N,N-Difluoromethylamine

by Thomas D. Padrick and George C. Pimentel*

Chemistry Department, University of California, Berkeley, California 94720 (Received April 25, 1972) Publication costs assisted by the U. S. Air Force Office of Scientific Research

Hydrogen fluoride and deuterium fluoride chemical laser emission has been observed due to elimination from N_1N -difluoromethylamine and its deuterated analogs. Gaseous methyl iodide- N_2F_4 -Ar mixtures at or near 250°K are photolyzed through Vycor. Hydrogen fluoride laser emission is observed from $CH_3NF_2^{\dagger}$, CH_2 -DNF₂[†], and $CHD_2NF_2^{\dagger}$ and equal-gain temperature measurements indicate a vibrational population ratio $N_1/N_0 = 0.47 \pm 0.02$ from each precursor. Deuterium fluoride laser emission is observed from $CD_3NF_2^{\dagger}$ and $CHD_2NF_2^{\dagger}$ with population ratio $N_2/N_1 = 0.66$ from each precursor, but no DF emission was observed from $CH_2DNF_2^{\dagger}$. The relative intensities and population ratios indicate that laser emission is associated with the first elimination step only, $CH_3NF_2^{\dagger} \rightarrow CH_2$ ==NF + HF[†], and that in the mixed H-D precursors, HF elimination is 2.5 times more probable than DF elimination. The average vibrational energy imparted to HF is, within experimental uncertainty, equal to the average internal energy per vibrational degree of freedom, in accord with statistical theories of unimolecular decomposition.

Introduction

Laser emission has been reported¹ due to the elimination of vibrationally excited HF from CH_3NF_2 produced in the reaction between CH_3 and N_2F_4 . In this earlier work (which will, hereafter, be called I) a number of interesting questions were raised concerning the detailed chemical processes that are involved. Chemical studies have shown that HCN is produced,^{2,3} but they do not indicate whether the elimination occurs in one or in two steps. Nor, of course, do they indicate how the vibrational excitation might be apportioned if two steps are involved. We report here experiments based upon isotopically substituted methyl radicals that bear upon these questions.

Experimental Section

The experimental apparatus described in I was used with only slight modifications. All experiments used a Vycor laser tube fitted with NaCl Brewster angle windows. The deuterated methyl iodides, CD_3I (ICN Chemical & Radioisotope Div.), CH_2DI (Isotopes), and CHD_2I (Thompston Packard, Inc.), were purified by low temperature, bulb-to-bulb distillation *in vacuo*.

Results

As background for the interpretation of laser emissions from the deuterated diffuoromethylamines, a number of additional experiments were performed with the $CH_3I-N_2F_4$ system. The effect of added inert gas, noted in I, was studied in more detail and the equalgain temperature measurement⁴ was repeated under conditions of better control. These results are reported first, followed, in turn, by those involving CD_3I , CH_2DI , and CHD_2I .

 $CH_3I-N_2F_4$. Figure 1 shows the effect of inert gas (argon or methane) on the intensity and time to threshold for CH₃I-N₂F₄ mixtures photolyzed at 253°K. While the partial pressures of N₂F₄ and CH₃I were held constant (respectively at 0.27 and 1.1 Torr) the argon partial pressure was increased from 5.6 (Figure 1a) to 10.7 Torr (Figure 1b) and then to 15.7 Torr (Figure 1c). The time to threshold increased from 15 to 23 μ sec and then to 31 μ sec while the intensity steadily decreased. With 20 Torr argon, no laser emission occurred. Figure 1d shows the laser emission obtained with 1.1 Torr CH_4 and 5.5 Torr argon. Both the intensity and the time to threshold, 23 μ sec, suggest that 1 Torr CH_4 has an effect equivalent to at least 5 Torr Ar. In agreement with this conclusion, a mixture that contained 2 Torr CH₄ and 5 Torr Ar gave no laser emission.

To permit detailed comparison of the laser emissions of the various isotopically substituted diffuoromethylamines, it was necessary to establish more accurately the equal-gain temperature, T_{eg} , for CH₃NF₂. The problem of poor reproducibility in equal-gain temperature experiments has been under study in these laboratories⁵ and has clearly been related to mode spacing. In I, a 1-m optical cavity was used, which provides a longitudinal mode spacing of 0.005 cm⁻¹ (150 MHz).

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(2) J. W. Frazer, J. Inorg. Nucl. Chem., 16, 63 (1960).

⁽³⁾ C. L. Bumgardner, E. L. Lawton, and H. Carmichael, Chem. Commun., 1079 (1968).

⁽⁴⁾ J. H. Parker and G. C. Pimentel, J. Chem. Phys., 51, 91 (1969).
(5) M. J. Molina and G. C. Pimentel, *ibid.*, 56, 3832 (1972); see also, M. J. Molina, Ph.D. Dissertation, University of California, Berkeley, 1972.



Figure 1. Total HF laser emission from 0.27 Torr N_2F_4 , 1.1 Torr CH₃I, and various pressures of buffer gas: 253°K, 490 J flash energy; (a) 5.6 Torr argon; (b) 10.7 Torr argon; (c) 15.7 Torr argon; (d) 5.5 Torr argon plus 1.1 Torr CH₄.

This implies that, in an equal-gain experiment, the highest-gain longitudinal mode for either of the two transitions may miss the line center by as much as 0.0025 cm^{-1} . Since this is comparable to line widths under our experimental conditions, the gain of both transitions can vary capriciously from experiment to experiment due to slight cavity length changes. With the 1-m cavity, this caused the measured value of $T_{\rm eg}$ to vary over a range of 60°. To correct this difficulty, the experiments were repeated with a 2-m optical cavity, halving the mode spacing. Reproducibility was very much better and measurements over a 20° range were sufficient to establish $T_{\rm eg}$ reliably.

Clues to the effectiveness of rotational equilibrium, which is essential to the equal-gain technique, are provided by the sequencing of the observed transitions.⁶ Figure 2 shows the sequencing observed in the photolysis of 12 Torr of a 1:4:20 mixture of N₂F₄: CH₃I:Ar at 248°K. The first transition is P₁₋₀(4). The second transition to reach threshold is P₂₋₁(5), preceding by 5 µsec the emission by P₁₋₀(6), the $1 \rightarrow 0$ transition that directly pumps P₂₋₁(5). This shows there is not strong communication between connected transitions, which means that rotational equilibration is good.

Eleven equal-gain determinations were carried out with a 1:4:20 mixture of N₂F₄: CH₃I: Ar. The total pressure was varied from 7 to 22 Torr and no pressure dependence could be discerned. Except for one measurement at 235°K, all values were in the range 246– 255°K. The absence of pressure dependence implies that *J*-dependent pressure-broadening effects and vibrational relaxation are negligible. The average value of T_{eg} for the P₁₋₀(4) and P₁₋₀(5) transitions is

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Figure 2. Sequencing of the HF transitions observed in the photolysis of 12 Torr of a 1:4:20 mixture of N₂F₄:CH₃I:Ar: 248°K, 490 J flash energy.



Figure 3. DF laser emission observed in the photolysis of 12 Torr of a 1:4:20 mixture of $N_2F_4:CD_3I:Ar: 248^{\circ}K$, 490 J flash energy.

249°K with a standard deviation $\sigma = 5.4^{\circ}$ ($\sigma_{11} = 1.6^{\circ}$ K). From this value of T_{eg} and the equal-gain temperature equations,^{4,5} we calculate $N_1/N_0 = 0.47 \pm 0.01$ for the CH₃NF₂ elimination laser.

 $CD_3I-N_2F_4$. Figure 3 shows the total DF laser emission and also that due to $P_{2-1}(6)$, as observed after photolysis of 12 Torr of a 1:4:20 mixture of N_2F_4 : CD_3 -I:Ar at 248°K. The DF laser emission reached threshold about 4 μ sec later than the HF emission shown in Figure 2, but the integrated detector signal exceeded that for HF under exactly the same conditions. In three pairs of experiments, the DF/HF integrated intensity ratio averaged 1.55 with an average

⁽⁶⁾ K. L. Kompa, J. H. Parker, and G. C. Pimentel, J. Chem. Phys., 49, 4257 (1968).



Figure 4. Sequencing of the DF transitions in the N_2F_4 : CD₃I: Ar experiment shown in Figure 3.

deviation of 0.26. We shall use such area ratios as relative measures of the amounts of HF and DF emission in the mixed isotope experiments; the ratios are not directly interpretable because the DF gain is undoubtedly lower than that for HF but the detector is more sensitive in the DF spectral region. Figure 4 shows the sequencing; the first v = 1-0 transitions to reach threshold were $P_{1-0}(5)$ and $P_{1-0}(6)$, each about 2 μ sec after $P_{2-1}(5)$ and $P_{2-1}(6)$.

Table I lists the results of equal-gain determinations. The average value of T_{eg} for the $P_{2-1}(5)$ and $P_{2-1}(6)$ transitions is 242°K with estimated uncertainty ± 6 °K. This value of T_{eg} corresponds to $N_2/N_1 = 0.66 \pm 0.01$.

 $CH_2DI-N_2F_4$. Photolysis of 12 Torr of a 1:4:20 mixture of N₂F₄: CH₂DI: Ar at 253°K produced HF laser emission but no DF emission, even at higher total pressure, 24 Torr. The HF emission included the same transitions as CH₃I and it displayed threshold time, intensity, and duration that were all quite similar to those obtained from CH₃I (compare Figure 5a and 1a). Equal-gain determinations, listed in Table I, gave T_{eg} = 254 ± 6°K for the P₁₋₀(4) and P₁₋₀(5) transitions. This corresponds to $N_1/N_0 = 0.48 \pm 0.01$.

 $CHD_2I-N_2F_4$. Figure 5b shows the total emission observed from 12 Torr of a 1:4:20 mixture of N₂F₄: CHD_2I : Ar at 253°K. Both HF and DF emission are included, as shown in Figure 5c, which is the total laser emission transmitted by an interference filter, which blocks all HF emission and transmits about 73% in the DF spectral range. In six pairs of experiments like that shown in Figures 5b and 5c, the DF/HF area ratio was measured to provide an estimate of the relative

Table I: EPlus Methyl	qual-Gain Iodide	Tempera	tures for N_2F_4	
Isotopic species	Total pressure, ^a Torr	HF/DF	Transition	$T_{eg,b}^{reg,b}$ °K
${ m CH_{3}I}$	7-22 ^c	\mathbf{HF}	$P_{1-0}(4)/P_{1-0}(5)$ Av	249 ± 3
$\mathrm{CD}_3\mathrm{I}$	$8\\8\\12$	DF DF DF	$P_{2-1}(5)/P_{2-1}(6)$ Av	$241 \\ 236 \\ 249 \\ 242 \pm 6$
$\mathrm{CH}_{2}\mathrm{DI}$	10 12 17	HF HF HF	$P_{1-0}(4)/P_{1-0}(5)$ Av	$252 \\ 255 \\ 254 \\ 254 \pm 6$
CHD₂I	$12 \\ 12 \\ 12 \\ 15 \\ 15 \\ 12 \\ 15 \\ 12 \\ 15 \\ 12 \\ 12$	HF HF HF HF	$P_{1-0}(4)/P_{1-0}(5)$ Av	$241 \\ 238 \\ 255 \\ 235 \\ 242 \pm 5$
	$\frac{12}{16}$	DF DF	$P_{2-1}(5)/P_{2-1}(6)$ Av	$249 \\ 238 \\ 243.5 \pm 8$

^a All methyl iodides were studied at the same relative composition, N₂F₄: CH_nD_{3-n}I: Ar = 1:4:20. ^b Uncertainties specified are $2\sigma_n$ where $\sigma_1 = 5.4$ °K, taken from the CH₃I experiments and $\sigma_n = \sqrt{5.4/n}$ where *n* is the number of measurements averaged. ^c Eleven measurements, $\sigma_1 = 5.4$ °K, $\sigma_{11} = 1.6$ °K (see text).



Figure 5. Laser emission from photolysis of N_2F_4 and partially deuterated methyl iodides: $253^{\circ}K$, 490 J flash energy; (a) HF emission from 12 Torr of a 1:4:20 mixture of N_2F_4 : CH₂DI:Ar; (b) HF + DF emission from 12 Torr of a 1:4:20 mixture of N_2F_4 : CHD₂I:Ar; (c) DF emission only from sample b (73% transmission filter).

probability of DF and HF elimination. The DF area was divided by the filter transmission factor, 0.73, and then subtracted from the combined HF and DF area to give the HF area. The six experiments gave an average DF/HF intensity ratio of 0.36 with a standard

deviation of 0.16. If we interpret this ratio with the aid of the area ratio obtained from CD_3NF_2 and CH_3-NF_2 , 1.55, the results suggest that $19 \pm 8\%$ of the hydrogen fluorides eliminated from CHD_2NF_2 are DF and $81 \pm 8\%$ are HF. The first transitions to reach threshold were the same as for CH_3I and CD_3I , *i.e.*, $1 \rightarrow 0$ transitions for HF and $2 \rightarrow 1$ transitions for DF.

Equal-gain studies were conducted for both the HF and DF emissions, as summarized in Table I. For HF from CHD₂NF₂, $T_{eg} = 242 \pm 5^{\circ}$ K for the P₁₋₀(4) and P₁₋₀(5) transitions, to give $N_1/N_0 = 0.46 \pm 0.01$. For DF from CHD₂NF₂, $T_{eg} = 243.5 \pm 8^{\circ}$ K for the P₂₋₁(5) and P₂₋₁(6) transitions, to give $N_2/N_1 = 0.66 \pm 0.01$.

Discussion

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The sequence of reactions we must consider is as follows.

$$CH_3 + N_2F_4 \longrightarrow CH_3NF_2^{\dagger} + NF_2 \qquad (1)$$

$$CH_3 + NF_2 \longrightarrow CH_3NF_2^{\dagger\dagger}$$
 (1a)

$$CH_3NF_2^{\dagger} \longrightarrow CH_2 = NF^{\dagger} + HF^{\dagger}$$
 (2)

$$CH_2 = NF^{\dagger} \longrightarrow HCN + HF^{\dagger}$$
(3)

The energy available for elimination depends upon whether reaction 1 or 1a is operative, so that question is considered first. Then the effect of argon will be discussed, again because of its importance to the laser performance. Thereafter, the significance of the laser emissions observed from the isotopically substituted species can be assessed.

Production of $CH_3NF_2^{\dagger}$. In I, it was assumed that reaction 1 initiates the elimination that accounts for the laser emission. In contrast, Brus and Lin feel that (1a) accounts for the HF elimination, both in their room temperature studies⁷ and in I. This proposal is plausible under their experimental conditions, where the N_2F_4/NF_2 ratio is maintained near 50 by the dimerization equilibrium. In a footnote (and without details) Brus and Lin⁷ refer to an RRKM estimate of $k_{1a}/k_1 \sim$ 100 at 300°K. If this estimate is accepted, it can be coupled with the room temperature N_2F_4/NF_2 equilibrium ratio to indicate that the CH_3NF_2 formed by (1a) is twice that formed by (1).

The experimental conditions used in I and in the present work give quite a different picture. With temperatures in the range $240-255^{\circ}$ K, and N₂F₄ pressures near 1 Torr (as were used in some experiments), the N₂F₄/NF₂ ratio is near 1000 and the NF₂ equilibrium pressure has dropped to 10^{-3} Torr. This must slow down reaction 1a 20-fold and, if (1a) were the dominant pumping reaction, there should be a dramatic increase in the time to reach threshold, which is not observed. Furthermore, the NF₂ pressure is now one or two orders of magnitude lower than the CH₃ partial pressure produced by the flash.⁸ Since (1a) probably has about the same rate constant as the CH₃ + CH₃ reaction, the

amount of CH_3 consumed in (1a) would decrease to only a small fraction of that lost to ethane formation, again drastically impairing laser performance. Since overall laser gain attributable to elimination is rather little affected by temperature, reaction 1a cannot be the dominant pumping reaction at the low temperatures.

These difficulties are eliminated if reaction 1 is also a significant pumping reaction. The $k_{1a}/k_1 \sim 100$ estimate, if applicable at the low temperatures, would indicate that the CH_3NF_2 produced by (1) would be ten times larger than that formed by reaction 1a. There is, however, significant reason for believing that k_{1a}/k_1 is much smaller than 100. The reactions CH₃ + $X_2 \rightarrow CH_3X + X$ can be regarded as prototypes for reaction 1. In the series Cl_2 , Br_2 , and I_2 , as the X_2 bond energy decreases from 57 to 45 kcal, and then to 35 keal, the activation energy decreases from 3.6 to 0.7 kcal and then to 0 kcal.⁹ Since the bond energy of N_2F_4 , 20 kcal, is even lower than that of I_2 , the comparison indicates that reaction 1 has zero activation energy. This implies that k_{1a}/k_1 is probably nearer unity and not much dependent upon temperature. With this estimate, over 99% of the CH₃NF₂ comes from reaction 1 at 250°K and (1a) becomes unimportant. We conclude that, at the low temperatures used in our experiments, reaction 1 is both the dominant source of CH_3NF_2 [†] and the effective pumping reaction.

Effect of Inert Gases. The delay and weakening of the laser emission caused by added argon or methane (see Figure 1) implies a deactivation process. This cannot be attributed to HF vibrational deactivation by argon because argon is known to be quite ineffective. Airey and Fried¹⁰ estimate that more than 2×10^4 argon-HF collisions are needed, on the average. In the conditions appropriate to Figure 1b, there are about 100 HFargon collisions per microsecond (at 10 Torr pressure) but the time to threshold is nearly double the 15 μ sec threshold time observed at 5 Torr total pressure. Yet in 15 μ sec, an average HF molecule would have encountered no more than about 750 argon atoms, an order of magnitude too low to account for the delay.

Deactivation of excited $CH_3NF_2^+$ before elimination offers another possible explanation of the inert gas pressure effect. Ross and Shaw¹¹ have estimated the rate constant for the elimination of HF from excited CH_3 - $NF_2^{\dagger}^{\dagger}$ to be $10^{10.3}$ sec⁻¹, which gives a half-time of

⁽⁷⁾ L. E. Brus and M. C. Lin, J. Phys. Chem., 75, 2546 (1971).

⁽⁸⁾ T. Ogawa, G. A. Carlson, and G. C. Pimentel, *ibid.*, **74**, 2090 (1970).

^{(9) (}a) See H. S. Johnston and P. Goldfinger, J. Chem. Phys., **37**, 100 (1962); (b) see A. F. Trotman-Dickenson and G. S. Milne, Nat. Bur. Stand. (U. S.), Data System, **9** (1967), from $E^{\pm}(M/HBr) = E^{\pm}(M/Br_2) = 2.0$, $E^{\pm}(M/HBr) - E^{\pm}(M/I_2) = 1.0$ (av), $M = CH_3$; (c) M. C. Flowers and S. W. Benson, J. Chem. Phys., **38**, 882 (1963). Note: measured value $E^{\pm} = 1.5$ considered by authors to be ≈ 1 kcal high.

⁽¹⁰⁾ J. R. Airey and S. F. Fried, Chem. Phys. Lett., 8, 23 (1971).

⁽¹¹⁾ D. S. Ross and R. Shaw, J. Phys. Chem., 75, 1170 (1971).

 3.6×10^{-11} sec. This half-time means that at 10 Torr, with one collision every 10^{-8} sec, elimination could not be affected by collisions. It must be remembered, of course, that Ross and Shaw are dealing with CH₃NF₂†† formed from CH₃ + NF₂ (reaction 1a), rather than from CH₃ + N₂F₄, as in the present experiments. Hence our excitation is lower by the N-N bond energy in N₂F₄, 20 kcal, and by whatever energy is partitioned into the NF₂ fragment, which we estimate to be 10 kcal or more. With perhaps 30 kcal less excitation, the rate of elimination could be appreciably slower. Nevertheless, we do not regard this as a likely explanation of the argon effect.

The observations are consistent with the interpretation that methyl radicals with excess translational and/or internal energy are required in reaction 1. In I, the activation energy, E_2^{\pm} , for elimination from CH₃NF₂ was shown to exceed 30 kcal on the basis of the known stability of CH₃NF₂. Ross and Shaw¹¹ offer two additional estimates based on deactivation studies, RRK or RRKM modelling, and the usual array of assumptions about collision efficiency, effective number of oscillators, and the nature of the transition state. These estimates place E_2^{\pm} between about 35 and 42 kcal/mol. Brus and Lin⁷ offer another estimate, 38 kcal, also based upon RRKM modelling. We will use this last value as a mean, with an uncertainty fixed by the range, $E_2^{\pm} = 38 \pm 5$ kcal/mol.

The internal energy available for elimination depends upon ΔH_1 , the exothermicity of reaction 1 and the energy division between the product fragments. In I, ΔH_1 was estimated to be about -60 kcal, assuming that the CN bond energy is the same as in methylamine. 85 kcal (as derived from tabulated heats of formation¹² for CH₃NH₂, CH₃, and NH₂). However, Dykstra, et al.,¹³ have presented kinetic evidence that suggests the diffuoromethylamine CN bond energy is only 56 kcal while Ross and Shaw¹¹ estimate 60 kcal. Accepting the latter figure implies that $\Delta H_1 = -40$ kcal. As indicated in I, the CH₃NF₃ might receive about 83% of the energy that goes into vibration (at most, 33 kcal) and only 44% of the energy that goes into translation. Thus, the lower CN bond energy, taken with the 38 kcal activation energy estimate, implies that reaction 1 produces CH₃NF₂[†] that cannot eliminate HF. The energy deficit, which would probably be in the range 5-15 kcal, might be made up by reactions involving "hot" methyl radicals.

The energy imparted to a photolytic CH₃ can be estimated. If photolysis occurs near 2576 Å (the peak of the CH₃I absorption band), the quanta carry 111 kcal/mol of energy, 57 kcal more than the C–I bond energy. Hancock and Wilson¹⁴ have measured the energy distribution between the photolysis products and conclude that about 5/6 of the bond ruptures give excited iodine atoms, $I(^{2}P_{1/2})$, and $^{1}/_{6}$ give ground state atoms, $I(^{2}P_{3/2})$. When $I(^{2}P_{1/2})$ is formed, the CH₃ fragment receives about 27 kcal of translational energy and 5.5 kcal of internal energy (vibration and rotation). When $I({}^{2}P_{*/_{2}})$ is formed, Hancock and Wilson find that the CH₃ fragment is given about 41 kcal of translational energy and 11 kcal of internal energy.¹⁴ The internal energies lodged in CH₃, 5.5 and 11 kcal, compare favorably to the 10 kcal estimate of Bass and Pimentel.¹⁵ This estimate is based on the assumption that the Franck-Condon principle is operative, which suggests that most of the internal energy is placed in vibrational excitation of the ν_{2} "umbrella" mode. The work of Callear and Van den Bergh¹⁶ also supports this contention. These workers found that vibrationally excited methyl radicals are produced in the photolysis of dimethylmercury.

The Ar: N₂F₄ and CH₃I: N₂F₄ ratios are 20 and 4, respectively. This suggests that most of the CH₃ translational energy will be lost in collisions with Ar or CH_aI before a reactive collision occurs. Removal of vibrational energy is more difficult, however. Callear and Van den Bergh¹⁶ found that it takes about 200 Ar collisions or 35 CH_4 collisions to deactivate their vibrationally excited methyl radicals. This relative deactivation efficiency is reasonably consistent with the observation, shown in Figure 1, that CH_4 delays and attenuates the laser emission about 4 to 8 times as effectively as does Ar. All of the data are consistent with the interpretation that excited methyl radicals are formed and that they contain internal energies of 5 to 10 kcal, probably enough to activate the diffuoromethylamine above its critical energy for HF elimination.

This conclusion implies that the energy held by CH_3NF_2 [†] just before elimination is quite close to the activation energy, which we have taken to be 38 ± 5 kcal.

Isotopic Comparisons. Table II summarizes the vibrational populations implied by the equal-gain temperature data in Table I. For both HF and DF, the derived population ratios are found to be independent of the parent. This fact, coupled with the observation that DF emits weakly from CHD_2NF_2 and not at all from CH_2DNF_2 , permits some conclusions about the elimination process. For example, consider a two-step elimination in which HF† excitation is identical with the two steps (reactions 2 and 3). Such a model would explain the constancy of the population ratios, but the DF emission from CHD_2NF_2 would be expected to be

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⁽¹³⁾ A. J. Dykstra, J. A. Kerr, and A. F. Trotman-Dickenson, J. Chem. Soc. A, 105 (1967).

⁽¹⁴⁾ G. Hancock and K. R. Wilson, Proceedings of the Esfahan Symposium on Fundamental and Applied Physics, Ali Javan, Ed., Aug 29-Sept 5, 1971.

⁽¹⁵⁾ C. D. Bass and G. C. Pimentel, J. Amer. Chem. Soc., 83, 3754 (1961).

⁽¹⁶⁾ A. B. Callear and H. E. Van den Bergh, Chem. Phys. Lett., 5, 23 (1970).

between 1/2 and 2/3 as intense as observed from CD₃- NF_2 , depending upon whether HF elimination is strongly favored or whether HF and DF elimination are equally probable. (The $k_{\rm H}/k_{\rm D}$ ratio found for the fluoroethanes,¹⁷ $k_{\rm H}/k_{\rm D} = 3.1$, would give DF emission 0.55 times that from CD_3NF_2 .) The observed intensity, 19% of the CD₃NF₂ emission, contradicts this model. If a two-step elimination is pictured in which reaction 3 gives a lower vibrational excitation than reaction 2, the weakness of the DF emission from CHD₂- NF_2 can be explained by assuming that H is preferentially eliminated in the first step, as suggested by the behavior of the fluoroethanes.¹⁷ However, this leads to the expectation that the N_1/N_0 ratio for HF should be higher from CHD₂NF₂ than from CH₃NF₂ and that the N_2/N_1 ratio for DF should be lower than from CD₃NF₂. The constancy of the population ratios is now in conflict with the model. These contradictions are not avoided by assuming simultaneous ejection of two hydrogen fluorides.

Isotopic species	$_{N_1/N_0}^{\rm HF}$	${ m DF}_{N_2/N_1}$
${ m CH_2NF_2}\ { m CH_2DNF_2}\ { m CHD_2NF_2}\ { m CHD_2NF_2}\ { m CD_3NF_2}$	0.47 0.48 0.46^{b}	0.66^{b} 0.66

^a All population ratios carry an estimated uncertainty of ± 0.01 . ^b Intensities suggest that 81% of eliminations give HF and 19% give DF.

We are left with the interpretation that reaction 3 does not occur within the time scale of our observations. Since only reaction 2 is effective in pumping, the constancy of population ratios becomes reasonable. The CH₂DNF₂ and CHD₂NF₂ results merely indicate a preferential elimination of H over D, as would be expected in any case. The DF intensity from CHD₂NF₂ suggests that HF elimination per H atom is 2.5 times more probable than DF elimination per D atom. This is in reasonable accord with the fluoroethane result¹⁷ quoted earlier, $k_{\rm H}/k_{\rm D} = 3.1$.

Energy Distribution. The RRKM theory of unimolecular decomposition contains the postulate that the internal energy is randomly distributed among the internal degrees of freedom of the energized molecule.¹⁸ Our data furnish some information about the energy disposed in one degree of freedom and, hence, an opportunity to test this statistical hypothesis. This was attempted in I, but with the premise that the sum of the exothermicities of reactions 2 and 3 was accessible. Since the present work indicates only the first step, re-



Figure 6. Energy diagram for HF elimination from CH₃NF₂.

action 2, is involved in the pumping, the significance of the data must be reassessed.

Figure 6 shows a schematic representation of the thermochemistry for reactions 2 and 3. We assume that CH_3NF_2 † contains just the 38 ± 5 kcal needed to surmount the presumed activation energy barrier. The exothermicity of reaction 2 and reaction 3 is relatively well known; the most uncertain element is the C-N bond energy, as mentioned earlier.

$$\Delta H_2 + \Delta H_3 = \Delta H_f^{\circ}(\text{HCN}) + 2\Delta H_f^{\circ}(\text{HF}) + D_0(\text{CH}_3-\text{NF}_2) - \Delta H_f^{\circ}(\text{CH}_3) - \Delta H_f^{\circ}(\text{NF}_2) = 32.3 + 2(-64.8) + 60 - 33.2 - 10.3 = -80.8 \text{ kcal}$$

The exothermicity of reaction 2 is more difficult to guess. If the C==NF bond energy is taken to be double that of C-NF₂, as is consistent with the relative magnitudes of CN bond energies listed by Cottrell,¹⁹ then ΔH_2 is -33 kcal. If the overall exothermicity is assumed to be equally divided between reactions 2 and 3, then $\Delta H_2 = -40$ kcal. We will take the latter figure as our best estimate.

This value of ΔH_2 leads to an internal energy in CH₃NF₂† equal to 38 + 40 = 78 kcal with an uncertainty of perhaps 10 kcal. If this energy is divided equally among the 15 vibrational degrees of freedom, there is about 5.2 kcal/degree of freedom.

This result can be compared to the information provided by our equal-gain temperature measurements. For HF, we find $N_1/N_0 = 0.47$. Furthermore, the observation that $v = 1 \rightarrow 0$ reaches threshold before the $v = 2 \rightarrow 1$ transition implies that $N_2/N_1 \leq 0.45$. If no higher levels are excited, the average energy in vibration is ≤ 6.0 kcal. If the N_2/N_1 ratio were 0.25 and $N_3/N_2 = 0$, the average energy would drop to 5.0 kcal, but it would rise to 5.5 again if N_3/N_2 also were 0.25.

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⁽¹⁸⁾ See, for example, K. Dees, D. W. Setzer, and W. S. Clark, J. Phys. Chem., 75, 2231 (1971).

⁽¹⁹⁾ T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 1958.

The DF ratio, $N_2/N_1 = 0.66$, gives similarly reasonable results. For example, if we assume for DF that N_1/N_0 $= N_2/N_1 = 0.66$ and $N_3 = N_4 = 0$, the average energy is 6.0 kcal; if $N_1/N_0 = N_3/N_2 = 0.33$ and $N_2/N_1 =$ 0.66, the average energy is 5.0 kcal. Plainly, these indications of the average energy in the HF or DF vibrational motion are consistent with the statistical estimate within the uncertainty that must be ascribed to the comparison.

Elimination from $CH_2=NF$. The conclusion that reaction 3 plays no role in the laser emission must be rationalized with the chemical evidence that hydrogen cyanide is a final product.^{2,3,11} In this regard, it is perhaps significant that in all of this earlier work, reaction 1a was probably responsible for much of the CH_3 -NF₂† formation. It is possible that CH_3NF_2 † from reaction 1 will eliminate only one HF molecule (reaction 2) while CH_3NF_2 † from reaction 1a can eliminate two (reaction 2 followed by reaction 3). Another possibility is that reaction 3 occurs even in our experiments, but on a much slower time scale than needed to affect the laser emission.

To evaluate these alternatives, it becomes interesting to try to estimate the energy received by $CH_2 = NF^{\dagger}$. A natural starting point, in the light of the previous section, is to assume a statistical distribution among the degrees of freedom. As reaction 2 occurs, five of the fifteen vibrational degrees of freedom of CH₃NF₂ become translations and rotations. We might assume that these degrees of freedom will receive 5/15 of the available 80 ± 10 kcal, or 27 kcal. This energy will mainly go to the light fragment but, in any case, will probably be ineffective in aiding elimination. The remaining 53 kcal might be divided between CH₂==NF and HF in proportion to the numbers of vibrational degrees of freedom, in which case CH_2 =NF would receive 90%, or 48 kcal. This estimate is somewhat larger than the 38 kcal activation energy deduced for elimination from CH_3NF_2 [†]. However, the activation energy for elimination from the imine is probably at least 10 kcal higher than for the diffuoroamine, judging by the activation energy for elimination from vinyl fluoride, estimated to be \sim 71 kcal/mol by Simmie, et al.,²⁰ and ~81 kcal/mol by Cadman and Engelbrecht,²¹ compared to that for fluoroethane, 60 kcal/ mol.²² These considerations all suggest that the energy available for elimination from CH_2 =NF† is marginally close to the activation energy. This makes creditable the explanation that two steps of elimination can occur from CH_3NF_2 † formed in reaction 1a but only one step from CH_3NF_2 † formed in reaction 1.

Conclusions

These experiments lead then to the rather unexpected, hence interesting, conclusion that the reaction between CH_3 and N_2F_4 is only marginally effective in initiating elimination from $CH_3NF_2^{\dagger}$ and it does not encourage significantly the second step elimination from CH_2 ==NF[†]. Reaction 2 needs energetic assistance from "hot" methyl radicals and reaction 3 does not seem to occur at all on the time scale of the laser experiment.

With this clarification of the important processes, it is possible to verify, for the CH_3NF_2 elimination, that the energy entering the HF vibrational degree of freedom is close to what is expected on the basis of a statistical energy distribution. This not only adds a useful experimental tiepoint for statistical theories of unimolecular decomposition but it also provides a working hypothesis for understanding the low vibrational excitation already displayed in elimination reactions^{1,23-26} and for predicting the behavior of new, similar reactions.

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