

Reactions of Gaseous, Halogenated Propene Radical Cations with Ammonia: A Study of the Mechanism by Fourier Transform Ion Cyclotron Resonance

Michael Büchner, Andreas Nixdorf, and Hans-Friedrich Grützmacher*

Abstract: The gas-phase ion-molecule reactions of the radical cations of 2-chloropropene ($1^{+\bullet}$), 2-bromopropene ($2^{+\bullet}$), and 2-iodopropene ($3^{+\bullet}$), as well as of the corresponding three 3,3,3-trifluoropropenes ($4^{+\bullet}$ – $6^{+\bullet}$) with ammonia have been studied by FT-ICR mass spectrometry complemented by ab initio calculations of the reaction thermochemistry. In all cases a deprotonation of the 2-halopropene radical cations by ammonia is distinctly exothermic. In spite of this, the substitution of the halo substituent by NH_3 is the main reaction pathway for $1^{+\bullet}$ and $2^{+\bullet}$ and is still competing for the slowly reacting iodo derivative $3^{+\bullet}$. In the latter case deprotonation generates not only NH_4^+ , but

also the proton-bridged dimer $[\text{H}_3\text{N} \cdots \text{H}^+ \cdots \text{NH}_3]$. These effects prove that the first addition step of the substitution by an addition-elimination mechanism of the haloalkene radical cations can compete effectively with exothermic deprotonation and occurs without noticeable activation energy. In fact it appears likely that the deprotonation of the unsaturated radical cations proceeds also by an addition-elimination process. The calculation of the reaction enthalpy

Keywords: ion-molecule reactions • mass spectrometry • nucleophilic substitution • radical ions • reaction mechanisms

shows that addition of NH_3 to the ionized 3,3,3-trifluoro-2-halopropenes $4^{+\bullet}$ – $6^{+\bullet}$ is especially exothermic. Experimentally this effect is not only reflected in the increased reaction efficiency of the substitution product, even in the case of the iodo derivative $6^{+\bullet}$, but also in competing fragmentations of the strongly excited distonic intermediates generated by the addition step. This corroborates the postulate that the variation of the rate constants with the substituents, which is observed for the reactions of ionized haloalkenes with ammonia, is caused by the excess energy released in the initial addition step.

Introduction

The detection of radical cations as reactive intermediates has initiated an increasing number of studies of their reactivities in solution^[1] and in the gas phase.^[2] These studies reveal that, in particular, organic radical cations exhibit a high reactivity that is attributed to their electron deficiency and which has been termed electron hole catalysis.^[3] In line with this concept unsaturated organic radical cations display fast reactions with electron-rich donor molecules and generate a variety of reaction products by addition, substitution, and/or fragmentation reactions. However, owing to the short lifetime of most organic radical cations in solution it is difficult to obtain information about the details of the reaction mechanisms and to determine which structural factors control the reaction rates.^[4] 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.

Recently, we have performed a systematic study of the gas phase reactions of mono- and dihalogenated arenes^[5] 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 through an addition-elimination mechanism. The kinetics and the rather low reaction efficiency of less than 15 % show that the first addition step of the aromatic substitution process is rate-determining. This was explained by the configuration mixing model of Shaik and Pross^[6] of polar organic reactions. However, further studies revealed that the mechanisms of the aromatic substitution via radical cations is more complex and includes rearrangement steps between addition of the nucleophile and elimination of the halo substituent.^[5b,c]

In the case of gas phase substitution reactions of olefinic radical cations the addition of the nucleophile is not expected to be the rate-determining step.^[2a] This was corroborated by FT-ICR studies of the ion-molecule reactions of the radical

[*] Prof. Dr. H.-F. Grützmacher, M. Büchner, Dr. A. Nixdorf
Lehrstuhl I für Organische Chemie, Fakultät für Chemie
der Universität Bielefeld
Postfach 10 01 31, D-33501 Bielefeld (Germany)
Fax: (+49) 521-106-6417
E-mail: gruetzmacher@chema.uni-bielefeld.de

reactants

Markovnikov orientation

anti-Markovnikov orientation

substitution products

Scheme 1. Substitution reaction of haloethene radical cations with ammonia.

More experimental information is needed to understand the extraordinary reactivity of olefinic radical cations and the course of their reactions with nucleophiles. In particular, the successful competition of addition to the ionized double bond of the haloalkene radical cation against deprotonation by a basic nucleophile should be verified unequivocally. Further, the role of the excess energy imparted to the intermediate distonic ion by an exothermic addition step should be examined further. Thus, we complemented the previous investigations by a study of the ion-molecule reactions of ionized 2-halopropenes **1–3** and 3,3,3-trifluoro-2-halopropenes **4–6** with ammonia using FT-ICR spectrometry.

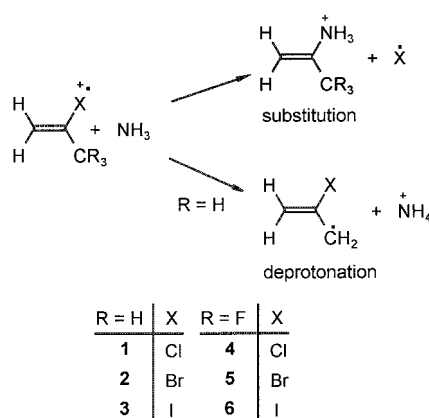
The radical cations of the 2-halopropenes **1–3** should be distinctly more acidic than the previously studied ionized vinyl halides because deprotonation of a propene radical cation yields a stabilized allyl radical. Therefore, the radical cations **1–3** are well-suited for an investigation of the competition between addition and deprotonation of unsaturated organic radical cations by basic substrates. It will be shown that, surprisingly, the substitution reaction of radical cations **1–3** is still observed in spite of the exothermic deprotonation by ammonia, thus corroborating a fast addition step of the nucleophile to the ionized double bond. In the case of all ionized 2-halopropenes the addition step generating a β -distonic ion by addition of ammonia is expected to be more exothermic than for ionized haloethenes. This effect should be especially increased for the radical cations of the 3,3,3-trifluoro-2-halopropenes **4–6**. Further, deprotonation of **4–6** is not expected to interfere with substitution because of the missing methyl group. Hence, the radical cations **4–6** are expected to reveal more clearly effects of a chemical activation during the addition step on the further fate of the excited intermediate distonic ions. It will be shown that this is indeed the case, and that the large excess energy present in the distonic ion results in additional fragmentations. The results of the kinetic experiments for 2-halopropene radical cations **1^{•+}–3^{•+}** will be discussed first and will be followed by a discussion of the reactions of the radical cations **4^{•+}–6^{•+}** with ammonia.

Abstract in German: Die Ion/Molekül-Reaktionen von Radikalkationen der 2-Halogenpropene $1^{+\bullet}-3^{+\bullet}$ und der 3,3,3-Trifluor-2-halogenpropene $3^{+\bullet}-6^{+\bullet}$ mit Ammoniak in der Gasphase werden mit Hilfe der FT-ICR-Massenspektrometrie untersucht und durch Ab initio-Rechnungen zur Thermodynamik der verschiedenen Prozesse ergänzt. Die Deprotonierung der 2-Halogenpropen-Radikalkationen durch Ammoniak ist danach in allen Fällen deutlich exotherm. Trotzdem ist für $1^{+\bullet}$ und $2^{+\bullet}$ die Substitution des Cl- bzw. Br-Substituenten die Hauptreaktion und auch im Fall des langsamer reagierenden I-Derivats $3^{+\bullet}$ eine intensive Konkurrenzreaktion. Im letzteren Fall wird bei der Deprotonierung nicht nur NH_4^+ gebildet, sondern auch das protonenverbrückte Dimer $[\text{H}_3\text{N}\cdots\text{H}^+\cdots\text{NH}_3]$. Diese Befunde beweisen, daß der erste Additionsschritt im Additions/Eliminierungsmechanismus der Substitution wie die Deprotonierung ohne größere Aktivierungsschwelle verläuft. Berechnungen der Reaktionsenthalpie zeigen, daß die Addition von NH_3 an die ionisierten 3,3,3-Trifluor-2-halogenpropene $4^{+\bullet}-6^{+\bullet}$ besonders exotherm ist. Im Experiment zeigt sich dies nicht nur durch erhöhte Reaktionsgeschwindigkeitskonstanten des gesamten Prozesses, sondern auch durch zusätzliche Fragmentierungen des hoch angeregten distonischen Zwischenprodukts. Dies stimmt mit der Vorstellung überein, daß die Abstufung der Geschwindigkeitskonstanten der Reaktionen ionisierter Halogenalkene mit Ammoniak durch die unterschiedliche Überschußenergie im Additionsprodukt bestimmt wird.

Results and Discussion

Thermochemistry: In discussing ion-molecule reactions in the gas phase at very low pressures studied by FT-ICR spectrometry, it should be noted that these reactions occur in isolated collision complexes of the reactants without energy exchange with the surroundings. These collision complexes are *electrostatically activated* by the energy gained from ion/dipole and ion/induced dipole interactions, and this excess energy may be used to induce chemical transformations within the complex. A consequence of the lack of any additional (thermal) activation is that only exothermic processes are observed, and that the experimental rate constants of the chemical reactions are not directly related the internal barrier or activation energy of a chemical reaction within the complex. Hence it is useful to accompany the experimental rate measurements by a theoretical calculation or estimation of the minima and other stationary points along the MERP of the ion-molecule reaction to get a better basis for the discussion of the experimental results.

The parallel reactions shown in Scheme 2 for 2-halopropene radical cations 1^{+*} – 3^{+*} and ammonia are



Scheme 2. Substitution and deprotonation of halopropene radical cations **1**–**6** with ammonia.

expected to occur because of the distinct gas-phase acidity of the propene radical cation^[9] and also from consideration of the results obtained for ion-molecule reactions of ionized vinyl halides with ammonia.^[7, 8] The heat of formation (ΔH_f) of chloroethene, bromoethene, and their radical cations are known with high accuracy,^[10] and the MERP of their reaction with ammonia has been calculated by high-quality ab initio methods.^[7] Further, ΔH_f of many C_2 , C_3 , and C_4 alkenes, their radical cations, and of other radicals are known reliably.^[10] These data can be combined to calculate the minima along the MERP of the reactions of 2-chloropropene 1^{+*} with ammonia at the MP2/6-31G* level of theory, making extensive use of isodesmic reactions and anchoring the relative heats of formation at $\Delta H_f(\text{chloroethene}^{+*}) = 999 \text{ kJ mol}^{-1}$ (238.8 kcal mol⁻¹).^[10] and $\Delta H_f(\text{chloroethene}^{+*}) = 1027 \text{ kJ mol}^{-1}$ (245.4 kcal mol⁻¹).^[10] The specific isodesmic reactions used and the relevant data are given in the

Appendix. In most cases more than one isodesmic reaction has been calculated to arrive at a value of a specific ΔH_f . The results deviate by less than $\pm 10 \text{ kJ mol}^{-1}$, which also corresponds to the estimated limits of error of most of the experimental data used, and this is sufficient for a discussion of the trends of the thermochemistry between the closely related reactions studied here. The ΔH_f of 1^{+*} , of the reaction intermediates, and of reaction products obtained are given in Table 1. These data have been used for the construction of the

Table 1. Calculated heats of formation of reactants, intermediates, and products of the reactions of 2-halogenopropene radical cations 1^{+*} – 3^{+*} and 3,3,3-trifluoro-2-chloropropene radical cation 4^{+*} with ammonia.

	ΔH_f [kJ mol ⁻¹]	Reaction	ΔH_f [kJ mol ⁻¹]
2-chloropropene ⁺⁺ (1 ⁺⁺)	940		
NH ₃	–46 ^[a]		
distonic adduct (Markovnikov)	691	addition, Markovnikov	–203
distonic adduct (anti-Markovnikov)	722	addition, anti-Markovnikov	–172
2-propenyl-ammonium cation	641		
Cl atom	121 ^[a]	substitution	–132
2-chloroallyl radical	112		
Ammonium cation	632 ^[a]	deprotonation	–150
2-bromopropene ⁺⁺ (2 ⁺⁺)	990		
NH ₃	–46 ^[a]		
distonic adduct (Markovnikov)	743	addition, Markovnikov	–201
2-propenyl-ammonium cation	641		
Br atom	112 ^[a]	substitution	–191
2-bromoallyl radical	171		
Ammonium cation	632 ^[a]	deprotonation	–141
2-iodopropene ⁺⁺ (3 ⁺⁺)	994		
NH ₃	–46 ^[a]		
distonic adduct (Markovnikov)	786	addition, Markovnikov	–162
2-propenyl-ammonium cation	641		
I atom	107 ^[a]	substitution	–200
2-iodoallyl radical	227		
Ammonium cation	632 ^[a]	deprotonation	–89
trifluoro-2-chloropropene (4 ⁺⁺)	507		
NH ₃	–46 ^[a]		
distonic adduct (Markovnikov)	85	addition, Markovnikov	–376
distonic adduct (anti-Markovnikov)	131	addition, anti-Markovnikov	–330
2 – (3,3,3-trifluoro-propenyl)-ammonium cation	61		
Cl atom	121 ^[a]	substitution	–279

[a] taken from ref. [10]

schematic MERP shown in Figure 1. The activation energy for the 1,2-NH₃ shift between the isomeric distonic adduct ions was shown previously not to depend much on the substitution type^[7] and was taken from the published MERP of the chloroethene radical-cation reaction.

The substitution reaction of 1^{+*} by ammonia is distinctly more exothermic than the reaction of the chloroethene radical cation (132 kJ mol⁻¹ vs. 116 kJ mol⁻¹), but the exothermicity of the addition step forming the Markovnikov adduct is almost identical. The new feature of the MERP of the reaction of 1^{+*} with ammonia is the deprotonation reaction yielding the 2-chloroallyl radical and NH₄⁺; this is very exothermic, as expected.

It is known that the result of isodesmic reactions often does not depend on the level of the ab initio method used.^[11] This

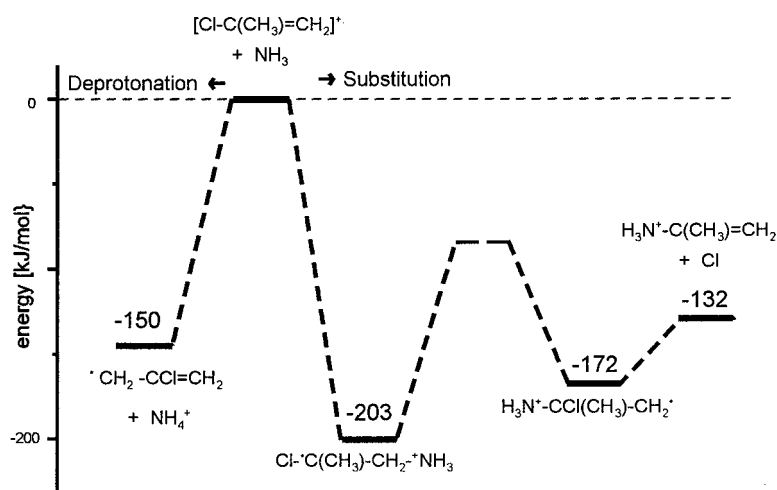


Figure 1. MERP (minimum reaction energy path) for deprotonation and substitution of 2-chloropropene radical cations 1^{++} by ammonia.

has been confirmed in the present case by a calculation the isodesmic reactions for 1^{++} and its products also by the lower level methods MP2/3-21G and MP2/STO-3G. Hence, the ΔH_f necessary for the construction of the MERPs of the reactions of the bromo and iodo derivatives 2^{++} and 3^{++} , and of the 3,3,3-trifluoro-2-propene radical cation 4^{++} with ammonia have been determined only by these methods. While this may introduce increased uncertainty into the ΔH_f values obtained, the main source of error is the limited number of ΔH_f of reference compounds for the iodo derivative **3**, the trifluoro derivative **4**, and their radical cations. For example, the ΔH_f of iodoethene and iodopropene had to be estimated by Benson's incremental method, and in the case of **4** only the ΔH_f of the 3,3,3-trifluoropropene,^[10] the 2,2,2-trifluoroethyl,^[10] and the 3,3,3-trifluoropropyl radical^[10] are known. Nonetheless, the ΔH_f obtained (see Table 1) can be used semiquantitatively to discuss the variation of the reaction energies with changing the substituents. For the reactions of the 2-bromopropene radical cation 2^{++} the MERP is essentially identical to that of the chloro derivative 1^{++} with exception of the reaction enthalpy (ΔH_r) of the substitution, which is more exothermic by approximately 60 kJ mol⁻¹. A similar result has been obtained by high-quality ab initio calculations of the MERPs of the corresponding haloethene radical cations.^[7] The ΔH_r of the substitution of the iodo substituent of 3^{++} by ammonia exhibits a further increase, as expected, owing to the small bond energy of the C–I bond cleaved, but the addition step generating the Markovnikov adduct and the deprotonation yielding a 2-iodoallyl radical and NH_4^+ are distinctly less exothermic by about 40 and 60 kJ mol⁻¹, respectively. This trend is expected because of the increased stabilization of the reactant alkene radical cation by an iodo substituent at the double bond, which is also reflected in the decreased ionization energy of iodoethene^[10] and the decreased stabilization of a radical by an α -iodo substituent. For 3^{++} , a deprotonation yielding an allene and an iodine atom is also slightly exothermic by 15 kJ mol⁻¹, whereas the analogous process is endothermic and almost thermoneutral in the case of 1^{++} and 2^{++} , respectively.

Compared with the 2-chloropropene reaction system of 1^{++} the MERP of the reaction of the 3,3,3-trifluoro-2-chloropropene radical cation 4^{++} with ammonia exhibits a strong increase in the exothermicity of the first addition step by 70 kJ mol⁻¹ and also of the total substitution reaction. These effects can be attributed to a combination of a stabilization effect of the CF_3 substituent on the radical site of the distonic Markovnikov adduct ion and on a destabilization of the reactant alkene radical ion. The first effect is seen by the difference of 30 kJ mol⁻¹ of the ΔH_f of the 2,2,2-trifluoroethyl radical and the ethyl radical^[10] (relative to the corresponding ethanes), and the second effect increases the ionization energy of 3,3,3-trifluoropropene to 10.95 eV by more than 1 eV, relative to propene.^[10] This corroborates the calculated CF_3 effects on the MERP of 4^{++} .

Summarizing, the results of an estimation and ab initio calculation of the MERPs of the reaction of 2-halopropene radical cations with ammonia assure the expected effects of the substituents on the reaction thermochemistry. In particular the deprotonation of all three halopropene radical cations by ammonia is distinctly exothermic and can be expected always to compete effectively with the substitution reaction. Further, in the series of the ionized 2-chloro-, 2-bromo-, and 2-iodopropene the substitution reaction becomes increasingly more exothermic, while the effect of the halo substituents on the initial addition step is opposite. Finally, the substitution reaction of the 3,3,3-trifluoropropene radical cations is indeed distinctly more exothermic than that of the ionized 2-halopropenes and, in particular, exhibits a very exothermic initial addition step of ammonia to the ionized double bond.

Reactions of 2-halopropene radical cations **1–3 with ammonia:** The rates of exothermic proton transfer between small ions and basic molecules are expected to approach the ion-molecule collision rate. Hence, deprotonation of the radical cations of **1–3** should override any other parallel ion-molecule reaction that exhibits a bottle neck on the MERP, because of entropic effects or the presence of a substantial activation energy. The experimental ion-intensity vs. reaction-time curves (kinetic plot) obtained for the reaction of 2-halopropene radical cations 1^{++} , 2^{++} , and 3^{++} with ammonia are shown in Figure 2. In all three cases the decay of the 2-halopropene radical cations follows exactly pseudo-first-order kinetics, and the bimolecular rate constants (k_{bi}), the reaction efficiencies of the total reaction, and the branching ratio between deprotonation and halogen substitution are given in Table 2.

The efficiencies of the total reaction of 1^{++} and 2^{++} are rather large and approach the collision rate, while that of the iodo derivative 3^{++} is distinctly smaller. It is clearly seen from Figure 2 that substitution of the halogen atom in 1^{++} – 3^{++} by the NH_3 group to form the product ion with $m/z = 58$ competes effectively with proton transfer to the ammonium ion ($m/z = 18$), in spite of the distinctly exothermic deproton-

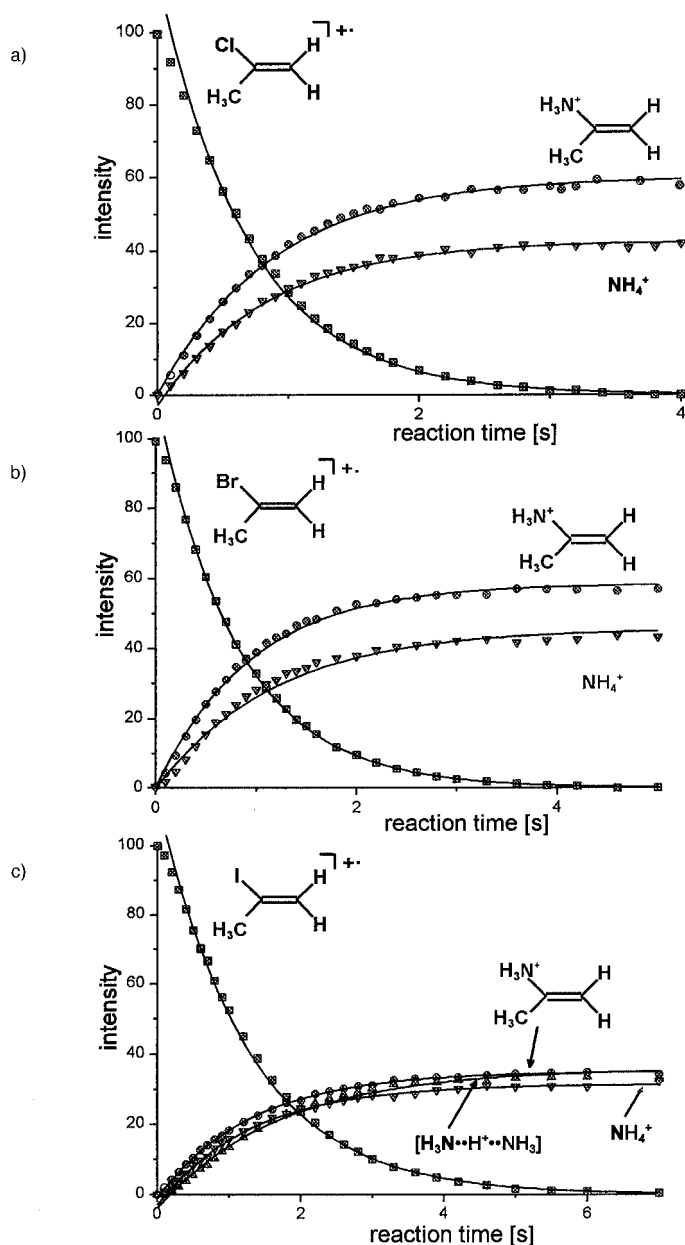


Figure 2. Plot of ion intensity vs. reaction time (kinetic plot) for the reaction of a) 2-chloropropene radical cations $1^{+\bullet}$, b) 2-bromopropene radical cations $2^{+\bullet}$, and c) 2-iodopropene radical cations $3^{+\bullet}$ with ammonia.

Table 2. Kinetic parameters for the reaction of 2-halopropene radical cations with ammonia.

	$k_{bi} \times 10^{-10}$ [cm ³ mol ⁻¹ sec ⁻¹]	Efficiency [%]	Branching ratio substitution/deprotonation
$1^{+\bullet}$	17.8	84	58:42
$2^{+\bullet}$	15.7	77	56:44
$3^{+\bullet}$	7.47	37	35:31:34 ^[a]

[a] m/z 35 (proton-bridged dimer of ammonia).

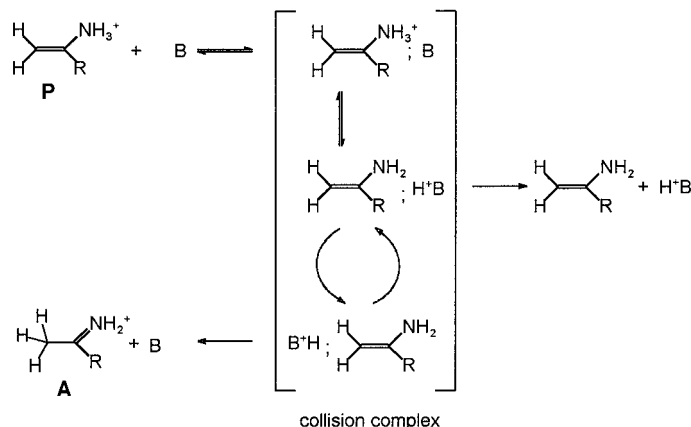
ation process. Substitution is still the main process for the chloro and the bromo derivatives $1^{+\bullet}$ and $2^{+\bullet}$, which also show an almost identical branching ratio for the deprotonation and substitution. This similar behavior of $1^{+\bullet}$ and $2^{+\bullet}$ in their reactions with ammonia is in agreement with the similar

MERPs calculated for these processes (see previous section). The efficiencies of 49 % and 43 % of the substitution process of $1^{+\bullet}$ and $2^{+\bullet}$, calculated from the branching ratio, are slightly larger and smaller, respectively, than the values obtained for this process of ionized vinyl chloride and vinyl bromide (57 % and 35 %^[7]). This suggests that the increased total reaction efficiencies of the halopropenes $1^{+\bullet}$ and $2^{+\bullet}$ are due to the additional deprotonation reaction.

In the case of the less reactive iodopropene radical cation $3^{+\bullet}$, deprotonation is the main process. Interestingly, deprotonation yields not only ammonium ions ($m/z = 18$), but also the proton-bridged dimer of ammonia [$H_3N \cdots H^+ \cdots NH_3$] ($m/z = 35$). Under the experimental conditions used, the reaction of $3^{+\bullet}$ proceeds to yield about equal amounts of the substitution product ($m/z = 58$), ammonium ions ($m/z = 18$), and the proton-bridged dimer ($m/z = 35$). From this branching ratio an efficiency of only about 13 % is calculated for the substitution process. A decrease of the efficiency of the gas-phase substitution reaction of haloalkene radical cations with decreasing strength of the carbon–halogen bond has been observed before^[7] and will be discussed further in the next section. The origin of this effect is very likely a smaller amount of excess energy in the distonic addition product of the first reaction step. Here it is of interest to note that even in the case of the slowly reacting $3^{+\bullet}$, substitution is still competitive with regard to deprotonation by ammonia. Again, this observation excludes a direct substitution mechanism of the S_N2 type in ionized haloalkenes, which is entropically demanding and which would impose an activation barrier on the reaction path. Instead, the substitution proceeds by at least two reaction steps of an addition-elimination mechanism, with a fast first addition step that evidently overrides even exothermic deprotonation. This is only conceivable if the collision complex of a 2-halopropene radical cation and ammonia collapses quickly to the β -distonic addition product without any activation barrier. Thus, the results obtained here confirm the ab initio calculations of the MERP of ionized vinyl halides with ammonia^[7] and of the addition of ethene radical cations to neutral ethene,^[12] which show no activation barrier for the addition of the electron-rich neutral reaction partner to the ionized alkene double bond. This ease of addition of nucleophiles also explains the high reactivity of alkene radical cations in solution generated electrochemically or by single-electron-transfer reactions.

To complete the examination of the substitution reaction of the 2-halopropene radical cations $1^{+\bullet}$ – $3^{+\bullet}$ with ammonia, the structure of the $C_3H_8N^+$ product ion was verified by a gas-phase titration experiment^[13] from which the proton affinity (PA) of the neutral C_3H_7N precursor (conjugate base) of the product ion can be determined. It has been shown previously for the substitution-product ion of vinyl halide radical cation with ammonia, that originally a vinyl ammonium ion is the only reaction product, which isomerizes more or less quickly by a shuttle mechanism^[14, 7] into the more stable, protonated aldiminium ion during deprotonation. Accordingly, the deprotonation of the $C_2H_6N^+$ product ions by a reference base with a PA between the PA of vinylamine and acetaldimine exhibits bimodal kinetics.^[7] If the 2-propenyl ammonium ion generated by the substitution from $1^{+\bullet}$ – $3^{+\bullet}$ behaves analo-

gously, the proton shuttle during deprotonation converts the 2-propenyl ammonium ion **P** (initially formed) into an acetone immonium ion **A** (Scheme 3), and deprotonation of the product ions $C_3H_8N^+$ by a suitable base should again exhibit bimodal kinetics; this can be used to estimate the PA of the neutral C_3H_7N precursor of **P** and **A**.



Scheme 3. Shuttle mechanism for the base-catalyzed tautomerization of protonated enamines and ketimines in the gas phase.

The PA of the appropriate conjugate bases of C_3H_7N were calculated by AM1, which is known to reproduce the PA within $\pm 20 \text{ kJ mol}^{-1}$,^[15] yielding $PA(2\text{-propenylamine}) = 881 \text{ kJ mol}^{-1}$ and $PA(\text{acetone imine}) = 923 \text{ kJ mol}^{-1}$ (experimental value 934 kJ mol^{-1} ^[10a]). As expected, the PA of acetone imine is considerably larger than that of 2-propenylamine. From these values it is concluded that a reference base with a $PA < 870 \text{ kJ mol}^{-1}$ does not deprotonate the $C_3H_8N^+$ product ions and a base with a $PA > 940 \text{ kJ mol}^{-1}$ quickly deprotonates all $C_3H_8N^+$ product ions, while the deprotonation by a base with a PA around 900 kJ mol^{-1} should exhibit bimodal kinetics. Indeed, this is observed experimentally. With ammonia ($PA = 854.0 \text{ kJ mol}^{-1}$ ^[10a]) and methylamine ($PA = 899.0 \text{ kJ mol}^{-1}$ ^[10a]) no deprotonation is observed, while complete deprotonation is achieved with diethylamine ($PA = 952.4 \text{ kJ mol}^{-1}$ ^[10a]). The kinetic plots for the deprotonation of the $C_3H_8N^+$ product ions by ethylamine ($PA = 911.8 \text{ kJ mol}^{-1}$ ^[10a]) and dimethylamine ($PA = 929.5 \text{ kJ mol}^{-1}$ ^[10a]) are shown in Figure 3. Deprotonation by both amines exhibits clearly the bimodal kinetics of a fast exothermic proton transfer and of a slow endothermic or thermoneutral deprotonation. However, owing to the different capabilities of the amines to act as a catalyst for the proton shuttle, the fractions of quickly and slowly deprotonated ions $C_3H_8N^+$ are different.

From these kinetic data the PA of the two isomers of the neutral C_3H_7N precursors are limited to $899 \text{ kJ mol}^{-1} < PA(C_3H_7N(I)) < 914 \text{ kJ mol}^{-1}$ and $930 \text{ kJ mol}^{-1} < PA(C_3H_7N(II)) < 952 \text{ kJ mol}^{-1}$ or $906 \pm 7 \text{ kJ mol}^{-1}$ and $941 \pm 11 \text{ kJ mol}^{-1}$, respectively; this is in reasonable agreement with the calculated PA of the conjugate bases, 2-propenylamine and acetone imine, of the expected products. This absolutely analogous behavior of the reaction products of the substitution of ionized haloethenes and halopropenes

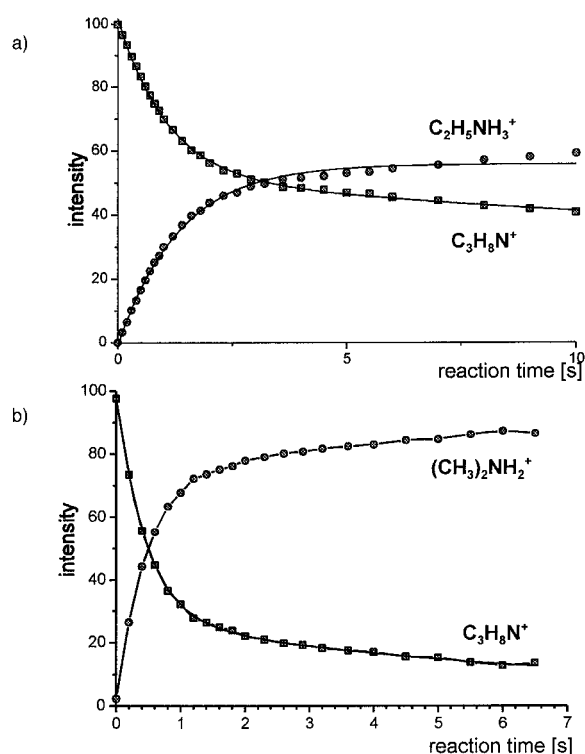
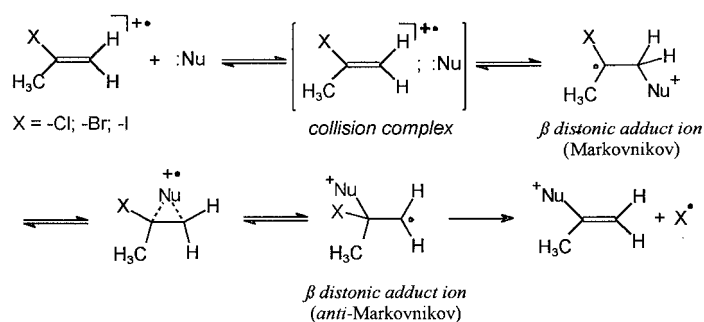


Figure 3. Plot of ion intensity vs. reaction time for the deprotonation (gas-phase titration) of the substitution product $C_3H_8N^+$ (from **2**⁺) by a) ethylamine ($PA = 911.8 \text{ kJ mol}^{-1}$ ^[10a]), and b) dimethylamine ($PA = 929.5 \text{ kJ mol}^{-1}$ ^[10a])

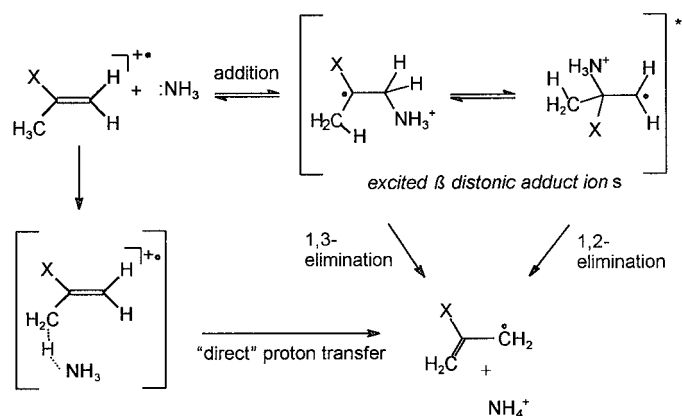
with ammonia confirms that both substitution reactions take identical routes^[7] to homologous products, in spite of the much more effective competition of the deprotonation of the radical cations in the case of the 2-halopropenes. Therefore, addition of ammonia results in isomeric β -distonic ammonium ions, corresponding to Markovnikov and anti-Markovnikov orientation, and interconversion by a 1,2- NH_3 shift before the halogen atom is lost from the less stable anti-Markovnikov product as depicted in Scheme 4.



Scheme 4. Mechanism of nucleophilic substitution reaction of ionized halopropenes **1**⁺–**3**⁺.

In addition to confirming the addition-elimination mechanism for the nucleophilic substitution of aromatic and olefinic radical cations, the results presented here also suggest a special mechanism of the deprotonation reaction of these unsaturated radical cations. In particular the deprotonation of

the iodo derivative $3^{+\bullet}$ yielding a proton-bridged dimer of ammonia ($m/z=35$) is not explained easily by a simple proton-transfer mechanism. Generally it is assumed that deprotonation of radical cations by a base occurs through a loose transition state structurally related to a proton-bridged complex of the base and the radical formed by deprotonation. This critical configuration is reached by a direct approach of the base onto the acidic hydrogen atom (Scheme 5) within the collision complex of the reactants, followed by a rapid proton transfer if the reaction is exothermic.



Scheme 5. Mechanisms of deprotonation of ionized halopropenes $1^{+\bullet}$ – $3^{+\bullet}$ by ammonia.

In the case of the alkene radical cations studied here, the nucleophilic base is also trapped competitively in the collision complex by addition to the double bond. However, if the further substitution process of the addition product is slow, the addition product will dissociate back to the complex of reactants, which once again are available for a deprotonation reaction. A consequence of this picture of the dynamics of the reaction of the 2-halopropene radical cations with ammonia is that the total reaction efficiency should always approach the collision rate, because deprotonation is exothermic and fast for all three radical cations $1^{+\bullet}$ – $3^{+\bullet}$. However, the experiment shows that in the case of the iodo derivative $3^{+\bullet}$ not only is the substitution process slow, but also the exothermic deprotonation is slow, as shown by the decreased total reaction efficiency. An obvious explanation of this effect is that deprotonation does not occur independently of the substitution, but proceeds via the distonic addition product (Scheme 5). A *syn*-1,2-elimination in the anti-Markovnikov adduct as well as a 1,3-elimination in the preferred Markovnikov adduct should exhibit a considerable activation barrier that requires sufficient excess energy in the addition product for the elimination of NH_4^+ . Since the adduct ion derived from $3^{+\bullet}$ is less excited than in the case of the chloro and bromo derivatives $1^{+\bullet}$ and $2^{+\bullet}$, deprotonation by this mechanism is also reduced and may in fact need a second ammonia molecule to surmount the activation barrier. However, additional and more focussed experiments are needed to substantiate these ideas about a special deprotonation mechanism of unsaturated radical cations.

Reactions of 3,3,3-trifluoro-2-halopropene radical cations $4^{+\bullet}$ – $6^{+\bullet}$ with ammonia: The 3,3,3-trifluoro-2-halopropene radical cations lack the methyl group that could be easily deprotonated with ammonia. Hence, substitution of the 2-halogen substituent is expected to be the only efficient process observed for the reactions of $4^{+\bullet}$ – $6^{+\bullet}$ with ammonia. The bimolecular rate constants (k_{bi}) and reaction efficiencies of these reactions are presented in Table 3, and Figure 4 displays, as an example, the kinetic plot for the reaction of the bromo derivative $5^{+\bullet}$ and the iodo derivative $6^{+\bullet}$ with ammonia.

Table 3. Kinetic parameters for the reaction of 3,3,3-trifluoro-2-halopropene radical cations with ammonia.

	$k_{\text{bi}} \times 10^{-10}$ [$\text{cm}^3 \text{mol}^{-1} \text{sec}^{-1}$]	Efficiency [%]
$4^{+\bullet}$	17.9	88
$5^{+\bullet}$	17.4	87
$6^{+\bullet}$	10.7	54

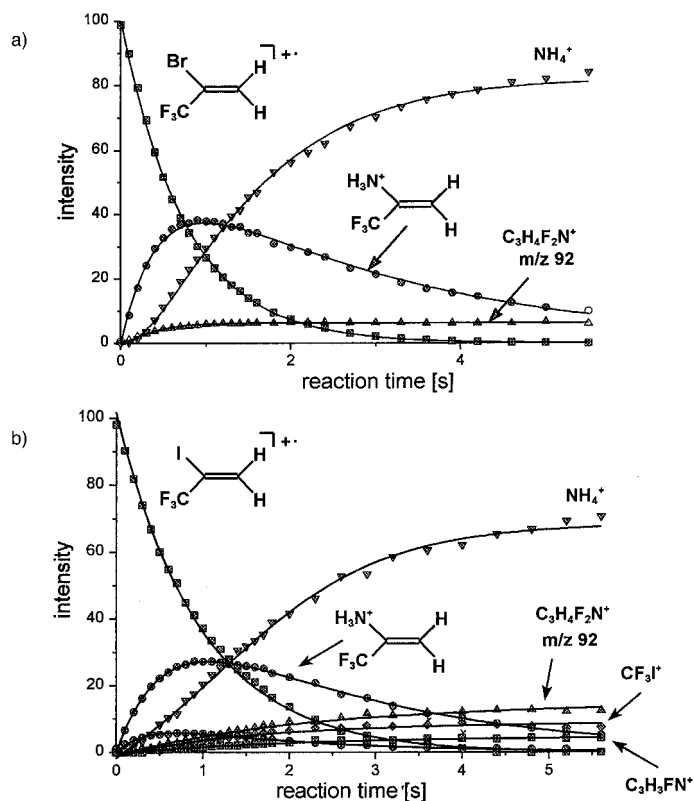


Figure 4. Plot of ion intensity vs. reaction time (kinetic plot) for the reaction of a) 3,3,3-trifluoro-2-bromopropene radical cations $5^{+\bullet}$, and b) 3,3,3-trifluoro-2-iodopropene radical cations $6^{+\bullet}$ with ammonia.

For all three 3,3,3-trifluoro-2-halopropene radical cations $4^{+\bullet}$ – $6^{+\bullet}$ excellent pseudo-first-order kinetics were observed, and the k_{bi} obtained from the decay of these radical cation show that the reaction is very efficient for the chloro and bromo derivatives $4^{+\bullet}$ and $5^{+\bullet}$. The reaction again proceeds essentially with the ion-molecule collision rate, while the iodo substituted radical cation $6^{+\bullet}$ exhibits a reduced reaction efficiency. Contrary to the original expectation, the ammo-

nium ion is the only abundant reaction product at long reaction times for all three radical cations $4^{+\bullet}$ – $6^{+\bullet}$ (Figure 4). However, an inspection of the ion-intensity vs. reaction-time curves of the ammonium ion and the expected substitution-product ion $C_3H_5NF_3^+$ reveals that the ammonium ion clearly arises from a deprotonation of the substitution product $C_3H_5NF_3^+$, which accordingly exhibits a maximum of its intensity during the reaction. The deprotonation of the $C_3H_5NF_3^+$ ion was corroborated in a separate experiment by isolation of the $C_3H_5NF_3^+$ ions and ejection of all other ions from the FT-ICR cell after an appropriate reaction time yielding the product ion $C_3H_5NF_3^+$ with sufficient intensity. Following the isolation, a complete deprotonation of the $C_3H_5NF_3^+$ ions by ammonia was observed. Evidently, the CF_3 -substituent lowers the PA of the conjugate base 2-(3,3,3-trifluoropropenyl)amine below the PA of ammonia (854 kJ mol^{-1} [10]), so that the corresponding ammonium $C_3H_5NF_3^+$ ion, which is the expected substitution product of $4^{+\bullet}$ – $6^{+\bullet}$, is quickly deprotonated with ammonia. This effect of the strongly electron-withdrawing CF_3 group on the PA is well documented for carbonyl compounds, ethers, and amines, [10] which exhibit PA values 50 – 100 kJ mol^{-1} lower than the corresponding CH_3 substituted derivatives. The PAs of 2-(3,3,3-trifluoropropenyl)amine (817 kJ mol^{-1}) and trifluoroacetone imine (833 kJ mol^{-1}), which are the conjugate bases of the possible reaction products, are both below the PA of ammonia.

Besides the $C_3H_5NF_3^+$ ion and the ammonium ion, the reaction of $4^{+\bullet}$ – $6^{+\bullet}$ with ammonia forms product ions with $m/z=92$ in moderate yields, and the iodo derivative $6^{+\bullet}$ generates additional ions with $m/z=219$, $m/z=199$, and $m/z=196$. Accurate mass determination of these ions, from the high-mass-resolution capability of the FT-ICR spectrometer of $m/\Delta m \approx 300\,000$, proves unequivocally the following elemental composition for these ions: $m/z=92 \equiv C_3H_4NF_2^+$, $m/z=219 \equiv C_3H_4NF_2I^+$, $m/z=199 \equiv C_3H_3NFI^+$, and $m/z=196 \equiv CF_3I^+$. The formation of a $C_3H_4NF_2^+$ ion corresponds to the loss of HF from the regular substitution product $C_3H_5NF_3^+$. An inspection of the ion-intensity vs. reaction-time curves shows that this second product ion ($C_3H_4NF_2^+$) is formed in parallel to the main product ion and not by a consecutive elimination of HF caused by attack of ammonia on $C_3H_5NF_3^+$. Obviously the excess energy present in the β -distonic ion created by a very exothermic addition of ammonia to the 3,3,3-trifluoro-2-halopropenes $4^{+\bullet}$ – $6^{+\bullet}$ not only induces the loss of the halogen substituent, but is sufficient to provoke additional elimination of HF in the still energetically excited substitution product before the products separate from the reaction complex. In line with this argument, the excited β -distonic intermediate arising from the addition of ammonia to the iodo derivative $6^{+\bullet}$ eliminates one and two molecules HF instead of losing iodine to yield the ions $m/z=219$, $C_3H_4NF_2I^+$ and $m/z=199$, $C_3H_3NFI^+$, respectively. The structures of these ions were not examined, but the elimination of HF from assorted ions driven by the thermodynamic stability of HF is well known in mass spectrometry. [16] The most obvious mechanism is a 1,4-HF elimination from the Markovnikov-adduct ion yielding the radical cation of a 3,3-difluoro-2-haloallylamine, and the structure of the adduct ion

calculated by ab initio methods indeed indicates an interaction between a proton of the NH_3^+ group and a fluorine atom from the CF_3 group. It is not well understood, however, why the $C_3H_4NF_2I^+$ and $C_3H_3NFI^+$ ions are formed only during the reaction of the 3,3,3-trifluoro-2-iodopropene radical cation $6^{+\bullet}$. The addition of ammonia to the other radical cations $4^{+\bullet}$ and $5^{+\bullet}$ is even more exothermic leading to an even more chemically activated β -distonic ion. It should be noted that the reaction efficiency for $4^{+\bullet}$ and $5^{+\bullet}$ corresponds almost to the collision limit because of this large excess energy available in the reaction intermediate. It may be that the large excess energy of these intermediates reduces the life-time of the distonic ions so much that elimination of HF is bypassed because of the tight transition state necessary. Similarly, the formation of CF_3I^+ ($m/z=196$) as a product of the reaction of $6^{+\bullet}$ with ammonia is unprecedented and surprising. Without further information the reaction pathway yielding this ion from the β -distonic intermediate is difficult to visualize, but clearly requires the rearrangement of an excited ion. Hence, the formation of all these additional product ions during the reaction of the radical cations of 3,3,3-trifluoro-2-halopropenes 4 – 6 with ammonia demonstrate convincingly the presence of an especially large amount of excess energy in the intermediates of these reactions, as expected from the thermochemical calculations. Further, these results show that the reactions following the formation of the excited β -distonic ion by addition of ammonia to the alkene radical cations are controlled at least as well by dynamic effects as by thermochemistry. Thus, the efficiency of the reactions of the haloalkene radical cations with ammonia increases from the haloethenes to the corresponding 3,3,3-trifluoro-2-halopropenes as expected from the calculated MERPs. This shows that in this series there is an increasing release of excess energy during the first addition step to drive the subsequent reaction. By the same effect of a decrease of the chemical activation of the distonic intermediates in each series of ionized chloro-, bromo-, and iodoalkene, the decrease of the substitution reaction efficiency is explained. However, although the distonic intermediate derived from the iodo derivative $6^{+\bullet}$ is less chemically activated than its chloro and bromo analogues derived from $4^{+\bullet}$ and $5^{+\bullet}$, it nevertheless exhibits more side reactions with greater abundance. This mixture of effects still makes it difficult to predict the course and the rate constants of the total reaction of ionized alkenes with electron-rich reactants.

Experimental Section

FT-ICR spectrometry: All FT-ICR experiments were performed in a Spectrospin Bruker CMS 47X FT-ICR instrument, [17] equipped with an InfinityTM [18] cell of 6 cm length, a 4.7 T superconducting magnet, a 24 bit/128 kword Aspect 3000 computer and an external ion source. [19]

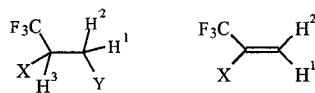
Kinetic measurements: Ions were generated by 25 eV electron impact (EI) from the halopropenes and an ion source pressure of 10^{-6} mbar. The mixture of the ions produced was focused into the FT-ICR cell by means of a transfer optic. The trapping voltages of the back and front plates were set to 1 ± 0.1 V and the voltages of the excitation plates to 0.0 ± 0.1 V. The ions under study were selected by broad-band (frequency sweep) ejection of 88 V_{p-p} and rf pulses of 14 V_{p-p} fixed-frequency (single shots) ejections. The

ejection process was finished after 15–20 ms. To remove any excess kinetic energy prior to reaction, the ions were thermalized by collisions with argon added by a pulsed valve (opened for 8–15 ms). The argon was removed after a delay time of 0.5–1.0 s. Fragment ions and product ions formed during this period were again ejected by single shots of 14 V_{p-p}. This method has been described in detail previously.^[5a] Ammonia as reactant gas was introduced into the FT-ICR cell continuously by a leak valve resulting in a constant pressure of 3×10^{-8} to 8×10^{-8} mbar. The pressure readings of the ionization gauge were corrected for the sensitivity of the neutral gas used^[20] and were calibrated by rate measurements of the reaction $\text{NH}_3^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ \text{NH}_2^+$ ($k_{\text{bi}} = 21 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).^[21] The sensitivity for NH_3 was taken from ref. [20]. The reaction-time delay varied from 1.5 ms to 10 s. After the reaction time, all ions were excited by a frequency sweep of 88 V_{p-p} with a step width of 7.8 kHz and an excitation pulse of 8 μs . FT-ICR spectra were averaged by 8 data acquisition circles and recorded by 32 k data points for 30 different reaction times. Peak intensities were obtained by exponential multiplication and Fourier transformation of the time domain signal. For kinetic evaluation, peak intensities of the magnitude spectra were normalized to the sum of all ions detected at each reaction time. By fitting these data to an exponential function by means of the Microcal Origin 4.5 program,^[22] the reaction rate constants k_{exp} were obtained. The bimolecular rate constants k_{bi} were calculated by use of the number density of the neutral reactant derived from the corrected pressure. The efficiencies of the reaction is given by $k_{\text{bi}}/k_{\text{col}}$. The collision rate constant k_{col} was calculated by the method of Su and Chesnavich.^[23]

Gas phase titration experiments: Gas phase titration experiments were performed by generation of the substitution product by chemical ionization (CI) in the external CI source of ammonia and 2-bromopropene. The ions were focused into the FT-ICR cell and deprotonated by the titration base present in the FT-ICR cell at a constant pressure. The determination of the deprotonation efficiency followed the procedure described above for the kinetic measurements. However, the thermalization of the cations had to be omitted, because otherwise an erroneous ratio of the isomers may be observed due to uncontrolled reaction during this period. Amines with proton affinities^[10] from 899 to 998 kJ mol⁻¹ were used as titration bases.

Materials and reagents: Ammonia (99.8%; Merck), methanol (>99.9%; Merck), 2-chloropropene **1** (>97%; Fluka) and 2-bromopropene **2** (>99%; Fluka) were obtained commercially.

Synthesis of 2-iodopropene 3 and 2-halo-3,3,3-trifluoropropenes 4–6: The purity of 2-iodopropene and of the 2-halo-3,3,3-trifluoropropenes synthesized in this work were analyzed by gas chromatography (Hewlett Packard HP 5890 Series II equipped with a 30 m SE54 capillar column, a VG Autospec mass spectrometer and a Bruker AC250P ¹H NMR spectrom-



eter). For ¹H NMR characterization the protons of **4–6** are labeled as indicated in the structures given below. The 2-halo-3,3,3-trifluoropropenes **4–6** were prepared by a two step synthesis, starting with the addition of the

halogen to 1,1,1-trifluoropropene, which generates the corresponding 1,2-dihalo-3,3,3-trifluoropropenes. These were transformed by elimination of HX to the corresponding 2-halo-3,3,3-trifluoropropenes according to a modified method of R. N. Hazeldine and K. Leedham with KOH/EtOH as the base.^[24]

Synthesis of 2-iodopropene 3: 2-chloro-2-iodopropene was synthesized by the reaction of 2-chloropropene with concentrated hydroiodic acid.^[25] 2,2-diiodopropene was synthesized by stirring 2-chloro-2-iodopropene (4.5 g, 22.0 mmol), sodium iodide (15.0 g, 100.0 mmol) and acetone (50 mL) for three days at ambient temperature. Distilled water (100 mL) was added to the reaction mixture, and the aqueous layer was washed three times with dichloromethane (100 mL). The combined dichloromethane layers were washed three times with distilled water and dried over anhydrous sodium sulfate. The solvent was removed by vacuum (15 mbar). The crude product was distilled at 0.03 mbar into a liquid-nitrogen-cooled Schlenk tube yielding 2,2-diiodopropene (0.23 g, 0.8 mmol). ¹H NMR (250 Hz, CDCl₃, 25 °C; TMS): $\delta = 3.00$ (s, 6H; $-\text{CH}_3$); MS (70 eV, EI): m/z (%): 296 (23) [M^{++}], 254 (7) [I_2^+], 169 (100) [$\text{C}_3\text{H}_6\text{I}^+$], 128 (8) [HI^+], 127 (19) [I^+]; 42 (15) [C_3H_6^+], 41 (67) [C_3H_5^+], 40 (6) [C_3H_4^+], 39 (30) [C_3H_3^+]. 2-iodopropene was obtained from the 2,2-diiodopropene by elimination of hydroiodic acid.

General procedure for synthesis of 2-halo-3,3,3-trifluoropropenes: 1,1,1-trifluoropropene was condensed at -30° to -40°C into a two neck reaction flask and the halogen was introduced as a gas (Cl_2) or as a liquid (Br_2 , ICl) into the stirred 1,1,1-trifluoro-propene until the typical color of the halogen persisted in the reaction mixture. Then the reaction mixture was stirred at -30°C for another hour. After warming up, the excess halogen was removed with a diluted aqueous solution of sodium bisulfite. The aqueous layer was separated, and the organic layer was washed three times with distilled water, dried over phosphorus pentoxide, filtered, and fractionated by distillation at normal pressure to yield the 1,2-dihalo-3,3,3-trifluoropropenes. These were converted into the 2-halo-3,3,3-trifluoropropenes by treatment with KOH/EtOH at -10°C . After neutralization of the reaction mixture with hydrochloric acid the 2-halo-3,3,3-trifluoropropenes were extracted with hexane and purified by distillation.

1,2-Dichloro-3,3,3-trifluoropropene: B.p. 53°C ; purity (by GC): 98.0%; ¹H NMR (250 Hz, CDCl₃, 25 °C; TMS): $\delta = 4.34$ (m, 1H; CH^2), 3.97 (dd, 1H; CH^2), 3.73 (dd, 1H; CH^1).

2-chloro-3,3,3-trifluoropropene (4): This very volatile compound (b.p. 15°C) was distilled directly from the reaction mixture after warming up and neutralization with hydrochloric acid. The yield was not determined. ¹H NMR (250 Hz, CDCl₃, 25 °C; TMS): $\delta = 6.07$ (ddt, 2H; CH^2), 5.79 (dd, 2H; CH^1); MS (70 eV): m/z (%): 132 (39)/130 (100) [M^{++}], 113 (12)/111 (37) [$\text{M}^{++} - \text{F}$], 95 (100) [$\text{C}_3\text{F}_3\text{H}_2^+$], 87 (11)/85 (34) [CF_2Cl^+], 75 (40) [$\text{C}_3\text{F}_3\text{H}^+$], 69 (87) [CF_3^+], 63 (29)/61 (81) [$\text{M}^+ - \text{CF}_3$], 26 (20) [C_2H_2^+].

1,2-dibromo-3,3,3-trifluoropropene: B.p. 116°C ; purity (by GC): 98%; ¹H NMR (250 Hz, CDCl₃, 25 °C; TMS): $\delta = 4.44$ (m, 1H; CH^2), 3.88 (dd, 1H; CH^2), 3.64 (dd, 1H; CH^1).

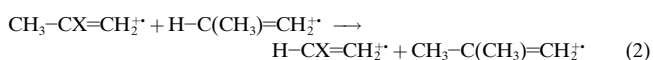
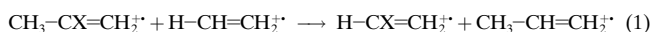
2-bromo-3,3,3-trifluoropropene (5): Yield: 91%; b.p. 34°C ; purity (by GC): >95%; ¹H NMR (250 Hz, CDCl₃, 25 °C; TMS): $\delta = 6.50$ (q, 1H; CH^2), 6.03 (q, 1H; CH^1); MS (70 eV, EI): m/z (%): 176 (65)/174 (65), [M^{++}], 157 (12)/155 (19) [$\text{M}^{++} - \text{F}$], 131 (14)/129 (14) [CF_2Br^+], 107 (24)/105 (25) [$\text{M}^{++} - \text{CF}_3$], 95 (100) [$\text{C}_3\text{F}_3\text{H}_2^+$], 75 (39) [$\text{C}_3\text{F}_3\text{H}^+$], 69 (71) [CF_3^+], 26 (26) [C_2H_2^+].

1-chloro-3,3,3-trifluoro-2-iodopropene: Purity (by GC): 99.0%; ¹H NMR (250 Hz, CDCl₃, 25 °C; TMS): $\delta = 4.45$ (m, 1H; CH^2), 3.95 (q, 1H; CH^2), 3.84 (dd, 1H; CH^1). The compound decomposed during heating.

3,3,3-trifluoro-2-iodopropene (6): The thermally labile iodide **6** was sampled into a liquid-nitrogen-cooled flask during distillation. Yield: 50%; b.p. 56°C ; purity (by GC): 98%; ¹H NMR (250 Hz, CDCl₃, 25 °C; TMS): $\delta = 6.95$ (q, 2H; CH^2), 6.30 (dd, 2H; CH^1); MS (70 eV): m/z (%): 222 (100) [M^{++}]; 203 (23) [$\text{M}^{++} - \text{F}$]; 177 (8) [CF_2I^+]; 153 (5) [$\text{M}^{++} - \text{CF}_3$]; 128 (25) [HI^+]; 127 (71) [I^+], 95 (24) [$\text{C}_3\text{F}_3\text{H}_2^+$]; 75 (92) [$\text{C}_3\text{F}_3\text{H}^+$], 69 (85) [CF_3^+].

Appendix

The experimental heats of formation (ΔH_f) used for the calculation of the isodesmic reactions are given in Table 4. The $\Delta H_f(\text{chloroethene}^{++})$ and $\Delta H_f(\text{bromoethene}^{++})$ are well known. However, in the case of iodoethene only the ionization energy of $9.30 \pm 0.10 \text{ eV}$ is tabulated. Combining this with the ΔH_f of 2-iodoethene derived by the increment system of S. W. Benson^[26] yields $\Delta H_f(\text{iodoethene}^{++})$ given in Table 4. The NIST Webbook contains two values for $\Delta H_f(2\text{-chloropropene})$, and the value of $-24.7 \text{ kJ mol}^{-1}$ has been selected for the further calculations, since this value is more consistent with Benson's increments.^[26] No experimental values for $\Delta H_f(2\text{-bromopropene})$ and $\Delta H_f(\text{iodopropene})$ are available, and these ΔH_f have been estimated with Benson's increments.^[26] Isodesmic reactions of the following type [Eqs. (1) and (2)], in which the halogen substituent and either an H atom or a CH_3 substituent change their places, have been used for the calculation of $\Delta H_f(2\text{-halopropene}^{++})$.



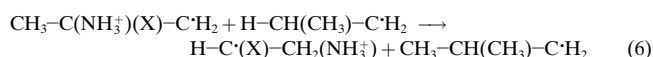
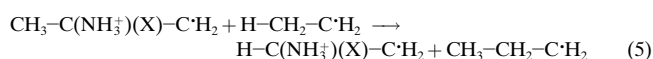
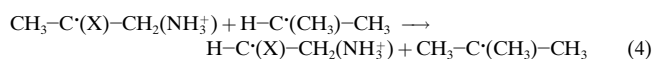
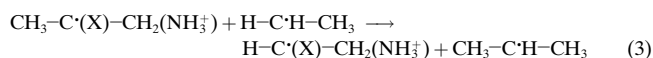
In the case of 2-bromopropene⁺⁺ and 2-iodopropene⁺⁺ the values obtained in this way were confirmed by isodesmic reactions of a halogen interchange with 2-chloropropene⁺⁺ and chloroethene⁺⁺, which had been calculated at

Table 4. Experimental heats of formation^[a] used for isodesmic reactions.

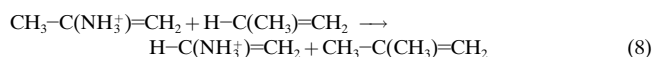
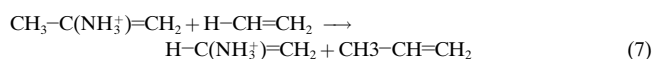
	ΔH_f [kJ mol ⁻¹] ^[a] neutral	Ionization energy [eV] ^[a]	ΔH_f [kJ mol ⁻¹] radical cation ^[b]
chloroethene	35.3 ± 1.4	9.99 ± 0.02	999
bromoethene	79.2 ± 1.9	9.82 ± 0.03	1027
iodoethene	129 ^[c]	9.30 ± 0.1	1026
chloropropene	-24.7		
bromopropene	27 ^[c]		
iodopropene	82 ^[c]		
ethene	52.5 ± 0.5	10.5138	1014
propene	20.4 ± 0.5	9.73 ± 0.01	939
isobutene	-18.0 ± 1.0	9.22 ± 0.02	509
3,3,3-trifluoropropene	-614 ± 7	10.95 ± 0.1	441
ethyl radical	118.8 ± 4		
n-propyl radical	100.0 ± 2.1		
isopropyl radical	92.0 ± 2.1		
isobutyl radical	66.9 ± 2.1		
tert.butyl radical	46.0 ± 2.5		
2,2,2-trifluoroethyl radical	-517 ± 8		
3,3,3-trifluoropropyl radical	-536 ^[d]		
allyl radical	163.2 ± 2		
methallyl radical	121.3 ± 2		

[a] Taken from ref. [10] if not otherwise stated. [b] Calculated from ΔH_f (neutral) and the ionization energy. [c] Calculated by the incremental method of S. W. Benson.^[26] [d] Calculated from the electron affinity data given in ref. [10].

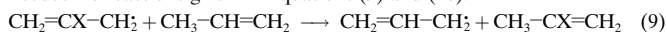
the MP2/6-31G* level of theory. Similarly, the distonic ions generated by the addition of NH₃ to the haloalkene radical cations in the Markovnikov and anti-Markovnikov mode were treated in the isodesmic reactions as substituted alkyl radicals [Eqs. (3), (4), (5), and (6)].



Since the ΔH_f of the distonic ions formed by addition of NH₃ to the radical cation of iodoethene are not available, a second set of isodesmic reactions were used, in which the distonic ions were equilibrated with the radical cations of the appropriate 2-halopropenes. The ΔH_f of substitution product 2-propenyl ammonium cation was obtained from the ΔH_f of its lower homologue vinyl ammonium cation by comparing with alkenes in the isodesmic reactions given in Equations (7) and (8).



Finally, the ΔH_f of the 2-haloallyl radical cations were calculated from the isodesmic reactions given in Equations (9) and (10).



The ΔH_f of the relevant species derived from 3,3,3-trifluoro-2-chloropropene were calculated by analogous sets of isodesmic reactions with the corresponding species derived from 2-chloropropene and 3,3,3-trifluoropropene, with its radical cation, the 2,2,2-trifluoroethyl radical and the 3,3,3-trifluoropropyl radical as references.

Acknowledgments: The financial assistance of this work by the VW-Stiftung (*Schwerpunkt intra- und intermolekularer Elektronentransfer*) is gratefully acknowledged. The FT-ICR spectrometer used for this work was a grant of the Deutsche Forschungsgemeinschaft. We thank the Fonds der Chemischen Industrie for additional financial assistance.

Received: February 9, 1998 [F994]

- [1] a) L. P. Johnstone, N. P. Schepp, *J. Am. Chem. Soc.* **1993**, *115*, 6564–6576; b) J. P. Dinnocenzo, D. R. Lieberman, T. R. Simpson, *J. Am. Chem. Soc.* **1993**, *115*, 366–367; c) G. Trampe, J. Mattay, S. S. Steenken, *J. Phys. Chem.* **1989**, *93*, 7157–7165; d) S. J. Steenken, C. J. Warren, B. C. Gilbert, *J. Chem. Soc. Perkin Trans. 2* **1990**, 335–342; e) M. Yasuda, Y. Matsuzaki, K. Shima, C. Pac, *J. Chem. Soc. Perkin Trans. 2* **1988**, 745–751; f) O. Hammerich, V. D. Parker, *Adv. Phys. Org. Chem.* **1984**, *20*, 56–189; g) B. Reistöen, V. D. Parker, *J. Am. Chem. Soc.* **1991**, *113*, 6954–6958; h) T. Drewello, N. Heinrich, W. P. M. Maas, N. M. M. Nibbering, T. Weiske, H. Schwarz, *J. Am. Chem. Soc.* **1987**, *109*, 4810–4818.
- [2] a) N. Heinrich, W. Koch, J. C. Morrow, H. Schwarz, *J. Am. Chem. Soc.* **1988**, *110*, 6332–6336; b) S. S. Shaik, A. Pross, *J. Am. Chem. Soc.* **1989**, *111*, 4306–4312; c) J. K. Cho, S. S. Shaik, *J. Am. Chem. Soc.* **1991**, *113*, 9890–9891.
- [3] P. A. Pabon, N. L. Bauld, *J. Am. Chem. Soc.* **1984**, *106*, 1145–1146.
- [4] For a recent example see P. Maslak, W. H. Chapman, Jr., T. M. Vallombroso, Jr., B. A. Watson, *J. Am. Chem. Soc.* **1995**, *117*, 12380–12389.
- [5] a) D. Thölmann, H.-F. Grützmaier, *J. Am. Chem. Soc.* **1991**, *113*, 3281–3287; b) D. Thölmann, H.-F. Grützmaier, *Int. J. Mass Spectrom. Ion Processes* **1992**, *117*, 415–440; c) D. Thölmann, S. Hamann, H.-F. Grützmaier, *Int. J. Mass Spectrom. Ion Processes* **1994**, *137*, 43–54.
- [6] a) S. S. Shaik, *Acta Chem. Scan.* **1990**, *44*, 205–221; b) S. S. Shaik, E. J. Canadell, *J. Am. Chem. Soc.* **1990**, *112*, 1446–1452; c) A. Pross, *J. Am. Chem. Soc.* **1986**, *108*, 3537–3538; d) S. S. Shaik, *J. Am. Chem. Soc.* **1981**, *103*, 3692–3701; e) A. Pross, S. S. Shaik, *J. Am. Chem. Soc.* **1981**, *103*, 3702–3709.
- [7] A. Nixdorf, H.-F. Grützmaier, *J. Am. Chem. Soc.* **1997**, *119*, 6544–6551.
- [8] D. Thölmann, D. Flottmann, H.-F. Grützmaier, *Chem. Ber.* **1991**, *124*, 2349–2356.
- [9] a) C. H. DePuy, S. Gronert, S. E. Barlow, V. M. Bierbaum, R. Damrauer, *J. Am. Chem. Soc.* **1989**, *111*, 1968–1973; b) F. G. Bordwell, J. P. Cheng, *J. Am. Chem. Soc.* **1989**, *111*, 1792–1795.
- [10] a) NIST Chemistry WebBook (<http://webbooknist.gov/chemistry/>), NIST Standard Reference Database No. 69, August **1997**. b) NIST Standard Reference Database 19A, *NIST Positive Ion Energetics Database*, Vers. 1.1, National Institute of Standards and Technology, Gaithersburg (USA), **1989**.
- [11] W. J. Hehre, L. Radom, P. von R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, **1985**.
- [12] J. Alvarez-Idaboy, L. A. Erikson, T. Fangström, S. Lunell, *J. Phys. Chem.* **1993**, *97*, 12737–12741.
- [13] H. H. Büker, H.-F. Grützmaier, M. E. Crestoni, A. Ricci, *Int. J. Mass Spectrom. Ion Processes* **1997**, *160*, 167–181.
- [14] a) D. K. Bohme, *Int. J. Mass Spectrom. Ion Processes* **1992**, *115*, 95–110; b) A. J. Chalk, L. Radom, *J. Am. Chem. Soc.* **1997**, *119*, 7573–7578.
- [15] a) M. J. S. Dewar, K. M. Dieter, *J. Am. Chem. Soc.* **1986**, *108*, 8075–8086; b) D. M. Myton, R. J. O'Brien, *Anal. Chem.* **1991**, *63*, 1201–1205.
- [16] D. A. Stams, T. D. Thomas, D. C. MacLaren, D. Ji, T. H. Morton, *J. Am. Chem. Soc.* **1990**, *112*, 1427–1434.

- [17] M. Allemann, H. Kellerhals, K. P. Wanczek, *Int. J. Mass Spectrom. Ion Phys.* **1983**, *91*, 139–142.
- [18] P. Caravatti, M. Allemann, *Org. Mass Spectrom.* **1991**, *26*, 514–518.
- [19] P. Kofel, M. Allemann, H. Kellerhals, K. P. Wanczek, *Int. J. Mass Spectrom. Ion Physics* **1985**, *65*, 97–103.
- [20] J. E. Bartmess, R. M. Georgiadis, *Vacuum* **1983**, *33*, 149–153.
- [21] V. G. Anicich, *J. Phys. Chem. Ref. Data* **1993**, *22*, 1506.
- [22] Microcal Origin 41, Microcal Software Inc., Northampton MA 01060 (USA), **1996**.
- [23] T. Su, W. J. Chesnavich, *J. Chem. Phys.* **1982**, *76*, 5183–5185.
- [24] R. N. Hazeldine, K. Leedham, *J. Chem. Soc.* **1952**, 3483–3490.
- [25] A. Oppenheim, *Justus Liebigs Ann. Chem.* **1868**, *Suppl. VI*, 353–375.
- [26] S. W. Benson, *Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters*, Wiley, New York, **1976**.
-