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Reactions of Gaseous Vinyl Halide Radical Cations with Ammonia. A Study of Mechanism by Fourier-Transform Ion Cyclotron Resonance Spectrometry and *ab Initio* Molecular Orbital Calculation

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Abstract: The reactions of the radical cations of vinyl chloride (**1**) and vinyl bromide (**2**) with ammonia in the gas phase have been studied by FT-ICR spectrometry and *ab initio* molecular orbital calculations. The FT-ICR experiments show that vinyl halide radical cations react mainly by substitution of the halogen atom, yielding $C_2H_6N^+$ product ions and moderately by formation of NH_4^+ with a total reaction efficiency of 57% (**1**⁺) and 35% (**2**⁺), respectively. The initial formation of NH_3D^+ from **1-d₃**⁺ and **2-d₃**⁺ establishes a direct deprotonation of the radical cations by NH_3 . *Ab initio* calculations confirm an exothermic deprotonation for all possible halovinyl radicals as the neutral product. The structure of the substitution product ions $C_2H_6N^+$ was investigated by CA mass spectrometry and gas-phase titration experiments. The results show the presence of vinylammonium ions **5**⁺ and acetaldiminium ions (**6**⁺) in the product ion mixture, but additional experiments reveal that **6**⁺ is generated by a base catalyzed isomerization of initially formed **5**⁺ (“shuttle mechanism”). The reaction energy profiles of the reactions of the vinyl halide radical cations **1**⁺ and **2**⁺ with ammonia were calculated by *ab initio* methods. The addition of NH_3 is very exothermic for both radical cations generating chemically activated distonic ammonium ions in the first reaction step. The addition proceeds regioselectively (Markovnikov and anti-Markovnikov), yielding preferentially an unreactive distonic ion by the Markovnikov orientation. This intermediate has to rearrange by a 1,2- NH_3 shift before eventually decomposing into vinylammonium ions **5**⁺ by loss of the halogen atom. It is suggested that this rearrangement corresponds to the “bottle neck” of the substitution process. The activation energy of the 1,2- NH_3 shift in the chloro- and bromo-substituted distonic ion is not significantly different, but the increased chemical activation of the chloro derivative results in an increased reaction efficiency for the total substitution process for the vinyl chloride radical cation. The *ab initio* calculations reveal further that the generation of the more stable substitution product acetaldiminium ion **6**⁺ is inhibited by a large activation barrier for the hydrogen rearrangements necessary within the intermediate distonic ion.

Introduction

The detection of radical cations as intermediates in organic reactions has initiated an increasing number of studies of their reactivities in solution¹ and in the gas phase.² These studies reveal that unsaturated organic radical cations exhibit a high reactivity toward electron-rich donor molecules and generate a variety of reaction products. However, owing to the short lifetime of most organic radical cations in solution it is difficult to obtain information about which factors control the reactions³ and to determine the details of the reaction mechanisms. In contrast, even very reactive gaseous radical cations are easily

investigated by appropriate mass spectrometric techniques, and a study of the gas-phase ion/molecule reactions of unsaturated organic radical cations can display many details of the reaction mechanisms, in particular in combination with pertinent theoretical calculations of the reaction system.

Recently, we have performed a systematic study of the gas-phase reactions of mono- and dihalogenated arenes^{2d,f,g} with ammonia and simple amines via radical cations using Fourier-transform ion cyclotron resonance (FT-ICR) spectrometry. These reactions result in the substitution of one halogen substituent by the nucleophile by an addition/elimination mechanism. The kinetics and the low reaction efficiency of less than 15% of the reactions of the aromatic radical cations^{2d,f,g} show that the first addition step of this aromatic substitution process is rate determining. This was explained by the configuration mixing model of Shaik and Pross⁴ for polar organic reactions. Further studies reveal that the detailed mechanisms of the aromatic substitution via radical cations is rather complex and includes rearrangement steps between addition of the nucleophile and elimination of the halogeno substituent.^{2f,g}

In the case of a gas-phase substitution reaction of olefinic

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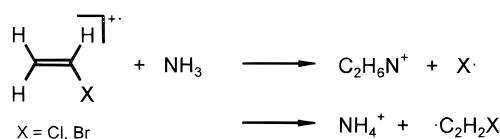
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(3) For a recent example, see: Maslak, P.; Chapman, W. H., Jr.; Vallombroso, T. M., Jr.; Watson, B. A. *J. Am. Chem. Soc.* **1995**, *117*, 12380.

(4) (a) Shaik, S. S. *Acta Chem. Scand.* **1990**, *44*, 205. (b) Shaik, S. S.; Canadell, E. *J. Am. Chem. Soc.* **1990**, *112*, 1446. (c) Pross, A. *J. Am. Chem. Soc.* **1986**, *108*, 3537. (d) Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* **1989**, *111*, 4300. (e) Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3702.

Scheme 1



radical cations the addition of the nucleophile is not expected to be the rate-determining step.^{2a} This was corroborated by preliminary FT-ICR study of the ion/molecule reactions of 1,2-dichloro- and dibromoethenes with ammonia, methylamine, or dimethylamine via radical cations.^{2e} In this case substitution of one halogen substituent occurs with a rather high efficiency although the reaction rate constants were still distinctly below the collision rate constant. Further, the structures of the substitution products were not obvious, and the reactions of 1,1-dichloroethene radical cations were different from those of the 1,2-isomer.^{2e} This latter observation suggests an interesting regioselectivity for the addition of the nucleophile to ionized haloalkenes which are asymmetrically substituted. Thus, the apparently simple substitution of haloalkene radical cations is very likely also a complex multistep reaction, and more experimental information is needed to understand the extraordinary reactivity of olefinic radical cations and the course of their reactions with nucleophiles. Therefore, we complemented the previous investigations by a study of the ion/molecule reactions of ionized vinyl chloride (1) and vinyl bromide (2) with ammonia and other small donor molecules using FT-ICR spectrometry and molecular orbital calculations. Here, we report the results for the reaction with ammonia (Scheme 1) with special emphasis on the determination of the structure of the substitution products and a calculation of the reaction energy profile.

The vinyl halides **1** and **2** are asymmetrically substituted and should allow the detection of effects of regioselectivity during the addition of the nucleophile to the ionized double bond. Further, Br is a better "leaving group" from radical cations than Cl because of its lower C–X bond energy which allows a study of leaving group effects on the rate of the overall process. Finally, vinyl halides are sufficiently small to apply *ab initio* methods of a reasonable high level of theory to the calculation of the reaction potential energy profile. Thus, these vinyl halide radical cations are well suited for a detailed investigation of the mechanism of the reaction of unsaturated organic radical cations with donor substrates. The results of the kinetic experiments and of the investigation of the structure of the reaction product ions will be discussed first and will be followed by a discussion of the reaction energy profile of this prototype of a substitution reaction of olefinic radical cations. It will be shown that the first addition step of the nucleophile to the ionized vinyl halide is indeed fast but occurs primarily with the "wrong" regioselectivity for substitution, and that the necessary rearrangement of the initial distonic ion is apparently the "bottle neck" of the overall reaction.

Experimental Section

Compounds. Ammonia, vinyl chloride (**1**) and vinyl bromide (**2**), and all other reagents are commercially available. The purity of all compounds was checked by gas chromatography and mass spectrometry and was in all cases > 99%. So all compounds were used without further purification. Vinyl chloride-*d*₃ radical cation (**1-d**₃^{•+}) was generated in the ion source by electron impact induced fragmentation of 1,2-dichloro-1,1,2,2-tetradeuterioethane which was prepared by the following procedure.⁵

1,2-Dichloro-1,1,2,2-tetradeuterioethane. Thionyl chloride (20.2 g, 169.5 mmol) was added slowly to a mixture of dry 1,1,2,2-tetradeuterioethylene glycol (2.80 g, 42.2 mmol) and dry pyridine (6.70 g 85.9 mmol). A very vigorous reaction occurred and the liquid darkened considerably. The mixture was refluxed for 2 h and then poured under vigorous stirring into ice-cold water. The organic layer was washed with 5% sodium hydroxide solution and with water and was dried over Na₂SO₄. Pure 1,2-dichloro-1,1,2,2-tetradeuterioethane was obtained by distillation at 81 °C. Yield: 1.11 g (10.8 mmol, 26%). MS (70 eV, EI) *m/z*: 106 (3.4) [C₂D₄37Cl₂^{•+}], 104 (21.7) [C₂D₄35Cl³⁷Cl^{•+}], 102 (34.0) [C₂D₄35Cl₂^{•+}], 69 (15.4) [C₂D₄37Cl^{•+}, C₂D₃35Cl^{•+}], 67 (72.7) [C₂D₄35Cl^{•+}, C₂D₃37Cl^{•+}], 65 (15.4) [C₂D₃35Cl^{•+}], 53 (21.6) [CD₂37Cl^{•+}], 51 (68.3) [CD₂35Cl^{•+}]. C₂D₄35Cl₂: mol weight calcd 101.9941, found 101.9942 (by FT-ICR mass spectrometry at *m/Δm* = 200,000).

Vinyl bromide-*d*₃ (**2-d**₃) was prepared according to Schaefer et al.⁶ by base-induced dehydrohalogenation of 1,2-dibromo-1,1,2,2-tetradeuterioethane. The deuterium content of 1,2-dichloro-1,1,2,2-tetradeuterioethane and vinyl bromide-*d*₃ was >98% (by mass spectrometry).

Mass Spectrometry. Ion/molecule reactions were investigated with a Spectrospin Bruker CMS 47X FT-ICR instrument⁷ equipped with 4.7 T magnet and an external EI/CI-ion source.⁸ The standard cylindrical ICR cell was used for rate measurement, while experiments to determine the structure of product ions C₂H₆N⁺ were performed with an Infinity cell.⁹ The vinyl halide radical cations 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 FT-ICR cell containing ammonia at an appropriate constant background pressure of 10^{–8}–10^{–7} mbar. The ¹²C₂H₃X^{•+} ions (X = ³⁵Cl or ⁷⁹Br) 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 isotopomers of the vinyl halide radical cations. The isolated radical cations were thermalized by collision with argon introduced into the ICR cell by a pulsed valve as described before.^{2d} 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 vinyl halide radical cations during this procedure. The time for the reaction of ¹²C₂H₃X^{•+} ions with ammonia was varied from 1.5 ms to 15 s. Then, all ions in the FT-ICR 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 32K data points for 20–30 different reaction times, and 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 *vs* 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 *vs* the reaction time and by taking into account the number density of ammonia in the FT-ICR cell. The number density was calculated from the pressure of the neutral reagent gas in the FT-ICR cell which was measured by an ion gauge located between the FT-ICR cell and the turbomolecular pump. Therefore, the readings of the ion gauge were not only corrected for the sensitivity of ammonia as the neutral gas¹⁰ but also calibrated for the pressure within the FT-ICR cell by measuring the rate constant for NH₃^{•+} + NH₃ → NH₄⁺ + NH₂. A value of *k*_{bi} = 22 × 10^{–10} cm³ molecule^{–1} s^{–1} was used for the rate constant of this reaction.¹¹ The normalized efficiency (in %) of the ion/molecule reaction is given by *k*_{bi}/*k*_{coll}. The collision rate constant *k*_{coll} was calculated using the method of Su and Chesnavich.¹²

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The collision activation (CA) mass spectra of the product ions and reference ions $\text{C}_2\text{H}_6\text{N}^+$ were obtained by a double-focussing mass spectrometer VG AutoSpec using 70 eV electron impact ionization, an electron current of 200 μA , an ion source temperature of 180 $^\circ\text{C}$, and an accelerating voltage of 8 kV. The $\text{C}_2\text{H}_6\text{N}^+$ product ions were generated within the CI ion source by the admission of vinyl chloride or vinyl bromide into the CI-plasma of ammonia gas at a suitable pressure to maximize the yield of $\text{C}_2\text{H}_6\text{N}^+$ product ions. The $\text{C}_2\text{H}_6\text{N}^+$ reference ions were generated from electron impact-induced fragmentation of an appropriate precursor. The $\text{C}_2\text{H}_6\text{N}^+$ ions were selected by the magnetic sector and focused into the field-free region between the magnetic sector and the second electrostatic analyzer of the AutoSpec mass spectrometer. Helium was used as a collision gas and was introduced at such a rate into the collision cell that the intensity of the main ion beam was reduced to about 30% of its original value. The CA mass spectra were obtained by scanning the deflecting voltage of the electrostatic analyzer, and the relative abundances of the reported CA spectra are the averages of at least 12 scans.

Computational Details. *Ab initio* molecular orbital calculations were performed by the GAUSSIAN 92 program¹³ 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 set¹⁴ using gradient procedures.¹⁵ For double- ζ level calculations a Huzinaga basis set¹⁶ 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. The heat of formation of the vinyl halide radical cations and haloethenyl radicals listed in Table 2 and 3 have been computed with the MOLPRO 92 suite of *ab initio* programs¹⁷ using a restricted reference wave function for the geometry optimizations ((RF/DO(DP))) and correlation contributions were considered on CERA-1/VTZ(f,2d,p) level of theory. Details of these computations will be published elsewhere. Harmonic vibrational wavenumbers were computed in order to characterize the stationary points on the potential energy hyper surfaces as minima (for equilibrium structures) or saddle points (for transition state structures) and to estimate the zero-point vibrational energies E_{vib}^0 . The latter energies were scaled by an empirical factor of 0.9 to account for the systematic overestimation of vibrational frequencies by the Hartree–Fock calculations.¹⁸ The frozen core approximation FC-(U)MPn was used for all perturbation calculations. Single point calculations were performed at the (U)MP4(SDTQ)/D95** of theory. Unfortunately, a spin-unrestricted wave function can contain contributions from unwanted spin states. These may distort significantly the potential hypersurface. For that reason spin-projected FC-UMP4 energies (PMP4) have been calculated to obtain improved values of the potential energies. The absolute energies were corrected for the zero-point vibrational energy contribution in order to calculate the reaction enthalpies ΔH_r^0 at 0 K. The enthalpy of formation, ΔH_f^{298} and proton affinity, PA, at 298 K were derived from the corresponding calculated values using standard statistical thermodynamics.¹⁹

Results and Discussion

Kinetic Measurements. Vinyl chloride radical cations (1^+) and vinyl bromide radical cations (2^+) react with ammonia,

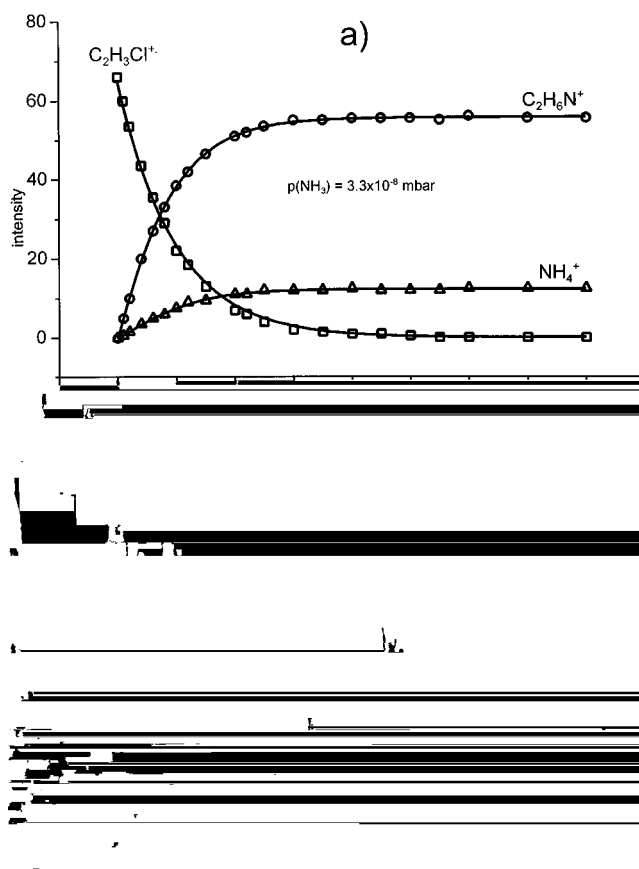


Figure 1. Ion intensity *vs* reaction time plot for reaction of (a) 1^+ with NH_3 and (b) 2^+ with NH_3 .

Table 1. Rate Constants, k_{bi} , and Efficiencies (eff) of the Reaction of Mono- and 1,2-Dihaloethene Radical Cations with NH_3

compound		k_{bi}^a	k_{coll}^a	eff %
$\text{H}_2\text{C}=\text{CHCl}^+$	(1^+)	12.3	21.6	57
$\text{H}_2\text{C}=\text{CHBr}^+$	(2^+)	7.2	20.6	35
<i>cis</i> - $\text{HCIC}=\text{CClH}^+$	(3^+_{tr})	12.5	20.8	60
<i>trans</i> - $\text{HCIC}=\text{CClH}^+$	(3^+_{cis})	12.5	20.8	60
$\text{HBrC}=\text{CBrH}^+$	(4^+)	8.5	20.0	43

^a In units of $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. ^b Recalculated from ref 2e.

generating $\text{C}_2\text{H}_6\text{N}^+$ ions and NH_4^+ ions as ionic products in close analogy to the reactions of the 1,2-dihaloethene radical cations.^{2e} Figure 1a,b show the kinetic plot obtained for 1^+ and its deuterated derivative $1\text{-}d_3$. The bimolecular rate constants k_{bi} and the efficiencies of the reactions are collected in Table 1 which includes also the previously determined rate constants k_{bi} for the reactions of the radical cations of *cis*- and *trans*-1,2-dichloroethene, 3^+_{cis} and 3^+_{tr} , and 1,2-dibromoethene 4^+ (mixture of stereoisomers) with NH_3 .²⁰ All reactions are quite fast with an efficiency between 35% and 60%, and there is no significant difference between the reactivity of the mono- and 1,2-disubstituted haloethene radical cations. The reactions of the mono- and dichloroethene radical cations are consistently more efficient than those of the bromo derivatives. This unusual result was confirmed by measuring directly the relative rates with ammonia in a mixture of 1^+ and 2^+ to avoid any ambiguity due to the determinations of the NH_3 partial pressure. The reason for the increased reactivity of the chloro ions is not evident from these experiments alone but this result shows clearly that the dissociation of the bond to the leaving group is

(20) The values of k_{bi} and the reaction efficiency given in Table 1 for the reaction of 3^+ with NH_3 are slightly larger than those in ref 2e because the deprotonation of 3^+ has been not included previously.

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not rate determining for the total substitution process. As will be discussed later this effect arises from an increased chemical activation by the initial addition of NH_3 to the vinyl chloride radical cation $\mathbf{1}^{\bullet+}$.

Of the two product ions observed for the reactions of $\mathbf{1}^{\bullet+}$ ($[\text{C}_2\text{H}_6\text{N}^+]/[\text{NH}_4^+] = 2.9$) and

Table 4. CA-Mass Spectra^a of C₂H₆N⁺ Ions 6⁺–8⁺ and of NH₃ Substitution Product Ions of 1⁺ and 2⁺

precursor	ion	<i>m/z</i>															
		43	42	41	40	39	38	30	29	28	27	26	25	24	22	18	17
(CH ₃) ₃ CHNH ₂ ⁺	6 ⁺	8.1	17.0	11.6	9.0	4.5	2.8	0.5	3.0	20.4	8.4	6.4	1.5			6.0	0.7
(CH ₃) ₂ NH ₂ ⁺	8 ⁺	4.9	12.6	8.3	7.5	4.5	3.0	1.3	3.9	40.1	9.2	0.8				3.8	
C ₆ H ₅ OCH ₂ CH ₂ NH ₂ ⁺ ^b	7 ⁺	4.4	8.9	6.1	5.8	2.8	2.8	5.8	2.3	31.2	11.7	9.1	2.7			6.2	
H ₂ C=CHCl ⁺ + NH ₃	5 ⁺	10.4	12.1	10.2	8.3	4.1	2.1	0.8	2.5	15.5	9.5	9.4	2.5	0.6	1.2	7.0	6.4
H ₂ C=CHBr ⁺ + NH ₃	5 ⁺	9.8	12.5	10.7	7.0	3.5	2.5	0.8	2.5	16.0	11.7	8.5	4.7	0.5	1.0	5.6	4.2

^a Intensity normalized to sum of fragment ion intensity. ^b Generated by 14 eV electron impact.**Table 5.** Experimental and Calculated Proton Affinities^a of Conjugated Bases C₂H₅N of ions 5⁺–8⁺

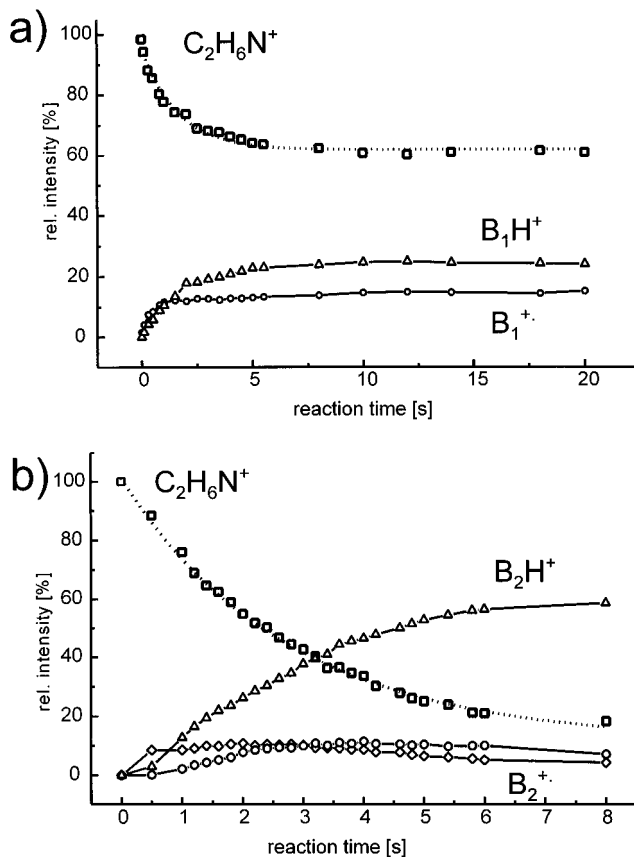
compound, C ₂ H ₅ N	ion	PA	
		calc ^b	exp
vinylamine ^e	5 ⁺	927	
vinylamine ^f	5 ⁺	866	864 ^g
acetaldimine	6 ⁺	905	893 ^c
aziridine	7 ⁺	915	903 ^d
<i>N</i> -methylformaldimine	8 ⁺	891	
ammonia	NH ₄ ⁺	868	854 ^d

^a In kJ/mol. ^b By MP4/6-311++G** and corrected for thermodynamical contributions. ^c References 23a. ^d Derived from data in ref 22. ^e C-protonation. ^f N-protonation. ^g From this work.

is a very characteristic feature of the CA mass spectrum of the C₂H₆N⁺ product ions only. Hence, these CA mass spectra prove unambiguously the presence of C₂H₆N⁺ ions with a structure different from 6⁺–8⁺, but it is difficult to decide whether the C₂H₆N⁺ product ions consist only of a single species or represent a mixture of isomers.

Structure of the C₂H₆N⁺ Product Ions by Gas-Phase Titration. More conclusive information about the structure of the C₂H₆N⁺ product ions is obtained by their “gas-phase titration”²⁶ with a series of reference bases of appropriate gas-phase basicity (GB). In these titration experiments the kinetics of the deprotonation of a gaseous mixture of isomeric ions by a set of reference bases of known GB are measured in separate experiments. A fast and efficient proton transfer is observed only for exoergic proton transfer. Thus, if the GB of the reference base is placed between the GB of the neutral conjugated bases of the ions in the mixture, bimodal kinetics are observed for the deprotonation because only the more acidic ions will react efficiently. The bimodal kinetic curve obtained may be examined by curve-fitting procedures to separate the ion mixture into two sets of isomeric ions with their corresponding conjugate bases being less and more basic than the reference base. Repeating this experiment with a series of reference bases allows a semiquantitative analysis of the ion mixture and an estimation of the GB (or PA) of the conjugated bases of the unknown ions by bracketing. This PA determination is very advantageous for an identification of ions because many PA are tabulated or may be calculated reliably by *ab initio* methods.

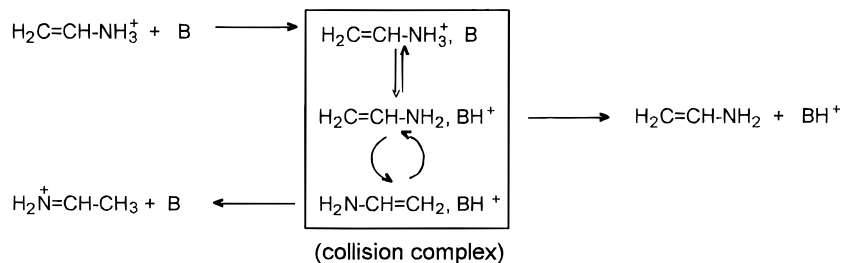
The PA of acetaldimine^{23a} and aziridine²² are known, but the PA of vinylamine and *N*-methylformimin have not been determined directly by experiment.^{23b} Therefore, for consistency the PA of all precursors of 5⁺–8⁺ were calculated by *ab initio* methods (Table 5). A comparison of the experimental and calculated PA in the case of acetaldimine (for 6⁺) and aziridine (for 7⁺) shows that the PA calculated by MP4/6-311++G** are overestimated by ~12 kJ/mol. For vinylamine both the PA for a protonation at the terminal C-atom (yielding 6⁺) and at the amino group (yielding 5⁺) were calculated. C-protonation is favored by 61 kJ/mol, in good agreement with the calculations

**Figure 2.** Plot of ion intensity *vs* reaction time for the deprotonation of C₂H₆N⁺ product ions by (a) 3-fluoroaniline (PA 866 kJ/mol²²); (b) 2-phenylpropene (PA 866 kJ/mol²²).

of Eades et al.^{23b} Taking into account the systematic error of the calculated PA, a PA(vinylamine) of about 860 kJ/mol is expected for N-protonation, slightly larger than the PA(NH₃).

The PA data (Table 5) predict fast deprotonation of 5⁺ and 6⁺, but not of 7⁺, by bases of PA < 903 kJ/mol. A complete and efficient deprotonation without any side reaction is observed during the reaction of the C₂H₆N⁺ product ions from the reactions of 1⁺ and 2⁺ with the strong base tributylamine (PA 985 kJ/mol²²). Thus, no C₂H₆N⁺ product ions that are reluctant to deprotonation are present in the ion mixture. A complete deprotonation of the C₂H₆N⁺ product ions is also observed by the weaker base 2-chloropyridine (PA 897 kJ/mol²²). Bimodal kinetics are observed for this process, but the slower process is too fast for the endoergic deprotonation of the aziridinium ion 7⁺ and is more compatible with the nearly thermoneutral deprotonation of 6⁺ (or probably 8⁺). Further decreasing the PA of the titration base results in a fast deprotonation of only one component of the ion mixture. This is still observed for reaction with 3-fluoroaniline (PA 866 kJ/mol²²; Figure 2a), but no deprotonation occurs by *N*-methylformamide (PA 861 kJ/mol²²). This sets the PA of the least basic component of the mixture to 864 ± 2 kJ/mol, in reasonable agreement with the estimated PA for N-protonation of vinylamine. Thus, the gas-

Scheme 3



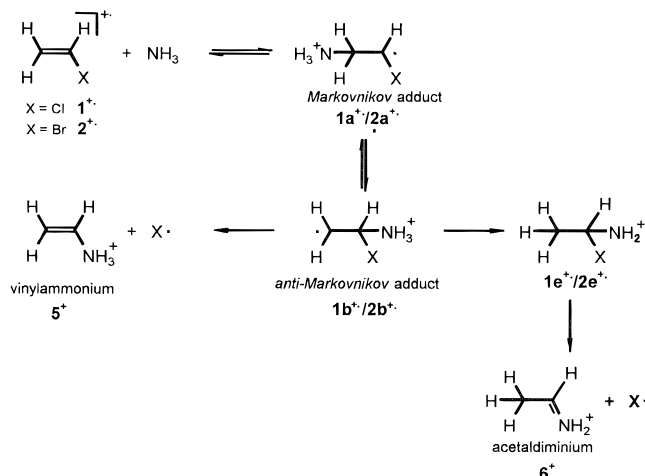
phase titration experiments indicate that the C₂H₆N⁺ product ions are apparently a mixture of vinylammonium ions (5⁺) and acetaldiminium ions (6⁺). The additional presence of the *N*-methylformamidinium ion (8⁺) in the product ion mixture cannot be excluded completely. However, in view of the extensive skeletal rearrangements necessary to generate 8⁺ during the substitution reaction the presence of this ion is not very likely.

However, the quantitative composition of the C₂H₆N⁺ ion mixtures varies considerably with the PA and the chemical nature of the reference base used for the gas-phase titration. As will be shown elsewhere²⁷ this is due to a base catalyzed tautomerization of 5⁺ into 6⁺ (Scheme 3). In the case of PA-(5) < PA(base) < PA(6), the base picks up a proton from 5⁺ within the initial collision complex formed by 5⁺ and a molecule of the base and generates a new product complex consisting of the neutral vinylamine and the protonated base. This product complex may dissociate or return the proton to the terminal C atom of the neutral vinylamine generating the more stable acetaldiminium ion (6⁺) in an exothermic process. Clearly, the amount of isomerization 5⁺ → 6⁺ depends on the branching ratio of these competing processes. A similar "shuttle mechanism" has been described before for small molecules with two basic sites.²⁸ However, to our knowledge this is the first time that such a strong influence not only of the PA of the catalytic base but also of its chemical structure has been observed. An interesting example is the titration of the C₂H₆N⁺ product ions with 3-fluoroaniline and 2-phenylpropene, respectively, shown in Figure 2a,b. The PA of 3-fluoroaniline and 2-phenylpropene are identical,²² but 2-phenylpropene is a "bad proton shuttle", and only less than 13% of the C₂H₆N⁺ product ions have isomerized into 6⁺ and are not deprotonated, compared to 65% in the case of the "good proton shuttle" 3-fluoroaniline. It is difficult to find a similar isomerization mechanism which involves also the *N*-methylformamidinium ion (8⁺). Therefore, these experiments evidence that ions 8⁺ are absent, that the presence of acetaldiminium ions (6⁺) among the C₂H₆N⁺ product ions is very likely an artefact of the titration experiment, and that initially only vinylammonium ions (5⁺) are formed during the reaction of 1⁺ and 2⁺ with NH₃.

Reaction Energy Profile. For a more explicit picture of the reaction steps occurring in the collision complex of 1⁺ and 2⁺ with NH₃ before dissociation either back to reactants or to the final products the possible reactions pathways have been established by the *ab initio* methods discussed in Computational Details. A key feature of the resulting mechanism is the regioselective addition of the NH₃ during the first step which may occur either at the α-position (Markovnikov-addition) or at the *ipso*-position (anti-Markovnikov addition) to the halogen substituent producing the distonic ions 1a⁺ and 1b⁺ or 2a⁺ and 2b⁺ (Scheme 4).

Of these distonic ions only the anti-Markovnikov products 1b⁺ or 2b⁺ dissociate directly into the vinylammonium ions

Scheme 4



5⁺ by loss of Cl[•] or Br[•], while any energetically appropriate fragmentation of the Markovnikov addition products 1a⁺ and 2a⁺ requires rearrangements. These rearrangements correspond either to hydrogen shifts which result eventually in the molecular ions 1e⁺ and 2e⁺ of 1-haloethylamines which decompose subsequently into acetaldiminium ions 6⁺, or to a 1,2-shift of the NH₃ group converting 1a⁺ and 2a⁺ into the anti-Markovnikov products 1b⁺ and 2b⁺ for further reaction to 5⁺.

The enthalpies of reaction, Δ*H*_r, of the individual reaction steps, calculated by *ab initio* methods (see Computational Details) have been used to construct the reaction energy profiles for the reaction of the ionized vinyl halides 1⁺ and 2⁺. The reaction energy profile for the substitution reactions of the ionized vinyl chloride 1⁺ and vinyl bromide 2⁺ are very similar with an exception to be discussed below. The reaction energy profile of 1⁺ is shown in Figure 3. The structure of lowest energy found for the addition complex of NH₃ to 1⁺ is the Markovnikov adduct 1a⁺ in which the radical site of the distonic ion is stabilized by the adjacent chloro atom. By the level of theory used no activation barrier was found for the addition step. This agrees with *ab initio* calculations of the polymerization of ethene radical cations, which were found to add to a neutral ethene molecule without a barrier.²⁹ The anti-Markovnikov adduct 1b⁺ is 30 kJ/mol higher in energy than 1a⁺, and this distonic ion 1b⁺ dissociates without a barrier by elongation of the C–Cl bond into the final products vinylammonium ion (5⁺) and Cl[•]. For these products the substitution of 1⁺ is exothermic by −116 kJ/mol. The formation of the acetaldiminium ion (6⁺) would be exothermic by −184 kJ/mol. However, starting from the anti-Markovnikov adduct 1b⁺ a formation of 6⁺ requires an 1,3-hydrogen shift from the ammonium moiety to the radical site, generating the molecular ion of 1-chloroethylamine 1e⁺ which is higher in energy by 30 kJ/mol than the β-distonic ion 1b⁺. The calculations indicate

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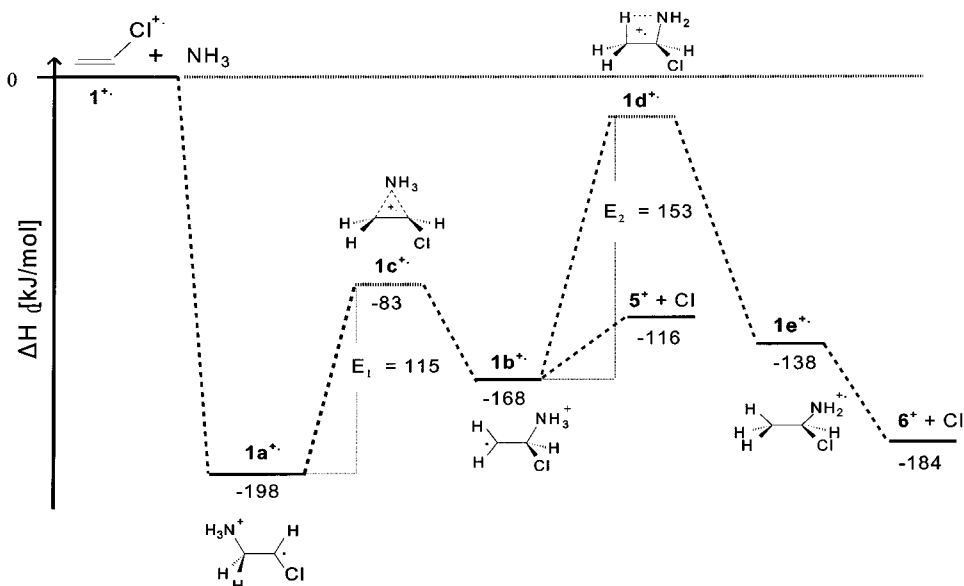


Figure 3. Reaction energy profile of the reaction of vinylchloride $1^{\bullet+}$ with NH_3 .

that likely the molecular ion $1e^{\bullet+}$ is kinetically unstable and decomposes without a barrier into 6^+ and Cl^{\bullet} , but the rate-determining step for this route of a substitution is the H rearrangement. As anticipated from the behavior of other distonic ammonium ions^{30,31} the 1,3-hydrogen shift in $1b^{\bullet+}$ via transition state $1d^{\bullet+}$ requires the large activation energy of 153 kJ/mol. Thus, in view of the dissociation into 5^+ by direct loss of Cl^{\bullet} the intermediate $1b^{\bullet+}$ has no chance to realize the acetaliminium ion 6^+ as the more stable product ion by the hydrogen rearrangement pathway although transition state $1d^{\bullet+}$ is still 15 kJ/mol below the energy limit established by the reactants $1^{\bullet+}$ and NH_3 .

Although the anti-Markovnikov adduct $1b^{\bullet+}$ decomposes without any significant energy barrier to the products 5^+ and Cl^{\bullet} , the initial intermediate formed regioselectively by the addition of NH_3 to $1^{\bullet+}$ is certainly the more stable Markovnikov adduct $1a^{\bullet+}$. Since $1a^{\bullet+}$ cannot produce the substitution products directly, it renders either back-dissociation or rearrangements to an isomeric distonic ion more disposed for the loss of Cl^{\bullet} . In the first case, the preferred formation of $1a^{\bullet+}$ leads to a "dead end" of the substitution reaction, and only that fraction of the collision complexes which eventually breaks down into the anti-Markovnikov adduct $1b^{\bullet+}$ will react by loss of Cl^{\bullet} . Thus, the reduced reaction efficiency of the substitution is determined by the regioselectivity of the addition step and the ratio $1a^{\bullet+}/1b^{\bullet+}$ initially formed. In the second case, $1a^{\bullet+}$ may rearrange by a 1,2-hydrogen shift into an α -distonic ion $\text{ClCH}_2\text{CHNH}_3^+$ as an intermediate suitable for the loss of Cl^{\bullet} , or may interconvert into $1b^{\bullet+}$ by an 1,2-shift of the NH_3 group. An *ab initio* calculation of the activation energy for the rearrangement of $1a^{\bullet+}$ into the α -distonic ion by an 1,2-hydrogen shift results in a prohibitively large barrier of 186 kJ/mol for this process, in agreement with the large activation energies reported for 1,2-hydrogen shifts in other distonic ions.³⁰ Hence, this rearrangement is excluded. The transition state $1c^{\bullet+}$ connecting $1a^{\bullet+}$ and $1b^{\bullet+}$ by the 1,2- NH_3 shift is located 115 kJ/mol above $1a^{\bullet+}$. The calculated activation energy for the 1,2- NH_3 shift as well as the structure of the transition state $1c^{\bullet+}$ compare well with the results of L. Radom et al. for the 1,2- NH_3 shift in the β -distonic isomer of the ethylamine radical cation.³¹ In spite of the quite large activation energy of the

1,2- NH_3 shift, the transition state $1c^{\bullet+}$ is still 83 kJ/mol below the energy limit defined by the reactants. Therefore, interconversion $1a^{\bullet+} \rightleftharpoons 1c^{\bullet+} \rightleftharpoons 1b^{\bullet+}$ is clearly an alternative to back dissociation of $1a^{\bullet+}$. In this case, the reaction efficiency of the substitution is determined by the competition between back-dissociation and rearrangement of $1a^{\bullet+}$ into $1b^{\bullet+}$, and the transition state $1c^{\bullet+}$ corresponds to the bottle neck of the total substitution reaction because of its tight cyclic structure.

As mentioned above the reaction energy profile for the reaction of the bromo derivative $2^{\bullet+}$ with NH_3 is qualitatively identical to that of the chloro ion $1^{\bullet+}$. In particular, the activation barriers for the 1,2- NH_3 shift converting the Markovnikov addition product $2a^{\bullet+}$ into the anti-Markovnikov product $2b^{\bullet+}$ and for the hydrogen rearrangement routes for the rearrangements of $2a^{\bullet+}$ or $2b^{\bullet+}$ are identical to the case of the chloro derivative. Obviously, the exchange of the Cl substituent by Br has no effect on the relative energy of the transition state especially of the 1,2- NH_3 shift. However, quantitatively the reaction of the vinyl bromide radical cation ($2^{\bullet+}$) with NH_3 differs from that of the chloro derivative $1^{\bullet+}$ by the reaction enthalpy of the total process, which is more exothermic for $2^{\bullet+}$ as expected from the cleavage of the weaker C–Br bond, and the reaction enthalpy of the first addition step $2^{\bullet+} + \text{NH}_3 \rightarrow 2a^{\bullet+}$ which is distinctly less exothermic (–184 kJ/mol) than the addition of NH_3 to ionized vinyl chloride (–198 kJ/mol). This is a consequence of the better stabilization of the radical site by Cl than by Br. In line with this explanation the energies of the anti-Markovnikov adduct ions $1b^{\bullet+}$ and $2b^{\bullet+}$ relative to the reactants are again nearly identical, since the Cl or Br substituent is now in the remote β -position to the radical site.

As a consequence of the different reaction enthalpy of the initial addition step, the bromo derivative $2a^{\bullet+}$ is less chemically activated than chloro derivative $1a^{\bullet+}$ by the preceding addition step. If both intermediates have to rearrange into the reactive anti-Markovnikov product ions $1b^{\bullet+}$ and $2b^{\bullet+}$ for the substitution to occur, they have to pass identical activation barriers and very similar transition-state structures on their way to the products 5^+ and Cl^{\bullet} or Br^{\bullet} . Thus, the energetically less excited bromo derivative $2a^{\bullet+}$ is expected to react with a lower reaction efficiency in spite of the increased exothermicity of the total process. In fact, preliminary RRKM calculations using the structures and energies calculated for $1a^{\bullet+}$ and $1c^{\bullet+}$ or $2a^{\bullet+}$ and $2c^{\bullet+}$ indicate that the calculated difference of 14 kJ/mol of

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excess energy between the distonic ions $1\text{a}^{+\bullet}$ and $2\text{a}^{+\bullet}$ is clearly sufficient to explain a difference in the reaction efficiencies of about a factor 2 experimentally observed for the reactions of chloroalkene and bromoalkene radical cations.

Conclusion

The results of the investigation of the reactions of vinyl halide radical cations with ammonia by a combination of FT-ICR spectrometry, tandem-mass spectrometry, and by *ab initio* calculation of the reaction energy profiles reveal further interesting aspects of the mechanisms of unsaturated organic radical cations with nucleophiles. Deprotonation and substitution of the halogen substituent, which are observed experimentally, turn out to be both exothermic. Nevertheless, it is remarkable that an entropically quite demanding substitution can compete with such a simple process as proton transfer and is in fact the main reaction pathway for vinyl halide radical cations at thermal energies. Obviously, the addition of the nucleophile NH_3 to the double bond of the ionized vinyl halide proceeds quickly in the collision complex without any noticeable energy barrier and severe steric constraints. Indeed, *ab initio* calculations detect no activation barrier for the addition of NH_3 to the double bond of the ionized alkene, in marked contrast to the reactions of aromatic radical cations.^{2d}

Nonetheless, the efficiencies of the vinyl halide radical cations with NH_3 are distinctly below the collision rate and are significantly smaller for the ionized vinyl bromide $2\text{a}^{+\bullet}$ than for ionized vinyl chloride $1\text{a}^{+\bullet}$. This effect is due to differences of the chemical activation of the distonic ions generated by the initial addition step. The addition of NH_3 to ionized vinyl chloride is more exothermic than addition to ionized vinyl bromide because of the better stabilization of the radical site in the chloro-distonic ion. Hence, in this latter ion more excess energy is available for the subsequent reaction steps than in the bromo derivative. This result reinforces the fact that the reactions of the radical cations of unsaturated organic compounds with nucleophiles in the diluted gas phase are dominated by chemically activated species. Thus, the rate constants and dynamics of these reactions are expected to depend strongly also on entropic effects.

Further, it has been shown by gas-phase titration experiments of the $\text{C}_2\text{H}_6\text{N}^+$ ions arising from the substitution of the halogen substituent by NH_3 that these ions correspond to vinylammonium ions 5^+ and that the much more stable acetaldiminium ions (6^+) are not formed. Subsequent isomerization of 5^+ into 6^+ by a 1,3-sigmatropic H shift is blocked by a large activation barrier. Interestingly however, this isomerization is catalyzed in a collision complex of the vinylammonium ion (5^+) with a suitable base by a shuttle mechanism. This base-induced proton shuttle is very likely a general mechanism for the isomerization of large protonated and multifunctional molecules because of the rather long lifetime expected for the respective collision complexes. In the present case obviously only vinylammonium ions (5^+) arise from the reaction of ammonia with ionized vinyl halides by an *ipso*-substitution of the halogen substituent most probably by an addition/elimination mechanism.

The analysis of the reaction energy profiles of the substitution reaction of ammonia with vinyl halide radical cations calculated by *ab initio* methods suggests that the reduced efficiency of the substitution is due to a regioselective addition of ammonia to the α -C atom of the ionized vinyl halide (Markovnikov orientation). This preferred Markovnikov addition requires an additional rearrangement step to arrive at the substitution product. The least energy demanding rearrangement corresponds to a 1,2-shift of the ammonium group generating the anti-Markovnikov isomer of the addition product. This rearrangement appears to be the bottle neck of the substitution reaction yielding eventually the vinylammonium ion.

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