ±10% error in the observed separation. On the basis of this treatment the apex angles of digermyl ether and digermyl sulfide are found to be 111^{+26}_{-18} and 116^{+21}_{-13}, respectively. As a check, the observed and calculated P − R separations of disilyl ether and sulfide were treated in the same manner yielding apex angles of 170^{+10}_{-37} for the ether and 101^{+15}_{-10} for the sulfide which agree rather well with other estimates.[2,7,10]

The difference in geometry between disilyl ether and digermyl ether is supported by the fact that the vola-

(15) T. D. Goldfarb, J. Chem. Phys., 39, 2860 (1963).
(16) S. L. Gerhard and D. M. Dennison, Phys. Rev., 43, 197 (1933).

tilities of disilyl ether and disilane are similar (b.p. -15.2 and $-14.5°$, respectively), whereas digermyl ether with a maximum vapor pressure of 66 mm. at $0°$ is appreciably less volatile than digermane (v.p. of 243 mm. at $0°$) thus suggesting a considerably larger dipole moment for $(GeH_3)_2O$. In view of the near equality of the electronegativities of germanium and silicon, this result is in agreement with a highly bent Ge–O–Ge skeleton.

If the near linearity of the Si–O–Si linkage in disilyl ether is correctly explained[10] as a result of a $(p \rightarrow d)\pi$-bonding contribution, then this contribution to the bonding in digermyl ether would be negligible if it has a highly bent skeleton as indicated by the above result. The difference in bonding between germanium and silicon may appear surprising since the covalent radii, electronegativities, and ionization potentials of the two elements are almost identical. None of these properties, however, reflects the difference in spatial distributions of the 3d- and 4d-orbitals and their relative abilities to form π-type bonds with oxygen 2p-orbitals. Indeed, bonding properties reflect relatively small perturbations on electron distributions and the very low bending frequency of disilyl ether[6] resulting from a low angle-bending force constant suggests that a small change in orbital overlap or repulsion terms could appreciably change the equilibrium angle.

Rare Gas Ion Reactions with Ammonia[1]

BY G. R. HERTEL AND W. S. KOSKI

The fractional yields and the relative cross sections for rare gas ion reactions with ammonia have been determined for the 3 to 200 e.v. energy region. The results are in rough agreement with the Massey–Burhop theory; however, anomalies are present. The implication of these results is discussed with respect to the recently proposed mechanism for rare gas sensitization for the production of hydrazine in the gas phase radiolysis of ammonia.

Introduction

Recently Lampe, et al.,[2] had occasion to investigate hydrazine formation in the gas phase radiolysis of ammonia. Deuterons were used as a source of ionizing radiation and the influence of the addition of Kr and Ne on the yield of hydrazine was investigated.

The yield of hydrazine increased by a factor of about 20 when the irradiated gas composition was changed from 90 mole % Ne in a Ne–NH_3 mixture to 90 mole % Kr in a Kr–NH_3 mixture. The proposed mechanism in the pure NH_3 case consisted of the ionization of NH_3 to produce NH_3^+ and NH_2^+ which was followed by the reactions

$$NH_3^+ + NH_3 \longrightarrow NH_4^+ + NH_2$$

$$NH_2^+ + NH_3 \longrightarrow NH_3^+ + NH_2$$
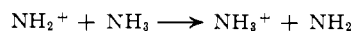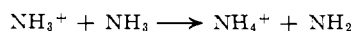
The neutralization of NH_4^+ was considered to be the only important neutralization process. The reactions proposed were

$$NH_4^+ + e \longrightarrow NH_3 + H$$

$$NH_4^+ + e \longrightarrow NH_2 + H_2$$
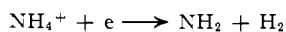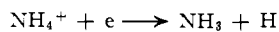
Hydrazine formation was pictured as resulting from the recombination of two amino radicals. On the basis of the work of McDonald, Kahn, and Gunning,[3]

(1) This work was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Contract AF 49(638)-481.

(2) F. W. Lampe, W. S. Koski, E. R. Weiner, and W. H. Johnston, *Intern. J. Appl. Radiation Isotopes*, **14**, 231 (1963).

(3) C. C. McDonald, A. Kahn, and H. E. Gunning, *J. Chem. Phys.*, **22**, 908 (1954).

it was concluded that hydrazine is efficiently destroyed by hydrogen atoms in the reactions

$$N_2H_4 + H \longrightarrow N_2H_3 + H_2$$

$$N_2H_4 + H \longrightarrow NH_2 + NH_3$$
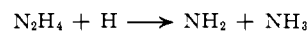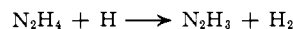
Therefore in this proposed mechanism the primary reason for the low G-value for hydrazine production is the destruction of hydrazine by hydrogen atoms.

In the presence of Kr or Ne, rare gas ions are produced by the deuteron bombardment, and charge exchange occurs between the rare gas ion and NH_3. The semiquantitative theory of Massey and Burhop[4] may be expected to be applicable. In this theory the maximum cross section for charge exchange is expected to occur for the condition

$$v_m = a \, |\Delta E| / h$$

and for $v \ll v_m$ the expression for the cross section will be of the form

$$\sigma \sim e^{-a|\Delta E|/4hv}$$

where v = relative ion velocity, v_m = relative ion velocity at maximum cross section, $a = \sim 7 \times 10^{-8}$ cm., ΔE is the energy defect and is the difference between the recombination energy of the bombarding ion and the energy required to produce the particular state of the product ion.

In the presence of Xe^+, the ion NH_3^+ would be expected to be produced in largest yield, whereas other

(4) H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, New York, N. Y., 1952, p. 478.