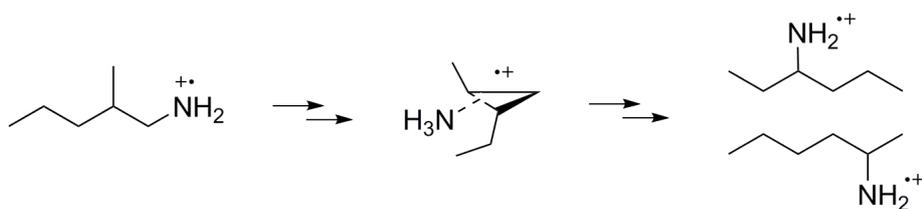


## Den Simple Spaltning

Alifatiske radikalers og kationradikalers  
spaltning, omlejring og hydrogenbindinger i gasfase

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Steen Hammerum

Kemisk Institut  
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Denne afhandling er af Det Natur- og Biovidenskabelige Fakultet ved Københavns Universitet antaget til offentligt at forsvares for den naturvidenskabelige doktorgrad, doctor scientiarum (dr. scient.).

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*De vises ord er som pigge,  
og som søm er de sat i tætte rækker,  
de er formet af én hyrde.  
Men ud over det: Min søn, lad dig advare!  
Der er ingen ende på de mange bøger der skrives,  
og den megen læsning bliver man træt af.*

*Præd. 12, 11-12 (1993 overs.)*

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## **Forord**

Når man søger at sammenfatte en stor del af det der i faglig sammenhæng har optaget en i 25 år rettes opmærksomheden mod den rolle tilfældet har haft, og mod den rolle andre mennesker har spillet for det der lykkedes. De fleste venner og fødselshjælpere må forblive unævnt, men jeg havde forstået meget lidt og nået meget mindre hvis ikke det havde været for Peter J. Derrick og Henri E. Audier og deres generøsitet som venner og som fagfæller, eller for Tore Vulpius og Theis I. Sølling og deres inspiration og modspil. Og Thorbjørn.

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# Den Simple Spaltning

## Alifatiske radikalers og kationradikalers spaltning, omlejring og hydrogenbindinger i gasfase

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## The simple cleavage

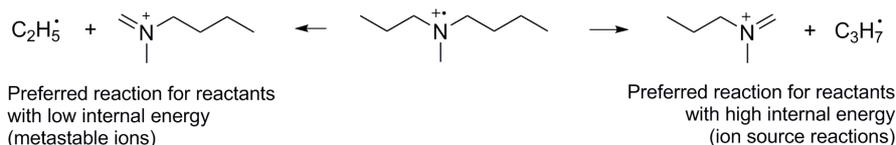
### The cleavage, rearrangement and hydrogen bonds of gas-phase aliphatic radicals and radical cations

Aliphatic radicals and radical cations undergo two characteristic unimolecular reactions, CC-bond cleavage and intramolecular hydrogen atom abstraction; numerous illustrative examples can be found in textbooks of mass spectrometry and radical chemistry.

The traditional view of the simple CC-cleavage in aliphatic radical cations is that it is a barrier-free (apart from the reaction endothermicity) uncomplicated homolysis of a single bond adjacent to a heteroatom. However, an explanation why this reaction would not be expected to have an enthalpy barrier is apparently not readily available.



A related textbook observation is that competing simple cleavage reactions in the mass spectrometer usually involve preferential loss of the larger alkyl radical. Disturbingly, the reasons for this behavior are never set out, even though the reaction thermochemistry suggests that loss of the smaller radical ought to be preferred; that is also the outcome observed for the (lower-energy) metastable ions.



The present studies took these observations as starting points, to examine the unimolecular simple cleavage of gas-phase radical cations, employing ionized aliphatic amines and ethers as suitable substrates. The scope soon expanded to include those simple cleavage reactions that do in fact have barriers (when bond fission takes place at a branching point), to include that amine radical cations readily isomerize by reversible intramolecular hydrogen atom abstraction, that the resulting distonic ions exhibit intramolecular hydrogen bonding between the alkyl radical and ammonium ion parts of the ion, and that the distonic ions could further isomerize by reactions that modify the heavy-atom framework prior to CC-cleavage.

The description of unimolecular reactions at low pressure is often based on RRKM theory; the transition state properties depend on the critical energy of the reactions and on the internal energy and degrees of freedom of the reactant. However, cleavage reactions that proceed without an intermediate energy barrier, that is, without a classical saddle-point transition state, require a variational treatment, since the position of the transition state on the reaction coordinate varies with the internal energy of the reactant. Earlier transition states for more highly energized reactants and, in turn, energy dependent *transition state switching*. The energy dependent reversal of the branching ratio of competing simple cleavage reactions illustrate this situation.

The primary tools used in these studies are mass spectrometers, for MIKE spectroscopy, and composite ab initio methods, for computational thermochemistry. The mass spectrometers used were P. J. Derrick's unusually large instrument(s) in Australia and England, and commercial instruments in France and Denmark (VG and Jeol); regrettably, neither of these is still operational. The computational results form the thermochemical infrastructure necessary to examine the mechanisms of reaction and the properties of reactants; it trails the experiments by several years in most cases, as adequate methods and computers were not available when the studies were planned and executed, even though it turns out that we guessed well.

The structure of the dissertation is as follows:

The first four chapters outline the background of the investigations, and provide examples of the reactions studied, description of the mass spectrometry experiments, and discussion of the particular use made of traditional RRKM theory.

Chapters 5-7 deal with the simple CC-cleavage of aliphatic radical cations, with emphasis on the competition between near-identical reactions, taking the  $\alpha$ -cleavage of tertiary amines as the prototype simple cleavage, and Chapter 8 deals with incomplete cleavage reactions.

Chapters 9-11 examine the isomerization of aliphatic amine radical cations, in particular the skeletal rearrangements that eventually allow CC-cleavage reactions that are not possible for those amine molecular ions that retain their initial structure.

The inter- and intramolecular hydrogen bonding of alkyl radicals is described in Chapter 12, and Chapter 14 outlines the computational thermochemistry methods employed throughout.

Some material appears in more than one chapter, to avoid extensive cross-referencing, and each chapter has a separate list of literature references.

**Chapter 1** introduces the questions that initially led to these studies and the reasons why the results are presented in Danish. Briefly, the opinion expressed is that we need to maintain Danish as an active language for professional communication concerning chemistry. Particularly to avoid speaking Pidgin among ourselves or broken Danish when addressing the public at large.

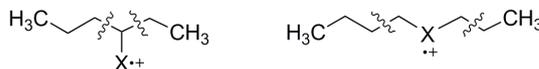
**Chapter 2** summarizes the reactions discussed in the succeeding chapters, highlighting the isomerization and cleavage reactions of ionized aliphatic amines in the gas phase; setting the stage so to speak.

**Chapter 3** describes the mass spectrometry technique used for most of the experiments, mass analyzed ion kinetic energy spectroscopy (MIKE).

**Chapter 4** discusses the conceptual framework of the present work, the traditional RRKM/QET theory, emphasizing the importance of the effective internal energy distribution of the metastable molecular ions. This is determined by the thermochemistry of the most important ion-source reactions. It will be particularly narrow when the critical energy of the ion-source reactions is low, because then most of the high-energy segment of the initial molecular ion population is removed (by fragmentation). Conversely, the energy distribution of the surviving metastable molecular ions will be broader when the ion-source reactions have relatively high critical energy, because the population of molecular ions with internal energy close to threshold is then depleted less effectively.

Of particular relevance, when simple cleavage would be relatively energy demanding, such as by fission of  $-\text{CH}_2-\text{CH}_2-$  units which requires some  $100 \text{ kJ mol}^{-1}$ , the metastable molecular ions will have a considerably wider energy distribution (and may in turn undergo a wider variety of reactions) than when cleavage would be by fission at branching points, requiring only some  $50 \text{ kJ mol}^{-1}$ .

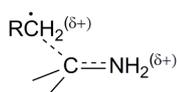
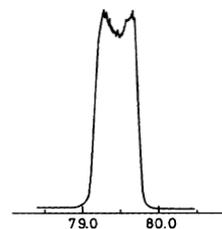
**Chapter 5** describes the intramolecular competition between nearly identical simple cleavage reactions, demonstrating that thermochemistry accounts satisfactorily for the branching ratio of low-energy ions



(metastable molecular ions), whereas variational transition state theory is required to describe the competing reactions of ions with considerable internal energy (bond cleavage in the mass spectrometer ion source without classical enthalpy-maximum transition states). The dichotomy gives rise to serious transition state switching.

The experimental finding, that low-energy molecular ions preferentially expell the smaller alkyl radical in competing reactions, whereas high-energy ions expell the larger radical, that is, that the  $k(E)$  curves cross, is well reproduced by the variational treatment.

**Chapter 6** considers the influence of energy barriers on simple cleavage reactions of branched-chain amine molecular ions. These barriers are often hidden, that is, passage requires less energy than the final separation of products. The presence of intermediate barriers can be demonstrated computationally, can be explained using valence bond theory, and can sometimes be verified by examining the kinetic energy release accompanying dissociation in mass spectrometers.

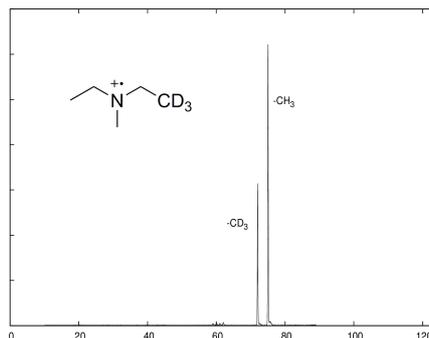


*Metastable peak for loss of  $\text{CH}_3\cdot$  from the tert-butylamine molecular ion, confirming the presence of an enthalpy barrier.*

The simple cleavage is not a straight-forward uncomplicated homolysis of a single bond. The transition state is polar with a significant charge-transfer contribution (partial positive charge on the incipient alkyl radical); it follows that elimination of methyl radicals will have a particularly pronounced enthalpy barrier. The closely related CC-cleavage of alkoxy radicals exhibits considerably higher barriers, probably because charge transfer stabilization of the alkoxy transition state entails charge separation.

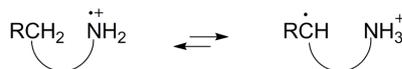
**Chapter 7** examines the secondary kinetic deuterium isotope effects on radical cation cleavage. The effects are caused by zero-point vibrational energy differences, but the observed magnitude of the isotope effects is determined of a number of additional factors.

RRKM theory provides a useful framework for the interpretation of the isotope effect variations caused by critical energy differences, for the changes arising from degrees-of-freedom differences and from the presence of competing reactions, as well as from the modification of instrumental parameters. The CC-cleavage causes two  $sp^3 \rightarrow sp^2$  conversions, and these are responsible for the zero-point energy differences that result in  $\alpha$ -secondary isotope effects. The CH/CD stretching vibration changes caused by hyperconjugation are predominantly responsible for  $\beta$ -secondary effects.



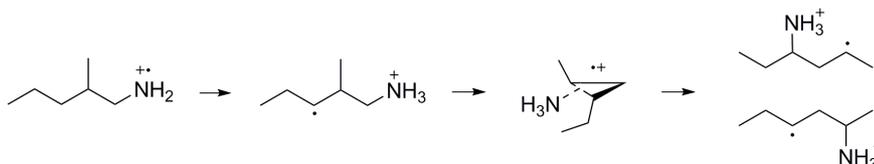
**Chapter 8** discusses the possible formation of ion-molecule complexes as the result of incomplete cleavage of radical cations. The presence of these species long enough for us to talk about them can in certain instances be substantiated (rarely done). The internal energy of complexes with appreciable lifetime is very low, which favors formation by cleavage at branching points. There is some evidence that simple cleavage reactions may be reversible.

**Chapter 9** is concerned with the intramolecular hydrogen atom abstraction reactions of saturated aliphatic radical cations with heteroatoms, examining the energy barriers and the reversibility.



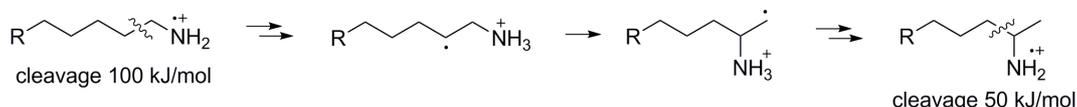
The competition between H-abstraction and CC-bond cleavage in primary and secondary amine radical cations favors cleavage when this takes place at a branching point. The distonic ions formed by H atom transfer from C to N are key intermediates when amine radical cations isomerize by modification of the heavy-atom skeleton as described in Chapters 10 and 11.

**Chapter 10** describes the formation and reactions of the intermediate [cyclopropane-NH<sub>3</sub>]<sup>+</sup>· ion-molecule complexes that mediate the migration of NH<sub>3</sub> and modification of the carbon skeleton observed to precede the fragmentation of many primary amine radical cations.

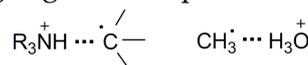
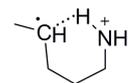


The key process is the interconversion of  $\gamma$ -distonic amine isomers by cyclization-ring opening, as proposed by Audier. The thermochemistry of the rearrangement requires that the intermediate cyclopropanes are at least disubstituted. Secondary and tertiary amine molecular ions do not isomerize in this manner, whereas ionized ethers do.

**Chapter 11** deals with the isomerization of protonated aminoalkyl radicals by 1,2-migration of NH<sub>3</sub>. This reaction allows  $\beta$ -distonic amine radical cations to rearrange, allowing otherwise unlikely CC-cleavage reactions. Primary and secondary amine radical cations isomerize in this manner, tertiary amines do not.



**Chapter 12** describes the properties of alkyl radicals as hydrogen bond acceptors. A computational study of the isomerization of ionized amines demonstrated an unusual stabilization of the *gauche* conformers of  $\gamma$ - and  $\delta$ -distonic amine radical cations owing to intramolecular N-H<sup>+</sup>...C· hydrogen bonding, and it turns out that alkyl radicals are quite generally good hydrogen bond acceptors toward ionic proton donors. The stabilization of binary ionic hydrogen bonded adducts is not a proper measure of the strength of the hydrogen bonding, but it does highlight the dependence on the acidity of the proton donor and on the ionization energy of the alkyl radical. The latter emphasizes the importance of charge exchange among the interactions that make up a hydrogen bond; in ionic systems, this entails delocalization of charge rather than charge separation.



**Chapter 14** describes the computational methods employed in the present studies as tools to establish a consistent and reliable thermochemical framework for the arguments and mechanisms used to understand the properties and reactions of the systems studied. G3-type composite ab initio methods were used throughout, with CBS-QB3 calculations and Benson-type estimates for control and consistency purposes.

**Chapter 15** attempts a summary of sorts across the dissertation.