[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILL.]

The Thermal Cyclization of Hexafluorobutadiene to Hexafluorocyclobutene[1,2]

BY E. W. SCHLAG AND W. B. PEATMAN[3]

RECEIVED OCTOBER 7, 1963

The kinetics of the cyclization of hexafluorobutadiene has been studied in the high pressure region. The reaction by all criteria appears to be a very clean homogeneous reversible unimolecular isomerization with no apparent side reactions, either gaseous or as polymer, and proceeds to within a few per cent of completion. The equilibrium constant (butadiene/cyclobutene), was determined to be $K_{eq} = e^{4.78 \pm 0.09}e^{-11,700 \pm 106/RT}$, and from this the forward rate constant was found to be $k_1 = 10^{12.03}e^{-35,380 \pm 19/RT}$ sec.$^{-1}$, and hence the reverse rate constant $k_2 = 10^{14.12}e^{-47,080 \pm 19/RT}$ sec.$^{-1}$. k_2 is directly comparable to the hydrocarbon analog, the isomerization of cyclobutene to 1,3-butadiene, which proceeds to completion, but with a normal pre-exponential factor. The quantitative reversal of this isomerization upon fluorine substitution has analogs, although less dramatic, in the dimerizations of fluoroolefins. Some explanations of this apparently general effect are discussed; however, more experimental data are needed before one can come to an unequivocal conclusion about the origin of this effect.

The reactions of fluorocarbons show many interesting features, particularly when contrasted to their hydrocarbon analogs. Nevertheless, there have been few quantitative studies of fluorocarbon reactions in sharp contrast with the amount of such work done on hydrocarbons. Some of the quantitative work on fluorocarbons, on more detailed examination, has been shown to involve at least a slight amount of a heterogeneous side reaction. It is known that in some cases small amounts of such products indicate the participation of a rather large heterogeneous component in the parent reaction. Most interest in fluorocarbons has been limited to a study of preparative possibilities or of its thermochemistry.

The study reported here involves a simple, reversible unimolecular isomerization reaction of a fluorocarbon. Other studies have usually been dimerizations of fluoroolefins to cyclobutane analogs. Simple ring systems usually undergo unimolecular decomposition to give the corresponding open compounds.[4] An example is the unimolecular isomerization of cyclobutene to butadiene studied extensively by Walters and coworkers.[4a,b] Hexafluorocyclobutene has, however, been prepared quantitatively from the open compound hexafluorobutadiene at 450°.[5] This was substantiated by a few equilibrium measurements of this system by Haszeldine and Osborne[6] in the 550–700° range. The fluorination thus produces an almost complete reversal of the isomerization. Simple fluorocarbon cyclizations of small ring systems find an analog in hydrocarbon chemistry only for reactions in the photoexcited state, where the cyclic form has been recovered.[7]

Experimental

Materials.—Hexafluorocyclobutene and hexafluorobutadiene were obtained from Peninsular Chemresearch and introduced into the system by a bulb-to-bulb distillation. Infrared spectra were made of each and compared with the published spectra of two compounds[8] in order to verify the identity of the compounds. Gas–liquid chromatographic analysis indicated that the compounds contained less than 0.5% of total impurities. Nitric oxide (Matheson, 99.0%) was distilled from a slush bath at −160°. Oxygen was used as received from Linde.

Apparatus and Procedure.—A conventional vacuum system was employed. The reactor was a 444-cc. Pyrex vessel in an air furnace adjusted to a vertical temperature gradient of ±0.1° or better. Temperatures were measured with frequently calibrated (melting points of zinc, lead, and tin) chromel–alumel thermocouples and a K-2 potentiometer. The analysis was made by g.l.c. (Kel-F 3 oil on firebrick) employing a thermistor cell as the detector. Only ratios of peaks were used. These were repeatedly found to agree within 2% with standard samples for all ratios from 0.1 to 10.0.

The reaction was allowed to proceed continuously, samples being withdrawn at periodic intervals for analysis. Samples were taken by expansion into a 20-cc. vessel. The consequent reduction in the pressure did not produce any fall-off in the rate constant (*cf.* Table I). Expansions into 50-cc. volumes were made in order to see if any dead space correction appeared necessary. No change in rate constant was observed, and hence no such correction was necessary.

In most unimolecular reactions, seasoning the vessel walls with products is essential to obtain reproducibly low rate constants which are then taken to be homogeneous. In this study it was found that a seasoning with $^1/_3$ atm. of reactants for 10 hr. at 265° or a seasoning with $^1/_3$ atm. of cyclopropane for 10 hr. at 450° (a proven recipe for the cyclopropane isomerization) produced identical results. Both conditions were used to obtain the rate constants of this study (Table I). Furthermore, treating the vessel with 1 atm. of oxygen for 20 hr. at 450° (runs labeled D in Table I) produced the same rate constant. Similarly, packing the vessel with glass wool, thereby increasing the surface to volume ratio by a factor of at least 33, had no measurable effect on the rate constant (*cf.* runs labeled C, Table I). It appears that this reaction, in the temperature region studied, is remarkably unaffected by wall conditions and therefore is probably homogeneous.

The raw data from the g.l.c. charts was punched on cards, and a least-squares reduction of the data was carried out on a computer.

Results

Nature of the Reaction.—The rate constants are given in Table I and span a temperature range of about 192–266° in a pressure region of 1 to 18 mm. This was confirmed to be in the high pressure region of the reaction, as is reasonable from the complexity of the molecule. For example, the cyclobutene isomerization is

---

[1] This work was supported by a grant from the Petroleum Research Fund of the American Chemical Society. Acknowledgment is made to donors of said fund.

[2] Abstracted from the thesis submitted by W. B. P. for the degree of Master of Science.

[3] Abbott Fellow.

[4] A few of the many examples are: (a) W. Cooper and W. D. Walters, *J. Am. Chem. Soc.*, **80**, 4220 (1958); (b) W. P. Hauser and W. D. Walters, *J. Phys. Chem.*, **67**, 1328 (1963) (we thank Professor Walters for letting us see a preprint of this paper); (c) C. T. Genaux and W. D. Walters, *J. Am. Chem. Soc.*, **73**, 4497 (1951); (d) F. Kern and W. D. Walters, *Proc. Natl. Acad. Sci.*, **38**, 937 (1952); (e) C. T. Genaux, F. Kern, and W. D. Walters, *J. Am. Chem. Soc.*, **75**, 6196 (1953); (f) H. O. Pritchard, P. Sowden, and A. F. Trotman-Dickenson, *Proc. Roy. Soc.* (London), **A218**, 416 (1953); (g) H. R. Gerberich and W. D. Walters, *J. Am. Chem. Soc.*, **83**, 4884 (1961); (h) H. M. Frey, *Trans. Faraday Soc.*, **58**, 957 (1962).

[5] M. Prober and W. T. Miller, Jr., *J. Am. Chem. Soc.*, **71**, 598 (1949).

[6] R. N. Haszeldine and J. E. Osborne, *J. Chem. Soc.*, 3880 (1955).

[7] R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 3982 (1962); **84**, 4141 (1962); **83**, 3280 (1961); **85**, 3048 (1963).

[8] (a) J. C. Albrighe and J. R. Nielsen, *J. Chem. Phys.*, **26**, 370 (1957); (b) J. R. Nielsen, M. Z. El-Sabban, and M. Alpert, *ibid.*, **23**, 324 (1955).

TABLE I

LIST OF $(k_0)_{av}$

Run[a]	Temp., °C.	Initial pressure in reactor, mm.	$(k_0)_{av} \times 10^5$, sec.$^{-1}$	$(k_0)_{av}$ cor. to 200.0°, $\times 10^5$, sec.$^{-1}$
1	198.5	7.73	4.33	4.89
2A	198.8	7.72	4.42	4.86
3	200.2	7.72	4.92	4.84
4	205.5	7.81	7.34	4.76
5	206.2	4.13	8.06	4.96
6	203.0	7.79	6.31	4.98
7	192.6	6.39	2.73	4.97
8	191.8	9.74	2.57	4.99
9	191.6	8.42	2.48	4.90
10	217.3	7.40	18.4	4.88
11	216.6	7.96	17.6	4.91
12	216.6	18.33	18.0	5.02
13C	194.7	7.85	3.22	4.93
14C	194.6	7.85	3.19	4.93
				$(k_0)_{av}$ cor. to 262.0° $\times 10^3$, sec.$^{-1}$
15	266.2	8.77	4.94	3.81
16	262.8	8.63	4.15	3.95
17A	261.0	7.80	3.67	3.91
18A	260.4	8.93	3.51	3.88
19	259.7	2.44	3.34	3.86
20	263.1	9.78	4.19	3.92
21B	262.8	9.08	4.08	3.97
22	263.1	8.47	4.13	3.86
23D	265.2	8.39	4.69	3.85
24D	265.1	9.32	4.64	3.83
25	266.1	9.51	4.94	3.85
26	266.7	8.23	5.11	3.83
27E	259.3	~2	3.15	3.73
28	258.6	1.04	2.97	3.67
29C	246.4	8.28	1.40	3.80
30C	246.4	8.86	1.40	3.80

[a] 2A, 17A, 18A contained *seriatim* 5, 10, and 15% NO. 21B contained 11% O_2. 13C, 14C, 29C, 30C were packed vessel runs. 23D, 24D were run in an unseasoned reactor. 27E hexafluorobutadiene used was 99.9% pure.

just beginning to fall off here.[4b] Since fluorination will lower the frequencies of the molecule, this reaction should be even further into the high pressure region for equal pressures.

Since some small peaks appeared on the g.l.c., it was of interest to see if these would change during the reaction. It can be seen from Table II that a reacted and an unreacted sample had essentially the same amount of these impurities. A further purification of a sample by g.l.c. produced no change in the rate constant (run 27E, Table I). Furthermore, a run taken to 75% reaction was analyzed by infrared and found to agree with a corresponding synthetic sample. Since it was possible that a side reaction occurs, but that the products are not trapped (say polymers), it was decided to compare the total peak area on g.l.c. of a reacted *vs.* an unreacted sample of identical size. It can be seen from Table II that all the reactants that were inserted into the reactor, and allowed to react up to 90% completion, were recovered as products (within 0.5% error of the method). This effectively demonstrates that neither volatile nor nonvolatile products were produced by side reactions.

TABLE II

MASS BALANCE

Run	Init. press.,[a] cm.	Procedure	Peak area per unit pressure: Open C_4F_6	Cyclo C_4F_6	Other	Total C_4F_6
A	11.45	Unpyrolyzed	386	0.0	1.59	386
B	11.45	Unpyrolyzed	384	0.0	1.70	384
C	11.45	Pyrol. at 267.4°	302	92.9	1.70	395
D	11.45	Pyrol. at 267.4°	45.3	321	1.66	366
A	11.50	Unpyrolyzed	385	0.0	1.67	385
B	11.45	Pyrol. at 267.1°	57.6	317	1.69	374
C	11.45	Unpyrolyzed	383	0.0	1.70	383
D	11.45	Pyrol. at 267.1°	94.0	291	1.73	385
E	11.50	Unpyrolyzed	385	0.0	1.74	385

[a] Pressure measured in 20-cc. volume at room temperature.

Furthermore, it was decided to check on the possibility of free radical reactions occurring to some lesser extent. Up to 15% of nitric oxide had no effect on the reaction (runs labeled A, Table I). Similarly, 11% oxygen had no effect on the reaction (run 21B, Table I).

Measurement of first-order rate constants as a function of per cent conversion, up to 90% reaction, showed only a 1.7% spread in the values with no trend.

It was concluded that this reaction is a homogeneous first-order reaction, unaffected by side reactions, free radical or otherwise, and hence unimolecular in character. The only product of this isomerization of hexafluorobutadiene is hexafluorocyclobutene, with a trace of a back reaction. (Some telomerization reactions have been reported for this compound,[5] but only for a temperature range below the one considered here.)

Equilibrium Constant.—Since this reaction appears to be well behaved to high conversion, efforts were made to determine the equilibrium constant. By extending the resolution of the g.l.c. slightly, this became possible (25 ft. of 11% Kel-F 3 on 30–60 mesh firebrick at 0°). Identical equilibrium values were obtained approaching it from either reactants or products (*cf.* Table III). The range of temperature was increased to a 260–375° range to increase the precision of the measurements. A plot of these data is seen in Fig. 2 along with the corresponding values of ΔH and ΔS for this reaction. (For purposes of comparison the equilibrium constant was defined with butadiene as product; see Fig. 3.) Haszeldine and Osborne[6] obtained values of 8.0 and 11.0 at 580°. The data of this study extrapolate to a value of 8.1, which should be considered excellent agreement. The value of the equilibrium constant was of further use in generating a reverse rate constant by indirect means, which is the

TABLE III

LIST OF EQUILIBRIUM CONSTANTS

Temp., °C.	$K_{eq} \times 10^{3a}$	Temp., °C.	$K_{eq} \times 10^{3a}$
Hexafluorobutadiene[b]		Hexafluorocyclobutene[b]	
260.4	1.92	313.8	5.38
261.0	1.9	313.9	5.32
262.8	2.0	314.2	5.44
262.8	2.5	Hexafluorobutadiene[b]	
263.1	2.12	314.5	5.50
263.1	2.18	314.9	5.60
263.1	2.11	374.7	14.6
264.4	2.12	375.0	14.3
265.1	2.12	375.1	14.3
265.2	2.57	Hexafluorocyclobutene[b]	
266.2	1.9	375.2	14.2
286.8	3.33	375.3	13.6
287.2	3.33		

[a] Defined as butadiene/cyclobutene. [b] Reactant.

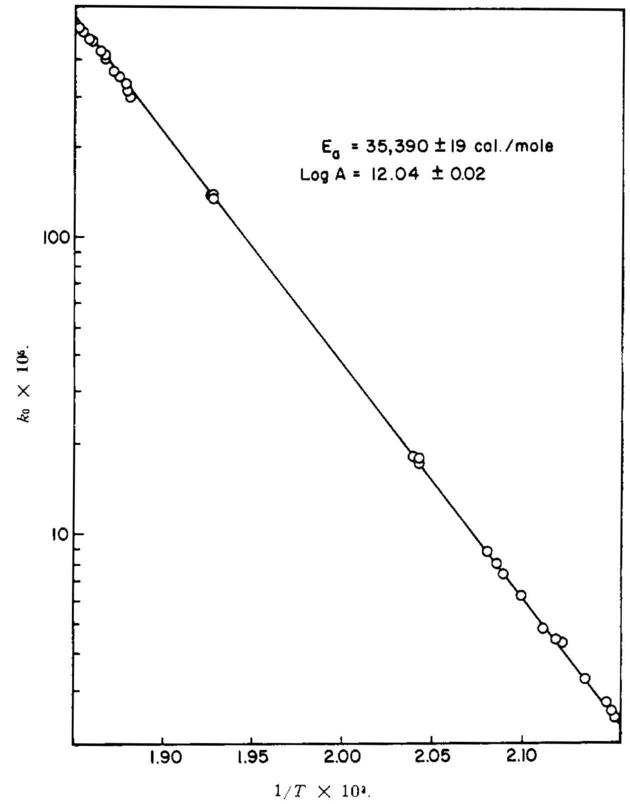

Figure 1.

direction in which the hydrocarbon reaction was studied.[4a,b]

Rate Constant.—The first-order rate constant in the range 192–267° has been computed for the over-all reaction (k_0, where $k_0 = k_1 + k_2$) and for the respective forward (k_1) and reverse (k_2) rate constants using the equilibrium constant determined in this study. The data are plotted in Fig. 1. As can be seen from the data in Table IV, k_0 virtually equals k_1 since the equilibrium is so far on the side of products.

TABLE IV

	E_a, cal./mole	Prob. err., cal./mole	log A	Prob. err.
		A^a		
$(k_0)_{av}{}^b$	35,380	33	12.03	0.03
k_0	35,390	19	12.04	.02
k_1	35,380	19	12.03	.02
k_2	47,080	19	14.12	.02
		B^a		
$(k_0)_{av}$	35,300	30	11.99	0.03
k_0	35,310	18	12.00	.02
k_1	35,300	18	11.99	.02
k_2	46,970	18	14.07	.02

[a] A, probable error representing only experimental spread; B, probable error representing only experimental spread with temperatures corrected for self-heating. [b] $k_0 = k_1 + k_2$; k_1 is the rate constant for the formation of cyclobutene, and k_2 the rate constant for the reverse process. k_0 was computed for every point in every run; $(k_0)_{av}$ is the average value of k_0 for a given run.

Since the reaction is exothermic one might expect a higher effective temperature in the vessel than measured at the walls. This self-heating effect has been calculated,[9] and the result on the rate constants is shown in the set B of Table IV. This affected the measured temperature by at most ~0.3°. It can be seen from these data that the experimental spread (determined by least squares) in the determination of the activation energy is extremely small. If one now wishes to add to this random error an extreme of systematic errors, this would still amount to an error of less than 250 cal./mole. All data reported here, however, have been given in terms of the experimental probable error.

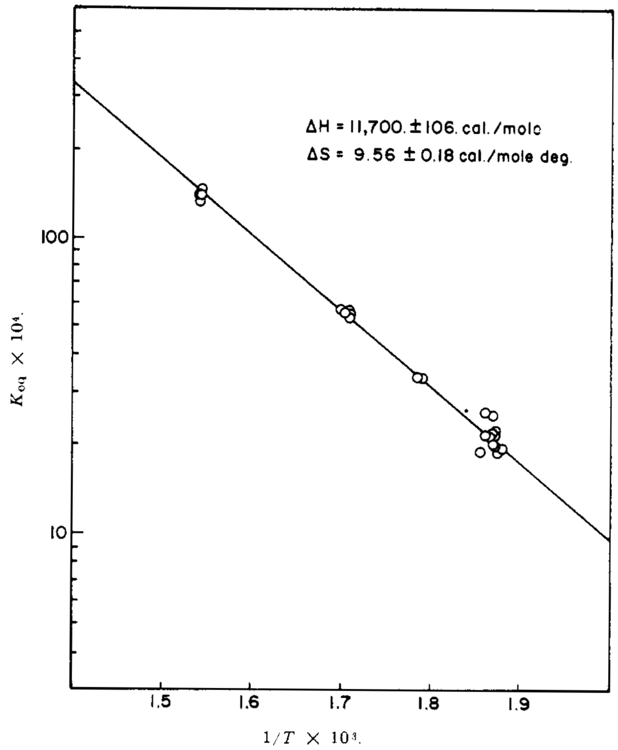

Figure 2.

Discussion

It is easiest to summarize the results of this work with a suitable reaction coordinate diagram (Fig. 3). For purposes of comparison the hydrocarbon diagram has also been included. Unfortunately no estimate of its heat of reaction could be found; bond energy calculations are probably not very reliable for this case. The approximate entropies for the various processes have also been indicated. A value of $\Delta S^* = 0$ e.u.[4a] has been suggested for the hydrocarbon reaction as being within the error, since any negative value did not appear reasonable In any case, it appears that whereas for the hydrocarbon reaction the activated complex is probably about isostructural with the cyclic species, this is not true for the fluorocarbon reaction. In that sense this reaction resembles cycloalkane decompositions which are characterized by an as large or larger value for ΔS^*.[10]

The fact that fluorination almost quantitatively reverses this reaction seems to be part of a general effect in fluorocarbon systems, where it is found that in going from olefinic to saturated linkages a greater exothermicity is observed for fluorocarbon systems. In the case studied here the effect is sufficiently large to offset any instability due to strain energy in the cyclic species. While there appear no directly comparable reactions of a

---

(9) (a) S. W. Benson, "Foundations of Chemical Kinetics," McGraw-Hill, Book Co., Inc., New York, N. Y., 1960, pp. 427–431; (b) 8 × 10^{-5} cal. cm.$^{-1}$ deg.$^{-1}$ sec.$^{-1}$ was used as the value for the coefficient of thermal conductivity for C_4F_6.

(10) For a short review see R. L. Brandaur, B. Short, and S. M. F. Kellner, *J. Phys. Chem.*, **65**, 2269 (1961).

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 sp^3 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 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.

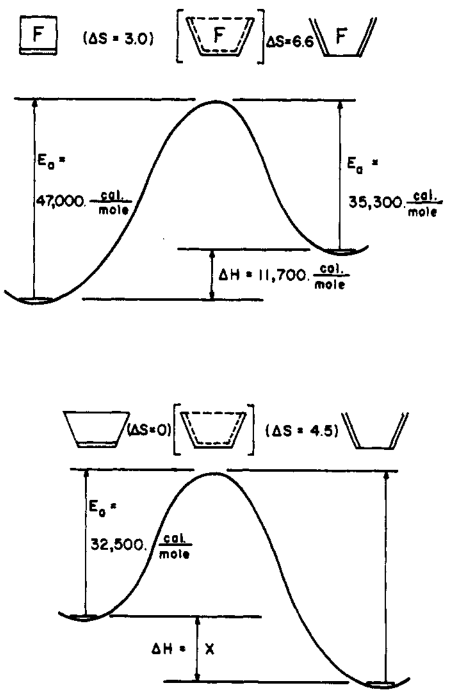

Fig. 3.—Reaction diagram.

Acknowledgment.—We thank Dr. R. L. Burwell, Jr., for some helpful comments on the manuscript.

---

(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).

(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

RECEIVED SEPTEMBER 3, 1963

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

---

(1) This research was supported by the Air Force under Grant No. 277-63 monitored by the Air Force Office of Scientific Research of the Air Research and Development Command. Presented in part at the International Symposium on Molecular Structure and Spectroscopy, Tokyo, Japan, September, 1962.