

H₂ Elimination from Protonated Methylene Imine Derivatives in the Gas Phase. A Mechanistic Study Involving *para* Substituents

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The title reaction has been studied by gas phase physical methods and employing different substituents. The reaction mechanism is discussed on the basis of data from kinetic energy release measurements. No substituent effect on the kinetic energy release of the reaction could be detected. It is inferred that the reaction is a 1,2-elimination, but that the reaction centre is tilted towards the carbon side of the central C-N bond. This is in line with previous experimental and theoretical work concerning the model system CH₂NH₂⁺.

The dynamics of elimination reactions have been extensively studied for ions in the gas phase. It is well documented that the partitioning of the reverse critical energy in general is not statistical; kinetic energy releases (translational energy of the separated fragments) range from zero to almost one hundred per cent.¹ The kinetic energy release in a reaction is intimately related to the shape of the potential energy surface (PES) of the reaction system, and to the detailed dynamics of the ensemble of reacting ions. No simple theory can therefore be expected to give a totally satisfactory explanation of this complex matter, although Derrick and coworkers have demonstrated a simple and useful method for the calculation of the kinetic energy release. The only requirement for using their method is some knowledge of the shape of the PES around the transition state of the reaction.²

We have been particularly interested in the mechanisms of H₂ elimination from various precursor ions. In an earlier paper³ we reported studies of isotope effects on the kinetic energy release associated with hydrogen loss from protonated methylene imine, CH₂NH₂⁺. Isotopic labelling showed that the reaction is a specific 1,2-

elimination, but from the isotope effect data it was concluded that the reaction centre is heavily tilted towards the carbon side of the C-N bond (Fig. 1). Recently, Derrick and coworkers were able to confirm this proposal by high level quantum chemical calculations.⁴ Similar mechanisms (skewed 1,2 eliminations) have also been inferred from experimental and theoretical work on the related systems CH₂OH⁺ and C₃H₇⁺.^{5,6} In order to obtain further evidence for or against this mechanism, we decided to look for possible substituent effects. After some introductory experiments we ended up with a useful candidate for the reaction, which is shown in Scheme 1. Seven *para* substituents ranging in σ^+ values between -1.3(NO₂) and 0.31 (Br) were chosen in order to uncover any susceptibility of the transition state to changes in the electronic environment.

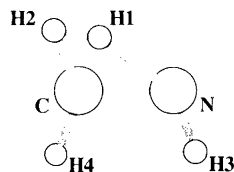
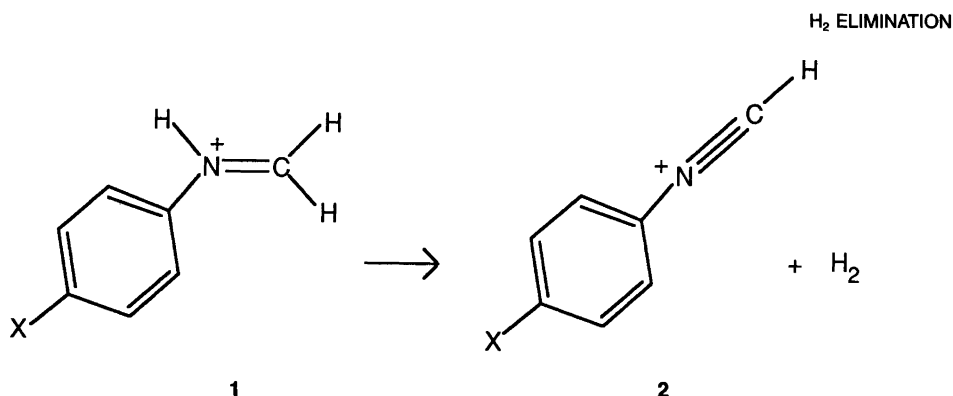


Fig. 1. Transition state for the reaction CH₂NH₂⁺ → CHNH⁺ + H₂.

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Scheme 1.

Because the system is too large for a precise theoretical calculation of the PES, no attempt was made to compare the experimentally obtained data with model data. The purpose of this paper is therefore a qualitative discussion of the mechanism based on the experimental data.

Experimental

The kinetic energy release measurements were done using an AEI MS 902 mass spectrometer. The decompositions taking place in the first field-free region of the instrument were recorded by the voltage scan technique.^{7,8} To obtain optimum energy resolution, the monitor slit was narrowed. In order to avoid interference from collisional activation processes,⁸ the pressure in the analyser region was kept well below 0.2 mPa.

Measurements of ionization and appearance energies were done according to the method of Johnstone and McMaster.⁹ Appearance energy determinations were made for daughter ions from metastable ion decompositions, and not directly on daughter ions formed in the ion source. This procedure was chosen in order to be certain that the daughter ions were formed in the process of interest and not by some other route. The disadvantage of this method compared to measurement of daughter ions formed in the ion source is the great loss of sensitivity. Daughter ion spectra were collected by the B/E-scan technique on a 7070F mass spectrometer (VG Analytical, Manchester, U.K.). Neutral precursors for **1** (para-substituted *N*-methyl anilines) were synthe-

sized according to standard methods described in the literature.¹⁰

Results and discussion

The 70 eV mass spectra showed that all the *N*-methyl anilines lose a hydrogen atom, thus forming abundant ions of structure **1**. These ions have several decomposition pathways available, and the most pronounced is HCN (or HNC) loss. Loss of H₂ accounts for less than 10% of the total daughter ion abundance in all cases, and was too weak to be detected in the case of the NO₂-substituted analogue. The experimental results are given in Table 1.

Previous isotopic labelling experiments have uniquely proven that H₂ loss from CH₂NH₂⁺ is a specific 1,2-elimination.³ It was important to show that the mechanism had not changed drastically upon derivatisation. Therefore the methyl deuteriated analogue of the unsubstituted ion **1** was prepared. Only loss of HD was found, which supports the above assumption.

It is remarkable that within experimental uncertainty the measured kinetic energy release value (Table 1) for the reaction is independent of the substituents. The mean value, $T = 0.48$ eV, is large but lower than that found for the underivatized system (CH₂NH₂⁺), which releases $T = 0.68$ eV.³ This finding shows that derivatisation in the *para* position has little influence on the reaction mechanism, and that the results therefore are representative of the model system (CH₂NH₂⁺).

In order to establish the thermochemistry of the unsubstituted system (X=H), we measured the ionization energy of the neutral precursor,

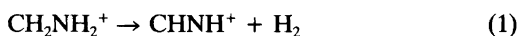
⁸ For a survey of metastable scan techniques, see Ref. 7b.

Table 1. Experimental data for the reactions investigated.

X	(M-1)/M ^a	Rel. H ₂ -loss/% ^b	T _{min} /eV ^c
NH ₂	0.25	<1	T.w. ^d
OH	0.93	<1	T.w.
CH ₃	1.40	7	0.48
H	1.23	8	0.48
Cl	1.14	2	0.47
Br	0.76	2	0.50
NO ₂	0.05	N.o. ^e	—

^aAbundancies of **1** relative to the molecular ion in the normal 70 eV mass spectra. M-1 may also have a contribution from ions formed by H-loss from other parts of the molecular ion. No attempt to correct for this has been made. ^bRelative abundancies of H₂-loss in the daughter ion spectrum of **1**. (B/E constant scan). The dominant process is loss of HCN, except for the nitro-substituted variant. ^cMeasured across the horns of the dish-shaped peak. There has been some dispute about the choice of method for obtaining *T* values. We have adopted the convention recommended in Ref. 15. Estimated standard deviation = 0.01 eV. ^dToo weak for precise measurement, ^eNot observed.

N-methyl aniline (IE = 7.98 ± 0.05 eV) and the appearance energies of **1** (AE = 11.2 ± 0.1 eV) and of **2** (AE = 15.0 ± 0.2 eV). This means that the forward activation energy for **1** → **2** is 367 ± 30 kJ mol⁻¹. The corresponding value for the reaction



is 412 ± 30 kJ mol⁻¹.¹¹ Unfortunately, we were not able to generate **2** by an independent route (a process without reverse activation barrier). The reverse activation energy could therefore not be determined. For reaction (1), the value for the reverse activation energy is 213 ± 30 kJ mol⁻¹.

It is well documented over a period of more than 50 years that ionic reactions in polar media show pronounced kinetic substituent effects.¹² One example is the solvolysis of *t*-cumyl chlorides in 90 per cent aqueous acetone,¹³ which is used as the standard for the determination of the σ⁺ constants. For this and many other reactions the kinetic substituent effect, and thereby variations in the activation energies, stems from different susceptibilities of the transition state and the re-

actant ground state to substituents. It is therefore reasonable to expect that substituents also may influence the reverse activation energy for a reaction, provided that the transition state and the product ground state have different susceptibilities to the substituents. Many examples of substituent effects on kinetic energy release are known, and have been interpreted to be due to changes in the reverse activation energy.¹⁴ The absence of a substituent effect in the present case may therefore simply reflect invariance of the reverse activation energy upon substitution. This in turn means that both the transition state structure and the product ion **2** depend on the nature of the substituent in the same way.

It is important to realize, however, that the kinetic energy release also depends on the dynamics of the reaction, i.e. on the motions of the reacting system on its way from transition state to products. Both the masses of the atoms and the strengths of the individual bonds (force constants) are in general of relevance. We believe that mass effects upon substitution may be neglected in this case. The position of the substituent is remote from the reaction centre (the part of the molecule involved in the decomposition), and only the moments of inertia are slightly affected upon substituent change. This leaves the effect of bond strengths to be considered.

Only bonds in the closest neighbourhood of the two departing hydrogens are able to compete for the reverse activation energy. It has previously been demonstrated that bonds which are not formed or broken during H₂ elimination are important for the redistribution of the reverse activation energy when the reaction coordinate is mechanically coupled to the secondary bond vibration. This effect is pronounced when the reaction centre is tilted towards the secondary bond.

There is much evidence in the literature for *para*-substituent effects on infrared frequencies and force constants in aromatic compounds. One should therefore expect different strengths (force constants) of the N-C(ring) bond, depending on the substituent. The absence of a substituent effect on the kinetic energy release in the present case probably means that this bond is very loosely coupled to the reaction coordinate. This indicates that the transition state is tilted towards the methylene carbon as found for the CH₂NH₂⁺ system.

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