

Unimolecular Decomposition of 1,2- and 2,2-Bis(difluoramino)propane

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Abstract: The pyrolyses of 1,2- and 2,2-bis(difluoramino)propane were carried out at 650 and 750°, respectively, and at 10⁻³ to 10⁻² Torr. The major reaction of 1,2 isomer is stepwise loss of both NF₂ groups to yield propylene, this process being the microscopic reverse of the addition of N₂F₄ to olefins. Minor reactions include dehydrofluorination and migration of fluorine from nitrogen to carbon. The 2,2 isomer decomposes completely by initial C-N scission, followed by both (1) migration of fluorine from nitrogen to carbon with subsequent fragmentation yielding both the syn and anti isomers of CH₃C(NF)F, and (2) loss of fluorine to yield (CH₃)₂C=NF. The strengths of the C-N bonds in the 1,2 and 2,2 isomers are about 55 and 45 kcal/mol, respectively. In a limited study, 1,1-bis(difluoramino)propane, pyrolyzed at 650°, undergoes C-N scission followed by fluorine migration to yield both the syn and anti isomers of HC(NF)F.

Recent studies of organic compounds containing NF₂ groups have provided information concerning both their preparation and their chemistry.¹ However, the only account of the gas-phase decomposition of these materials is that of Cerfontain² who reported that the pyrolyses of the N₂F₄ adducts of *trans*-stilbene and anthracene at 220° lead mainly to the formation of the parent aromatic hydrocarbon. We have carried out a study of the thermal decomposition of two bis(difluoramino)alkanes.

Initial studies in sealed Pyrex ampoules showed that the decomposition proceeded mostly by a surface-catalyzed dehydrofluorination and yielded primarily polymeric products at all but the lowest conversions.

To minimize these wall effects, we used for the present study a variation of the technique of very-low-pressure pyrolysis (VLPP) described by Benson, *et al.*³ In their apparatus, molecules are passed through a reactor at about 10⁻³ Torr and acquire energy primarily by colliding with the heated walls. If they gain sufficient energy before leaving the reactor, the molecules decompose unimolecularly. Chain processes are not possible owing to the low pressure, and wall-catalyzed decomposition is minimized by operation at high temperatures. The effluent is passed directly into a mass spectrometer.

In our modification of this procedure, the reactor is run so that the pressures are about an order of magnitude higher than in VLPP, and the effluent is condensed in a liquid nitrogen trap. The materials can then be isolated and submitted for analysis by vpc, ir, and nmr.

This paper discusses the study of two compounds that have two NF₂ groups per molecule, 1,2-bis(difluoramino)propane (I) and 2,2-bis(difluoramino)pro-

pane (II). Since in I the NF₂ groups are arranged



vicinally whereas in II the arrangement is geminate, it was of interest to look for differences in both reaction path and kinetics for the decomposition of these two compounds.

Experimental Section

Materials. Compounds I and II are both known to be sensitive to shock, and the neat materials were handled carefully in small quantities at all times. Compound I was obtained from Dr. Manfred Czieles of the Naval Ordnance Station, Indian Head, Md. It was received and stored in 50% solution in CH₂Cl₂ and separated just before use. Compound II was obtained from the Aerojet General Corp. in solution in Arochlor 1248. It too was separated just before use.

Apparatus and Procedure. The reactor is a fused, silica cylinder, 10 cm long and 2.2 cm in diameter, with an exit aperture 0.95 cm in diameter. The material to be studied is stored in a sample bulb at several Torr and allowed to diffuse through a needle valve at a rate that gives 10⁻³ to 10⁻² Torr in the reactor. The residence time is about 10 msec. The oven heating and insulation are like those described in ref 3a, except that in this case, the current to the main heater is controlled by a Model SCR stepless temperature controller.⁴

Experiments were run for 5 to 10 hr. Materials emerging from the reactor were collected in a large liquid nitrogen cooled trap, and at the end of a run the condensate was vacuum transferred to a smaller U-trap. This secondary trap was then removed from the system, and the contents were analyzed. In some cases the pyrolysis products were transferred directly to a gas ir cell for ir analysis of the entire mixture of products. Gas chromatographic analysis was carried out on toluene solutions of the product mixtures, using a 6-ft column of 20% didecyl phthalate on 45/60 firebrick. The separated components were cleanly isolated and submitted individually for ir, nmr, or mass spectrometric analysis.

The mass balances were approximately 50%, and the trapping efficiency was better than 90%. Thus, the difficulties in isolation were not so much those of trapping volatile compounds, but rather subsequent reactions that apparently occur in condensed N₂F₄ systems. This kind of problem is found as well in condensed N₂O₁-hydrocarbon systems.⁵ A nonvolatile yellow residue, which was

(1) (a) A. Logothetis and G. Sausen, *J. Org. Chem.*, **31**, 3689 (1966); (b) K. Baum and H. Nelson, *J. Amer. Chem. Soc.*, **88**, 4459 (1966); (c) S. K. Brauman and M. E. Hill, *ibid.*, **89**, 2127 (1967); (d) *ibid.*, **89**, 2131 (1967); (e) A. J. Dijkstra, J. A. Kerr, and A. J. Trotman-Dickenson, *J. Chem. Soc. A*, 582 (1966); (f) *ibid.*, 105 (1967); (g) *ibid.*, 864 (1967).

(2) H. Cerfontain, *J. Chem. Soc.*, 6602 (1965).

(3) (a) S. W. Benson and G. N. Spokes, *J. Amer. Chem. Soc.*, **89**, 2525, 6030 (1967); (b) *J. Phys. Chem.*, **72**, 1182 (1968); (c) K. King, D. Golden, G. N. Spokes, and S. W. Benson, *Int. J. Chem. Kinet.*, **3**, 411 (1971).

(4) Manufactured by West Instrument Corp., Schiller Park, Ill.
(5) R. Shaw, private communication.

water soluble and contained ionic fluoride, was consistently formed in the trap. The residue was otherwise uncharacterized.

N-Fluoriminoacetyl Fluoride [$\text{CH}_3\text{C}(\text{NF})\text{F}$]. This material was isolated from the pyrolysis of II as a 50:50 mixture of its syn and anti isomers. The mass spectrum of the syn-anti mixture of $\text{CH}_3\text{C}(\text{NF})\text{F}$ showed an intense parent peak (m/e 79) plus four lesser peaks corresponding to ions resulting in loss of F or N from the C_2 fragment. CH_3^+ was the most intense peak. The two isomers were separated by gas chromatography. Their individual nmr spectra each show a doublet of doublets centered at τ 7.93 for



the syn isomer and at τ 7.76 for the anti isomer with $J_{\text{HCF}^{\text{syn}}} = 12$ cps; $J_{\text{HNF}^{\text{syn}}} = 6$ cps; $J_{\text{HCF}^{\text{anti}}} = 13$ cps; and $J_{\text{HNF}^{\text{anti}}} = 8$ cps. The structural assignments are based on the assumption that a cis geometry of F and CH_3 groups results in a larger spin coupling than a trans geometry.^{1a,c}

2-(N-Fluorimino)propane [$(\text{CH}_3)_2\text{C}=\text{NF}$]. This material was also isolated from the pyrolysis of II, and since we have no compelling evidence bearing on its structure, the assignment is speculative. The nmr spectrum of the material isolated by gas chromatography consists of an unsymmetrical triplet centered at τ 8.1 with $J = 5.0$ cps between the first and second peaks and $J = 3.8$ cps between the second and third peaks. This pattern may be considered to be that of two overlapping doublets; thus, the nmr spectrum is consistent with the assigned structure. The mass spectrum is not easily interpreted.

Results

In the pyrolyses of I and II, I decomposed in the range 650 to 750° and II in the range 450 to 550°. Table I summarizes the detailed product analyses for

Table I. Product Data for the Pyrolysis of 1,2- and 2,2-(NF_2) $_2\text{C}_3\text{H}_6$

Reactant (temp, °C)	Products	Percentage of product mixture ^a
1,2-(NF_2) $_2\text{C}_3\text{H}_6$ (650-750)	Propylene	~95
	N_2F_4	<i>c</i>
	$\text{CH}_3\text{C}(\text{NF})\text{CN}^b$	~5
	CH_3CN	
	FCH_2CN	
	HCN	
2,2-(NF_2) $_2\text{C}_3\text{H}_6$ (450-550)	Unidentified	62
	$\text{CH}_3\text{C}(\text{NF})\text{F}^d$ (anti and syn)	
	N_2F_4	<i>c</i>
	HCN	11
	CH_3NF_2	6
	$(\text{CH}_3)_2\text{C}=\text{NF}^e$	21

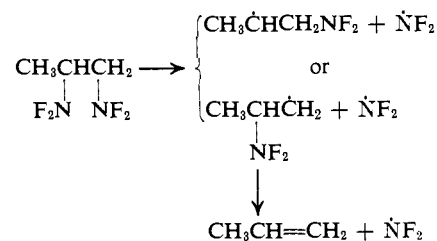
^a Identification of these compounds was made by analysis by ir, nmr, and mass spectrometry. Percentages are based on gas chromatography peak areas. SiF_4 was observed in most experiments, identified by its ir absorption at 9.8 μ . ^b Reference 1a. ^c The N_2F_4 was identified qualitatively by ir. ^d A new compound. See Experimental Section. ^e Tentatively identified. See Experimental Section.

the pyrolyses. Although N_2F_4 was undoubtedly a major product in the decomposition of both compounds, it was noted only qualitatively, and the results will be discussed with this reservation in mind.

Discussion

1,2-Bis(difluoramino)propane. Propylene is the major product from the decomposition of I (Table I); this suggests that the principal reaction is the reverse of

the stepwise addition of N_2F_4 to olefins, studied by Dijkstra, Kerr, and Trotman-Dickenson (DKT).^{1e-g}

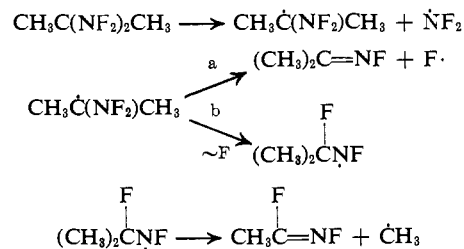


At the lower pressures within the reactor, compounds such as alkyl difluoramines are not in their first-order kinetic region, and for this reason, the kinetic parameters governing the reactions could not be obtained by a simple Arrhenius treatment of the data. On the other hand, since the pressure in the system was about an order of magnitude higher than in the VLPP procedure, we could not use the kinetic analysis employed by Benson, *et al.*^{3c}

A rough analysis in terms of RRK theory,⁶ however, showed that the activation energy for the C-N scission was about 55 kcal/mol.⁷ This value compares well with the DKT value of 56 kcal/mol.^{1f,8}

The minor products isolated, including CH_3CN , FCH_2CN , and HCN, are probably the result of wall-promoted reactions, although the case for $\text{CH}_3\text{C}(\text{NF})\text{CN}$ is not clear since it results from the loss of three molecules of HF from I, and it has been shown⁹ that vibrationally excited alkyldifluoramines can undergo unimolecular dehydrofluorination.

2,2-Bis(difluoramino)propane. The major products from the pyrolysis of II at 450 to 550° are the syn and anti isomers of $\text{CH}_3\text{C}(\text{NF})\text{F}$, and $(\text{CH}_3)_2\text{C}=\text{NF}$. A mechanistic scheme explaining the formation of these products is one involving two paths for decomposition of the radical formed initially by C-N scission.



The fluorine atom rearrangement by path b is unusual. A radical generated at an NF_2 -bearing carbon generally proceeds to the fluorimine.^{10,11} In such cases, however, photolytic methods of fluorine-promoted hydrogen abstractions were used, and the radicals were probably generated in a vibrationally excited

(6) G. Emanuel, Aerospace Corp., Report STR-0200(4240-20)-5, Jan 1969.

(7) The activation energy values estimated are probably good to ± 3 kcal/mol.

(8) In their study of the addition of N_2F_4 to several olefins, DKT found that the activation energies for the initial step, and for loss of NF_2 by the thermally equilibrated radical, were consistently of the same value to within 2 kcal/mol. Thus the C-N bond strength in the intermediate radical, C-CNF₂, is near zero.

(9) (a) D. S. Ross and R. Shaw, *J. Phys. Chem.*, **75**, 1170 (1971); (b) J. W. Frazer, *J. Inorg. Nucl. Chem.*, **16**, 63 (1960); (c) C. Bumgardner, E. Lawton, and H. Carmichaels, *Chem. Commun.*, 1079 (1968).

(10) J. P. Freeman, *Advan. Fluorine Chem.*, **6**, 287 (1970).

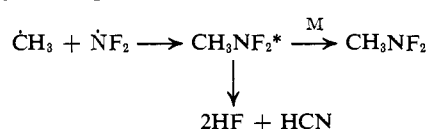
(11) It is conceivable that the C-F compound could arise from reaction of the imine with the fluorine atoms formed by path a. However, the fastest reaction in that case would be H-atom abstraction rather than addition.

state. The competitive energetics of the two possible reaction routes would then be unimportant, and N-F scission, the reaction with the looser transition state (and thus having the higher preexponential factor in its rate expression), would be dominant.

In the present case, however, the intermediate radical is thermally equilibrated. Moreover, since the rearrangement is 40 to 50 kcal/mol exothermic,¹² whereas the N-F scission is probably close to thermoneutral, the activation energy for b should be considerably lower than that for a. The rates of two reactions are thus competitive, and products from both are observed.

The lower temperature range for decomposition for II corresponds to an E_a for C-N scission of about 45 kcal/mol.⁷ The 10-kcal/mol bond weakening by α -NF₂ substitution is not unexpected; similar findings have been noted for aliphatic nitro compounds.¹³

The minor products, CH₃NF₂ and HCN, can be explained by the sequence⁹



although their formation could also be due to reactions on various surfaces in the system.

Fluorine migration was also observed in a limited study of the low-pressure pyrolysis of CH₃CH₂CH(NF₂)₂ (III) at 650°. Although the major path for de-

(12) This range is based on estimated bond strengths of 106 and 58 kcal/mol for C-F and N-F bonds, respectively; see J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

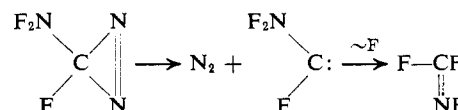
(13) G. M. Nazin, G. B. Manelis, and F. I. Dubovitskii, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 374 (1968).

composition of this material was simple dehydrofluorination, significant amounts of HC(NF)F¹⁴ and CH₃-CH₂NF₂ were observed in the product mixture, indicating that such a rearrangement was taking place, the ethyldifluoramine providing good evidence for the presence of ethyl radicals.¹⁵

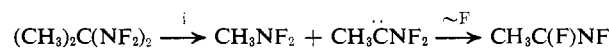
Acknowledgments. The work was supported by the U. S. Office of Naval Research under Contract Nonr 3760(00). The mass spectra were interpreted by Miss Julia Whittick. The authors are grateful for helpful discussions of this work with Drs. D. M. Golden, S. W. Benson, and R. Shaw.

(14) The structure of this material was determined solely from its ¹H nmr spectrum, a double pair of doublets, which suggests *ca.* a 70:30 mixture of the two isomers. The major isomer has a band centered at τ 2.1 with $J_{\text{HNF}} = 33$ cps and $J_{\text{HCF}} = 91$ cps. The band of the minor isomer is centered at τ 3.4 with $J_{\text{HNF}} = 27$ cps and $J_{\text{HCF}} = 84$ cps.

(15) R. Mitsch, E. Newvar, R. Koshar, and D. Dybvig, *J. Heterocycl. Chem.*, **2**, 371 (1965). They observed fluorine migration in an electron deficient species



Thus we might consider for II the generation of a similar species with subsequent rearrangement.



However, at least two facts contraindicate this mode of decomposition. (a) The formation of carbene requires formation of equal amounts of fluorimine and alkyldifluoramine, and at least for II, fluorimine is the major product. (b) We estimate the Arrhenius A factor for a process such as i to be about 10^{10} to 10^{11} sec⁻¹. A lower limit value for the activation energy can be estimated by considering that in i the net process is the breaking of the H₃C-C bond, which requires about 80 kcal/mol. Thus, $k_i \geq 10^{11-80/4.6RT}$ sec⁻¹, a value much too small to account for the observed rate of decomposition of II at 450°.

Rearrangements and Unimolecular Decompositions of Benzenoid C₉H₁₁⁺ Ions

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Abstract: Ions of composition C₉H₁₁⁺ have been generated within a mass spectrometer by electron impact. In terms of the structures of the carbonium ions which are believed to be generated at the threshold, the ions can be subdivided into two groups. Five ions (group 1) are generated as PhC₃H₈⁺ units and in these ions only the six hydrogens of the C₃ side chain become equivalent before unimolecular decomposition *via* loss of C₂H₄, C₃H₄, and C₆H₆. In contrast, CH₄ loss from the C₃ side chains is a specific 1,2 elimination and it is concluded that the reaction occurs in an excited state in which 1,2 shifts are forbidden. Five ions (group 2) are generated as carbonium ions containing di- or trisubstituted benzene rings and side chains of only one or two carbon atoms. These group 2 ions are apparently precluded (by the nature of the initially generated structures) from undergoing any facile unimolecular decompositions, and undergo rearrangements which render all 11 hydrogens in the ion equivalent prior to loss of C₂H₄, C₃H₄, and C₆H₆.

When positive ions decompose in the Nier-Johnson mass spectrometer *via* a metastable transition, they do so after existing for lifetimes of the order of 10 μ sec. Thus, the metastable ion is provided, in a molecular beam following electron impact, with internal energy sufficient for unimolecular decomposition, but

this decomposition does not occur until some 10⁸ vibrations of a given bond have taken place. Metastable transitions therefore normally occur in ions whose internal energies are only slightly (*e.g.*, 0-25 kcal) in excess of the required activation energy. It follows that if a given ion undergoes two or more com-