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Reactions of 2-bromopropene radical cation with amines—a study by FT-ICR spectrometry and DFT calculation

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Dedicated to Prof. Dr. Helmut Schwarz on the occasion of his 60th birthday.

Abstract

The reactions of the 2-bromopropene radical cation $\mathbf{1}^{\bullet+}$ with four amines (CH_3NH_2, $CH_3CH_2NH_2$, $(CH_3)_2NH$, and $(CH_3)_3N$) and CH_3SH were studied by Fourier transform-ion cyclotron resonance (FT-ICR) spectrometry and molecular orbital calculations. The ionization energy (IE) of $(CH_3)_2NH$, and $(CH_3)_3N$), respectively, are considerably below the IE(**1**). Consequently, fast electron transfer (ET) is the only reaction detected with $\mathbf{1}^{\bullet+}$. The amine radical cation formed undergoes a (known) fast secondary reaction with the neutral amine and generates the corresponding ammonium ion. ET is also exothermic (0.14–0.78 eV) for the other reactants, but in these reaction systems substitution of the Br atom of $\mathbf{1}^{\bullet+}$ by the nucleophile and oxidation of the nucleophile by hydride transfer to $\mathbf{1}^{\bullet+}$ competes efficiently with ET. The minimum energy reaction path (MERP) for the reaction system $\mathbf{1}^{\bullet+}/CH_3NH_2$ was analyzed by theoretical calculation of stationary points using DFT at the level B3LYP/6-31+G(3df,2p)//B3LYP/6-31G(d). The calculated MERP agrees to the general reaction scheme developed for the reactions of ionized alkenes with nucleophiles. In particular, the initial reaction step for substitution and oxidation, which competes with ET, is addition of the nucleophile to the ionized double bond. No energy minimum along the MERP was found with B3LYP/6-31G(d) corresponding to the encounter complex of $\mathbf{1}^{\bullet+}$ and CH_3NH_2, while both UHF/6-31(Gd) and MP2/6-31G(d) show this complex as an energy minimum. The charge and spin density of the complex is almost completely localized at the 2-bromopropene component, confuting any "hidden charge transfer" in the complex prior to further reactions. The initial addition step, which is strongly exothermic, can be viewed as an "*inner sphere*" ET which combines the single ET from the nucleophile to $\mathbf{1}^{\bullet+}$ with simultaneous bond formation between reactants. This "*inner sphere*" ET competes with "*outer sphere*" ET resulting only in charge exchange between the reactants. In the case of simple amines as nucleophiles, the "*outer sphere*" ET requires considerable reorganization of the amine structure. This is indicated by significantly higher *vertical* IE_v of the amines. Therefore, a fast ET prevails over fast addition of the nucleophile to the ionized double bond of $\mathbf{1}^{\bullet+}$ only if the IE_v(amine) is distinctly below IE(**1**).

Keywords: Ion/molecule reaction; 2-Bromopropene radical cation; Reaction mechanism; Electron transfer; Nucleophilic substitution; FT-ICR; DFT

1. Introduction

Exothermic electron transfer (ET) and exothermic proton transfer (PT) between organic molecules and

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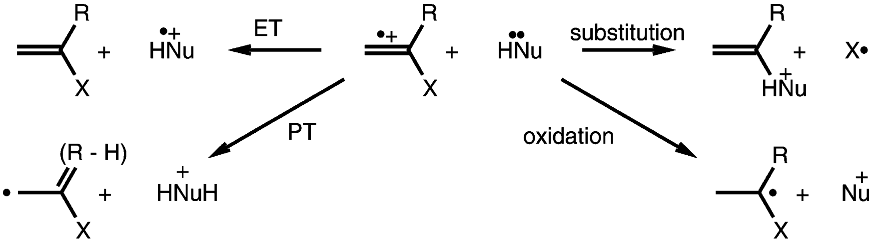
ions are exceptionally fast reactions, which overcome virtually any other chemical process between the reactants [1]. In the gas phase, these transfer reactions occur with a rate constant usually corresponding to the limit of the rate constant of ion/molecule collisions, i.e., every collision between the reactants results in a chemical change of the components. Therefore, the observation of an ion/molecule reaction which involves reaction steps of cleavage and making of chemical bonds and which nonetheless competes successfully with ET and PT is surprising and deserves a closer inspection. During our study of reactions of radical cations of unsaturated organic compounds with electron rich nucleophiles [2] we found such a reaction in the substitution of the bromo substituent of the radical cation of 2-bromopropene by methyl amine and ethyl amine.

Fourier transform-ion cyclotron resonance (FT-ICR) spectrometry is an excellent experimental tool for the investigation of ion/molecule reactions. However, the primary data accessible by this (and other mass spectrometric) experimental technique are the mass-to-charge ratio and the relative intensity of ions and the change of these data with reaction time. The other data necessary to “understand” a chemical reaction through its mechanistic details have to be inferred from other sources. For example, it is not obvious from experiment wether the reaction products arise from the collision complex of the reactants by a one-step or by a multi-step mechanism and which intermediates may be involved in the chemical transformation. Many of these questions can be ministered using methods of computational chemistry [3]. Consequently, the literature contains many studies of gas phase ion chemistry using “experiment and theory in concert” [4], excellent examples coming from the laboratory of Helmut Schwarz and his coworkers. One of us (H.-F.G.) remembers with pleasure when at the meetings of the German mass spectroscopy group in the 1960, a young student from Bohlmann’s group at the TU Berlin showed up who stressed very clearly the need of theoretical calculations to assist and confirm experimental results of mass spectrometric investigations. His nick-name given to him by other students was “der grüne Teufel” (“the green devil”) because he was rather unconventionally dressed (mostly in a green pullover) and had a tendency to ask them at their lectures piercing questions (“did you perform any meaningful calculations?”). It is well known, that unconventional dressing and piercing questions are still characteristics of Helmut Schwarz.

The radical cations of haloalkenes carrying the halogen at the double bond react in the gas phase with suitable nucleophiles HNu by a displacement of the halogen. Representative examples are the reactions of 2-halopropene radical cations with ammonia which yield N-protonated 2-propenyl amine [5]. A further characteristic reaction mode of the ionized haloalkenes with certain nucleophiles is discovered in the reaction of vinyl halide radical cations with primary and secondary alcohols as the nucleophile [6]. In these cases the alcohol is oxidized to the corresponding protonated aldehyde or ketone by a formal hydride abstraction from the carbinol C atom. An electron rich nucleophile corresponds to a Lewis base with a significant proton affinity (PA) or gas phase basicity (GB) and exhibits at the same time a low ionization energy (IE). As a consequence PT and ET between haloalkene radical cations and nucleophiles are likely reactions if these processes become exothermic. These four possible reaction modes are depicted in Scheme 1.

In fact, ET has been observed between the radical cations of halogenated ethenes and methyl amine, but substitution could be achieved easily through a reaction with inversed charge distribution of the reactants, i.e., of the radical cation of methyl amine and the neutral haloethenes. Further, PT from the 2-halopropene radical cations to ammonia was observed to compete with substitution [5] since the radical cation of a 2-halopropene is a strong acid yielding a resonance stabilized 2-haloallyl radical by deprotonation. It will be shown below that the reaction of the radical cation $\mathbf{1}^{\bullet+}$ of 2-bromopropene with methyl amine and ethyl amine is exceptional in that all four pathways shown in Scheme 1 are observed as competing processes. This is unexpected because the IE of methyl amine and of ethyl amine of 8.9 ± 1 and 8.8 eV, respectively, are distinctly below $\mathrm{IE}(\mathbf{\mathit{1}}) = 9.58 \pm 0.02\,\mathrm{eV}$ [7] which



Scheme 1. General reaction scheme of haloalkene radical cation with nucleophile HNu.

enables exothermic ET from $\mathbf{1}^{\bullet+}$. In addition, both amines are strong bases in the gas phase, so that PT is also expected to be a major reaction. To learn details of this unexpected behavior of the reaction of the 2-bromopropene radical cation $\mathbf{1}^{\bullet+}$ with methyl amine, the FT-ICR experiments were accompanied by theoretical calculations to get some insight into the mechanisms. The calculations were performed primarily using methods of density functional theory (DFT) which are more convenient than high level ab initio calculations and still are expected to produce reliable structures and relative energies of a minimum energy reaction path (MERP).

2. Experimental

2.1. FT-ICR spectrometry

All FT-ICR experiments were performed using a Spectrospin Bruker CMS 47X FT-ICR instrument [8], equipped with an infinity™ [9] cell, a 4.7 T superconducting magnet, a 24bit/128kword Aspect 3000 computer and an external ion source [10].

2.2. Kinetic measurements

Ions were generated by 25 eV electron impact (EI) from 2-bromopropene at an ion source pressure of 10^{-6} mbar. The mixture of the ions produced was focused into the FT-ICR cell by means of the 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 irradiation with the appropriate rf pulses ("single shots") of 14 V_{p-p}. This method has been described in detail previously [11]. Methyl amine (as well as other reactant gases) 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 [12] and were calibrated by rate measurements of the reaction $NH_3^{\bullet+} + NH_3 \rightarrow NH_4^+ + NH_2$ ($k_{bi} = 21 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) [13]. The reaction time delay varied from 1.5 ms to about 10 s. At the end of each 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 eight 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. Then, the relative intensity of the ions was plotted against the reaction time to create a "kinetic plot." By fitting these data to an exponential function using the Microcal Origin 4.5 program [14], the reaction rate constants k_{exp} were obtained. The bimolecular rate constants k_{bi} were determined form k_{exp} by using the number density of the neutral reactant derived from the corrected pressure. For convenience reaction efficiencies eff (%) $= 100 \times k_{\mathrm{bi}}/k_{\mathrm{cpt}}$ are used in the discussions. The capture rate constant k_{cpt} was calculated using the method of Su and Chesnavich [15].

2.3. Compounds

2-Bromopropene (**1**) and methyl amine, ethyl amine, dimethylamine, trimethyl amine and methyl thiol used as the neutral reactants were obtained commercially as pure compounds. The purity of all compounds was controlled by GC, and the compounds were sufficiently pure (>98%) to be used without further purification.

2.4. Calculation

Ab initio molecular orbital calculations and DFT calculations were performed by the GAUSSIAN 98 program [16]. The starting geometries of all species were selected by semi-empirical PM3 calculations, and the geometry of appropriate structures was fully optimized at the B3LYP level with the 6-31G(d) basis set. The spin-unrestricted formalism was used for all species. Harmonic vibrations were computed at this level of theory to characterize the stationary points on the potential energy hypersurfaces as minima (for equilibrium structures) or first order saddle points (for transition state structures) and to estimate the zero-point vibrational energy ZPE. Single point calculations were performed at the B3LYP/6-311+G(3df,2p) level of theory, and the corresponding electronic energies E_{el} were corrected by the ZPE taken from the corresponding B3LYP/6-31G(d) calculation. The frequencies of vibrations were used without any scaling to calculate the ZPE, since only relative zero-point energies E_0 were needed to construct the MERP. Additional ab initio calculations were performed for reactants and some intermediates and reaction products as indicated in the text. The unrestricted Hartree–Fock formalism (UHF) and geometry optimization with the basis set 6-31G(d) was used followed by single point calculation UHF/6-311+(3df,2p) of the optimized structures (UHF/6-311+G(3df,2p)//UHF/6-31G(d)). Also, harmonic vibrations were computed at UHF/6-31G(d) to characterize the stationary points on the potential energy hypersurfaces and to estimate the ZPE. These ZPE (without scaling of the frequencies) were used to correct the E_{el} from the UHF/6-311+(3df,2p) single point calculations. To inspect the effect of electron correlation, some calculations were repeated at the MP2 level of theory using the frozen core approximation (UMP2(FC)) and the basis set 6-31G(d) to optimize the geometries and to calculate the harmonic frequencies. In all calculations, spin contamination was not a problem, and $\langle S^2 \rangle$ was always close to the expected value of 0.7500.

3. Results and discussion

Besides methyl amine, CH_3NH_2; and ethyl amine, $CH_3CH_2NH_2$; the more basic dimethyl amine, $(CH_3)_2NH$ and trimethyl amine, $(CH_3)_3N$; as well as methanethiol (methyl mercaptane, CH_3SH) were chosen as reactants for the 2-bromopropene radical cation $\mathbf{1}^{\bullet+}$. The thermochemical data (ΔH_f^0, IE, GB and PA) of the amines and methanethiol as well as those of ammonia, NH_3, are given in Table 1.

The reaction of $\mathbf{1}^{\bullet+}$ with NH_3 has been studied before [5]. In this reaction system, substitution is the major reaction and PT is a minor reaction. (Note that in this reaction system PT is exothermic by 89 kJ mol^{-1}!) No ET is observed, indicating that with ΔIE of 0.6 eV between the reactants ET is too endothermic to occur under our experimental conditions. In contrast, the reactions of $\mathbf{1}^{\bullet+}$ with $(CH_3)_2NH$ and $(CH_3)_3N$ generate almost exclusively the amine radical cations by very fast ET. These ions undergo a fast secondary reaction with the excess of amine [17] present in the gas phase and produce the protonated amine as the final product ion. A small fraction of the protonated amines may arise by a direct PT from $\mathbf{1}^{\bullet+}$ but PT is clearly not a major reaction. The IEs of these two amines are

Table 1
Relevant thermochemical data [7] for the reactions of 2-bromopropene radical cation, $\mathbf{1}^{\bullet+}$, with amines and methanethiol

Compound	H_f^0 (kJ mol^{-1})	IE (eV)		PA (kJ mol^{-1})	GB (kJ mol^{-1})
		Adiabatic	Vertical		
NH_3	-45.94 ± 0.35	10.07 ± 0.02	10.82	853.6	819.0
CH_3NH_2	-23.0 ± 0.5	8.9 ± 0.1	9.64	899.0	864.5
$CH_3CH_2NH_2$	-84.5 ± 0.5	8.8 ± 0.1	9.50	912.0	878.0
$(CH_3)_2NH$	-19 ± 2	8.24 ± 0.08	8.95	929.5	896.5
$(CH_3)_3N$	-24 ± 2	7.80 ± 0.1	8.54	948.9	918.1
CH_3SH	-22.8 ± 0.59	9.439 ± 0.01	9.44	773.4	742.0
$H_2C{=}CBr{-}CH_3$, **1**	27[a]	9.58 ± 0.02			
$H_2C{=}CBr{-}CH_2^{\bullet}$	184.5[b]				
$H_2C{=}CH{-}CH_3$	20.41 ± 0.1	9.73 ± 0.01		751.6	722.7
$H_2C{=}CH{-}CH_2^{\bullet}$	171 ± 3	8.18 ± 0.07		736.0	707.4

[a] Estimated by increments from S.W. Benson, *Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters*, Wiley & Sons, New York, 1976.

[b] Estimated from isodesmic reaction $CH_2{=}CH{-}CH_3 + CH_2{=}CBr{-}CH_2^{\bullet} \rightarrow CH_2{=}CH{-}CH_2^{\bullet} + CH_2{=}CBr{-}CH_3$.

more than 1 eV below IE(**1**), so that fast ET is the expected outcome of these reactions. Therefore, no detailed kinetic analyses were performed. The kinetics of the reactions of $\mathbf{1}^{\bullet+}$ with CH_3NH_2, $CH_3CH_2NH_2$, and CH_3SH were completely investigated. The rate constants k_{bi} and reaction efficiencies eff obtained are listed in Table 2, and the corresponding kinetic plots are shown in Figs. 1–3. For theses three reactants all four reaction pathways shown in Scheme 1 are observed.

In principle, the reaction energy of ET is determined by the difference of the recombination energy (RE) of the reactant ion and the IE of the neutral reactant. However, it is common practice to replace the RE by the IE of the neutral precursor of the reactant ion. In this case ET from $\mathbf{1}^{\bullet+}$ to CH_3NH_2 and $CH_3CH_2NH_2$ is exothermic by 0.68 eV (65.6 kJ mol^{-1}) and 0.78 eV (75.3 kJ mol^{-1}), so that a priori a fast ET is expected as the predominant primary reaction, followed by a fast reaction of the amine radical cation with the neutral amine to generate the corresponding protonated amine as the final product ion. In fact, in the reaction system $\mathbf{1}^{\bullet+}/CH_3NH_2$, the amine radical cation $CH_3NH_2^{\bullet+}$, *m/z* 31, is observed as an intermediary primary product ion, and the protonated methyl amine $CH_3NH_3^+$, *m/z* 32, (80% total intensity) conforms to the main reaction product at the end of the reaction. However, the remaining 20% of the final total ion current are due to an ion $C_4H_{10}N^+$, *m/z* 72, which corresponds to N-protonated methyl 2-propenyl amine as the substitution product of $\mathbf{1}^{\bullet+}$ by CH_3NH_2 (Scheme 2, R = H). Moreover, a further primary product ion CH_4N^+, *m/z* 30, is observed, which transfers also a proton to CH_3NH_2 in a secondary reaction. The ion CH_4N^+

Table 2
Bimolecular rate constants, k_{bi}, capture rate constants, k_{cpt}, reaction efficiencies, eff, and branching ratios of the reaction of 2-bromo propene radical cation, $\mathbf{1}^{\bullet+}$

Reactant	k_{bi} ($\times 10^{-10}$, cm^3 molecule^{-1} s^{-1})	k_{cpt} ($\times 10^{-10}$, cm^3 molecule^{-1} s^{-1})	Eff (%)	Branching ratio subst./ox./ET/Pt
CH_3NH_2	17.5	16.0	≈100	1/0.6/1.2/<1
$CH_3CH_2NH_2$	13.6	14.5	94	1/4.3/10.9/<4
$(CH_3)_2NH$	n.d.	13.2	≈100	Principally ET
$(CH_3)_3N$	n.d.	11.7	≈100	Principally ET
CH_3SH	9.1	14.2	64	1/0.13/0.15/<0.13

Abbreviations: sust., substitution; ox., oxidation; ET, electron transfer; and PT, proton transfer.

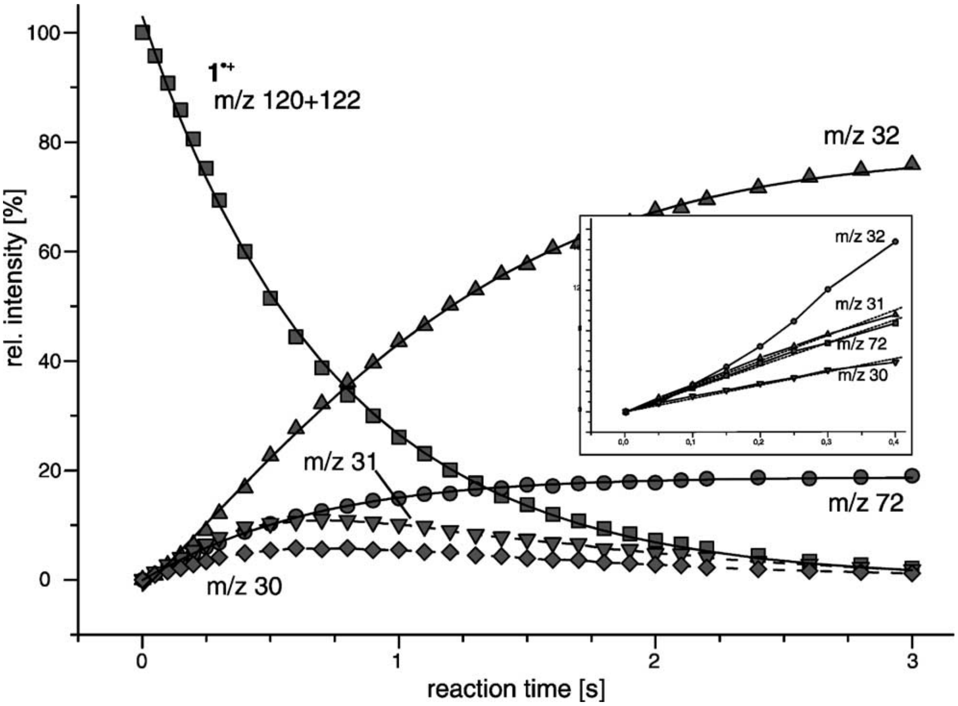


Fig. 1. Kinetic plot of the reaction of $\mathbf{1}^{•+}$ and methyl amine.

is N-protonated formimine $H_2C{=}NH_2^+$ (Scheme 2, R = H), which is generated by an oxidation reaction known from the ion/molecule reactions of the systems haloethene/CH_3NH_2 [6]. This shows, that $CH_3NH_3^+$ is produced by two secondary reactions and likely also by direct PT from $\mathbf{1}^{•+}$ as a primary reaction. (With $\Delta H_r = -136\,\text{kJ mol}^{-1}$, PT is even more exothermic than ET.) This explains the high abundance of $CH_3NH_3^+$ at the end of the reaction. Thus, ET, PT, substitution, and oxidation can be identified as primary reactions for $\mathbf{1}^{•+}$/CH_3NH_2 (Scheme 2). The branching ratio of these four processes was estimated by the "method of initial slopes" from the ion intensity curves of the kinetic plot at early stages of the reaction (see insert in Fig. 1) yielding substitution/oxidation/ET/PT = 1/0.6/1.2/<1. The intensity curve of $CH_3NH_3^+$, *m/z* 32, exhibits a distinct curvature even at the early stage of the reaction, and this prohibits an exact determination of the abundance of direct PT. Nonetheless it is clearly seen that PT is less abundant than substitution or ET. From the general mechanisms of the substitution reaction and oxidation reaction it is approved [5,6,18], that both processes involve the addition of the nucleophile to the ionized double bound as a initial reaction step. Therefore, competition in the reaction system $\mathbf{1}^{•+}$/CH_3NH_2 occurs actually between ET, PT and addition of CH_3NH_2 to $\mathbf{1}^{•+}$ with the result that addition is the most abundant primary process, distinctly favored not only over PT, but also over ET.

A parallel result is obtained for the reaction system $\mathbf{1}^{•+}$/$CH_3CH_2NH_2$. Again the radical cation $CH_3CH_2NH_2^{•+}$, *m/z* 45, is observed as a transient primary product ion and the protonated amine $CH_3CH_2NH_3^+$, *m/z* 46, (Scheme 2, R = CH_3), as the by far dominating final product ion. Substitution of the bromo atom of $\mathbf{1}^{•+}$ produces N-protonated ethyl propenyl amine, *m/z* 86, (Scheme 2, R = CH_3), and oxidation by hydride transfer generates the N-protonated acetaldimine ion, *m/z* 44, (Scheme 2, R = CH_3). The relative abundance of the substitution

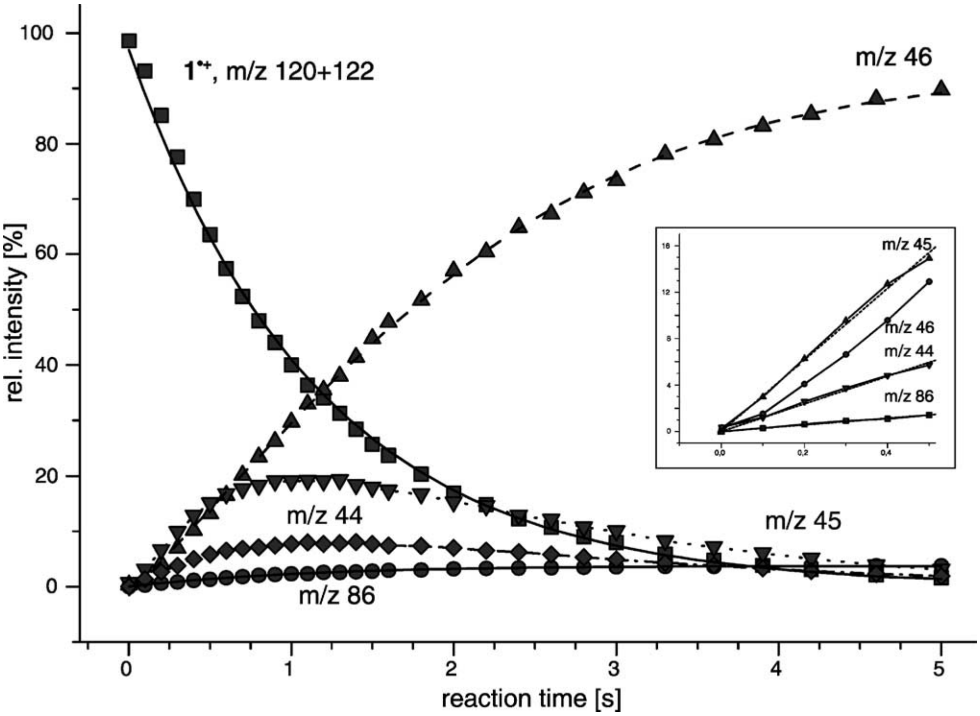


Fig. 2. Kinetic plot of the reaction of $\mathbf{1}^{\bullet+}$ and ethyl amine.

product ion is much lower as in the case of CH_3NH_2 as reactant, and oxidation is favored over substitution. This is obviously a result of the reduced bond energy of the C_α–H bond in $CH_3CH_2NH_2$ [19] which is cleaved during the generation of ion *m*/*z* 44 in the oxidation process [5]. An estimation of the branching ratio of the primary processes for $\mathbf{1}^{\bullet+}/CH_3CH_2NH_2$ results in substitution/oxidation/ET/PT = 1/4.3/10.9/<4 (see insert in Fig. 2) showing that in this reaction system exothermic ET is clearly favored, but nonetheless not strong enough to override completely addition of $CH_3CH_2NH_2$ to the ionized double bond of $\mathbf{1}^{\bullet+}$.

One reason for disfavoring ET in the reaction systems $\mathbf{1}^{\bullet+}/CH_3NH_2$ and $\mathbf{1}^{\bullet+}/CH_3CH_2NH_2$ could be that the usual assumption, that the RE can be numerically replaced by IE, is not valid for **1** and its radical cation, and that the actual RE of $\mathbf{1}^{\bullet+}$ is smaller by about 0.5 eV. In this case ET in both reaction systems would be only slightly exothermic. This hypothesis can be tested by the reaction of $\mathbf{1}^{\bullet+}$ with CH_3SH, because in this reaction system ET is only slightly exothermic by the (RE = IE) postulate (Table 1). Indeed, the corresponding kinetic plot (Fig. 3) shows that substitution giving the ion $C_4H_9S^+$, *m*/*z* 87, is the main process. Nevertheless, ET is observed producing the thiol radical cation $CH_3SH^{\bullet+}$, *m*/*z* 48, as a primary product ion and subsequently the protonated thiol $CH_3SH_2^+$, *m*/*z* 49, although with low abundance. This is in line with an only slightly exothermic ET (−0.14 eV) as predicted by using the IEs of **1** and of CH_3SH, and excludes that RE($\mathbf{1}^{\bullet+}$) is below the IE(CH_3SH) of 9.44 eV. In passing it should be noted that CH_3SH is considered a good nucleophile, in agreement with the predominance of substitution in $\mathbf{1}^{\bullet+}/CH_3SH$, and that only a trace of an oxidation product ion, *m*/*z* 47, is found. The ion *m*/*z* 47 corresponds to protonated thioformaldehyde $H_2C{=}SH^+$, and the formation of a C=S double bond by the oxidation process is not favorable. In summary, the experimental results show, that in the reactions of the

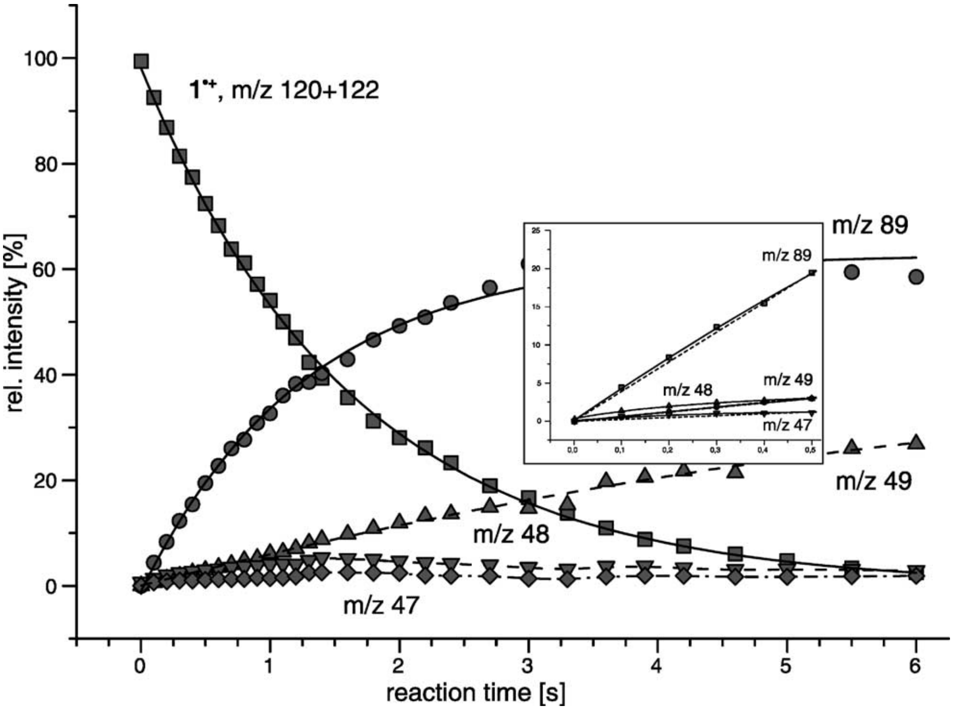
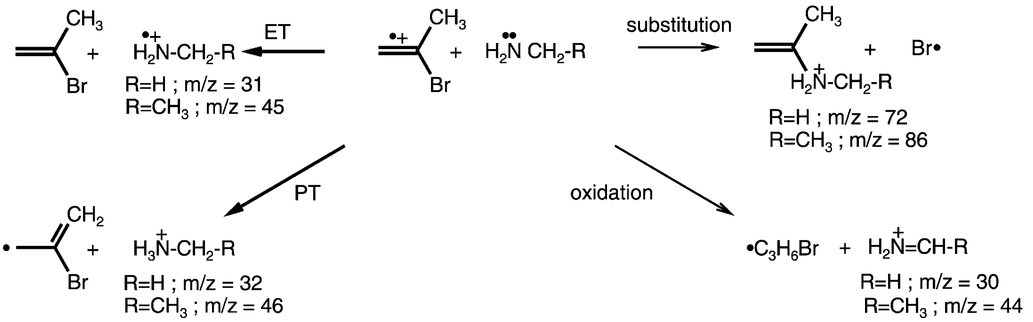


Fig. 3. Kinetic plot of the reaction of $\mathbf{1}^{\bullet+}$ and methanethiol.

radical cation $\mathbf{1}^{\bullet+}$ of 2-bromopropene with CH_3NH_2 and $CH_3CH_2NH_2$, the addition of the amine to the ionized C=C double bond competes effectively with ET although the latter process is significantly exothermic. In both reaction systems addition is followed by substitution of the bromo atom or by a hydrogen rearrangement resulting in the oxidation of the amine to the protonated aldimine, while the amine radical cations from the ET undergo a fast secondary reaction yielding the protonated amine.

A possible explanation for this result is a "hidden ET" within the collision complex of $\mathbf{1}^{\bullet+}$ and the amine resulting in a new complex of neutral **1** and the amine radical cation. It has been shown before that radical cations of amines react efficiently by addition to neutral alkenes [20] and arenes [21]. Therefore, it may



Scheme 2. Reaction of $\mathbf{1}^{\bullet+}$ with methyl amine (R = H) and ethyl amine (R = CH_3).

Table 3
Calculated total energies at 0 K, E_0, and energies of reaction, ΔE_0, for the reaction system 2-bromopropene radical cation/methyl amine ($\mathbf{1}^{\bullet +}/CH_3NH_2$)

Species	B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d)[a]		UHF/6-311+G(3df,2p)//UHF/6-31G(d)[a]	
	E_0 (hartree)	ΔE (kJ mol^{-1})[b]	E_0 (hartree)	ΔE (kJ mol^{-1})[b]
$\mathbf{1}^{\bullet +}$	−2691.095823	0	−2688.531501	0
CH_3NH_2	−95.835676		−95.184556	
1	−2691.432393	−25	−2688.831502	−54
$CH_3NH_2^{\bullet +}$	−95.508472		−94.905074	
CH_2=CBr–$CH_2^{\bullet}$	−2690.795873	−103	−2688.240072	−145
$CH_3NH_3^{+}$	−96.174917		−95.531135	
Complex	Not existent	−2783.730652	−38	
β-Distonic ion (C1)	−2786.986992	−146	−2783.779807	−167
β-Distonic ion (C2)	−2786.976803	−119	−2783.767868	−136
α-Distonic ion (C1)	−2786.965659	−90		
α-Distonic ion (C2)	−2786.967933	−96		
Methyl 2-propenylammoniumion	−212.869153	−114	−211.423177	−168
$Br^{\bullet}$	−2574.105730		−2572.357055	
2-Br-propyl radical	−2691.997044	−61	−2689.389937	−99
Formiminium ion	−94.957602		−94,363896	
TS(1,2-amine shift)	−2786.962420	−81		
TS1(1,4-H shift)	−2786.941443	−26		
TS2(1,4-H shift)	−2786.939948	−22		

[a] ZPE correction from frequency calculation with basis set 6-31G(d).

[b] Sum of ΔE_0 of ion and neutral product, relative to reactants.

be suspected that, after ET, **1** and the amine radical cation stay long enough in the ion/neutral complex for an internal ion/molecule reaction if the initial ET is only moderately exothermic and the excess energy of the complex is small. This hypothesis was examined by performing theoretical calculations on the MERP of the reaction of $\mathbf{1}^{\bullet +}$ with CH_3NH_2.

Principally, the calculation were performed using DFT at the level B3LYP/6311+(3df,2p)/–/B3LYP/6-31G(d) which has been shown to produce reliable reaction energies for open shell systems [22]. Additional ab initio calculations were done for reactants and selected species with the UHF model. Calculated zero-point energies, E_0, for stationary points along the MERP for the reaction system $\mathbf{1}^{\bullet +}/CH_3NH_2$ are presented in Table 3 together with the ΔE_0's relative to the reactants $\mathbf{1}^{\bullet +}$ and CH_3NH_2.

The correctness of the calculated ΔE_0's, which are obtained for $\mathbf{1}^{\bullet +}/CH_3NH_2$, can be checked by comparison with the experimental reaction enthalpies, ΔH_r, of -66 and $-136\,\mathrm{kJ\,mol^{-1}}$ for ET and PT (from data of Table 1). Using the basis sets 6-31G(d) and 6-311+G(3df,2p), respectively, the B3LYP model yields $\Delta E_0 = -31$ and $-26\,\mathrm{kJ\,mol^{-1}}$ for ET and $\Delta E_0 = -103\,\mathrm{kJ\,mol^{-1}}$ (both basis sets) for PT. The reaction energies calculated by B3LYP are obviously too positive for both processes. Since the IE(**1**) obtained with B3LYP is also too small by 0.4–0.6 eV, it may be possible that B3LYP overestimates specifically the stability of the radical cation $\mathbf{1}^{\bullet +}$. With the UHF model, $\Delta E_0 = -62$ and $-53\,\mathrm{kJ\,mol^{-1}}$ for ET and $\Delta E_0 = -148$ and $-145\,\mathrm{kJ\,mol^{-1}}$ for ET were calculated with the basis sets 6-31G(d) and 6-311+G(3df,2p). This is in better agreement with the experimental values. However, B3LYP and UHF agree in the order of relative stability of intermediates and products. Therefore, following the advise given in the literature [22], the B3LYP model was used to calculate the MERP for the reactions of $\mathbf{1}^{\bullet +}$ with CH_3NH_2. This MERP is shown in Fig. 4.

The mechanisms, which evolve from the calculated MERP for the substitution reaction and oxidation

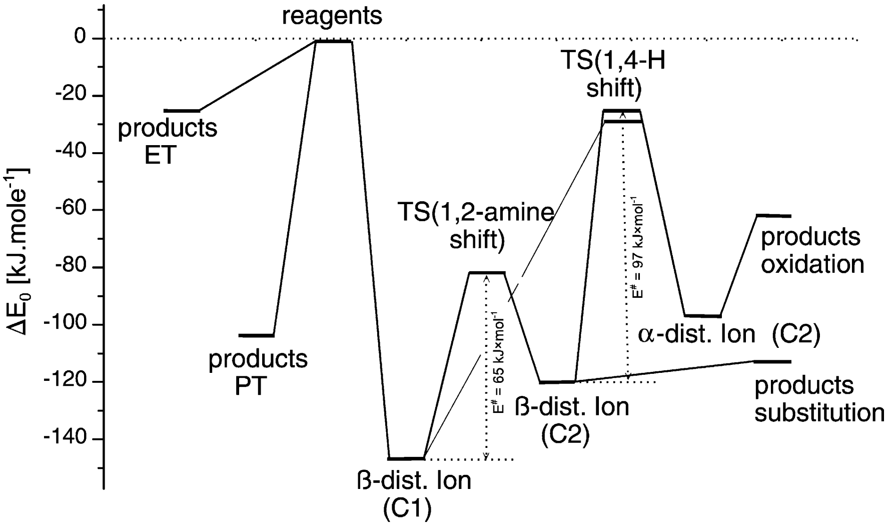
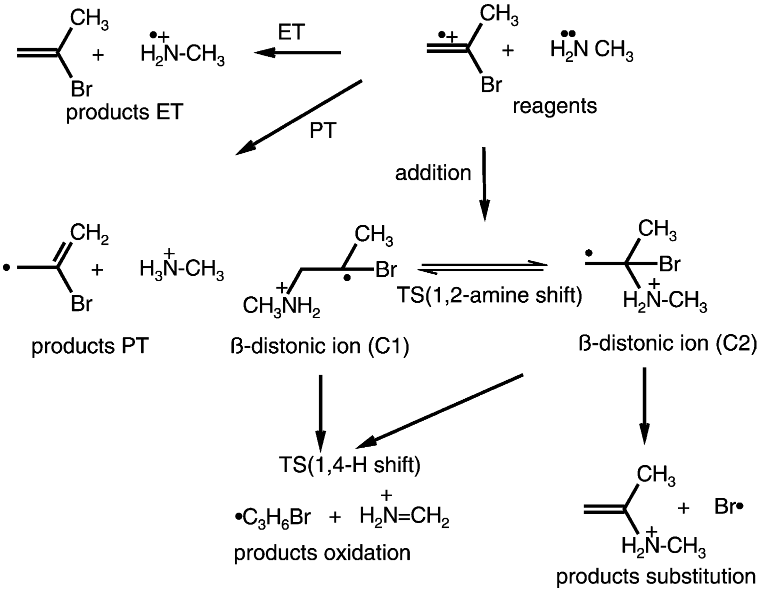


Fig. 4. MERP of the reactions of $\mathbf{1}^{\bullet+}$ and methyl amine (B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d)).

reaction of $\mathbf{1}^{\bullet+}/CH_3NH_2$, are in close analogy to those established for related systems [2]. Briefly, both reactions start by addition of CH_3NH_2 to the double bond of $\mathbf{1}^{\bullet+}$, generating two isomeric β-distonic ammonium ions by addition at each of the C atoms of the double bond (Scheme 3). The energy released by the exothermic addition drives the further reactions of the β-distonic ions either by loss of the bromo substituent or by a 1,4-hydrogen shift yielding a bromopropyl radical and N-protonated formimine. The latter process involves a considerable activation barrier for the 1,4-hydrogen shift. While both β-distonic ions can rearrange by an 1,4-hydrogen shift which requires the activation energy of 120 and 97 kJ mol^{-1}, respectively, only the less stable β-distonic ammonium ion, which is formed by addition at C(2) of $\mathbf{1}^{\bullet+}$, is able to eliminate Br by a β-cleavage to the radical site (Scheme 3). Both β-distonic ions interconvert by a 1,2-shift of CH_3NH_2 with a calculated activation energy of 65 kJ mol^{-1}. This activation energy is less than activation energies of 104 and 115 kJ mol^{-1} for the 1,2-shift of CH_3NH_2 and NH_3, respectively, in β-distonic ions generated from the vinyl chloride radical cation and CH_3NH_2 or NH_3 [18,20]. It is also smaller than the activation energy of 89 kJ mol^{-1} calculated by Radom et al. for the 1,2-NH_3-shift in the β-distonic isomer of the ethyl amine radical cation [23]. These latter activation energies have been calculated by high level ab initio models. It appears likely that the reduced activation energy for the 1,2-amine shift in the β-distonic ion derived from $\mathbf{1}^{\bullet+}$ arises from the increased stability of the transition state owing to the additional CH_3 group of the alkene.

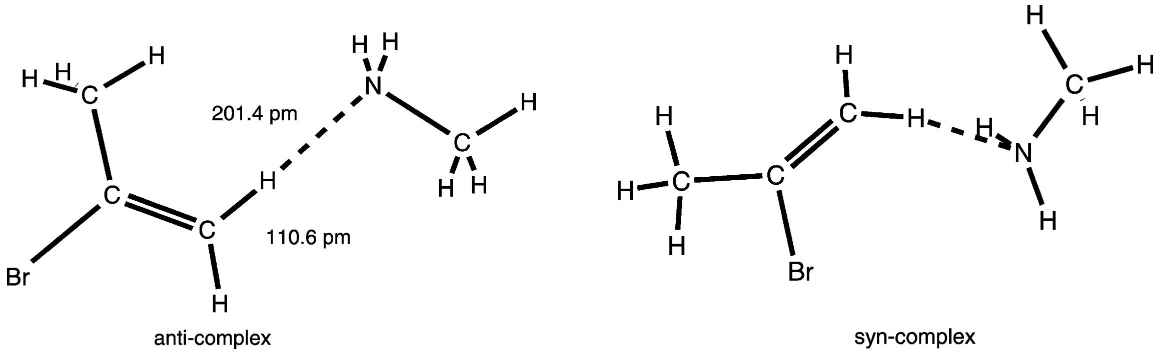
Regarding the competing primary ion/molecule reactions of $\mathbf{1}^{\bullet+}/CH_3NH_2$, the ΔE_0 calculated by B3LYP reveal that the addition of CH_3NH_2 is strongly exothermic by 146 and 119 kJ mol^{-1}, depending on the site of the addition. Addition is significantly more exothermic than ET and PT. Nonetheless, addition may proceed by an initial “hidden ET” in the collision complex of $\mathbf{1}^{\bullet+}$ and CH_3NH_2. On the way to locate the collision complex on the B3LYP energy hypersurface, semi-empirical PM3 (without fixing the charge at one component) was used first to detect suitable orientations of both components in the complex. Several orientations were found by PM3 which correspond to stable complexes and which were used as starting points for further geometry optimization by B3LYP/6-31G(d). However, in every case the end point of the optimization was the more stable isomer of the β-distonic ammonium ions. Obviously, a complex between $\mathbf{1}^{\bullet+}$ and CH_3NH_2 is not an energy



Scheme 3. Reaction mechanism of $\mathbf{1}^{\bullet+}$ with methyl amine (see MERP).

minimum on the B3LYP energy hypersurface, and the collision complex collapses without a barrier to the β-distonic onium ion. If the further geometry optimization of the PM3 geometries was performed by UHF/6-31G(3), two of the initial structures survived. These are shown in Scheme 4.

In these two structures, the molecule of CH_3NH_2 lies in the plane of the radical ion $\mathbf{1}^{\bullet+}$ near the terminal CH_2 group and the lone pair at the N atom of CH_3NH_2 points to one of the H atoms of the CH_2 group. The respective H–C bond of $\mathbf{1}^{\bullet+}$ is slightly stretched (110.6 pm compared to 108.6 pm) and the distance of 201.4 pm between the H atom and the amine N atom indicates a weak hydrogen bond. In the more stable one of the two complexes, the CH_3NH_2 molecule is positioned *anti* to the Br atom of $\mathbf{1}^{\bullet+}$, and by UHF/6-311+G(3df,2p)//UHF/6-31G(d) this complex is 38 kJ mol^{-1} below the sum of the ΔE_0's of the free reactants. It was suspected that the qualitatively different results of the calculations for the complex



Scheme 4. Ion/molecule complexes of 2-bromopropene radical cation and methyl amine (UHF/6-31G(d)).

($\mathbf{1}^{\bullet+}$+CH_3NH_2) using either B3LYP or UHF are due to electron correlation which is not considered by the UHF model. Therefore, optimizing of the geometry was repeated for separated reactants and complex using MP2(FC)/6-31G(d). The ΔE_0 calculated at this level of theory for the complex is 69 kJ mol^{-1} below the reactants, which is even more than using the UHF model. The structures obtained by UHF and MP2 are practically identical. According to the population analysis the charge density and the spin density are almost completely at the 2-bromopropene component of the complex, not at the CH_3NH_2 component. Thus, this complex contains certainly a neutral molecule of CH_3NH_2 and a radical cation of 1, and there is no indication of a "hidden ET." Further, the two structures of the complexes shown in Scheme 4 are not favorable for PT between the components. This would require a short distance between one of the H atoms of the methyl group of $\mathbf{1}^{\bullet+}$ and the lone pair of the N atom of methyl amine. This could be an explanation why addition and substitution also competes successfully with PT.

Two considerations may help to understand why in the reaction of $\mathbf{1}^{\bullet+}$ and CH_3NH_2 the addition of the amine to the ionized double bond of $\mathbf{1}^{\bullet+}$ beats the exothermic ET between reactants. First, according to the reactivity model of Shaik and Pross [24], the reaction of a radical cation with a nucleophile is depicted as the transfer of one electron from the lone pair of the nucleophile to the radical cation (which forms the corresponding neutral in the triplet state) simultaneously with the coupling of two electrons, one from each component, to create the new bond. This picture corresponds to a so called "*inner sphere ET*" which combines the transfer of a single electron with a bond forming process between electron donor and electron acceptor. Therefore, the competition between ET and addition in the system $\mathbf{1}^{\bullet+}/CH_3NH_2$ can be viewed as the competition between "outer sphere *ET*" and "inner sphere *ET*" [25]. According to the calculations, the latter is favored by a much greater exothermicity. Second, the Marcus model for ET [1a], [1b] requires the relaxation of the geometry of the neutral to that of the ion (and vice versa). A fast "outer sphere" ET would be a "vertical" process which yields an excited $CH_3NH_2{}^{\bullet+}$ radical cation with the geometry of the neutral amine. Hence, the *vertical* ionization energy, IE_v, of the amine is relevant for this fast process. The (adiabatic) IE and IE_v of simple aliphatic amines differ significantly. For CH_3NH_2 and $CH_3CH_2NH_2$, values from 9.58 to 9.64 eV and from 9.44 to 9.50 eV, respectively, are listed in the NIST data base [7]. As a consequence, a "vertical" ET from CH_3NH_2 to $\mathbf{1}^{\bullet+}$ would be thermoneutral or even slightly endothermic, and only that from $CH_3CH_2NH_2$ would be slightly exothermic. In contrast, the IE and IE_v of CH_3SH do not differ significantly. From these IE_v one would expect, that CH_3NH_2 and $CH_3CH_2NH_2$ behave similar to CH_3SH as reactants of $\mathbf{1}^{\bullet+}$, showing considerable competition between ET and addition, while the expected ET dominates only in the reactions of amines $(CH_3)_2NH$ and $(CH_3)_3N$ with considerably lower IE (and IE_v). This is indeed observed.

4. Conclusion

The investigation of the reactions of 2-bromopropene radical cation $\mathbf{1}^{\bullet+}$ with the methyl amines, ethyl amine, and methanethiol furnished additional details of the mechanisms of alkene radical cations with nucleophiles. As expected from their low IE, $(CH_3)_2NH$ and $(CH_3)_3N$ undergo a fast ET with $\mathbf{1}^{\bullet+}$, likely as the only primary reaction, and the amine radical cations react further with the excess of amine in the gas phase generating the corresponding protonated amine as the only product observed at the end of the reaction. The IE of CH_3NH_2, $CH_3CH_2NH_2$, CH_3SH are also definitely below the IE of **1**, but substitution of the Br atom of $\mathbf{1}^{\bullet+}$ and/or oxidation by hydride transfer to $\mathbf{1}^{\bullet+}$ compete efficiently with ET and PT in the case of these reactants. Substitution and oxidation reaction proceed both by addition of the neutral reactant to the ionized double bond of $\mathbf{1}^{\bullet+}$ which generates a β-distonic onium ion as a reactive intermediate. A calculation of the MERP of the reactions of CH_3NH_2 with $\mathbf{1}^{\bullet+}$ by DFT methods gives no indication for a deviation from this general reaction scheme. In particular, no ET in the collision complex of $\mathbf{1}^{\bullet+}$ and CH_3NH_2 can be detected. However, the addition step was found to be substantially more exothermic than ET and PT. From these results it is concluded that the encounter complex of $\mathbf{1}^{\bullet+}$ with an amine molecule can collapse quickly and without an activation barrier to the intermediate β-distonic ion. The addition step can be perceived as an "*inner sphere*" ET combining single ET with bond formation. Thus, the competition between ET and addition, which is observed during the reactions of $\mathbf{1}^{\bullet+}$ with amines or other nucleophiles, is another example of the competition between "*outer sphere*" and "*inner sphere*" ET. Such a competition is well known from dissociative ET to alkyl halides and S_{RN} reactions [1c], where ET competes with a bond breaking process. In the systems discussed here, it is a bond forming process which competes with ET. Because of this competition, "*outer sphere*" ET can prevail over fast addition only if it is not only exothermic as an *adiabatic* process, but also as a *vertical* process which requires no adjustment of the geometries of the species changing their charge state. In the case of methyl amine and ethyl amine, the great difference between the adiabatic IE and vertical IE show that the latter requirement is not satisfied.

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