

CNDO/2 STUDY OF THE DIFLUOROAMINO RADICAL DIMERIZATION*

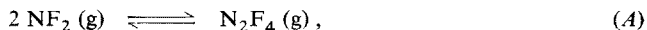
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Received February 17th, 1975

Absolute values of equilibrium constants were calculated for the dimerization of the difluoroamino radical. Both enthalpy and entropy terms were calculated by CNDO/2. The enthalpy was determined by means of the bicentricly rescaled energy. The entropy was determined by statistical thermodynamic calculations within the rigid rotor and harmonic oscillator approximations. Isomerism of tetrafluorohydrazine was taken into account. The relation of the equilibrium constant of dimerization to the spin density distribution is briefly discussed.

There are several gaseous molecule-radical equilibria¹ experimentally accessible at ordinary temperatures, for example systems involving NO and NO₂. The difluoroamino radical-tetrafluorohydrazine equilibrium (A)



also belongs to this family. Since the first synthesis of tetrafluorohydrazine in 1958 both equilibrium and rate processes of the system (A) have been extensively studied². The absolute values of the equilibrium constants of reaction (A) have been determined^{3,4} especially from measurements of pressure variation with temperature at constant volume. In these studies the standard enthalpy change of reaction (A) was determined on the basis of the second law treatment. Herron and Dibeler⁵ determined the relative values of the equilibrium constant mass spectrometrically. The equilibrium constant was also determined at room temperature by means of the UV³ and ESR (ref.⁶) spectroscopy. Molecular constants of the components of the process (A) were reviewed in refs^{2,7}. The principal progress in the interpretation of the equilibrium (A) was made by Lide and Mann⁸ who also discovered the isomerism of N₂F₄. The assumption of the *trans* and *gauche* N₂F₄ isomers in the statistical-thermodynamic calculation is described in ref.⁹. The energy difference between the two isomers has been estimated several times¹⁰⁻¹², but the results of different authors differ by as much as one order. A more recent thermodynamic analysis¹³ favours the results of Cardillo and Bauer¹¹. Kinetic studies were also performed on the recombination¹⁴ of NF₂ radical and on the dissociation¹⁵ of tetrafluorohydrazine. Tetrafluorohydrazine is used synthetically as a source of NF₂ radicals, in particular for introducing the difluoroamino group^{2,16}.

* Part VII in the series Calculation of Absolute Values of Equilibrium and Rate Constants; Part VI: *J. Fluor. Chem.* 6, 465 (1975).

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Reactivity of radicals represents a problem¹⁷ which has been widely studied theoretically. The important work has involved the calculation of absolute values of equilibrium and rate constants of reactions involving radicals. The equilibria associated with some radical dimerizations were interpreted both qualitatively¹⁸ and by quantitative quantum chemical semiempirical calculations¹⁹ of the equilibrium constants.

The compounds of nitrogen and fluorine have been examined rather well experimentally and have been the subject of numerous quantum chemical treatments. Their various molecular constants given by CNDO/2 and INDO are reviewed in ref.²⁰. The adaptation of CNDO/2 to reproduce heats of atomization was reported in refs^{21,22}. Estimates of the heats of formation by means of MINDO were reported by Ganguli and McGee²³. Important results on the force field of NF_3 were obtained by an *ab initio* calculation²⁴ with the gaussian basis set. These made it possible to exclude alternative sets of force constants which do not possess physical meaning but are compatible with the experimental data²⁵. CNDO/2 calculations²⁶ suggested a possible isomerism of the activated complex in the isomerization of difluorodiazine (N_2F_2). Hindered rotation around the N—N bond in N_2F_4 was studied by Wagner²⁷ on both semiempirical and nonempirical levels. The standard enthalpy change of the reaction (A) was determined in ref.²⁸ by *ab initio* calculations with the gaussian basis set.

The aim of this paper is to calculate the equilibrium constants, standard enthalpy and standard entropy changes of reaction (A) by means of statistical-thermodynamic methods in the ideal gas phase within the rigid rotor and harmonic oscillator approximations. All necessary molecular constants adopted originate from semiempirical CNDO/2 calculations.

METHODS OF CALCULATIONS AND RESULTS

A. *Energy function.* Molecular constants have been generated from CNDO/2 wave functions²⁰. With NF_2 and NF the CNDO/2 approximation was combined with the restricted open shell "half-electron" method^{29,30}.

B. *Compounds studied.* Besides the components of the process (A) — NF_2 , *trans*- N_2F_4 , *gauche*- N_2F_4 — all compounds of N and F for which a great deal of experimental information is available were also studied. The latter were NF , NF_3 , *trans*- N_2F_2 , *cis*- N_2F_2 , N_2 and F_2 . These six compounds were used for the determination of scaling factors for the two-centre components of the total CNDO/2 energy which were used in the calculations of heats of formation (see Part F).

C. *Molecular geometry.* The first step of the calculations was the full geometry optimization of all compounds studied. The optimization was based on the minimization of the total CNDO/2 energy. The automatic procedure reported by McIver and Komornicki³¹ and Pancif³² was used which links the explicit formulas for the first derivatives of the total energy with the iterative variable metric method. The starting points of the calculations were the partly optimized geometries reported by Pople and collaborators²⁰. The geometry parameters obtained are compared with the experimental data^{11,17,33} in Table I.

TABLE I
Molecular Geometries Given by CNDO/2^a

Molecule	Point group	Bond distances, 10 ⁻¹⁰ m		
		N—N	N—F	F—F
N ₂	D _{∞h}	1·140 (1·088 ^b)		
F ₂	D _{∞h}			1·119 (1·409 ^b)
NF (3Σ ⁻)	C _{∞v}		1·190 (1·51 ^b)	
NF ₂ (2B ₁)	C _{2v}		1·224 (1·363 ^c)	
NF ₃	C _{3v}		1·249 (1·371 ^b)	
<i>trans</i> -N ₂ F ₂	C _{2h}	1·241 (1·25 ^b)	1·239 (1·44 ^b)	
<i>cis</i> -N ₂ F ₂	C _{2v}	1·239 (1·214 ^b)	1·238 (1·384 ^b)	
<i>trans</i> -N ₂ F ₄	C _{2h}	1·362 (1·489 ^d)	1·251 (1·375 ^d)	
<i>gauche</i> -N ₂ F ₄	C ₂	1·359 (1·489 ^d)	1·251 (1·375 ^d)	

D. *Vibrational frequencies.* The calculation of frequencies of the normal vibrational modes was performed by the Wilson **FG** matrix technique³⁴ with the set of cartesian nuclear coordinates. The elements of the force constant matrix were evaluated numerically from the differences of the first derivatives of the total energy with respect to nuclear coordinates; successively equidistant shifts along all coordinates were assumed. The classification of the vibrational modes was based on the eigenvectors of the **FG** matrix and the matrix of potential energy distribution³⁵.

TABLE II
Stationary Points of the Potential Curve of the Hindered Rotation around the N—N Bond in N₂F₄ Given by Full Optimization of Molecular Geometries by CNDO/2

Dihedral angle °	Relative CNDO/2 energies kJ . mol ⁻¹	Type of the stationary point	
		potential curve	potential hypersurface
0·0	12·514	maximum	saddle point
69·7 ^a	0·0	minimum	minimum
130·2	6·262	maximum	saddle point
180·0 ^b	2·046	minimum	minimum

^a *gauche*-N₂F₄. ^b *trans*-N₂F₄.

TABLE I
(Continued)

FNF	Bond angles, °	
	NNF	torsion
106.6 (102.5 ^c)		
104.5 (102.2 ^b)	109.9 (115 ^b)	180
	114.6 (114.5 ^b)	0
104.8 (102.9 ^d)	104.5 (100.6 ^d)	180
104.8 (105.1 ^d)	{ 107.8 (104.3 ^d) 104.8 (100.1 ^d)	69.7 (67.1 ^d)

^a Experimental geometries in parentheses. ^b Ref. 7. ^c Ref. 33. ^d Ref. 11.

E. *Hindered rotation in N₂F₄*. Generally, the iterative variable metric method does not guarantee³¹ that the energy of a stationary point found on the energy hypersurface is a minimum. This also makes it possible to optimize the geometries of saddle points of the energy hypersurface which correspond to activated complexes in the theory of absolute reaction rates. Distinction between saddle points and minima can be made by means of eigenvalues of the **FG** matrix³⁴. Table II presents the order of energies of all stationary points on the energy hypersurface of the N₂F₄ molecule that lie on the potential curve for the hindered rotation around the N—N bond for the range <0; π> of the dihedral angle between the NF₂ groups.

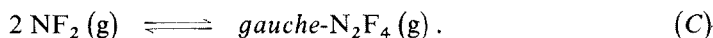
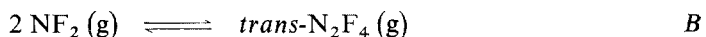
F. *Heats of atomization*. The total CNDO/2 energy cannot be applied directly to the determination of the zero point energy³⁶. Companion³⁷ has suggested the evaluation of heats of formation by means of two-centre terms of the total molecular energy. In this procedure the following relationship is assumed to be valid for the heat of formation at the absolute zero:

$$\Delta H_{at,0}^0 = \sum_{A < B} K_{AB} E_{AB} + k_0. \quad (1)$$

Here K_{AB} and k_0 are empirical scaling factors determined by fitting Eq. (1) to a suitable set of experimental data. The two-centre terms E_{NN} , E_{FF} and E_{NF} were chosen from the total CNDO/2 energies for the optimized geometries of all members of our set of systems (Table I). The experimental heats of atomization of the compounds used

in the scaling procedure were taken from ref.³⁸. The optimized scaling factors K_{NN} , K_{FF} , K_{NF} and k_0 were obtained from Eq. (1) by the least-squares treatment. These transformation constants were then used for the calculation of heats of atomization of NF_2 , *trans*- N_2F_4 and *gauche*- N_2F_4 from the two-centre energy terms. The heats of atomization computed in this way are compared with the experimental values in Table III. Optimization of the scaling factors for *trans*- and *gauche*- N_2F_4 was performed with a six-membered set (N_2 , F_2 , NF , NF_3 , *trans*- N_2F_2 , *cis*- N_2F_2); in the case of NF_2 , the N_2 molecule was disregarded. In the calculation according to Eq. (1) the zero-point energy was not taken into account.

G. Statistical-thermodynamic treatment. Knowledge of the molecular geometries and frequencies of vibrational modes makes it possible to construct the partition functions of the components of reaction (A) within the rigid rotor and harmonic oscillator approximation; from partition functions it is then possible to derive the thermodynamic functions. The partition functions were constructed as described in ref.¹⁹. To allow for the presence of a pair of *d*, *l* conformers of *gauche*- N_2F_4 , the $R \ln 2$ term was added to the entropy. Hence, it is possible in this way to arrive directly at the thermodynamic functions of the following two dimerizations



Nevertheless the experimental determination of equilibrium constants cannot provide characteristics of the partial dimerizations (B) and (C) but only of the total process (A). If a rigorous comparison with experiment is to be done, it is necessary to account

TABLE III

Heats of Atomization at the Absolute Zero

Molecule	$\Delta H_{\text{at},0}^0$, MJ . mol ⁻¹	
	obsd.	CNDO/2 ^a
NF_2 (g)	-0.57955 ^b	-0.57359 ^d
<i>trans</i> - N_2F_4 (g)	-1.24416 ^c	-1.23263 ^e
<i>gauche</i> - N_2F_4 (g)	-1.24178 ^c	-1.23709 ^e

^a Evaluated from the rescaled two-centre components of the total CNDO/2 energy. ^b Taken from ref.⁷. ^c Taken from ref.¹³. ^d Used scaling factors in (kJ . mol⁻¹ . eV⁻¹): $K_{\text{NN}} = 10.600$, $K_{\text{FF}} = 7.160$, $K_{\text{NF}} = 10.073$; $k_0 = 82.980$ kJ . mol⁻¹. ^e Used scaling factors in (kJ . mol⁻¹ . eV⁻¹): $K_{\text{NN}} = 12.031$, $K_{\text{FF}} = 0.698$, $K_{\text{NF}} = 6.516$; $k_0 = -126.296$ kJ . mol⁻¹.

for the weights of partial equilibria (B) and (C) in the observed process (A). Following the results of ref.⁹, the equilibrium constant, K_p , enthalpy and entropy changes, ΔH_T^0 and ΔS_T^0 , associated with the equilibrium (A) become:

$$K_p = K_p^{(t)} + K_p^{(g)}, \quad (2)$$

$$\Delta H_T^0 = K_p^{(t)}/K_p \cdot \Delta H_T^{0(t)} + K_p^{(g)}/K_p \cdot \Delta H_T^{0(g)}, \quad (3)$$

$$\Delta S_T^0 = K_p^{(t)}/K_p \cdot (\Delta S_T^{0(t)} + R \ln(K_p/K_p^{(t)})) + K_p^{(g)}/K_p \cdot (\Delta S_T^{0(g)} + R \ln(K_p/K_p^{(g)})), \quad (4)$$

where indices (t) and (g) refer to thermodynamic quantities of reactions (B) and (C), respectively. Table IV presents the results of the treatment according to formulas (2)–(4) and also gives the data for the partial dimerizations (B) and (C) for some selected temperatures. The main results of the statistical-thermodynamic treatment are presented in Table V, in which a comparison is made of ΔH_T^0 , ΔS_T^0 and $\log K_p$ given by CNDO/2 for the equilibrium (A) with their experimental counterparts. The entries of Table V cover boundary temperatures at which the experiment was performed^{3,4}.

DISCUSSION AND CONCLUSIONS

Experimentally, the equilibrium has been thoroughly examined. Its interesting feature is the isomerism of one reaction component. Since the calculations can be compared with the generous experimental data, one has an excellent opportunity to test the theoretical approach. Treatment of the process (A) as a result of two partial dimerizations (B) and (C) gives a new interpretation of the observed thermodynamic data. At present the evaluation of the entropy term, involving the full geometry optimization and the calculation of at least a harmonic force field, is feasible for the (A) type equilibria only on a semiempirical level. The nonempirical study of Hinchliffe and Cobb²⁸ is restricted to the evaluation of the enthalpy term. The calculated value differed from the experimental enthalpy¹³ by 37.2 kJ mol⁻¹. Though the result is very reasonable²⁸ in view of the fact that the electron correlation was not taken into account, it can hardly be used for the calculation of the absolute value of the equilibrium constant. From the family of semiempirical methods we selected the CNDO/2 method²⁰ because of its known good applicability²⁰ to the class of N—F compounds. Usually MINDO is preferred because it gives rather reliable heats of formation¹⁹. In our case, however, it is not manageable because the parametrization²³ is compatible with the standard molecular geometries, which excludes geometry optimization and construction of the force field. However the use of CNDO/2 requires the evaluation of the enthalpy term by rescaling the total energy. This problem was studied by Companion^{21,22,37} for several classes of compounds. Companion's idea was adopted in this paper but refinements to the following three points

were made. Optimization of the scaling factors was based on a set of compounds instead of a single compound. The experimental heats of atomization used originate from a single and recent source³⁸ and are reduced to absolute zero (in ref.²¹ to 298 K). In particular, the use of a correct heat of atomization for N_2 should be pointed out. Finally, the calculations on the total energies were performed for the optimized instead of experimental molecular geometries. Nevertheless the modifications just noted had no effect on the finding²¹ that no use may be made of a linear correlation between observed and calculated heats of atomization, although such a correlation was established by Isaacs for hydrocarbons³⁹. Calculation of the frequencies of vibrational modes made it possible to test the augmentation of the expansion (1) for the zero-point energy term in the form $(K_{\omega}/2) \sum_i \hbar\omega_i$. Though this correction is compatible with the physical sense of the CNDO/2 energy, the actual optimizations of scaling factors showed that it can be hardly accounted for. The reason is due to the fact that the two-centre terms E_{AB} are several orders higher in value than the vibrational term. The disregard of the N_2 molecule in the scaling set for the determination of the heat of atomization of NF_2 is justifiable with respect to the absence of the E_{NN} term with this radical. In our opinion, the agreement between the experimental and predicted heats of atomization is rather good (Table III). Rescaling of the two-centre terms did not change, however, an incorrect order of stabilities of *trans*- and *gauche*- N_2F_4 isomers given by CNDO/2 (Table II). Table II represents the final description of the energy curve for the hindered rotation on the CNDO/2 level. This is sufficient for the evaluation of the rate constant for the N_2F_4 isomerization, but the incorrect order of the two isomers makes such a calculation meaningless. It is noteworthy that nonempirical calculations²⁷ give a good account of the hindered rotation in N_2F_4 . It is interesting that the bond lengths in the stationary points found (Table II) are almost constant; the largest difference is $3 \cdot 10^{-13}$ m. This finding provides support for the assumption about the invariant bond lengths and bond angles which is made in MO studies of hindered rotation. The other geometry constants (Table I) are in good agreement with those reported by Popie and collaborators²⁰.

Up to now the rigid rotor and harmonic oscillator approximation represents a single accessible way for the use of quantum chemical methods. Utility of this approximation for calculations of equilibrium constants of chemical gas-phase reactions has been demonstrated previously⁴⁰. Use of the CNDO/2 method as a source of molecular constants for statistical-thermodynamic calculations is discussed in ref.⁴¹. Since CNDO/2 failed to give a realistic potential curve for N_2F_4 , the partition function of the hindered rotation was replaced by the vibrational partition function of the corresponding torsional mode.

The entries of Table IV permit us to determine how the individual isomers contribute to the characteristics of the (A) process. The enthalpy term is predominantly

TABLE IV
Basic Thermodynamic Characteristics^a Given by CNDO/2 for the Partial and Total Dimerizations of NF₂

T, K ^b	$\Delta H_T^0, \text{ kJ mol}^{-1}$			$\Delta S_T^0, \text{ J mol}^{-1} \text{ K}^{-1}$			$K_p, \text{ atm}^{-1}$		
	dimerization to								
	<i>trans</i>	<i>gauche</i>	<i>total</i>	<i>trans</i>	<i>gauche</i>	<i>total</i>		<i>trans</i>	<i>gauche</i>
298.15	-90.125	-94.581	-94.190	-183.702	-179.182	-177.107	$1.562 \cdot 10^6$	$1.624 \cdot 10^7$	$1.780 \cdot 10^7$
373.15	-90.171	-94.690	-94.141	-183.855	-179.521	-176.972	$1.044 \cdot 10^3$	$7.546 \cdot 10^3$	$8.591 \cdot 10^3$
423.15	-90.084	-94.646	-94.001	-183.638	-179.412	-176.624	$3.372 \cdot 10^1$	$2.050 \cdot 10^2$	$2.387 \cdot 10^2$
523.1	-89.698	-94.335	-93.527	-182.828	-178.763	-175.625	$2.552 \cdot 10^{-1}$	1.209	1.464

^a Standard state is ideal gas phase at 1 atm pressure. ^b We selected temperatures that are boundaries of the experimental temperature ranges of refs.^{3,4}.

TABLE V

Basic Thermodynamic Characteristics^a for the Total Equilibrium Process $2 \text{ NF}_2 (\text{g}) = \text{N}_2\text{F}_4 (\text{g})$ Determined Experimentally and by CNDO/2 Calculations

T, K	$\Delta H_T^0, \text{ kJ mol}^{-1}$		$\Delta S_T^0, \text{ J mol}^{-1} \text{ K}^{-1}$		$\log K_p, [K_p] = \text{atm}^{-1}$	
	obsd. ^b	calc.	obsd. ^b	calc.	obsd. ^b	calc.
298.15	-90.793	-94.190	-180.280	-177.107	6.056	7.251
373.15	-82.969	-94.141	-166.607	-176.972	2.910	3.934
423.15	-83.303	-94.001	-167.569	-176.624	1.530	2.378
423.3	-85.772	-94.001	-173.581	-176.622	1.517	2.374
523.1	-85.772	-93.527	-173.701	-175.625	-0.508	0.165

^a Standard state is ideal gas phase at 1 atm pressure. ^b Experimental data for the first 3 temperature from ref.³, the other from ref.⁴.

due to the enthalpy of the reaction (C), whereas with the entropy term the effect of the N_2F_4 isomerism is more distinct. Formally, it is possible to replace Eqs (2)–(4) by an alternative procedure *viz.* by making use of the partition function in which the summation extends over all energy of N_2F_4 (*i.e.* of both isomers). Numerically, this procedure would provide the same results as a procedure based on Eqs (2)–(4), which respects inherently the individuality of isomers. The thermodynamic data calculated for the partial processes (B) and (C) are useful for such an experiment which would permit to measure a single simple equilibrium (B) or (C).

Agreement between experimental and calculated data on the equilibrium process (A) is satisfactory (Table V). The results presented in Table V refer only to five selected temperatures, similar agreement between experimental and theoretical data was found within the whole experimental temperature range, however^{3,4}. A feeble point of the theoretical approach is the predicted incorrect order of the two isomers, which depreciates the enthalpy term. The entropy is affected by this failure to a lesser extent. Actually, the experimental entropy⁴ is reproduced rather closely.

Both experimental and theoretical data show that NF_2 is the predominating component of the gas phase at temperatures over 500 K. This is in contrast to most radicals. We present in Table VI the comparison of dimerizations of NH_2 and NF_2 radicals. MINDO/2 calculations¹⁹ suggest that hydrazine is dissociated to the same degree as tetrafluorohydrazine at 500 K at the temperature as high as 1600 K.

The calculated absolute values of ΔH_T^0 , ΔS_T^0 and K_p provide the full description of the equilibrium radical dimerization. Nevertheless it is expedient to look for a quantum chemical index, which is provided directly by standard MO calculations and which would account for the radical ability to coupling. Balaban⁴² treats the stability of nitrogen free radicals in terms of conjugation in the radical and steric compression in the dimer. Atkins and Symons¹⁸ suggest that differing tendencies of radicals to dimerization can be explained by the localization of the odd electron

TABLE VI

Comparison of the Thermodynamic Characteristics at $T = 500$ K for the Equilibrium Dimerizations of NH_2 and NF_2 Radicals

Process	ΔH_T^0 , kJ mol ⁻¹	ΔS_T^0 , J mol ⁻¹ K ⁻¹	$\log K_p$; $[K_p] = \text{atm}^{-1}$
$2 NH_2 (g) = N_2H_4 (g)^b$	-241.484	-154.674	17.148
$2 NF_2 (g) = N_2F_4 (g)^c$	-85.320	-172.882	-0.117 ^d

^a Standard state is ideal gas phase at 1 atm pressure. ^b According to ref.⁷. ^c According to ref.¹³.

^d This implies 49.7% dissociation of N_2F_4 at 1 atm pressure.

on that atom which is the site of coupling. This idea may be demonstrated with NH_2 and NF_2 by means of electron densities in singly occupied MOs given by restricted CNDO/2 calculations. The odd electron in NH_2 is fully localized in the $2p_z$ orbital of the nitrogen atom, whereas in NF_2 it is delocalized — the spin densities in nitrogen and fluorine p_z orbitals are predicted to be 0.754 and 0.123, respectively. Recent *ab initio* unrestricted Hartree-Fock calculations⁴³ suggest even more distinct delocalization of the spin density in NF_2 . The idea based on the spin densities gives a qualitatively correct picture. To give it a quantitative expression would mean to find a correlation between spin densities and ΔH_T^0 or K_p . Limits of such a treatment are conceivable, however, and the superiority of the approach to chemical reactivity by means of direct calculations of equilibrium constants is obvious.

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Translated by P. Čársky.