TABLE IV

SECONDARY ISOTOPE EFFECT ON MUTAROTATION OF DEUTERIO-D-GLUCOSE AND D-GLUCOSE-1-d (COMPARED TO ORDINARY D-GLUCOSE), 25°[a]

| | k_H/k_D | | | |
| | —H$_2$O— | | —D$_2$O— | |
Compound	In neutral soln.	In acid-catalyzed reaction	In neutral soln.	In acid-catalyzed reaction
Deuterio-D-glucose	1.17 ± 0.04	1.05 ± 0.03	1.16 ± 0.01	1.09 ± 0.04
D-Glucose-1-d	1.12 ± 0.03	1.09 ± 0.02	1.16 ± 0.01	1.05 ± 0.04

[a] The secondary deuterium isotope effect of deuterio-D-mannose in H$_2$O and D$_2$O is in the range of 1.1 to 1.2. The uncertainties in k_1 for mannose are considerably greater than those for glucose, the reaction rates being much faster. Consequently the numerical values for the secondary isotope effect for mannose are not included in Table IV.

TABLE V

RATE CONSTANTS OF MUTAROTATION OF GLUCOSE IN H$_2$O–D$_2$O MIXTURES, 25°

$k_N = k_{0,N} + k_{1,N} (HClO_4)$

	$k_{0,N}$	$k_{1,N}$
$N = 0$	0.0102	0.28
0.23	.0077	.27
.31	.0071	.26
.48	.0061	.26
.65	.0059	.22
1.0	.0029	.21

on carbon 1 or glucose, and none of the other C–D bonds have significant influence on the rate. This is a reasonable assumption, since carbon 1 is immediately adjacent to the reaction center where O–H bonds are broken and reformed during the rate-determining step. This situation is likewise quite consistent with the observations of Challis, Long and Pocker.[6]

The acid catalysis of mutarotation of glucose at 25°, in the range 0 to 0.04 M perchloric acid, also has been studied in H$_2$O–D$_2$O mixtures. For a given value of N, where N is the mole fraction of D$_2$O in the solvent mixture, the data yield linear plots of the observed rate constants $vs.$ the molarity of the acid catalyst. The results are summarized in Table V. The primary deuterium isotope effect is given by k_{H_2O}/k_N, where k_{H_2O} is the value of k for $N = 0$, and this increases with increase in N, as is expected. The failure of the Gross–Butler theory to predict the rates of acid-catalyzed mutarotation of glucose in H$_2$O–D$_2$O mixtures already has been discussed by Purlee.[18]

A few isolated experiments were carried out with glucose and deuterio-D-glucose in the pH range 7.8 to 8.45, using tris-(hydroxymethyl)-aminomethane buffers in aqueous medium. In every case, the rate constant for fully deuteriated glucose is smaller than for glucose. The secondary isotope effect, k_H/k_D, for a given pH in this pH region varies from 1.1 to 1.2.

(18) E. L. Purlee. J. Am. Chem. Soc., 81, 263 (1959).
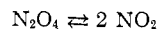

The Tetrafluorohydrazine–Difluoroamino Radical Equilibrium[1]

BY FREDERIC A. JOHNSON AND CHARLES B. COLBURN

Tetrafluorohydrazine and difluoroamino radicals were found to exist in equilibrium. The enthalpy and entropy changes of this reaction were determined by two independent methods. Measurement of the pressure dependence at constant volume was used to calculate a series of K_p's between 100 and 150°. K_f was obtained at five degree intervals in this temperature range by extrapolation of K_p to zero pressure. The enthalpy change by this method averaged 19.9 kcal./mole with no significant temperature dependence; the entropy change was 39.9 e.u. A spectrophotometric method based on the temperature dependence of the ultraviolet absorption of the difluoroamino radical gave an enthalpy change of 21.7 kcal./mole and an entropy change of 45.0 e.u.

Introduction

Only a few gaseous molecule–radical systems stable at ordinary temperatures are known. The reactions

$$N_2O_4 \rightleftharpoons 2 NO_2$$

and

$$N_2O_3 \rightleftharpoons NO + NO_2$$
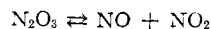
are perhaps the best known examples of this type of behavior and have been studied extensively by Bodenstein,[2] by Verhoek and Daniels[3] and by others. Another system in which a weak nitrogen–nitrogen bond is responsible for a similar molecule–

radical system is the tetrafluorohydrazine–difluoroamino radical equilibrium.

The low N–N bond strength in tetrafluorohydrazine results in the presence of detectable amounts of difluoroamino radicals even at ambient temperatures. The ultraviolet spectrum of tetrafluorohydrazine has a pressure and temperature dependent band whose maximum is at 260.2 mμ. This band is due to NF$_2$ radicals and observation of its variation with temperature and pressure offers a convenient means of completely characterizing the equilibrium. To check this method and to obtain data more easily at higher temperatures, the familiar measurement of pressure at constant volume allows calculation of equilibrium constants over a range of temperatures. The enthalpy

(1) This research was carried out under Army Ordnance Research Contract No. DA-01-021 ORD-5135.

(2) Bodenstein, Z. physik. Chem., 100, 68 (1922).

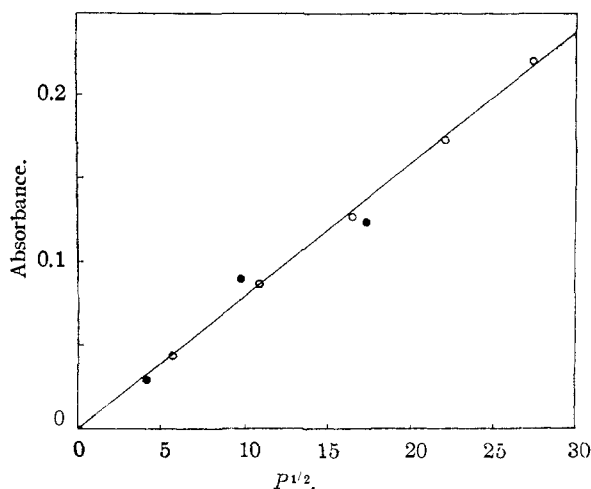(3) F. Verhoek and F. Daniels. J. Am. Chem. Soc., 53, 1250 (1931).

Fig. 1.—Absorbance *versus* the square root of pressure of N₂F₄. The solid points are at ambient temperature; the circles at 25.0°.

Fig. 2.—Log absorbance *versus* reciprocal temperature. Pressure of the gas is 430 mm. at 25°.

and entropy changes of the reaction are then evaluated from the temperature dependence of the equilibrium constant K_p.

Experimental

The tetrafluorohydrazine used in these investigations ranged from 99.5 to 99.9% in purity by mass spectrometric analysis. The chief impurities were nitrous oxide, nitric oxide and silicon tetrafluoride; the limits of detection of the contaminants by routine analysis were 0.10, 0.15 and 0.10%, respectively. Samples of tetrafluorohydrazine prepared from nitrogen trifluoride and copper[4] and from other sources were found to be identical and were used interchangeably.

A Beckman Model DK1 Recording Spectrophotometer was used in the optical work. The absorbance at various pressures was measured in 10 cm. quartz-windowed cylindrical cells equipped with a 0.5 mm. stopcock. Temperature was estimated to 0.1° from a thermometer graduated in 0.5°. Pressure was measured with an absolute mercury manometer protected with Kel-F #10 oil.[5] The temperature dependence of the absorbance at 260 mμ was investigated using the Beckman 92527 Temperature Regulated Cell Holder. Cylindrical quartz-windowed cells of 5 cm. path length were filled by freezing a measured amount of N₂F₄ in the cell with liquid nitrogen and sealing the glass inlet tube with a gas–oxygen torch. Kel-F 90 fluorocarbon grease[6] was used on all ground glass joints and stopcocks.

To avoid the possibility of undesired reactions, an all-glass system was used for the measurements of the temperature dependence of the pressure at constant volume. This apparatus was similar to that of Verhoek and Daniels,[3] except that Pyrex Bourdon gauges were used in this work instead of a glass diaphragm. The Bourdon gauges were similar to that described by Foord,[6] although a reference pointer was added as an aid in null detection. The three gauges used in the course of the investigation gave similar results except that #3 was somewhat more sensitive than the others. At each temperature, sets of five readings were averaged, the balance point being approached from the high and low pressure sides on alternate readings. The difference in balance point due to direction of approach appeared to be less than 0.05 mm. Groups of five readings had standard deviations (of the mean) of 0.05 to 0.20 mm. in the initial measurements; later work with gauge #3 and an Emil Greiner manometer with vernier[7] gave standard deviations of 0.02 to 0.10 mm.

The all-glass system consisted of the Bourdon gauge, a bulb of about 200-cc. capacity and a break-off tip for sam-
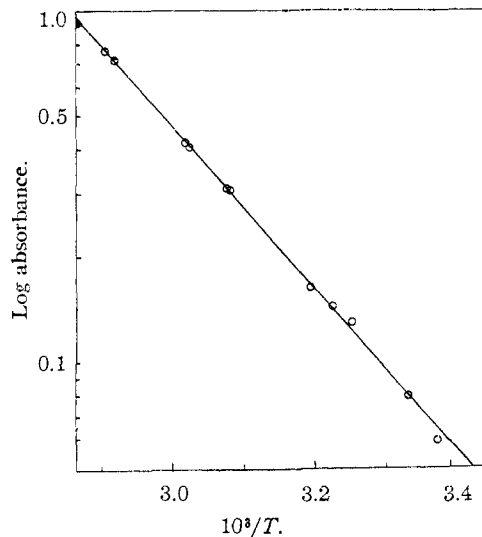
(4) C. B. Colburn and A. Kennedy, *J. Am. Chem. Soc.*, **80**, 5004 (1950).

(5) Trademark of Minnesota Mining and Manufacturing Company. St. Paul 6, Minnesota.

(6) Foord, *J. Sci. Instr.*, **11**, 126 (1934).

(7) Emil Greiner Company, New York City, New York.

pling after the run. Weighed amounts of tetrafluorohydrazine were condensed in the bulb with liquid nitrogen and sealed off with a torch. In the initial runs the volume was calibrated with carbon dioxide. When the degree of dissociation was found to be low, the volume was found from the pressure and weight of N₂F₄ with the appropriate small correction for dissociation. Very little attack on the glass was noted even after several hours at 150° and the same apparatus gave consistent results on re-use. At higher temperatures, however, etching occurred too rapidly for satisfactory operation. Mass spectrometric analysis after each run showed purity to be higher than 99% in each case except run III, this run was found to contain 2.4% nitric oxide and the results were discarded.

The thermostat consisted of a five-gallon vessel of oil agitated by an air-driven stirrer. Two 500-watt heaters operated from variable transformers could be adjusted sufficiently close to hold the bath to within 0.1° during the five-minute period required for a group of measurements.
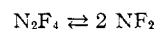
The mass spectra of tetrafluorohydrazine and the routine analyses were done with a Consolidated Model 620 mass spectrometer equipped with a metal inlet system.

Results and Discussion

Spectrophotometric.—The ultraviolet spectrum of N₂F₄ shows an absorption maximum at 260 mμ with a 20 mμ half width. The absorption at 260 mμ is wholly unexpected for a molecule with the structure of tetrafluorohydrazine. The resemblance of this poorly structured band to the NO₂ ultraviolet bands suggested its assignment to the difluoroamino radical.

As expected if an equilibrium concentration of NF₂ radicals were the source of the band, heating the ultraviolet cell causes an enormous enhancement of the absorbance. The fact that the absorbing species is involved in an equilibrium is proven by the return of the absorbance to its original value on cooling after the first and subsequent heating cycles.

A more rigorous proof that the reaction

$$N_2F_4 \rightleftarrows 2\ NF_2$$

is the equilibrium involved and that the difluoroamino radical is the absorbing species at 260 mμ is furnished by Fig. 1. If the absorbance at 260 mμ is plotted against the pressure of N₂F₄ to the one-half power, a straight line is obtained. This

behavior is that expected[8] if

$$\alpha = (K_p/4P)^{1/2} \quad (\alpha = \text{degree of dissociation})$$

for the equilibrium

$$A \rightleftharpoons 2 B$$

where $P_a \gg P_b$. No other explanation fits both the temperature and pressure dependence of the ultraviolet band.

The internal energy change for the reaction can be found from these data. Since

$$C_{NF_2} = \frac{A}{\epsilon L}$$

(where A is absorbance, ϵ is the molar absorbancy index in liters/mole-cm. and L is the path length in cm.), K_c is given by

$$K_c = \frac{A^2}{\epsilon^2 L^2 C_{N_2F_4}}$$

or

$$\ln K_c = 2 \ln A - \ln \epsilon^2 L^2 C_{N_2F_4} \qquad (1)$$

If the absorbancy index is assumed independent of temperature and the change in $C_{N_2F_4}$ is assumed negligible, the internal energy change can be obtained using the constant volume form of the integrated van't Hoff equation.

Figure 2 shows the log A plotted against reciprocal temperature. A good straight line is obtained, justifying the derivation and its assumptions. The line is represented by the equation

$$\log A = -\frac{2.31 \times 10^3}{T} + 6.62 \qquad (2)$$

The value of the internal energy change from the slope is 21.1 kcal./mole. The enthalpy change of 21.7 kcal./mole at 298° is found readily from the internal energy by the addition of RT.

The data of a run at much lower pressure (idealized[9] pressure of N_2F_4 was 0.75 mm.) are plotted as log absorbance versus $1/T$ in Fig. 3. The curvature in the line at higher absorbance values and the internal energy change of 17.5 kcal./mole from the apparently straight portion at lower absorbances are adequate demonstration that the fraction dissociated is no longer negligible with respect to unity at this pressure and temperature. However, useful information can be obtained from this plot by a curve-matching procedure. If one assumes a series of values of α at 150°, where A is equal to 0.201, the family of curves in Fig. 3 can be calculated using only the concentration of N_2F_4 and the previously found internal energy change of 21.1 kcal./mole. The assumption $\alpha = 0.90$ gives an excellent fit to the experimental points. This value permits estimation of such other characteristic parameters as the absorbency index ϵ, K_p and ΔS.

The absolute concentration of radicals can be found from the degree of dissociation since C_{NF_2} is 2α times the idealized $C_{N_2F_4}$. The molar absorbancy index of the difluoroamino radical can be calculated from the usual spectrophotometric equation since the concentration, the absorbance and the cell length are known; it is found to be 550 l./mole-cm. at 150°. A second value of 565 l./

(8) S. Glasstone, "Textbook of Physical Chemistry," 2nd Ed., D. Van Nostrand Co., Inc.. New York. N. Y.. p. 837.

(9) Idealized pressure will be used in the remainder of the paper to mean the pressure which would have existed if no dissociation had occurred.
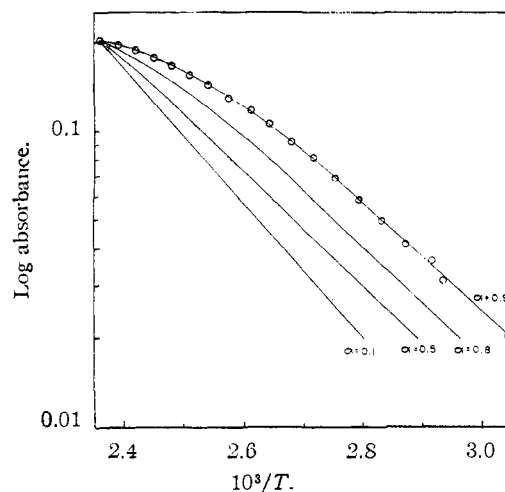

Fig. 3.—Log absorbance versus reciprocal temperature.

mole-cm. at 25° is calculated from the slope of Fig. 1. A K_p of 8.8×10^{-7} (atmospheres) at 25° is also found from α and ΔE and used in the evaluation of ϵ from Fig. 1.

The absorbancy index need not be accurate to permit finding the entropy change of the reaction. Equation 3 can be derived from the usual relationships and definitions given previously. The

$$\Delta F = (10.62 \times 10^3 R + RT) - RT(30.24 + 1 + \ln \frac{RT}{\epsilon^2 L^2 C_{N_2F_4}}) \quad (3)$$

resemblance of (3) to the thermodynamic identity $\Delta F = \Delta H - T\Delta S$ is obvious. Thence, ΔH is 21.7 kcal./mole as before, and the entropy change is 45.0 e.u.

An interesting observation on the rate of establishment of the equilibrium was made at 110°. The absorbance was found to vary in phase with the two degree–one minute fluctuation of the temperature regulated cell holder. This behavior appeared to exist at all temperatures above 22°. Further investigation of the dissociation and recombination rates is underway.

Pressure Variation with Temperature at Constant Volume.—Measurements on the Bourdon gauge apparatus consisted of pressure readings in mm. at 0° as read from the Greiner manometer. In other runs the appropriate corrections for mercury temperature and barometric pressure were applied. Because of the rather small degree of dissociation, corrections also were applied for the expansion of the Pyrex vessel—the coefficient of cubic expansion was taken[10] as 9.6×10^{-6} deg.$^{-1}$. The error in pressure readings was such as to cause maximum errors in α of 1% at 150° and 4% at 100°, corresponding to errors in K_p of approximately 2 and 8%, respectively.

The effect of temperature on the gauge was checked by a run with helium. An excellent straight line extrapolating to $-274.5°$ at zero pressure was obtained when pressure was plotted against temperature. Hence, little systematic drift of gauge null point with temperature was present.

The data of the Bourdon runs were plotted as

(10) N. A. Lange, "Handbook of Chemistry." 7th Ed.. Handbook Publishers, Inc., Sandusky, Ohio, 1949, p. 1641.

TABLE I

LEAST SQUARES "BEST" EQUATIONS
($\log K_p = A \times 10^3/T + B$)

A	B	ΔH	ΔS	$C \times 10^3$ (moles/l.)
4.130	8.257	18.90	37.79	25.8
4.172	8.379	19.09	38.34	19.8
4.142	8.315	18.95	38.05	16.8
4.236	8.522	19.38	39.00	14.07
4.239	8.530	19.40	39.03	10.74
4.454	9.009	20.33	41.23	5.36
4.299	8.619	19.67	39.44	4.70

log K_p *versus* reciprocal temperature in accordance with the familiar integrated form of the van't Hoff equation. The points were fitted by a least squares treatment assuming no error in $1/T$. The assumption that the enthalpy change is constant over this large temperature range is justified by the apparent linearity of the plot (statistical calculations also show that little temperature dependence is to be expected). The enthalpy and entropy changes derived from these plots are given in Table I for the seven runs, together with the least squares constants and the idealized concentrations of tetrafluorohydrazine.

The scatter of experimental points from the equations in Table I was such as to cause a probable error of 0.1 kcal./mole or less in the enthalpy and a probable error of 0.6 e.u. or less in the entropy change. These probable errors[11] remained essentially the same size for all the runs as a result of better technique during the later runs at lower pressure where the errors might have been expected to be relatively large. It is also plain from Table I that the enthalpy and entropy are concentration dependent.

From the least squares equations, K_p was calculated at 5° intervals between 95 and 155°. This procedure was necessary since, as a matter of experimental convenience, readings were not taken at exactly the same temperature in each run. At each temperature, straight line extrapolation to zero pressure was carried out by least squares. The values of K_f so obtained, and the enthalpy and entropy changes at the mid-point of a 10° interval are given in Table II. The calculated probable error in K_f is less than 4% at 50° and 8% at 100°, corresponding to uncertainties of 2 and 4% in α. These uncertainties might be reduced considerably by using a non-linear extrapolation since the K_p's form a smooth curve concave downward, but because all of the points are within expected error of the straight line, it was felt that no more detailed treatment was justified. The better internal consistency as evidenced by the standard deviations of ΔH and ΔS is due to the pooling of data in the least squares log K_p vs. $1/T$ equations.

Mass spectrometric cracking patterns[12] of tetrafluorohydrazine were obtained with the electrostatic plate heaters on and off. The absence in the heated plate pattern of the molecule–ion peak and other peaks involving the N–N bond make it

(11) L. Hammett, "Introduction to the Study of Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1952, p. 410.
(12) C. B. Colburn and F. A. Johnson, *J. Chem. Phys.*, **33**, 1869 (1960).

TABLE II

EQUILIBRIUM FUGACITY CONSTANTS, ENTHALPY AND ENTROPY

T, °C.	ΔH	ΔS	K_f	$\lambda(K_p = K_f + \lambda C)$
150	19.91	40.05	2.95×10^{-2}	1.63×10^{-1}
145	19.82	39.84	2.22	
140	20.05	40.39	1.67	1.09×10^{-1}
135	20.14	40.59	1.23	
130	19.50	39.04	9.09×10^{-3}	7.71×10^{-2}
125	19.91	40.06	6.74	
120	19.57	39.17	4.83	4.72×10^{-2}
115	19.81	39.77	3.48	
110	19.83	39.85	2.49	2.75×10^{-2}
105	20.06	40.43	1.75	
100	19.83	39.82	1.23	1.60×10^{-2}
Av.	19.85	39.90		

$$\sigma = 0.20 \quad \sigma = 0.48$$

apparent that tetrafluorohydrazine is essentially completely dissociated under the normal conditions of high temperature and low pressure prevailing in the ionizing section of the mass spectrometer. Less dissociation near ambient temperatures is shown by the presence of small 104, 85, 66 and 47 peaks in the pattern found with unheated electrostatic plates. Extrapolation of the K_f data permits estimation of the degree of dissociation at the normal operating temperature (170°) and 10^{-8} atmosphere as 99.99%; at 25° and 10^{-8} atmospheres the estimated degree of dissociation is 98%. These estimates are in good agreement with the observed patterns.

When handled by conventional vacuum techniques, tetrafluorohydrazine has a light to dark blue color. The color was originally attributed to trace impurities[4] and now is known to be a function of the concentration of NF_2 radicals in the gas phase prior to condensation. Samples condensed from cold gas (−30°) at relatively high pressures are water-white; samples condensed from gas at elevated temperatures and low pressures may be so dark as to appear blue-black. In general, the depth of color parallels the expected concentration of difluoroamino radicals in the gas phase provided the condensation is carried out rapidly with liquid nitrogen. Attempts to detect an absorption in the red visible spectrum were unsuccessful (10 cm. cell heated to 100° with one atmosphere pressure). Visual examination of gas at one atmosphere in a one meter tube shows no trace of color, while an equivalent number of atoms condensed to a liquid shows decided color. This comparison suggests that association in the condensed phase is responsible for the color. An investigation of spectra in the liquid phase and other colligative properties in the condensed phases has begun.

Comparison of Values.—Sufficient information exists on the N_2F_4 molecule and the NF_2 radical to compute entropies and heat capacities by classical statistical means.[13] These calculations confirm the experimental observations that ΔH is not strongly dependent on temperature in the range 25–150°. In neither of the experimental methods was a temperature dependence noted—the two

(13) K. Wilde and R. Ettinger, these laboratories, private communication.

kilocalorie difference in the results is thus due to experimental error and not to a change in ΔH with temperature. An average value of 20.8 kcal. ± 1 at 100° probably best represents the experimental results.

The entropy change found from statistical treatment of the molecular constants falls between the experimental values of 40 and 45 e.u. The experimental determinations show no significant temperature dependence, however, probably as a result of the relative magnitudes of experimental error and the real effect. The agreement among the three values is fair when the large effect of small systematic errors is considered.

The average ΔH of 20.8 kcal./mole ± 1 kcal. found in this work corresponds to the N–N bond dissociation energy in N_2F_4. The existence of a low bond energy has precedent[3] in N_2O_4 (14.6 kcal.) and in N_2O_3(10.2 kcal.). The similarity in behavior of these three systems may be taken as support of both the experimental enthalpy change and the estimated bond strength.

Loughran and Mader[14] have reported an N–N bond dissociation energy in N_2F_4 of 30 kcal/mole from the results of an electron bombardment study. However, this value is based on the assumption of an ionization process which does not occur in significant proportion under their experimental conditions. In view of our suggestion that the $NF_2{}^+$ peak is derived directly from NF_2 radicals, Loughran and Mader have reappraised[12] their calculations and now find an N–N bond strength of 20 ± 5 kcal. in agreement with our results.

Herron and Dibeler[15] recently have published the results of an appearance potential study on

N_2F_4 in which a mass spectrometer with an "open" ion source was used. The fragmentation pattern they find is essentially that we observe using an unheated source and likewise represents the tetrafluorohydrazine–difluoramino equilibrium displaced toward the radical by the low pressure only. Using literature data,[16,17] they derive an N–N bond dissociation energy in N_2F_4 of 56 kcal. by a method which involves $D(NF_2\text{-}F)$. This value of $D(NF_2\text{-}F)$ used by Herron and Dibeler results from an arbitrary division by Reese and Dibeler[17] of the N–F bond energy in NF_3 into an initial strong bond and two lesser bonds by analogy with ammonia.

We find that two methods of calculation using the relations $\Delta H_f(NF_2) = \Delta H_f(NF_3) + D(NF_2\text{-}F) - \Delta H_f(F)$ and $A(NF_2{}^+) = D(F_2N\text{-}F) + I(NF_2)$[18] give estimates of 55 and 57 kcal., respectively, for $D(NF_2\text{-}F)$. The remaining two N–F bond energies in NF_3 then average 70.4 kcal. (using the average of the two estimates above). This value is in excellent agreement with the average N–F bond strengths calculated for tetrafluorohydrazine (70.3 kcal. using N–N of 20.8 kcal.) and for the difluoramino radical (70.1 kcal. using $\Delta H_f(NF_2) = 9.4$ kcal.). The relatively facile preparation of tetrafluorohydrazine from NF_3 in the presence of a variety of fluorine acceptors may be taken as qualitative evidence that the first N–F bond in NF_3 is weaker than the remaining two.

Acknowledgments.—The authors wish to thank Mr. Al Kennedy for the mass spectral data and help in the calculation of bond energies. We are also grateful to Mr. Don Strahm for his assistance with the spectrophotometric work and to Dr. Carl Bumgardner for his interest and helpful discussions.

(14) E. D. Loughran and C. Mader, *J. Chem. Phys.*, **32**, 1578 (1960).

(15) J. T. Herron and V. H. Dibeler, *J. Am. Chem. Soc.*, **82**, 1555 (1960).

(16) G. T. Armstrong, S. Marante and C. F. Coyle, NBS Report 6584, National Bureau of Standards.

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

(18) $A(NF_2{}^+) = 14.2$ e.v. and $I(NF_2) = 11.8$ e.v.[12,14]

Thermodynamics of *cis–trans* Isomerizations. The 1,2-Difluoroethylenes

By Norman C. Craig and Eric A. Entemann

Received February 21, 1961

Equilibrium constants for the iodine-catalyzed reaction, *cis*-HFC=CFH = *trans*-HFC=CFH, have been determined over the temperature range 477–762°K. by gas chromatographic analysis. For this reaction, $\log K = -202.8/T + 0.02919$. $\Delta H^0 = 928$ cal./mole, and $\Delta S^0 = 0.134$ e.u./mole. The lower energy of *cis*-HFC=CFH compared with *trans*-HFC=CFH is considered in relation to previous results for the other symmetrically dihalogenated ethylenes. Previously unreported *trans*-HFC=CFH has been characterized.

Introduction

cis–trans Isomerizations are of considerable interest because of the simplicity of the reaction. From this point of view a particularly interesting series of such isomers is that of the dihalogenated ethylenes. For the *cis*-to-*trans* reaction, $\Delta H_0{}^0$ for the 1,2-diiodoethylenes[1] is about 2 kcal./mole exothermic, $\Delta H_0{}^0$ for the 1,2-dibromoethylenes[2] is within 0.1 kcal./mole of being zero, but $\Delta H_0{}^0$ for the 1,2-

dichloroethylenes[3] is nearly 0.5 kcal./mole endothermic. This last value may also be contrasted with those for the stilbenes,[4] decalins,[5] 2-butenes[6] and other *cis–trans* pairs in which the enthalpy of the *trans* isomer is also smaller. Pitzer and Hollenberg[3] have given a semi-quantitative interpretation of the lower energy of *cis*-1,2-dichloro-

(1) S. I. Miller, A. Weber and F. F. Cleveland, *J. Chem. Phys.*, **23**, 44 (1955).

(2) J. M. Dowling, P. G. Puranik, A. G. Meister and S. I. Miller, *ibid.*, **26**, 233 (1957).

(3) K. S. Pitzer and J. L. Hollenberg, *J. Am. Chem. Soc.*, **76**, 1493 (1954).

(4) R. B. Williams, *ibid.*, **64**, 1395 (1942).

(5) N. L. Allinger and J. L. Coke, *ibid.*, **81**, 4080 (1959).

(6) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *ibid.*, **57**, 876 (1935); E. J. Prosen, F. W. Maron and F. D. Rossini, *J. Research Natl. Bur. Standards*, **46**, 106 (1951).