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MECHANISM OF DIFLUOROAMINE DEAMINATIONS

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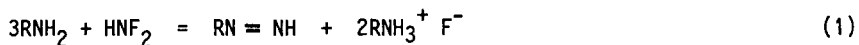
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SUMMARY

An alternative explanation of the reductive deamination with difluoroamine is suggested which does not involve the originally proposed formation of nitrogen monofluoride and Wolff-Kishner cleavage.

The reductive deamination of amines by difluoroamine has been discussed in terms of intermediate formation of nitrogen monofluoride [1, 2]. Some steps in the proposed mechanism seem questionable and hence an alternative view of the reaction is presented.

Bumgardner put forward a five step reaction scheme. The initial step was a proton transfer between difluoroamine and a more basic primary amine to form a salt with the difluoronitrogen (I) anion. This salt decomposed in a rate determining step to produce nitrogen monofluoride which inserted rapidly into the N-H bond of HNF₂. The product eliminated hydrogen fluoride with further amine to form a di-imine, which then extruded dinitrogen and left the alkane. The overall stoichiometry accords with



There is only indirect evidence for the intermediacy of a fluoronitrene (NF) in reactions, based mainly on reaction products and their stereochemistry. Le Noble [3] inferred such an intermediate in the alkaline decomposition of HNF₂ from a large positive volume of activation obtained from the pressure variation of rate. The suggested rate determining step was



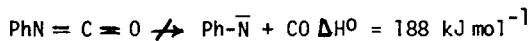
Even if this were the only explanation of a larger transition state, one has to transfer a mechanism obtained using a fully dissociated base in an aqueous medium to a relatively weak base in a non-aqueous medium.

Nitrogen monofluoride in a ground triplet state, isoelectronic with dioxygen, can be isolated in an argon matrix when fluorine azide decomposes [5]. However, it should be noted that NF is probably the least reactive nitrene. Just as CF₂ is much less reactive than CH₂, NF should be less reactive than NH whose organic chemistry, especially in solution, has been described as "meagre" by Lwowski [4]. Also the bonds being attacked are the least reactive since the reactivity order is tertiary > secondary > primary. Admittedly nitrogen monofluoride would be produced in a more active singlet state by spin conservation. Nevertheless one would expect the singlet to triplet relaxation to compete with the insertion reaction and hence lead to some stable dimer (N₂F₂) of which none was actually observed.

It has been shown that a thermal reaction which produces nitrene must not be too endothermic [6] otherwise the reaction will require too high an energy of activation. Thus phenyl nitrene is formed from the almost thermoneutral azide decomposition

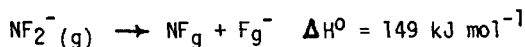


but not from the decomposition of the isocyanate



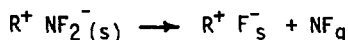
The suggested formation of NF from a complex fluoride needs to be tested thermochemically, especially in view of the unusual breakdown of a complex fluoride to its component fluorides at ambient temperatures.

The dissociation enthalpy



can be calculated from the following data [7, 8] ΔH_f^0 (NF₂, N, F, and F_g⁻) of 38, 473, 79 and 255 kJ mol⁻¹ respectively, the dissociation energy D₀⁰ (NF) of 332 kJ mol⁻¹ and the electron affinity EA(NF₂) of 222 kJ mol⁻¹. The EA value is the least reliable, but it does fit between anticipated upper and lower limits set by EA(F₂) of 290 and EA (CF₂) of 192 kJ mol⁻¹.

The gaseous dissociation enthalpy can be converted to a solid state value by using the difference between terms in Born-Haber cycles on each solid



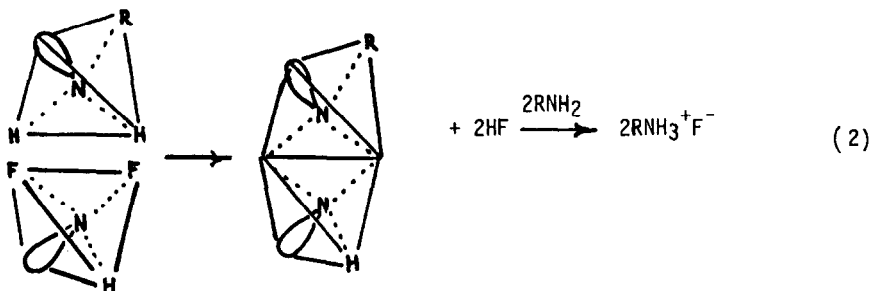
The gaseous dissociation enthalpy becomes more positive by

$$\left[U(\text{RNF}_2) - U(\text{RF}) \right] + EA(\text{NF}_2) - EA(\text{F}) + \Delta H_f^\circ(\text{NF}_2) - \Delta H_f^\circ(\text{F})$$

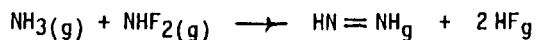
which amounts to about 140 kJ mol^{-1} . The difference in lattice energies between the salts shown in the first term has only a small positive value almost negligible compared with the other terms.

The resultant solid-state dissociation enthalpy of 360 kJ mol^{-1} can be converted to a free energy value of 300 kJ mol^{-1} after allowing for the entropy increase of about $200 \text{ JK}^{-1} \text{ mol}^{-1}$ due to the release of gaseous NF. The corresponding equilibrium constant is about 10^{-53} . It could be argued that even a minute amount of NF in equilibrium would not preclude a subsequent rapid reaction but the examples quoted earlier do not support this contention.

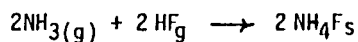
The proton transfer between difluoroamine and the more basic primary amine requires an apex interaction between two tetrahedrally shaped molecules. A closer approach is possibly by edge-wise interaction. On a statistical basis, fruitful apex encounters would be more probable because, although there are more edges than apices, the edges would need to be closely aligned compared with only random orientations for apex encounters. The effect of dipole-dipole interactions would greatly favour edge encounters over apex ones. The dipoles present in HNF_2 may not be completely predictable from electronegativity differences between atoms since it has been shown that O and N can be more basic than F towards proton action [9]. Nevertheless, the polarity $\delta^+ \delta^-$ still holds if NF_2 is considered as a group. The nitrogen in the primary amine, differing in polarity from that in the fluoroamine, would also lead to a longer distance dipole interaction. These polarities favouring edge-wise interaction suggest a far simpler route to the di-imine, as shown, without the need to form NF in an endo-ergonic reaction.



The reaction scheme 2) is at least thermodynamically favourable as can be judged from the change in bond energies between products and reactants. (The enthalpy for the simplest corresponding reaction for which data is available



can be calculated as -207 kJ mol^{-1} , and for the neutralization reaction



as -474 kJ mol^{-1} or -681 kJ mol^{-1} overall).

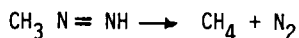
The cis-form is shown as the condensed product analogous to the more stable isomers of N_2F_2 or N_2H_2 . A linear condensation is rejected because it would require an unfavourable nitrogen catenation. The acidic character of difluoroamine is expressed by fluoride ion abstraction, rather than proton donation, a process reminiscent of acidity in anhydrous HF or HSO_3F systems.

The mode of decomposition proposed for the di-imine also seems improbable. It is compared with a Wolff-Kishner cleavage, a reduction carried out under highly alkaline conditions. In the original papers excess amine was provided by using amine to difluoroamine ratios between 4 and 6. In the last paper [2] the reactant ratio was only 3 and there was not enough amine left after formation of the di-imine to provide the basic conditions for its decomposition. Furthermore, extra amine is required to act as the solvent required for "a competing symmetrical solvation" - the explanation advanced for incomplete retention of configuration. The loose ion-pair proposed has another implication. Its non-rigidity would allow some degree of rotational freedom and hence produce the alkane containing hydrogen from both fluorinated and unfluorinated amines. This consequence could be tested using DNF_2 and checking the deuterium content of the alkane.

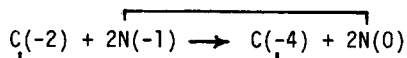
In the final extrusion of dinitrogen from di-imine it is helpful to examine any changes in oxidation number between reactants and products to indicate the direction of electron flow. The oxidation number concept has not been applied consistently to organic compounds [10, 11] but recently simpler rules for deriving oxidation numbers in covalent compounds

have been given [12] as well as examples of their use and limitations [13]. The Wittig reaction, for example, can be viewed as a neutralization of carbons, and the formation of diazonium salts as a neutralization of nitrogens.

In the extrusion reaction



all hydrogens remain in the +1 state, the carbon is reduced and the nitrogen oxidised in a redox reaction



It follows that electrons flow from N to C during reaction. Thus a partial ionization towards a carbanion, rather than a carbocation, is expected as Bumgardner suggests. To achieve a net retention of configuration at the incipient carbanion centre requires some geometrical restraint to stabilize the polarity. The only material available for this is the alkyl substituted ammonium fluoride formed in the reaction. If the cis-amine spans across the salt, which could be present in a heterogeneous reaction mix, a strong ion-dipole stabilization would help retention of configuration. Some rotation at the carbanion would be possible during nitrogen extrusion because the cation's positive charge would be spread over the peripheral hydrogens. According to this picture the alkane's hydrogen would derive exclusively from the difluoroamine and there would be a net retention of configuration.

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