Reaction of radical cations of 1,1-dihaloethenes with ammonia: substitution and base catalyzed tautomerization in sequence

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Abstract

The reactions of the radical cations of 1,1-dichloroethene (**1**) and 1,1-dibromoethene (**2**) with ammonia have been studied by Fourier transform ion cyclotron resonance (FTICR) spectrometry and ab initio molecular orbital calculations. Both radical cations exchange smoothly one of the halogen substituents by an ammonium group (reaction efficiency 60% and 35%, respectively) to yield a primary product ions $C_2H_5NX^+$ (X = Cl, Br). By using the experimental facilities of the FTICR method it is shown that the primary ions react further with ammonia producing ammonium ions by deprotonation and ions $C_2H_7N_2^+$ by addition of NH_3 and elimination of HX. Under the experimental conditions used the ion $C_2H_7N_2^+$ rapidly forms the proton-bound homodimer $N_2H_7^+$ of ammonia as the final reaction product ion. Ab initio calculations of the minimum energy reaction pathway as well as experimental results show that the primary product ion $C_2H_5NX^+$ corresponds to a N-protonated 1-halovinylamine ($CH_2=CX–NH_3^+$) generated by an addition/elimination mechanisms from **1**$^{·+}$ or **2**$^{·+}$ and NH_3. The proton affinity of the 1-chlorovinyl amine is estimated theoretically and experimentally to be about 15 kJ/mol less than that of NH_3, whereas the more stable tautomer acetimidehalogenide $CH_3–CX=NH$ is more basic than NH_3 by about 15 kJ/mol. This situation leads to a base catalyzed tautomerization of the initially generated N-protonated 1-halovinyl amine into the acetimidehalogenide which subsequently reacts with NH_3 to yield the proton-bound heterodimer of acetonitrile and NH_3, $[CH_3CN··H^+··NH_3]$. This latter species undergoes fast ligand exchange to produce the proton-bound homodimer of NH_3 $[H_3N··H^+··NH_3]$ as the final product ion. (Int J Mass Spectrom 195/196 (2000) 533–544) © 2000 Elsevier Science B.V.

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1. Introduction

The interaction of electron deficient radical cations derived from unsaturated organic compounds with electron rich nucleophiles is the key step of many reactions initiated by photoinduced electron transfer and related reactions [1]. The possibility to directly observe even highly reactive radical cations in the gas phase by mass spectrometry and Fourier transform ion cyclotron resonance (FTICR) spectrometry enables a study of the mechanisms of these reactions and helps to understand the chemistry of these reactive intermediates. In preceding articles we have investigated the reactions of the radical cations of halogenated benzenes [2,3], ethenes [4–6], and propenes [7] by using ammonia and methylamine as the nucleophile. The macroscopic chemical reaction of these systems corresponds to a substitution of a single halogen substitu-

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distonic intermediate
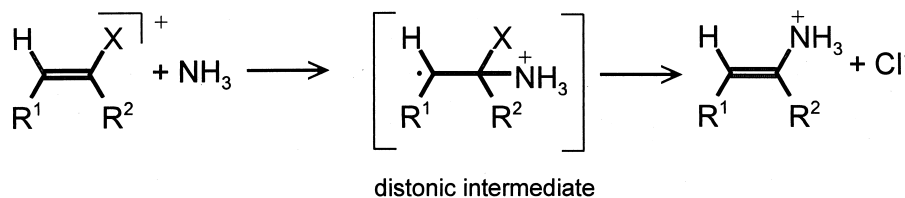
Scheme 1.

ent giving rise to protonated anilines and vinylamines, respectively, and additionally to deprotonation in the case of the halopropene radical cations. The determination of the kinetics of these ion/molecule reactions, assisted by ab initio calculations of the minimum energy reaction pathway (MERP) reveals that the substitution process principally follows an addition/elimination mechanism shown in Scheme 1 but very likely includes additional reaction steps for isomerization between the regioisomers of the intermediate distonic ion created by the addition step [5,7]. It is of interest to note that in the case of alkene radical cations the addition step is so fast that it can compete successfully even with exothermic deprotonation by the basic nucleophile [7]. This experimental observation confirms the conclusion derived from ab initio calculations that the addition of the nucleophile to the double bond of the alkene radical cations is very exothermic and does not require a significant activation energy.

The substitution of a halogen atom in ionized vinyl halides or 2-halopropenes results in the generation of N-protonated enamines [5,7]. Although the N-protonated enamines are distinctly less stable than their C^- protonated tautomers (protonated aldimines or ketimines [8]) they are usually the final product of the ion/molecule reaction between haloalkene radical cations and ammonia. Only if the conjugate base of the N-protonated enamine produced (the enamine itself) is less basic at the amino group than ammonia is the N-protonated enamine eventually deprotonated and the ultimate reaction product is the ammonium ion [7].

This general reaction scheme is also found for the reactions of the radical cations of polyhalogenated arenes [1] and of 1,2 dihaloethenes [3], which display substitution of only one halogen substituent. The

exception is the reaction of the radical cation of 1,1-dichloroethene with ammonia [3] where apparently both chloro atoms are substituted and which gives the proton-bound dimer of ammonia, $[H_3N \cdot \cdot H^+ \cdot \cdot NH_3]$, besides ammonium NH_4^+, as the final reaction products. There are some open questions with respect to the mechanism of this reaction sequence. First, the kinetics of this ion/molecule reaction indicates that substitution of the two chlorine atoms occurs by successive reaction steps, each requiring the attack of an ammonia molecule. Although it can be safely assumed that the first substitution occurs by the addition/elimination mechanism of unsaturated radical cations depicted in Scheme 1, the second chloro substituent is lost from an even-electron species, presumably a N^- protonated 1-chlorovinylamine, by addition of NH_3 and elimination of HCl. Certainly this has to occur by another type of mechanism than the first substitution. Second, it is not clear why the second substitution reaction is only observed for N-protonated 1-chlorovinylamines and not for the isomeric N-protonated 2-chlorovinylamines derived by monosubstitution from ionized 1,2-dichloroethene. Similarly, the radical cation of 1,2-bromoethene reacts with ammonia only by substitution of one bromine atom [3] although substitution of bromo by an amino group is substantially more exothermic than substitution of a chlorine atom. Finally, a formation of the proton-bound dimer of ammonia under the low pressure conditions in the FTICR cell during the experiments is rather surprising. It appears feasible that the 1-chlorovinylamine is less basic than the 2-chloro isomer because of the electron withdrawing nature of the Cl substituent next to the amino group, so that only the N-protonated 1-chlorovinylamine is deprotonated by ammonia. However, this would result primarily in the formation of NH_4^+ ions which are

indeed observed as in other cases. Nonetheless, it is only during the reaction of 1,1-dichloroethene radical cation with ammonia that the formation of the proton-bound dimer of ammonia is observed. This clearly shows that these dimer ions are not formed by clustering of the NH_4^+ ions with the excess of NH_3 present in the FTICR cell, but that the proton-bound dimer of ammonia is a genuine reaction product of one of the intermediates of the reaction of ionized 1,1-dichloroethene with ammonia. To get further information about this reaction sequence and to develop a detailed reaction mechanism we have repeated the study of the ion/molecule reaction of 1,1-dichloroethene radical cations $\mathbf{1}^{\cdot+}$ with ammonia by FTICR spectrometry, including in this study also the reactions of the 1,1-dibromoethene radical cations $\mathbf{2}^{\cdot+}$, and by verifying the suggested reaction pathways by ab initio calculations of relevant stationary points along the reaction coordinate. The results add further interesting details to the rich gas phase chemistry of the radical cations of alkenes and show a multistep reaction for the ionized 1,1-dihaloethenes in which base-induced isomerization of the primary reaction product 1-halovinyl ammonium ion and subsequent base induced HCl or HBr are the key steps.

2. Experimental

2.1. Compounds

Ammonia and 1,1-dichloroethene **1** are commercially available. The purity of **1** was checked by gas chromatography and mass spectrometry and was in all cases >99%. So **1** was used without further purification. The (unstable) 1,1-dibromoethene **2** was prepared freshly by the following procedure [9].

1,1-Dibromoethene 2: 21.5 g (81.0 mmol) of commercially available 1,1,2-tribromethane was treated with a solution of 7.9 g (80.2 mmol) CH_3COOK and 11.3 g (81.4 mmol) of K_2CO_3 in 65 ml of ethanol at 80 °C. After 3 h cold water was added until all inorganic material was dissolved and the 1,1-dibromoethene **2** was separated at the bottom of the reaction bottle. The crude **2** was washed several times with water, dried and purified by distillation. Yield 12.9 g (69 mmol; 85% of theory); boiling point 87–88 °C.

2.2. FT-ICR spectrometry

Ion/molecule reactions were investigated with a Spectrospin Bruker CMS 47X FTICR instrument [10] equipped with 4.7 tesla magnet, an external electron ionization/chemical ionization (EI/CI) ion source [11] and a cylindrical ICR Infinity cell [12]. The radical cations of the 1,1-dihaloethenes **1** and **2** were generated in the external ion source by electron impact at a nominal electron energy of 18–27 eV. All ions formed were transferred into the FTICR cell containing ammonia at an appropriate constant background pressure of 10^{-8}–10^{-7} mbar. The ions $\mathbf{1}^{\cdot+}$ or $\mathbf{2}^{\cdot+}$ were isolated by applying a broad band ejection ("chirp ejection," 88 V_{p-p}, 80 μs) followed by a series of single frequency pulses ("single shots," 14 V_{p-p}, 1.6 ms) to remove all ^{13}C, ^{37}Cl, and ^{81}Br isotopomers. The isolated radical cations were thermalized by collision with argon introduced into the ICR cell by a pulsed valve as described before [2,5]. After a delay time of 500 ms for removing argon any fragment ions or product ions formed during the cooling period were ejected again by single shots, and special care was taken to avoid any translational excitation of the isolated dihaloethene radical cations during this procedure. The time for the reaction of the dihaloethene radical cations with ammonia was varied from 1.5 ms to 22 s. At the end of the reaction period all ions in the FTICR cell were excited by an frequency sweep of 88 V_{p-p} with a step width of 7.8 kHz and an excitation pulse time of 8 μs. The mass spectra were recorded by 32 K data points for 20–30 different reaction times. Each mass spectrum is the average of at least 16 data acquisition sequences. After exponential multiplication of the time domain signal and Fourier transformation the peak intensities of the magnitude spectra were normalized to the sum of all ion detected at that reaction time and plotted versus the reaction time ("kinetic plot").

The bimolecular rate constants k_{bi} were calculated from the slope of a logarithmic plot of the relative

reactant ion intensity versus the reaction time and by taking into account the number density of ammonia in the FTICR cell. The number density was calculated from the pressure of the neutral reagent gas in the FTICR cell which was measured by an ion gauge located between the FTICR cell and the turbomolecular pump. The readings of the ion gauge were corrected for the sensitivity of ammonia as the neutral gas [13], and the pressure within the FTICR cell was calibrated by measuring the rate constant for $NH_3^{+\cdot}$ + $NH_3 \rightarrow NH_4^+$ + $\cdot NH_2$ (k_{bi} = 22 × 10^{-10} cm^3 molecule^{-1} s^{-1} [14]). The normalized efficiency (in percent) of the ion/molecule reaction is given by k_{bi}/ k_{coll} × 100, where the collision rate constant k_{coll} was calculated using the method of Su and Chesnavich [15]. The absolute error of k_{bi} corresponds usually to ±30%, and the main source of error is the determination of the partial pressure of the neutral reactant in the FTICR cell. Hence, the limit of error for relative rate constants is smaller and about ±10%.

2.3. Computational details

Ab initio molecular orbital calculations were performed by the GAUSSIAN 92 program [16] on a RS/6000 workstation or a SNI S600/20 computer. The geometries of all species were fully optimized at the Hartree-Fock level with the D95** basis set [17] by using gradient procedures [18]. For double-zeta level calculations a Huzinaga basis set [19] for the bromine atom ($13s10p4d/6s5p2d$) was used with an additional *d*-function exponent of 0.389. The spin-unrestricted Hartree-Fock formalism was used for the open shell radical cations and the restricted Hartree-Fock formalism for the closed shell species. Harmonic vibration of frequencies were computed to characterize properly the stationary points on the potential energy hypersurfaces as a minimum (for equilibrium structures) or a saddle point (for transition state structures) and to estimate the zero-point vibrational energy E_{vib}^0. The latter energy was scaled by an empirical factor of 0.9 to correct the systematic overestimation of vibrational frequencies by the Hartree-Fock calculations G1 [20]. The frozen core approximation FC-(U)MPn was used for all perturbation calculations. Single point calculations were performed at the (U)MP4(SDTQ)/D95** level of theory. Unfortunately, a spin-unrestricted wave function can contain contributions from unwanted spin states which may distort the potential hypersurface. For that reason spin projected FC-UMP4 energies (PMP4) have been calculated to obtain improved values of the potential energy. The absolute energy was corrected for the zero-point vibrational energy to calculate the reaction enthalpy ΔH_r^0 at 0 K. The enthalpies of formation, ΔH_f^{298} at 298 K were derived from the corresponding calculated values of ΔH_f^0 using standard statistical thermodynamics [21].

3. Results and discussion

The radical cations of 1,1-dichloroethene **1** and of 1,1-dibromoethene **2** react efficiently with ammonia. The kinetic plots are shown in Fig. 1, and in both cases the decay of the initial dihaloethene radical cations obeys strictly pseudo-first-order kinetics. The rate constants and reaction efficiencies of these ion/ molecule reactions are given in Table 1 together with those for the corresponding reactions of the 1,2-dihalo isomers for comparison. Both the radical cations of **1** and its isomer 1,2-dichloroethene display the same reaction efficiency of 60% toward ammonia, and the reaction efficiency of 35% of **2**$^{\cdot+}$ is also not significantly different from that of 1,2-dibromoethene radical cations. It has been observed before [3–7], that the reactivities of the radical cations of the bromo derivatives are clearly less those of the chloro compounds although the reactions of the ionized bromoalkenes are more exothermic. This is again observed for the reactions of the dihaloethene radical cations of **1** and **2** with ammonia. The origin of this effect is the exothermicity of the first addition step which provides the excess energy of the distonic intermediates to drive the reaction in the forward direction, and which is usually more exothermic for the addition of the nucleophile to the chloroalkene radical cation.

The kinetic plots of Fig. 1 show conclusively that in both cases the ion $C_2H_5NX^+$ (**1b**$^+$ X = Cl; **2b**$^+$ X = Br) is the primary reaction product, which is
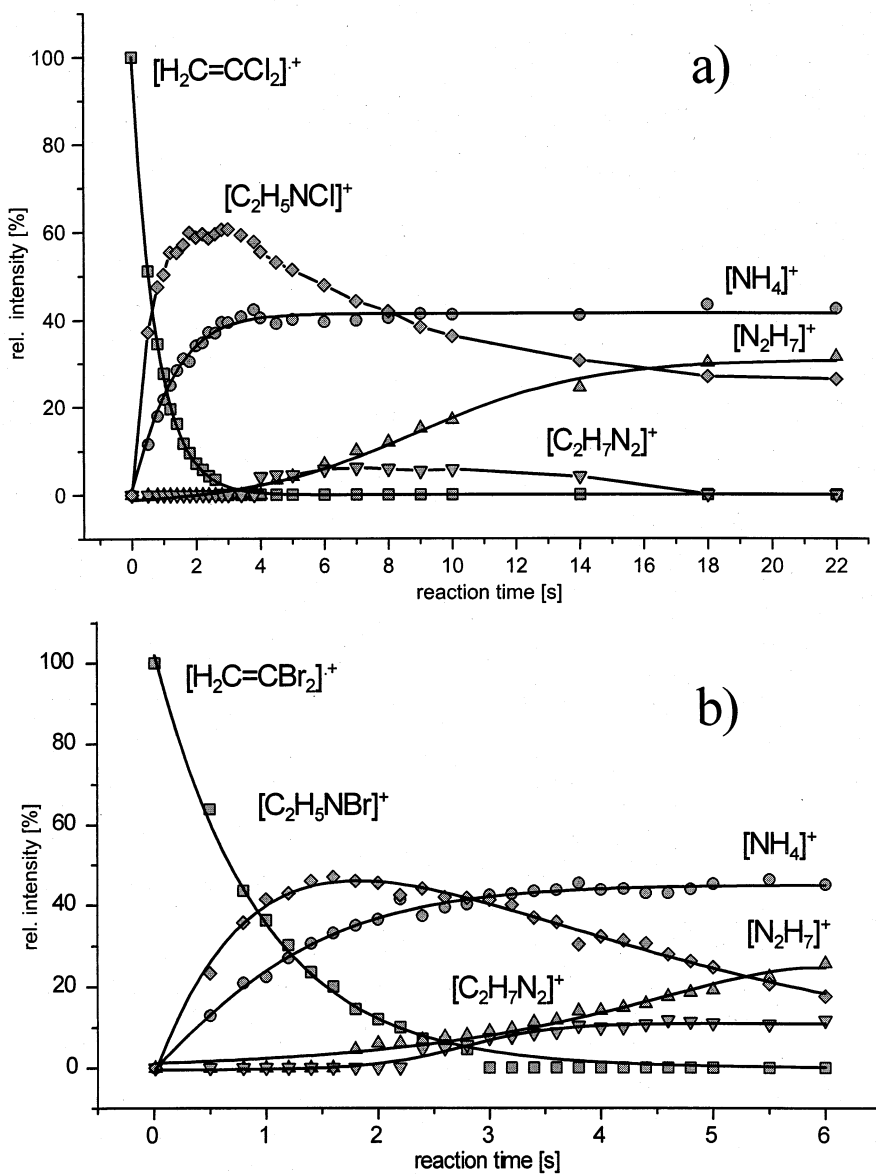
Fig. 1. Kinetic plot for the reaction of (a) the radical cation of 1,1-dichloroethene, $\mathbf{1}^{\cdot+}$, and (b) the radical cations of 1,1-dibromoethene, $\mathbf{2}^{\cdot+}$, with ammonia.

formed swiftly by substitution of one of the halogen substituents by NH_3 according to Scheme 1, $R^2 = Cl$, Br. However, it is not clearly seen from the kinetic plots whether NH_4^+ is also generated as a primary reaction product. In view of the low acidity of the vinyl halide radical cations [5,7] this is not very

likely. Note that the intensity of the ions NH_4^+ reaches a plateau already at the early stages of the reactions, whereas the intensity of $N_2H_7^+$, the proton-bound dimer of ammonia $[H_3N \cdot\cdot H \cdot\cdot NH_3]$, continues to increase. This does not agree with the formation of $N_2H_7^+$ by association of primarily formed NH_4^+ to

Table 1
Bimolecular rate constants, k_{bi}, and reaction efficiency of reaction of dihaloethen radical cations with ammonia

Ion	k_{bi} ($\times 10^{10}$ cm^3 molecule^{-1} s^{-1})	Reaction efficiency (%)
$H_2C=CCl_2^{\cdot+}$ ($1^{\cdot+}$)	124	60
$H_2C=CBr_2^{\cdot+}$ ($2^{\cdot+}$)	70	35
$HClC=CHCl^{\cdot+}$	125	60
$HBrC=CHBr^{\cdot+}$	85	43

additional NH_3. The MERP for the formation of the primary product ion $1b^{\cdot+}$ and $2b^{\cdot+}$ has been constructed by a ab initio calculations of the stationary points along the reaction coordinate. The MERPs, shown in Fig. 2, corroborate the mechanism expected from Scheme 1. The addition of NH_3 to the double bond of the radical cations $1^{\cdot+}$ and $2^{\cdot+}$ is very exothermic and gives rise to isomeric distonic ions $1a^{\cdot+}/2a^{\cdot+}$ and $1*a^{\cdot+}/2*a^{\cdot+}$ depending on a Markovnikov orientation or anti-Markovnikov orientation during the addition. The Markovnikov adducts $1a^{\cdot+}/2a^{\cdot+}$ are more stable, as expected from a stabilization of the radical electron by the adjacent halogen substituents, but only the anti-Markovnikov adducts are a reactive configuration for the loss of a halogen atom by β cleavage to the radical site. However, the excess energy of the energetically preferred distonic ions $1a^{\cdot+}/2a^{\cdot+}$ is much larger than the activation barrier separating the isomers, so that interconversion of the Markovnikov adducts $1a^{\cdot+}/2a^{\cdot+}$ and the anti-Markovnikov adducts $1*a^{\cdot+}/2*a^{\cdot+}$ is fast. Nonetheless, the exothermicity of the addition step is almost equal for the chloro derivative $1a^{\cdot+}$ and the bromo derivative $2a^{\cdot+}$. Hence, the lower reaction efficiency for the total reaction of $2^{\cdot+}$ with ammonia may be attributed to the larger activation barrier for the isomerization of $2a^{\cdot+}$ into $2*a^{\cdot+}$. In the case of the chloro derivative $1^{\cdot+}$ the MERP for generation of the N-protonated acetimidechloride $1c^+$ by a hydrogen shift within the distonic ion and subsequent fragmentation of an intermediate 1,1-dichloroethylamine radical cation was also explored by ab initio calculations. Formation of the N-protonated imidchloride $1c^+$ is much more exo-

thermic than formation of the N-protonated enamine $1b^+$. However, as in the case of the corresponding reaction of vinyl chloride radical cations [5], the 1,3-hydrogen shift within the distonic ion $1*a^{\cdot+}$ exposes a prohibitively large activation barrier for an effective total substitution process. This ensures that the N-protonated 1-halovinylamines $1b^+/2b^+$ are the primary reaction products.

The primary product ion $C_2H_5NX^+$ $1b^+/2b^+$ reacts further with ammonia, and an ion $C_2H_7N_2^+$ can be detected as the secondary product ion. Obviously the rate constants for the reaction of $1b^+$ and $2b^+$ with NH_3 are rather small, whereas the secondary ion $C_2H_7N_2^+$ exhibits the kinetic property of an reactive intermediate which reacts efficiently with NH_3 to generate the ions $N_2H_7^+$ as the final reaction product. To corroborate this reaction sequence the primary ions $1b^+$ and $2b^+$ have been isolated in the FTICR cell after an appropriate reaction time of $1^{\cdot+}$ and $2^{\cdot+}$, respectively, with ammonia to follow separately the secondary reaction with NH_3. The rate constants and efficiencies of these reactions are included in Table 2, and a kinetic plot for the reaction of $1b^+$ with NH_3 is shown in Fig. 3. This kinetic plot demonstrates unambiguously that the primary ions $1b^+$ and $2b^+$ react with NH_3 to yield ion $C_2H_7N_2^+$ as an primary product ion and to generate NH_4^+ and $N_2H_7^+$ as the final product ions. However, the decay of the ions $1b^+$ and $2b^+$ does not follow pseudo-first-order kinetics but exhibits bimodal behavior. This is most easily seen by plotting the intensity of ions $C_2H_5NX^+$ in a semilog plot [Fig. 3(b)] which results in a curved line for $\ln[C_2H_5NX^+]$. Further, the dependence of the intensity of the ion NH_4^+ on reaction time indicates that this ion is generated by a fast process while the product ion $N_2H_7^+$ arises much more slowly. The rate constant of the slow process has been determined by a curve fitting procedure, and the values given in Table 2 refer to this slow process.

It should be noted that parallel fast and slow reactions do not result per se in a deviation from first-order kinetics but show an experimental pseudo-first-order rate constant, which presents the sum of the constants of the parallel processes. The observation of a more complicated kinetic behavior for the reaction
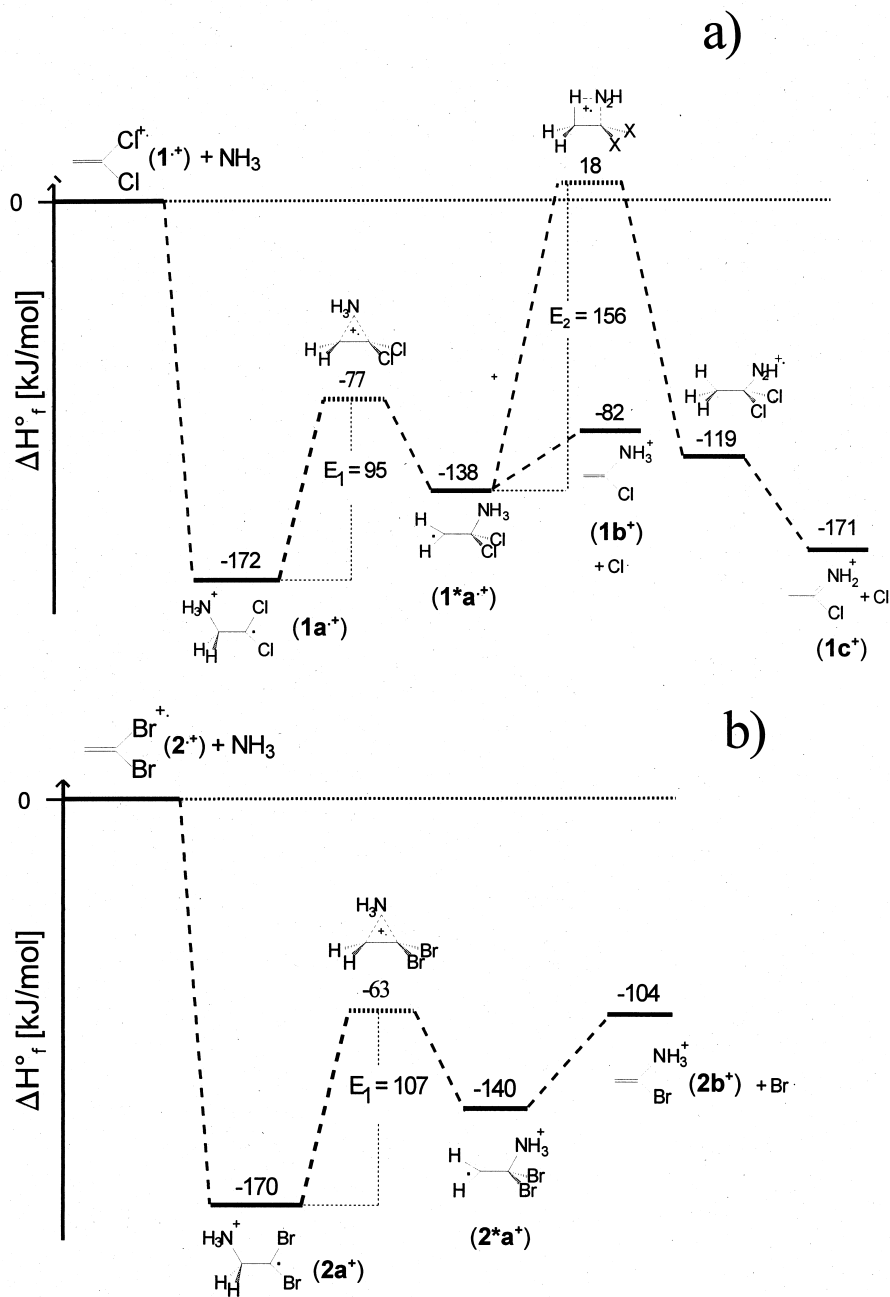
Fig. 2. Minimum energy reaction path (MERP) calculated by ab initio methods, of the reaction of (a) the radical cation of 1,1-dichloroethene, **1**$^{\cdot+}$, and (b) the radical cations of 1,1-dibromoethene, **2**$^{\cdot+}$, with ammonia.

Table 2
Bimolecular rate constants, k_{bi}, and reaction efficiency of the reaction of intermediate product ions with ammonia

Intermediate product ion	k_{bi} ($\times 10^{10}$ cm^3 molecule^{-1} s^{-1})	Reaction efficiency (%)
$C_2H_5NCl^+$	6	8
$C_2H_5NBr^+$	1.2	6
$C_2H_7N_2^{+\,a}$	3.2	15

[a] Increased error limit of $\pm 50\%$ because of low ion intensity.

of the primary product ions $C_2H_5NX^+$ with NH_3 therefore also implies a more complicated reaction mechanism. We suggest the mechanism depicted in Scheme 2 which includes, as a crucial step, the parallel deprotonation and tautomerization of the 1-halovinyl ammonium ion $C_2H_5NX^+$ (X = Cl: **1b**$^+$; X = Br: **2b**$^+$) arising from **1**$^{\cdot+}$ or **2**$^{\cdot+}$ and NH_3 as the typical primary reaction product by the addition/ elimination mechanism. This base-catalyzed tautomerization of **1b**$^+$ or **2b**$^+$ produces the more stable N-protonated acetimidehalogenides **1c**$^+$ or **2c**$^+$. In analogy to the tautomeric pair vinylamine/acetaldimine it is safe to assume that the acetimidehalogenides are more basic than the isomeric 1-halovinylamines. Thus, **1c**$^+$ or **2c**$^+$ are not deprotonated by NH_3 anymore but react by formation of the product ion $C_2H_7N_2^+$ by addition of NH_3 and elimination of HX. Eventually, the ion $C_2H_7N_2^+$ reacts again with NH_3 to yield the ion $N_2H_7^+$, which corresponds to the
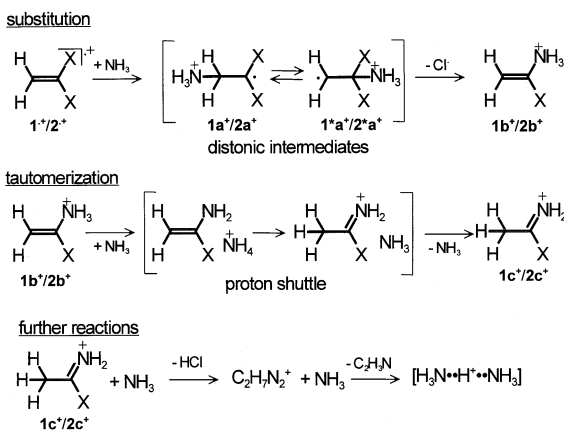
proton-bound dimer $[H_3N\cdot\cdot H^+\cdot\cdot NH_3]$. Although the reaction of the protonated acetimidehalogenides **1c**$^+$ and **2c**$^+$ is rather slow with a reaction efficiency below 10%, the final reaction step producing $N_2H_7^+$ is distinctly faster.

By now base-catalyzed isomerization of ions in the gas phase by a shuttle mechanism are well known [22], and a base-catalyzed tautomerization of protonated species by an 1,3 proton shift, which is forbidden by orbital symmetry rules, has been demonstrated before [5]. To demonstrate experimentally the base-catalyzed tautomerization of the 1-chlorovinyl ammonium ion **1b**$^+$ into the protonated acetimidechloride **1c**$^+$ and to estimate the proton affinity of the corresponding conjugated bases **1b** and **1c**, the product ions $C_2H_5NCl^+$ generated from **1**$^{\cdot+}$ and ammonia in the external CI ion source were isolated within the FTICR cell and were allowed to react subsequently with a series of bases (Table 3). No deprotonation is observed for acetone (PA 812.0 kJ/mol [23]) and formamide (PA 822.2 kJ/mol [23]) as reference bases whereas fast and complete deprotonation occurs by dimethylformamide (PA 887.5 kJ/mol [23]), methylamine (PA 899 kJ/mol [23]), and 4-fluoroaniline (PA 871.5 kJ/mol [23]). This includes the PA of all possible conjugate bases C_2H_4NCl of the product ions between 871 and 822 kJ/mol. Reference bases of intermediate PA deprotonate the product ions $C_2H_5NCl^+$ by a reaction exhibiting bimodal kinetics and show the presence of varying amounts of a quickly and a slowly deprotonating isomer (Table 3). This is clear evidence of an isomerization of a more acidic ion $C_2H_5NCl^+$ into a less acidic one by a shuttle mechanism [5]. In particular, about 51% of the ions $C_2H_5NCl^+$ react with 3-fluoroaniline (PA 867.3 kJ/mol [23]) by proton transfer whereas the remaining ions do not react. Further, the much weaker base diethyl ether (PA 828.4 kJ/mol [23]) deprotonates only 25% of the ions $C_2H_5NCl^+$. From these results the PA of the conjugated bases C_2H_4NCl of two isomeric ions are estimated to be 870 $\pm$ 5 and 825 $\pm$ 5 kJ/mol for the more and the less basic isomer. This is indeed a range of PA values including the PA of ammonia of 853.6 kJ/mol [23] as required for the mechanism depicted in Scheme 2. Further evidence
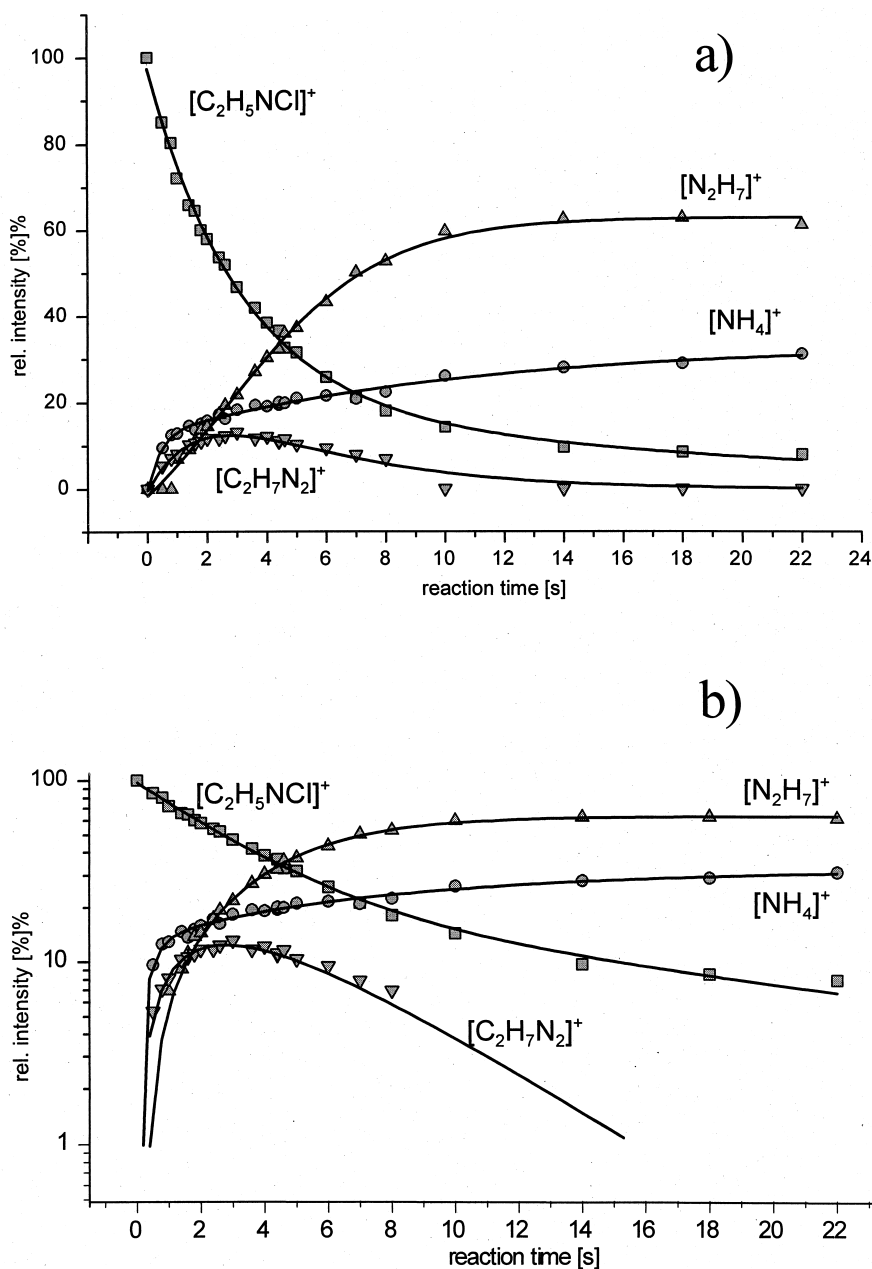

Scheme 2.

Fig. 3. Kinetic plot of the reaction of the primary product ion $C_2H_5NCl^+$ (from $1^{\cdot+}$ and ammonia) with ammonia.

for the structure of the ions $C_2H_5NCl^+$ was obtained by ab initio calculations [FC-MP4(SDTQ)/6-311++G**//RHF/D95**] of the PA of the C_2H_4NCl isomers 1-chlorovinylamine **1b** [absolute PA(calc.) = 835 kJ/mol] and acetimidechloride. **1c** [absolute PA(calc.) = 886 kJ/mol]. Both absolute values are too large by more than 10 kJ/mol, but the difference ΔPA to the PA of ammonia [absolute PA(calc.) = 860 kJ/mol; ΔPA = +26 kJ/mol and −25 kJ/mol] calculated at this level of theory agrees satisfactorily

Table 3
Gas phase titration of product ions $C_2H_5NCl^+$ by various bases

Titration base	PA (kJ/mol)[a]	Slow deprotonation (%)	Fast deprotonation (%)
Acetone	812	No reaction	
Formamide	822.2	No reaction	
Diethyl ether	828.4	75	25
Di-*n*-butyl ether	845.7	14	86
Di-*iso*-propyl ether	855.5	14	86
Di-*sec*-butyl ether	865.9	22	78
3-Fluoroaniline	867.3	49	51
4-Fluoroaniline	871.5	Fast monomodal deprotonation	
Dimethylformamide	887.5	Fast monomodal deprotonation	
Methylamine	899	Fast monomodal deprotonation	
2-Chloropyridin	900.9	Fast monomodal deprotonation	

[a] PA taken from [23].

with the experimentally observed ΔPA of $+16$ kJ/mol for **1b** and -20 kJ/mol for **1c**.

There are several plausible reactions to generate an intermediate ion $C_2H_7N_2^+$ by reaction of a protonated acetimidehalogenide with ammonia (Scheme 3). In solution, acetimidehalogenides react with ammonia by substitution of halogen to yield acetamidine. The same reaction may take place in the gas phase (path a) to form the very stable protonated amidinium ion $C_2H_7N_2^+$. However, it is also conceivable that ammonia attacks the protonated acetimidehalogenide as a base which induces the elimination of HX, and then
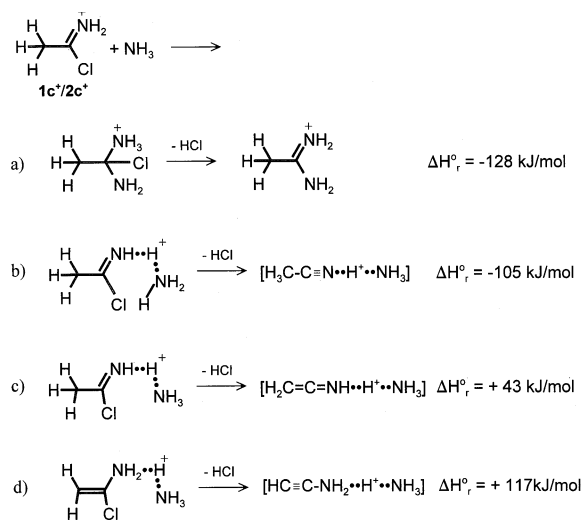
Scheme 3.

remains attached in a proton-bound heterodimer of ammonia and a species C_2H_3N. Depending on whether the elimination of HX occurs across the C–N bond or across the C–C bond of the protonated acetimidehalogenide, the C_2H_3N component of the heterodimer corresponds to acetonitrile or to ketimine (paths b and c). The reaction enthalpy ΔH_r of pathways a–c has been calculated for X $=$ Cl by ab initio methods, and the values of ΔH_r are indicated in Scheme 3. Additionally, the elimination of HCl from the protonated 1-chlorovinylamine $\mathbf{1b}^+$ yielding N-protonated ethinylamine (path d) has also been calculated and is included Scheme 3. The results show that pathways c and d are distinctly endothermic and cannot occur in the diluted gas phase of a FTICR cell in the absence of any additional activation. Although reaction pathways a and b are rather exothermic, the experimentally observed reaction is slow, indicating an activation barrier or "bottle neck" along the reaction coordinate. The substitution of Cl by ammonia of protonated acetimidechloride, either by a direct S_N2 mechanism or an addition/elimination process, is expected to exhibit a considerable activation barrier (path a), and in the case of the HCl elimination induced by a NH_3 molecule (path b) the specific structure of the multiply hydrogen bonded activated complex corresponds very likely to an entropic bottle neck. Although both the acetamidinium cation and the proton-bound heterodimer of NH_3 and acetonitrile are

potential candidates for the reaction product ion $C_2H_7N_2^+$ with respect to the reaction enthalpy of the formation from protonated acetimidehalogenides, a fast reaction with NH_3 to generate the proton-bound homodimer of ammonia is only expected for the proton-bound heterodimer of acetonitrile and NH_3, this reaction corresponds to a ligand switching in a proton-bound complex. Acetonitrile (PA = 779.2 kJ/mol [23]) is less basic than NH_3, and although acetonitrile has a larger dipole moment, ligand exchange by NH_3 to yield the proton-bound homodimer is expected to be a straightforward and exothermic reaction. In contrast, the reaction of the amidinium cation with NH_3 to generate the proton-bound dimer of ammonia requires a rather complicated rearrangement, and it is not likely that the very basic acetamidin (PA = 970.7 kJ/mol [23]) transfers a proton even if the transfer is assisted by a second NH_3 molecule. These arguments lead to the proton-bound heterodimer of acetonitrile and ammonia as the structure of the reactive intermediate ion $C_2H_7N_2^+$.

4. Conclusion

This more detailed study of the reaction of the radical cations of 1,1-dihaloethenes **1** and **2** with ammonia uncovers additional information about possible reactions of the highly reactive radical cations of unsaturated organics with electron rich nucleophiles [1]. The initial steps of the reactions of ionized **1** and **2** with ammonia in the gas phase follow the general reaction scheme developed for the reactions of monohalogenated alkenes [4–7] consisting of an addition/elimination mechanism for the substitution of the halogen substituent. By this mechanism, the first addition step is very fast without a noticeable activation barrier and gives rise to an energetically excited distonic ion which is the reaction intermediate controlling the formation of a N-protonated enamine as the first observable reaction product. The new and special feature of the reaction of the 1,1-dihaloethene radical cations is the production of a N-protonated 1-halovinylamine which tautomerizes by a 1,3-proton shift catalyzed by ammonia via a shuttle mechanism. The N-protonated vinylamines and enamines arising via this mechanism by the halogen substitution from the radical cations of vinyl halogenides [5], 2-halopropenes [7], and 1,2-dihaloethenes [4] are not acidic enough for proton transfer to ammonia, and the 1,1,1-trifluor-2-halopropenes [7] do this without the possibility of tautomerization. In the case of the N-protonated 1-halovinylamines studied here the neutral 1-halovinylamines, as the conjugated base of the reaction product, are less basic than ammonia, but the tautomeric acetimidehalogenides are stronger bases than ammonia. This enables base catalyzed tautomerization in the gas phase with ammonia as the catalyst, whereas in the other cases a tautomerization of the N-protonated enamine into the more stable N-protonated ketimine is achieved only if a suitable base is added by purpose [5]. In the next experimentally observable step of the total process of ionized 1,1-dihaloethenes with ammonia, the acetimidehalogenides undergo a base-catalyzed elimination of HX to produce a proton-bound heterodimer of acetonitrile and ammonia. This is also a new reaction type, and the details of this process are not completely understood. In particular, it will be of interest to establish by further experimental data the occurrence of the intermediate complex shown in Scheme 3, path b, with the multidentate hydrogen bonding of an ammonia molecule. It may well be that this special structure is responsible for the elimination of the HX molecule from the imidehalogenide, which would make NH_3 a very suitable catalyst for this process.

References

[1] (a) L.P. Johnstone, N.P. Schepp, J. Am. Chem. Soc. 115 (1993) 6564; (b) J.P. Dinnocenzo, D.R. Lieberman, T.R. Simpson, ibid. 115 (1993) 366; (c) G. Trampe, J. Mattay, S.S. Steenken, J. Phys. Chem. 93 (1989) 7157; (d) S.S. Steenken, C.J. Warren, B.C. Gilbert, J. Chem. Soc., Perkin Trans. 2 1990, 335; (e) M. Yasuda, Y. Matsuzaki, K. Shima, C. Pac, J. Chem. Soc., Perkin Trans. 2 1988, 745; (f) V.D. Parker, M.J. Tilset, J. Am. Chem. Soc. 109 (1987) 2251.

[2] D. Thölmann, H.-F. Grützmacher, J. Am. Chem. Soc. 113 (1991) 3281.

[3] (a) D. Thölmann, H.-F. Grützmacher, Int. J. Mass Spectrom. Ion Processes 117 (1992) 415; (b) D. Thölmann, S. Hamann, H.-F. Grützmacher, ibid. 137 (1994) 43.

[4] D. Thölmann, D. Flottmann, H.-F. Grützmacher, Chem. Ber. 124 (1991) 2349.

[5] A. Nixdorf, H.-F. Grützmacher, J. Am. Chem. Soc. 119 (1997) 6544.

[6] A. Nixdorf, H.-F. Grützmacher, Eur. J. Mass Spectrom. 5 (1999) 93.

[7] M. Büchner, A. Nixdorf, H.-F. Grützmacher, Chem. Eur. J. 4 (1998) 1799.

[8] O. Mó, M. Yáñez, M. Decouzon, J.-F. Gal, P.-C. Maria, J.-C. Guillemin, J. Am. Chem. Soc. 121 (1999) 4653.

[9] F.R. Jensen, R.A. Nees, J. Org. Chem. 37 (1972) 3037.

[10] M. Allemann, H. Kellerhals, K.P. Wanczek, Int. J. Mass Spectrom. Ion Processes 46 (1983) 139.

[11] P. Kofel, M. Allemann, H. Kellerhals, K.P. Wanczek, Int. J. Mass Spectrom. Ion Processes 65 (1985) 97.

[12] P. Caravatti, M. Allemann, Org. Mass Spectrom. 26 (1991) 514.

[13] J.E. Bartmess, R.M. Georgiadis, Vacuum 33 (1983) 149.

[14] N.G. Adams, D. Smith, J.F. Paulson, J. Chem. Phys. 72 (1980) 288.

[15] T. Su, W. J. Chesnavich, J. Chem. Phys. 76 (1982) 5183.

[16] M.J. Frisch, G.W. Trucks, M. Head-Gordon, P.M.W. Gill, M.W. Wong, J.B. Foresman, B-G. Johnson, H.B. Schlegel, M.A. Robb, E.S. Binkley, C. Gonzalez, R.L. Martin, D.J. Fox, F.J. Detrees, J. Baker, J.J.P. Stewart, J.A. Pople, GAUSSIAN 92, Gaussian, Pittsburgh, 1991.

[17] T.H. Dunning, P.J. Hay, in Modern Theoretical Chemistry, Plenum, New York, 1976, Chap. 1, pp. 1–28.

[18] H.B. Schlegel, J. Comp. Chem. 2 (1982) 214.

[19] S. Huzinaga, Gaussian Basis Set for Molecular Calculations, Elsevier, Amsterdam, 1984, p. 217.

[20] W.J. Hehre, L. Radom, P.v.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, Wiley, New York, 1986.

[21] D.A. McQuarrie, Statistical Thermodynamics, Harper & Row, New York, 1973.

[22] (a) D.K. Böhme, Int. J. Mass Spectrom. Ion Processes 115 (1992) 95; (b) A.J. Chalk, L. Radom, J. Am. Chem. Soc. 119 (1997) 7573.

[23] Nist Chemistry Webbook; Nist Standard Reference Database No. 69, August 1997.