

Appearance Potential Study of Tetrafluorohydrazine

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silane is made with a carbon orbital of unusually high s character and is therefore shortened nearly as much as the bond in the cyanide. A study of the C^{13} -H coupling in the proton magnetic resonance spectrum of H_3SiCH_3 would be desirable, since such data may be used¹² to estimate the state of hybridization of the carbon atom.

We wish to thank Mr. William E. Baitinger for help with the preparation of H_3SiCN . One of us (RCB) thanks the Purdue Research Foundation for financial support during a part of this work.

* Supported by the U.S. Atomic Energy Commission under contract with the Purdue Research Foundation.

¹ For relevant data see W. Gordy, W. V. Smith, and R. F. Trambarulo, *Microwave Spectroscopy* (John Wiley & Sons, Inc., New York, 1953), p. 371.

² R. W. Kilb and L. Pierce, *J. Chem. Phys.* **27**, 108 (1957).

³ A. G. MacDiarmid, *J. Inorg. & Nuclear Chem.* **2**, 88 (1956). See, however, references 5 and 7 which show that the normal cyanide is indeed obtained and not the isocyanide.

⁴ We are indebted to Professor Walter Edgell for the use of this instrument.

⁵ J. Sheridan and A. G. Turner, *Proc. Chem. Soc.* **1960**, 21.

⁶ In collaboration with Professor R. L. Livingston and Dr. C. N. R. Rao, one of us (RCB) is attempting to obtain the necessary value using the electron diffraction technique.

⁷ H. R. Linton and E. R. Nixon, *Spectrochim. Acta* **10**, 299 (1958).

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⁹ W. West and M. Farnsworth, *J. Chem. Phys.* **1**, 402 (1933).

¹⁰ This assumption of course does not imply that the true, equilibrium Si-H distance differs significantly from the Si-D distance, but applies only to the "effective" parameters derived from the I° values. See C. C. Costain, *J. Chem. Phys.* **29**, 864 (1958).

¹¹ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1945), p. 164.

¹² N. Muller and D. E. Pritchard, *J. Chem. Phys.* **31**, 1471 (1959).

Appearance Potential Study of Tetrafluorohydrazine*

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THE preparation and properties of tetrafluorohydrazine (N_2F_4) have been reported by Colburn and Kennedy.¹ A recent study of the microwave spectrum of the compound has given further information as to the structure of tetrafluorohydrazine.² We wish to report an estimate of the bond dissociation energy of the N-N bond in tetrafluorohydrazine as derived from appearance potential measurements.

A sample of tetrafluorohydrazine was obtained from Rohm and Haas Company, Redstone Arsenal Research Division, Huntsville, Alabama. The purity was quoted at 95+ % and was found to be 97% by mass spectral analysis. The major impurities of air and nitrous oxide

TABLE I. Mass spectrum of tetrafluorohydrazine.

Species	Relative abundance (70 v)	AP (v)
NF_2^+	57.6	11.8 ± 0.2
NF^+	100.0	15.0 ± 0.2
N_2^+	0.2	
F^+	6.6	
NF^{++}	0.3	
N^+	11.4	

were removed by standard low temperature distillation techniques, increasing the purity to 99%.

The mass spectrum of tetrafluorohydrazine and the observed appearance potentials are presented in Table I. The data were obtained using a Consolidated Electro-dynamics Corporation Model 21-103C mass spectrometer modified for appearance potential and excess kinetic energy studies.³ The appearance potentials were determined by the method of initial breaks. Excess kinetic energies were measured by using the metastable ion suppressor as a retarding potential device. Both procedures have been described previously.³ Krypton and argon were added as calibration standards for the appearance potential and excess kinetic energy measurements, respectively.

Since the fragmentation process producing NF_2^+ is probably complex, several mechanisms resulting in its formation may be postulated. However, reasonable arguments can be made for the preference of a single possibility, which is presented in Table II. A value for the bond dissociation energy, $D(F_2N-NF_2)$, may be calculated using the observed appearance potential (AP) for NF_2^+ if one knows the ionization potential (IP) of NF_2 and the bond dissociation energy, $D(FN-F)$. From our measured value of 14.6 v for the AP- (NF_2^+) from NF_3 , and Reese and Dibeler's estimate of 3.2 v for $D(F_2N-F)$,⁴ a value of 11.4 v for the IP(NF_2) was estimated. The value for $D(FN-F)$ was taken to

TABLE II. Fragmentation mechanisms postulated.

m/e 52	$AP(NF_2^+) = 11.8 \pm 0.2$			
	$e + N_2F_4 \rightarrow NF_2^+ + NF + F^- + e$			
	$D(F_2N-NF_2) = AP(NF_2^+) - IP(NF_2) - D(FN-F) + EA(F)^a$			
	11.8	-11.4	-2.7	+3.6
	$= 1.3 \pm 0.3$ v (30 kcal)			
	or $= 1.7$ using 11.0 for IP(NF_2) ^b			
m/e 33	$AP(NF^+) = 15.0 \pm 0.2$			
	$e + N_2F_4 \rightarrow NF^+ + NF + F^- + F + e$			
	$D(F_2N-NF_2) = AP(NF^+) - IP(NF) - 2D(FN-F) + EA(F)^a$			
	15.0	-12.0	-5.4	+3.6
	$= 1.2 \pm 0.3$ v (28 kcal)			

^a Excess kinetic measurements indicated that both NF_2^+ and NF^+ are formed with less than 0.2 v excess kinetic energy.

^b Footnote 4.

be 2.7 v.⁴ The proposed mechanism appears to be supported by the shape of the ionization efficiency curve, which exhibits a rather long tail in the appearance potential region. This would suggest, in the absence of excess kinetic energy of the ion, that the NF_2^+ fragment is being formed by a multiple fragmentation process.⁵

Table II also contains the most probable fragmentation mechanism for the formation of the NF_2^+ species. It can be seen that the mechanism is comparable to that written for the formation of NF_2^+ and gives a value for $D(\text{F}_2\text{N}-\text{NF}_2)$ in good agreement with the number calculated from the $AP(\text{NF}_2^+)$. The value for $IP(\text{NF})$ was taken to be 12.0 v⁴ and for $EA(\text{F})$ 3.6 v.⁴

From this study and the known physical properties of the compound, it has been concluded that the bond dissociation energy of the $\text{F}_2\text{N}-\text{NF}_2$ bond in tetrafluorohydrazine undergoing electron bombardment is 1.3 ± 0.3 ev.

* Work performed under the auspices of the U.S. Atomic Energy Commission.

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² D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.* **31**, 1129 (1959).

³ R. J. Kandel, *J. Chem. Phys.* **22**, 1496 (1954).

⁴ R. M. Reese and V. H. Dibeler, *J. Chem. Phys.* **24**, 1175 (1956).

⁵ F. H. Field and J. L. Franklin, *Electron Impact Phenomena* (Academic Press, Inc., New York, 1957), p. 12.

position, ρ_i 's are π densities on adjacent carbon atoms or more generally the corresponding diagonal elements of the spin density matrix.⁴ This is an approximate expression which neglects contributions from unpaired π density on noncontiguous atoms and from terms corresponding to off-diagonal elements of the spin density matrix. The data for C^{13} splittings in naphthalene negative ion combined with values of ρ_α and ρ_β calculated from proton hyperfine splittings^{5,2} yield $k_1 = 13.5$ gauss, $k_2 = -5.9$ gauss. These constants are in agreement with C^{13} splittings⁶ and π spin densities^{7,8} in triphenylmethyl- C^{13} and methyl⁹- C^{13} . In the case of triphenylmethyl- C^{13} the best agreement is obtained if the three rings are considered coplanar.⁸

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Spin Distribution in Naphthalene Negative Ion*

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THE ESR absorption spectrum of naphthalene negative ion with 53 atom percent C^{13} in one β position has been observed in dilute 1,2-dimethoxyethane solution at room temperature. This spectrum is well represented by a superposition on the spectrum of ordinary naphthalene negative ion of a spectrum in which each line has been doubled with a splitting of 1.2 gauss. One may relate this β C^{13} splitting and the previously determined α C^{13} splitting¹ with unpaired π -electron densities through an empirical equation suggested by the application of simple valence bond² or molecular orbital theory³ to a C—C fragment. This relationship may be written as follows:

$$S_n = 3k_1\rho_n + k_2\sum_i \rho_i,$$

where S_n is the hyperfine splitting from a C^{13} at position n , ρ_n is the unpaired π -electron density at this

Some Observations on Atomic Exchange in NO^*

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CLUSIUS and Schleich¹ have recently found that the vapor pressure ratios of isotopic nitric oxides, $\text{N}^{14}\text{O}^{16}/\text{N}^{15}\text{O}^{16}$ and $\text{N}^{14}\text{O}^{16}/\text{N}^{14}\text{O}^{18}$, are three to five times greater than the corresponding ratios for other diatomic molecules of comparable molecular weight and boiling point. They have used the strikingly high single-stage separation factor to enrich nitrogen-15 by distillation of nitric oxide, and have pointed out the attractive possibility of using this process to simultaneously concentrate the heavy isotopes of nitrogen and oxygen.² In order to obtain highly concentrated nitrogen-15 or oxygen-18 by distillation of a mixture of $\text{N}^{14}\text{O}^{16}$, $\text{N}^{15}\text{O}^{16}$, and $\text{N}^{14}\text{O}^{18}$, it is necessary to establish the equilibrium: $\text{N}^{15}\text{O}^{16} + \text{N}^{14}\text{O}^{18} \rightleftharpoons \text{N}^{14}\text{O}^{16} + \text{N}^{15}\text{O}^{18}$. In view of this it seemed of interest to measure the rate of exchange between isotopically labeled nitric oxide molecules.