Ion/molecule reactions of 2-chloro- and 2-bromopropene radical cations with methanol and ethanol—FT-ICR spectrometry and DFT calculations

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Abstract

Continuing the studies of ion/molecule reactions of haloalkene radical cations with nucleophiles, the reactions of the radical cations of 2-chloropropene, $1^{•+}$, and 2-bromopropene. $2^{•+}$, with methanol and ethanol, respectively, have been investigated by FT-ICR spectrometry and by computational analysis using DFT calculation (BHLYP/6–311 + G(2d,p)//BHLYP/6–31 + G(d) level). Only slow reactions (reaction efficiency <1%) are observed for $1^{•+}$/methanol and $2^{•+}$/methanol. Slow proton transfer is the main process for $1^{•+}$/methanol besides minor addition of methanol to $1^{•+}$ followed by loss of HCl or $^{•}$Cl. Addition of methanol accompanied by loss of $^{•}$Br is the exclusive process observed for $2^{•+}$/methanol. In contrast, both $1^{•+}$ and $2^{•+}$ react efficiently with ethanol yielding protonated acetaldehyde as the exclusive ($1^{•+}$) or by far dominant ($2^{•+}$) primary reaction product. The computational analysis of these ion/molecule reactions shows that in the case of $1^{•+}$/methanol and $2^{•+}$/methanol all processes are either endothermic or blocked by large activation energies. Nonetheless, addition of methanol to the ionized C—C double bond of $1^{•+}$ or $2^{•+}$ is exothermic, yielding in each case a pair of isomeric β-distonic methoxonium ions. A new reaction mechanism has been found for the HX (X = Cl, Br) elimination from the less stable isomer of the distonic intermediates. Further, an energetically favorable transition state has been detected for hydrogen atom transfer from the α-CH$_2$ group of alcohol to the halogenoalkene radical cations. These findings lead to a revised mechanism of the oxidation process and provide a plausible explanation for the excessive H/D exchange between $1^{•+}$ and CD$_3$OH during their slow reaction.
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1. Introduction

The radical cations of halogenoalkenes react efficiently with nucleophiles by the pathways shown in Scheme 1 [1]. The four reaction modes shown are (i) charge exchange or electron transfer (ET); (ii) proton transfer (PT); (iii) substitution of the vinylic halogen substituent; and (iv) oxidation of the nucleophile by hydride ion abstraction. These reactions have been extensively studied for radical cations of halogenoethenes and 2-halogenopropenes using ammonia or amines as nucleophiles [2]. A prototypical example is the re-

action of 2-bromopropene radical cation with methyl amine or ethyl amine, in which all four reaction pathways are observed in direct competition [3]. The reactions of mono- and di-halogenoethenes with simple aliphatic alcohols have also been investigated [4]. In these reaction systems, oxidation of the alcohol by the radical cation to the protonated aldehyde or ketone becomes important, in particular for ethanol or isopropanol as the neutral reaction partner.

To illustrate this point further, the ion/molecule reactions of the radical cations of 2-chloropropene **1** and 2-bromopropene **2** with methanol and ethanol have been investigated by Fourier transform ion cyclotron resonance (FT-ICR) spectrometry and by analyzing the minimum energy reaction pathways (MERP) with theoretical calculations. The two radical cations $1^{•+}$ and $2^{•+}$ display the

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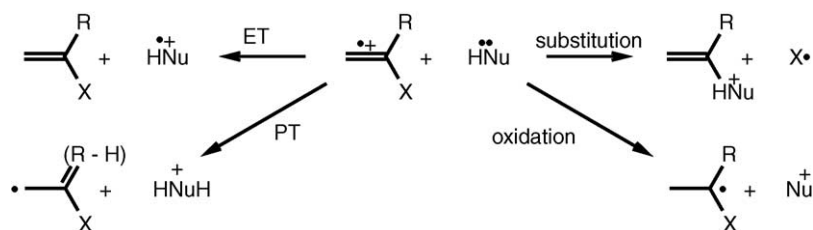
Scheme 1.

halogen substituent at the C–C double bond, which can be substituted by the alcohol via the usual addition/elimination mechanism of nucleophilic substitution at a $C(sp^2)$ atom mediated by radical cations [1]. Further, oxidation of the alcohol by formal hydride transfer to the halogenoalkene radical cation may occur if the activation barrier of the hydrogen migration during this process is not too large. Compared to the ionized halogenoethenes studied before, $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ are much more acidic owing to the additional methyl group at the ionized double bond. Thus, PT could prevail over all of the other ion/molecule reactions. However, it will be shown that the main reaction pathway which is observed for $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ depends clearly on the nature of the halogen substituent and of the alcohol.

2. Experimental

2.1. Compounds

2-Chloropropene **1** and 2-bromopropene **2** as well as methanol and ethanol were obtained commercially as pure compounds. The purity of these compounds was controlled by GC, and the compounds were sufficiently pure (>98%) to be used without further purification.

2.2. FT-ICR spectrometry

All FT-ICR experiments were performed using a Spectrospin Bruker CMS 47X FT-ICR instrument [5], equipped with an infinity^{TM} cell [6], a 4.7 T superconducting magnet, a 24 bit/128 kword Aspect 3000 computer and an external ion source [7].

2.2.1. Kinetic measurements

Ions were generated by 20–30 eV electron impact (EI) from the respective halogenopropene, and the mixture of the ions produced in the ion source 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 $1\,V \pm 0.1\,V$ and the voltages of the excitation plates to $0.0 \pm 0.1\,V$. The ions were selected by broad band (frequency sweep) ejection of $88\,V_{p–p}$ and by 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 "single shots" of $14\,V_{p–p}$. This method of ion generation has been described in detail previously [8]. Methanol and ethanol, respectively, 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 [9] and were calibrated by rate measurements of the reaction $NH_3^{\bullet+} + NH_3 \rightarrow NH_4^+ + NH_2^{\bullet}$ ($k_{bi} = 21 \times 10^{-10}\,cm^3$ molecule^{-1} s^{-1}) [10]. The reaction time delay varied from 1.5 ms to about 30 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 $8\,\mu s$. FT-ICR spectra were averaged by eight data acquisition cycles and recorded by 32 k data points for up to 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 [11], the pseudo-first order reaction rate constants k_{exp} were obtained. The reproducibility of k_{exp} is very good, but due to uncertainty in the measurement of the pressure of the neutral reactant the error in k_{bi} (and of eff) is about 30%. 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 of the neutral reactant in the FT-ICR cell. For convenience, reaction efficiencies eff (%) = $100 \times k_{bi}/k_{cpt}$ are used in the discussions. The collision rate constant k_c was calculated using the method of Su and Chesnavich [12].

2.3. Computational methods

All calculations have been performed with Gaussian 98 [13]. The potential energy surface of 2-halogenopropene radical cations $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ has been explored using the split valence all electron $6–31 + G(d)$ basis set in combination with the hybrid density functional Becke-half-and-half-LYP (BH-

Table 1
Bimolecular constant, k_{bi}, collision rate constant, k_c, and reaction efficiency, eff, of ion/molecule reaction between 2-chloropropene radical cation $1^{\bullet+}$ and 2-bromopropene radical cation $2^{\bullet+}$ with methanol and ethanol, respectively
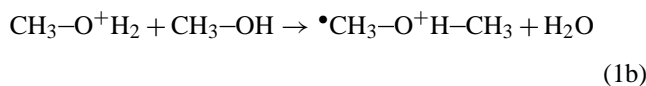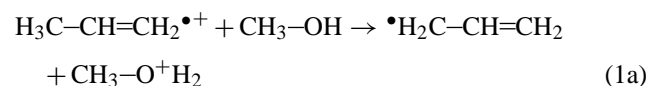
Reaction system	k_{bi} ($\times 10^{-10}$ (cm$^3 \times$ molecule$^{-1} \times$ s^{-1}))	k_{ADO} ($\times 10^{-10}$ (cm$^3 \times$ molecule$^{-1} \times$ s^{-1}))	eff (%)
$1^{\bullet+}$ + methanol	0.015	15.9	0.09
$2^{\bullet+}$ + methanol	0.13	15.0	0.9
$1^{\bullet+}$ + ethanol	7.35	17.0	43.0
$2^{\bullet+}$ + ethanol	6.02	14.3	42.21

LYP) [14]. This level of theory has given remarkably good results in previous studies of radical cations and their respective reactions with neutral nucleophiles [15]. Relative energies have then been calculated using the BHLYP functional in combination with the 6–311 + G(2d,p) basis set. Energies obtained at this level of theory are discussed in the text, if not mentioned otherwise. Combination with zero point energy (ZPE) correction and thermochemical corrections to the enthalpy H°_{298} at 298 K, respectively (based on the BHLYP/6–31 + G(d) harmonic vibrational analysis) yield total energy differences at 0 K denoted as ΔE_0 and standard enthalpy differences designated as ΔH°_{298}.

3. Results and discussion
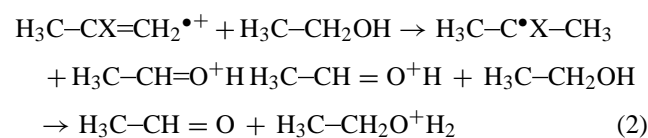
3.1. FT-ICR-spectrometric studies

The ionization energy (IE) of 2-chloropropene **1** and 2-bromopropene **2**, respectively, is significantly below the IE of methanol and ethanol [16]. Hence, direct electron transfer (ET) is not observed in the FT-ICR experiments if the ions are properly thermalized. However, the radical cations of propene and of larger alkenes are quite acidic because deprotonation at a position allylic to the ionized C–C double bond gives rise to a radical which is stabilized by allylic resonance. A test experiment showed that protonated methanol is the only primary ionic product of the reaction of propene radical cation with methanol (Eq. (1a)), which forms protonated dimethyl ether and water in a secondary process (Eq. (1b)). The primary reaction is efficient ($k_{bi} = 14.9 \pm 0.5 \times 10^{-10}$ (cm^3 molecule^{-1} s^{-1}); eff = 72%) which indicates an exothermic PT from the propene radical cation to methanol. An estimation of the reaction enthalpy of Eq. (1a) using known experimental data [16] yields $\Delta H^{\circ}_{298,r} = -12.5 \, (\pm 12) \, \text{kJ} \times \text{mol}^{-1}$, in good agreement with experimental observation.

$$H_3C-CH=CH_2^{\bullet+} + CH_3-OH \rightarrow {}^{\bullet}H_2C-CH=CH_2$$
$$+ CH_3-O^+H_2 \tag{1a}$$

$$CH_3-O^+H_2 + CH_3-OH \rightarrow {}^{\bullet}CH_3-O^+H-CH_3 + H_2O \tag{1b}$$

A similar exothermic PT is expected for the reactions of halogenopropenes $1^{\bullet+}$ and $2^{\bullet+}$ with methanol or ethanol. The kinetic plots for these four reaction systems are shown in Fig. 1, and the corresponding kinetic data are collected in Table 1. Contrary to expectation, efficient PT is not observed in any of these reaction systems.

The product of the secondary process, Eq. (1b), induced by protonated methanol, is observed as the main ionic product in the case of $1^{\bullet+}$/methanol, but the total efficiency of the reaction of $1^{\bullet+}$ with methanol is only eff = 0.09%. This low total reaction efficiency indicates, that all reaction channels according to Scheme 1 are either endothermic or blocked by large activation barriers. This is confirmed by theoretical calculations (see next section below). Besides slow endothermic PT, formation of ions C$_4$H$_8$O$^{\bullet+}$, m/z 72, and C$_4$H$_9$O$^+$, m/z 73, takes place which corresponds to substitution by addition of CH$_3$OH to $1^{\bullet+}$ followed by elimination of HCl and Cl, respectively. The only product ion found in the system $2^{\bullet+}$/methanol corresponds to substitution by loss of Br, and the total reaction is again not efficient (total eff = 0.9%), although eff is distinctly increased compared to $1^{\bullet+}$/methanol. Using ethanol as the neutral reactant, the reactions of both $1^{\bullet+}$ and $2^{\bullet+}$ are efficient with eff = 43% and 42%, respectively, and protonated ethanol C$_2$H$_5$–O$^+$H$_2$, m/z 47, is the main product at the end of the reactions. However, in both reaction systems protonated acetaldehyde H$_3$C–CH=O$^+$H, m/z 45, is observed as a primary product ion which is generated by oxidation of ethanol via a formal hydride transfer to $1^{\bullet+}$ or $2^{\bullet+}$. PT from the primary ion H$_3$C–CH=O$^+$H to ethanol is exothermic (PA(acetaldehyde) = +768.5 kJ × mol^{-1} [16]; PA(ethanol) = +776.4 kJ × mol^{-1} [16]), and the occurrence of this secondary process is proven by the shape of the ion intensity curves for H$_3$C–CH=O$^+$H and C$_2$H$_5$–O$^+$H$_2$ in the respective kinetic plots. The former one exhibits a maximum typical of an intermediate reaction product, and the latter one shows a sigmoidal curvature, as expected for the consecutive ion/molecule reactions of Eq. (2). Thus, it is doubtful whether any PT from $1^{\bullet+}$ or $2^{\bullet+}$ to ethanol occurs as a primary process.

$$H_3C-CX=CH_2^{\bullet+} + H_3C-CH_2OH \rightarrow H_3C-C^{\bullet}X-CH_3$$
$$+ H_3C-CH=O^+H \; H_3C-CH=O^+H + H_3C-CH_2OH$$
$$\rightarrow H_3C-CH=O + H_3C-CH_2O^+H_2 \tag{2}$$

The outcome of the ion/molecule reactions of the four reaction systems leads to the following conclusions.

Firstly, using methanol as the reactant, the low efficiencies for the total reactions of $1^{\bullet+}$ and $2^{\bullet+}$ indicate that all four reactions pathways according to Scheme 1 are more or
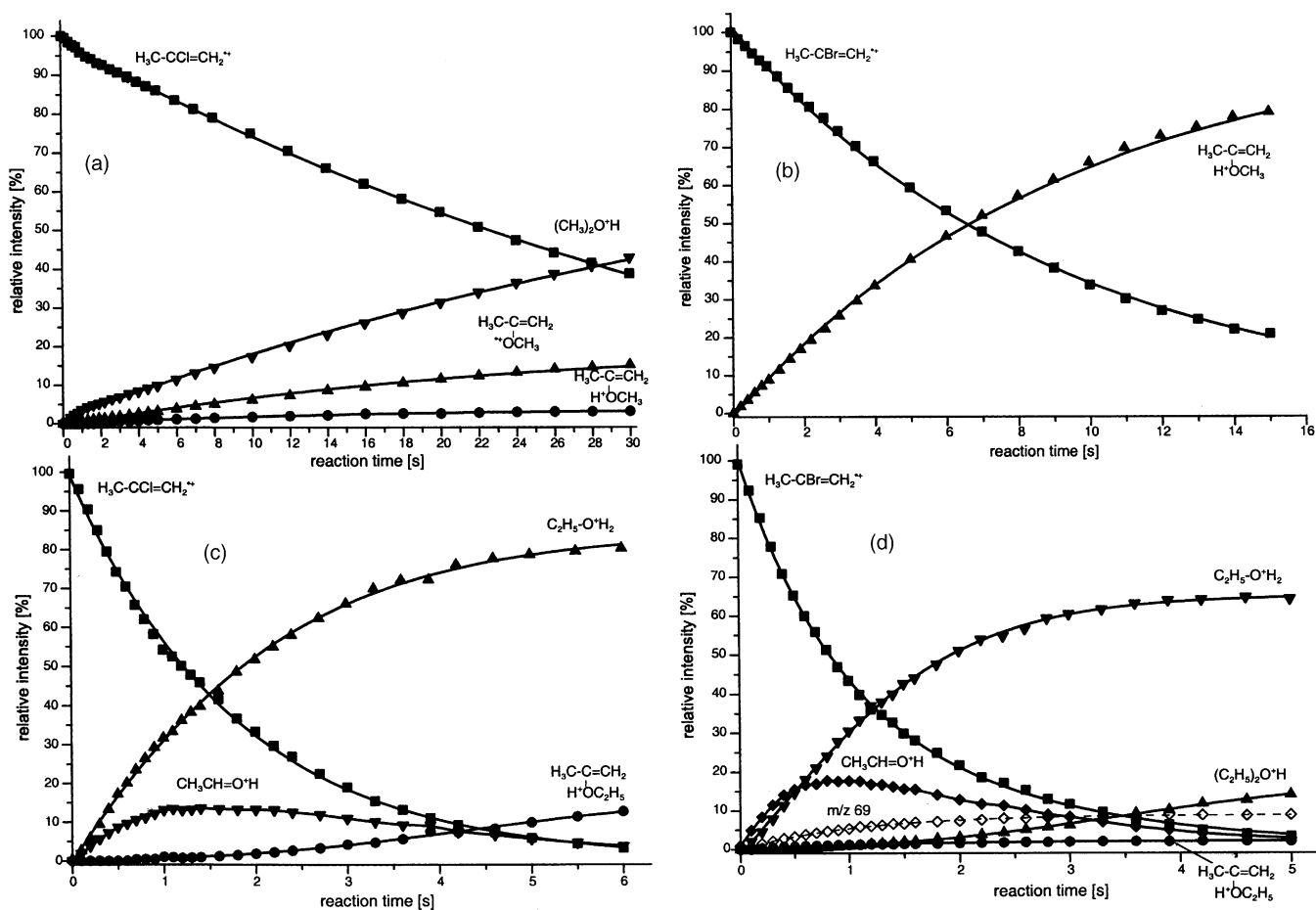
Fig. 1. Kinetic plots of the ion/molecule reaction of (a) 2-chloropropene radical cation $1^{\bullet+}$ and methanol; (b) 2-bromopropene radical cation $2^{\bullet+}$ with methanol; (c) 2-chloropropene radical cation $1^{\bullet+}$ with ethanol; (d) 2-bromoopropene radical cation $2^{\bullet+}$ with ethanol.

less endothermic. The increase of eff of the bromo derivative $2^{\bullet+}$ (compared to $1^{\bullet+}$) and the observation of substitution as the only reaction channel indicate that loss of Br is likely only slightly endothermic. Conversely, the loss of Cl from $1^{\bullet+}$ must be significantly endothermic because of the stronger C–Cl bond. Therefore, endothermic PT becomes now the main reaction pathway. Interestingly, the Cl substituent is lost during substitution not only as Cl atom, but also as HCl. The elimination of HX from halogenoalkene radical cations during the substitution by nucleophiles has not been observed before using FT-ICR spectrometry, although this reaction pathway is clearly more exothermic than loss of X. However, substitution and loss of HX has been observed as an intra-cluster reaction initiated by selective photoionization of mixed clusters of halogenoalkenes and methanol or ammonia [17]. Further, elimination of HCl has been observed during the substitution reactions of substituted chlorobenzene radical cations and chloronaphthalene radical cations if the direct loss of Cl becomes very slow [8,18]. The mechanism of the HCl elimination reaction is not known, but it must include a distinct activation barrier of H atom transfer to Cl to be overruled by the less exothermic loss of Cl atom.

Secondly, the dissociation energy of the C–H bond at the $C(\alpha)$ atom of ethanol is distinctly below that of the corre-

sponding bond in methanol. Cleavage of this bond is the crucial step during oxidation of alcohol by a formal hydride transfer to the alkene radical cation. Obviously the reduction of the $C(\alpha)$–H bond energy makes the oxidation process not only more exothermic but reduces also the activation barrier of the H atom migration in the distonic adduct ion during this process. Therefore, oxidation becomes the main reaction pathway both for $1^{\bullet+}$ and $2^{\bullet+}$.

The detailed reaction mechanisms for substitution and oxidation, which have been elaborated in earlier studies [1,4], are shown in Scheme 2. It is suggested that the first reaction step for both reaction pathways is a fast addition of the nucleophile to the ionized C–C double bond of the alkene. The addition step may be still exothermic even if all reaction pathways are endothermic, but then the only possible reaction of the β-distonic addition product is dissociation back into reactants. Energetically excited distonic ions are known to undergo extensive migrations of H atoms. There is a chance that such rearrangements take also place during the lifetime of the distonic addition product of methanol to $1^{\bullet+}$. Hence, the reaction of $1^{\bullet+}$ with trideuteromethanol, CD_3OH, was investigated. The corresponding kinetic plot is shown in Fig. 2, using the isotopomer $^{12}C_3{}^1H_5{}^{37}Cl$, *m/z* 78, of $1^{\bullet+}$ as the reactant ion. The main reaction product observed at the
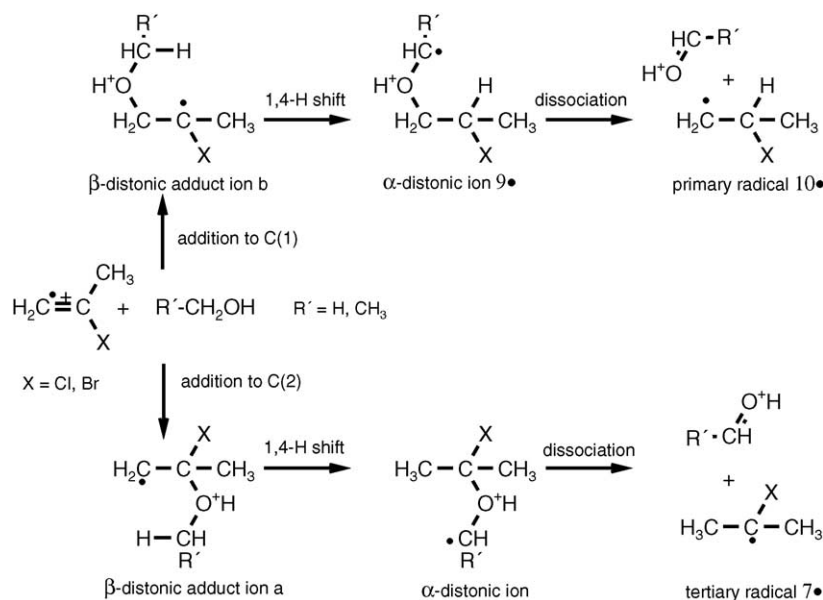
Scheme 2. Proposed mechanism of oxidation of alcohol by halogenoalkene radical cation.

final stages of the reaction is protonated bis-trideuteromethyl ether, $D_3C-O^+H-CD_3$, m/z 53, in agreement with the results from $1^{•+}/CH_3OH$. Product ions of substitution should be detected at m/z 75 ($^{12}C_4H_5D_3{}^{16}O$, loss of $H^{37}Cl$) and m/z 76 ($^{12}C_4H_6D_3{}^{16}O$, loss of ^{37}Cl). These ions are not found. Instead, an ion of elemental composition $^{12}C_4H_5D_4{}^{16}O$, m/z 77, is observed, although with low abundance. This ion corresponds to a substitution product ion derived from the monodeuterated derivative of $1^{•+}$. Indeed, abundant formation of

an ion $^{12}C_3H_4D^{37}Cl^{•+}$, m/z 79, is clearly seen at early stages of the reaction, and at later stages of the reaction even an ion $^{12}C_3H_3D_2{}^{37}Cl^{•+}$, m/z 80, is observed. Obviously, incorporation of D atoms from CD_3OH into $1^{•+}$ is faster than a reaction by substitution. An explanation for this observation is the occurrence of reversible H or D migrations in the excited distonic addition product of $1^{•+}$ and CD_3OH which is rapidly generated in an exothermic process and which eventually dissociates back to reactants. However, it should be mentioned
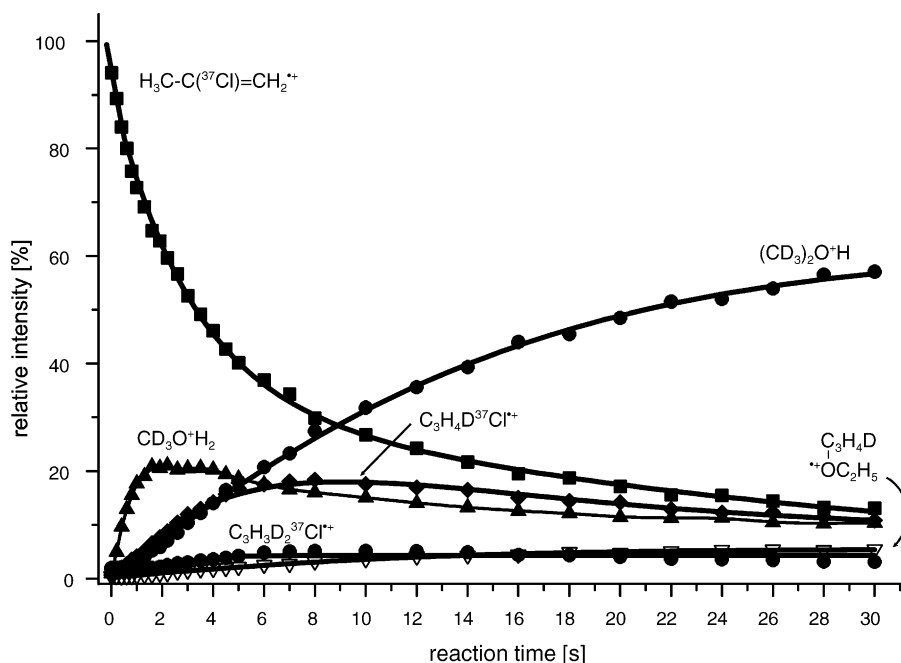

Fig. 2. Kinetic plot of the reaction of 2-chloropropene radical cation $1^{•+}$ (isotopomer $^{12}C_3{}^1H_5{}^{37}Cl$) with CD_3OH.

Table 2
Reaction enthalpies, ΔH°, of the ion/molecule reactions of chloropropene radical cation, $1^{\bullet+}$, with methanol[a]

	$\sum H^\circ_{298}$ (hartree × molecule^{-1})	ΔH°_{298} (kJ × mol^{-1})
Reactants		
$1^{\bullet+}$ + methanol	−692.699918	0
Products		
1-dista$^{\bullet+}$	−692.710491	−30.2
1-TS(isom)	−692.710739	−30.9
1-distb$^{\bullet+}$	−692.721372	−58.8
1-TSa(1,2Cl)	−692.693320	14.9
1-distc$^{\bullet+}$	−692.713047	−36.9
1-TSa(elim)	−692.700636	−4.4
$(3^{\bullet+} + HCl)_{complex}$	−692.752987	−141.8
$3^{\bullet+}$ + HCl	−692.748616	−127.9
$4^{\bullet+}$ + Cl$^\bullet$	−692.687422	32.8
1-TSa(1,3H)	−692.663147	94.1
$5^{\bullet+}$	−692.710486	−30.2
$6^{\bullet+}$ + Cl$^\bullet$	−692.736633	−96.4
1-TS(1,4H)	−692.707227	−21.7
$(11^+ + {}^\bullet CH_2OH)_{complex}$	−692.706038	−18.5
$CH_2=O^+H + \textbf{7}^\bullet$	−692.678625	55.9
1-TSb(1,3H)	−692.670063	75.9
$8^{\bullet+}$	−692.708610	−25.3
$11^+ + {}^\bullet CH_2OH$	−692.689413	27.6
1-TSb(1,4H)	−692.668226	80.7
$9^{\bullet+}$	−692.702150	−8.3
$CH_2=O^+H + \textbf{10}^\bullet$	−692.670954	76.0
$CH_3O^+H_2 + \textbf{13}^\bullet$	−692.68918	28.2

[a] For numbering of species see Schemes 3 and 4.

Table 3
Reaction enthalpies, ΔH°_{298}, of the ion/molecule reactions of bromopropene radical cation, $2^{\bullet+}$, with methanol[a]

	$\sum H^\circ_{298}$ (hartree × molecule^{-1})	ΔH°_{298} (kJ × mol^{-1})
Reactants		
$2^{\bullet+}$ + methanol	−2806.58900	0
Products		
2-dista$^{\bullet+}$	−2806.59751	−24.8
2-TS(isom)	−2806.59733	−24.3
2-distb$^{\bullet+}$	−2806,60725	−47.9
2-TS(1,2Br)	−2806.59633	−21.7
2-distc$^{\bullet+}$	−2806.60515	−44.9
2-TS(elim)	−2806.59731	−24.3
$(3^{\bullet+} + HBr)_{complex}$	−2806.63955	−135.2
$3^{\bullet+}$ + HBr	−2806.63601	−123.4
$4^{\bullet+}$ + Br$^\bullet$	−2806.59414	−13.5
2-TS(1,4H)	−2806,59333	−11.4
$\textbf{9}_{\textbf{Br}}^{\bullet+}$	−2806.59131	−8.6
$H_2C=O^+H + \textbf{7}_{\textbf{Br}}^\bullet$	−2806.56527	62.3
$H_2C=O^+H + \textbf{10}_{\textbf{Br}}^\bullet$	−2806.56161	69.4
$(11_{Br}^+ + {}^\bullet CH_2OH)_{complex}$	−2806,59844	−24.8
$11_{Br}^+ + {}^\bullet CH_2OH$	−2806.57581	32.1
$CH_3O^+H_2 + \textbf{12}_{\textbf{Br}}^\bullet$	−2806.57601	34.1

[a] For numbering of species see Schemes 3 and 4.

Table 4
Reaction enthalpies, ΔH°, of the ion/molecule reactions of chloropropene radical cation, $1^{\bullet+}$, and 2-bromopropene radical cation, $2^{\bullet+}$, with ethanol[a]

	$\sum H^\circ_{298}$ (hartree × molecule^{-1})	ΔH°_{298} (kJ × mol^{-1})
Reactants		
$1^{\bullet+}$ + ethanol	−731.973201	0
Products		
1*-dista$^{\bullet+}$	−731.989113	−44.3
1*-distb$^{\bullet+}$	−732.000132	−73.2
$4_{Et}^{\bullet+}$ + Cl$^\bullet$	−731.967218	15.7
1*-TSb(1,4H)	−731.951674	54.0
$\textbf{9}_{\textbf{Et}}^{\bullet+}$	−731.987651	−40.4
$CH_3-HC=O^+H + \textbf{7}^\bullet$	−731.985001	−31.0
$\textbf{1}_{\textbf{Et}}\textbf{-TS(1,4H)}$	−731.985536	−32.4
$CH_3-HC=O^+H + \textbf{10}^\bullet$	−731.977330	−10.8
$(11^+ + CH_3C^\bullet HOH)_{complex}$	−732.009815	−98.6
$CH_3CH_2O^+H_2 + \textbf{13}^\bullet$	−731.973403	−0.5
Reactants		
$2^{\bullet+}$ + ethanol	−2845.862284	0
Products		
2*-dista$^{\bullet+}$	−2845.875734	−37.8
2*-distb$^{\bullet+}$	−2845.887467	−66.0
$4^{*\bullet+}$ + Br$^\bullet$	−2845.873941	−30.6
$\textbf{2}_{\textbf{Et}}\textbf{-TSb(1,4H)}$	−2845.839345	57.7
$\textbf{9}_{\textbf{E,Br}}\textbf{t}^{\bullet+}$	−2845.876535	−39.9
$CH_3-HC=O^+H + \textbf{7}_{\textbf{Br}}^\bullet$	−2845.871648	−24.6
$\textbf{2}_{\textbf{Er}}\textbf{-TS(1,4H)}$	−2845.873555	−32.1
$CH_3-HC=O^+H + \textbf{10}_{\textbf{Br}}^\bullet$	−2845.867985	−15.0
$(11_{Br}^+ + CH_3C^\bullet HOH)_{complex}$	2845.899218	−99.4
$11_{Br}^+ + +CH_3C^\bullet HOH$	2845.799993	163.5
$CH_3CH_2O^+H_2 + \textbf{13}_{\textbf{Br}}^\bullet$	−2845.860230	5.4

[a] For numbering of species see Schemes 3 and 4.

that the computational study of the ion/molecule reactions of $1^{\bullet+}$/methanol indicates a somewhat different H/D exchange mechanism.

3.2. Computational studies

The potential energy surfaces of 2-chloropropene radical cation $1^{\bullet+}$ and 2-bromopropene radical cation $2^{\bullet+}$, respectively, and methanol were explored in detail using the 6–31 + G(d) basis set in combination with the hybrid density functional Becke-half-and-half-LYP (BHLYP). In the case of ethanol as the neutral reactant, only some stationary points were calculated which are relevant to the experimentally observed oxidation process. The results are collected in the tables of the supplement material. The data were used to calculate the reaction enthalpies ΔH°_{298} (Tables 2–4) and to construct the MERPs of the relevant processes (Figs. 3–5). The reaction system $1^{\bullet+}$/methanol has been particularly analyzed and will be discussed first, using the relative reaction enthalpies ΔH°_{298}, of Table 2 to construct a schematic MERP shown in Figs. 3 and 4. The corresponding structures are depicted in Scheme 3. PT from radical cation $1^{\bullet+}$ to methanol yielding protonated methanol $CH_3O^+H_2$ and 2-chloroallyl radical $\textbf{12}^\bullet$ is endothermic by +28.2 kJ × mol^{-1}. In contrast, addition of methanol to $1^{\bullet+}$ is exothermic and proceeds apparently without an enthalpic barrier to yield β-distonic radical cations $\textbf{1-dista}^{\bullet+}$ and $\textbf{1-distb}^{\bullet+}$, the latter
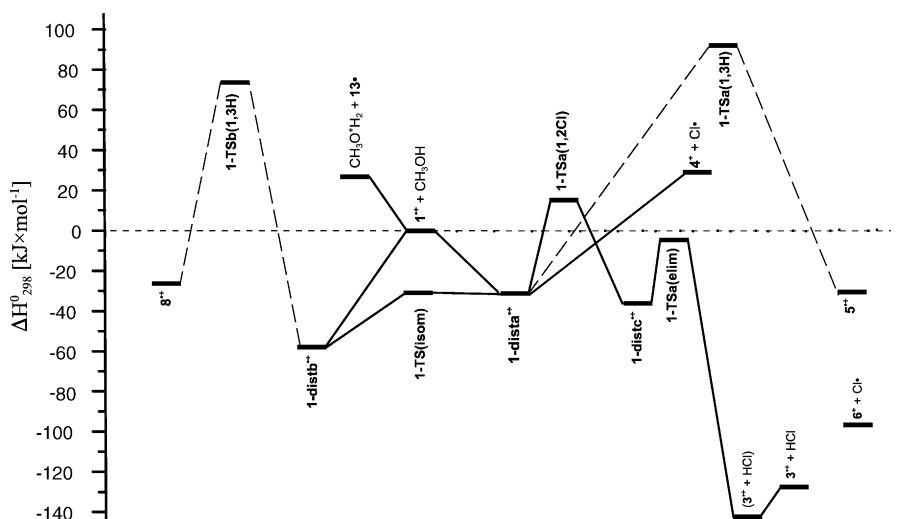
Fig. 3. Calculated MERP of the ion/molecule reactions of 2-chloropropene radical cation $1^{\bullet+}$ and methanol (except oxidation).

being $28.6 \, \text{kJ} \times \text{mol}^{-1}$ more stable than the former. These two primary addition products can easily interconvert through transition state **1-TS(isom)** located less than $1 \, \text{kJ} \times \text{mol}^{-1}$ above isomer **1-dista$^{\bullet+}$**.

Starting from **1-dista$^{\bullet+}$**, the most favorable reaction pathway leads through elimination of HCl to methyl 2-propenyl ether radical cation **3$^{\bullet+}$**. Relative to reactants, this reaction is very exothermic by $-127.9 \, \text{kJ} \times \text{mol}^{-1}$. Elimination of Cl atom alone and formation of protonated vinylether **4$^+$** is much less favorable and endothermic by $+32.8 \, \text{kJ} \times \text{mol}^{-1}$. However, the elimination of HCl requires obviously an activation enthalpy. Unexpectedly, an extension of the isomerization reactions of **1-dista$^{\bullet+}$** was found in the search for the transition state for the loss of HCl. The corresponding transition state **1-TS(elim)** was found at $-4.4 \, \text{kJ} \times \text{mol}^{-1}$ relative to reactants which is distinctly
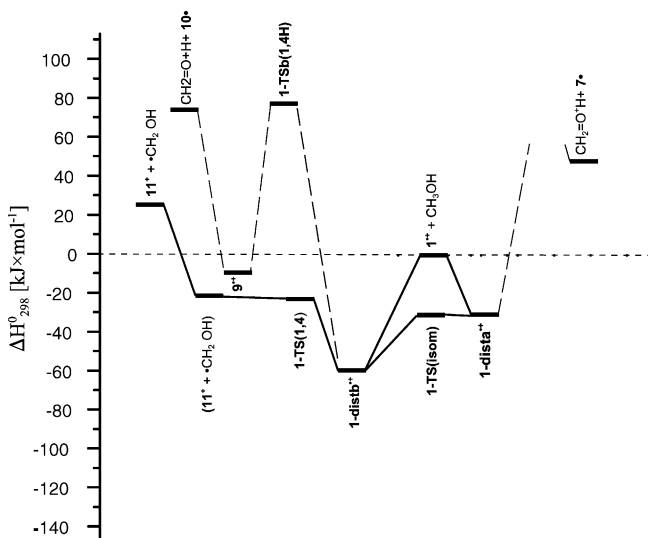
below the energy level given by PT and Cl substitution. However, **1-TS(elim)** does not connect the product complex ($3^{\bullet+} + \text{HCl}$)$_{\text{compl}}$ with **1-dista$^{\bullet+}$**, but with a third distonic intermediate **1-distc$^{\bullet+}$** which is derived from the former by a 1,2-Cl shift. Thus, HCl elimination via **1-TS(elim)** corresponds to a 1,3-elimination from **1-distc$^{\bullet+}$**. This agrees with the fact that generally 1,3-HCl elimination from radical cations of alkyl chlorides and cycloalkyl chlorides is preferred over 1,2-elimination [19]. 1,2-Cl shifts in distonic radical cations have been observed before [20] and are usually associated with rather large activation energies. In the present case of the isomerization **1-dista$^{\bullet+}$ → 1-distc$^{\bullet+}$**, the transition state **1-TS-1,2Cl** is located at $14.9 \, \text{kJ} \times \text{mol}^{-1}$ relative to reactants which corresponds to an ativation enthalpy of only $45.1 \, \text{kJ} \times \text{mol}^{-1}$ for the 1,2-Cl shift. Nonetheless, **1-TS-1,2Cl** represents the "bottle neck" for the elimination of HCl from **1-dista$^{\bullet+}$**. A *scan* calculation by increasing stepwise the C−Cl bond length of **1-dista$^{\bullet+}$** revealed that on leaving the Cl atom enters the path of isomerization and forms the more stable isomer **1-distc$^{\bullet+}$** because the dissociation into free **4$^{\bullet+}$** and Cl$^{\bullet}$ is endothermic. Since the transition state **1-TS(1,2Cl)** is located below **4$^{\bullet+}$** + Cl$^{\bullet}$, elimination of HCl by the route **1-dista$^{\bullet+}$ → 1-TS(1,2Cl) → 1-distc$^{\bullet+}$ → 1-TS(elim) → 3$^{\bullet+}$** + HCl eventually takes place instead of loss of Cl$^{\bullet}$. Obviously the general explanation for the rule, that substitution accompanied by loss of HX is only observed if loss of X is endothermic, is the energetically demanding 1,2-shift of X in the distonic intermediates, which has to precede loss of HX to enable 1,3-elimnation, and the tight transition states for isomerization and elimination.

Intramolecular hydrogen migration in **1-dista$^{\bullet+}$** through transition state **1-TSa-1,3H** yields the 2-chloro-2-methoxy-propane radical cation **5$^{\bullet+}$**. This latter product at $-30.2 \, \text{kJ} \times \text{mol}^{-1}$ is as stable as the primary addition product **1-dista$^{\bullet+}$** but the barrier for its formation is rather high at $+94.1 \, \text{kJ} \times \text{mol}^{-1}$ relative to reactants (Fig. 3). A C−Cl bond

Fig. 4. Calculated MERP of the oxidation reaction of 2-chloropropene radical cation $1^{\bullet+}$ and methanol.
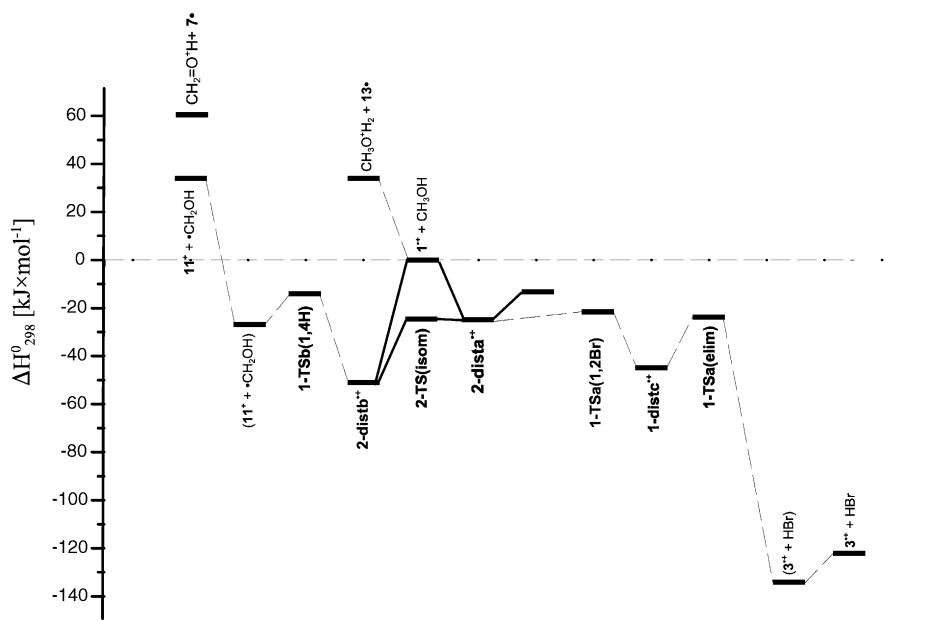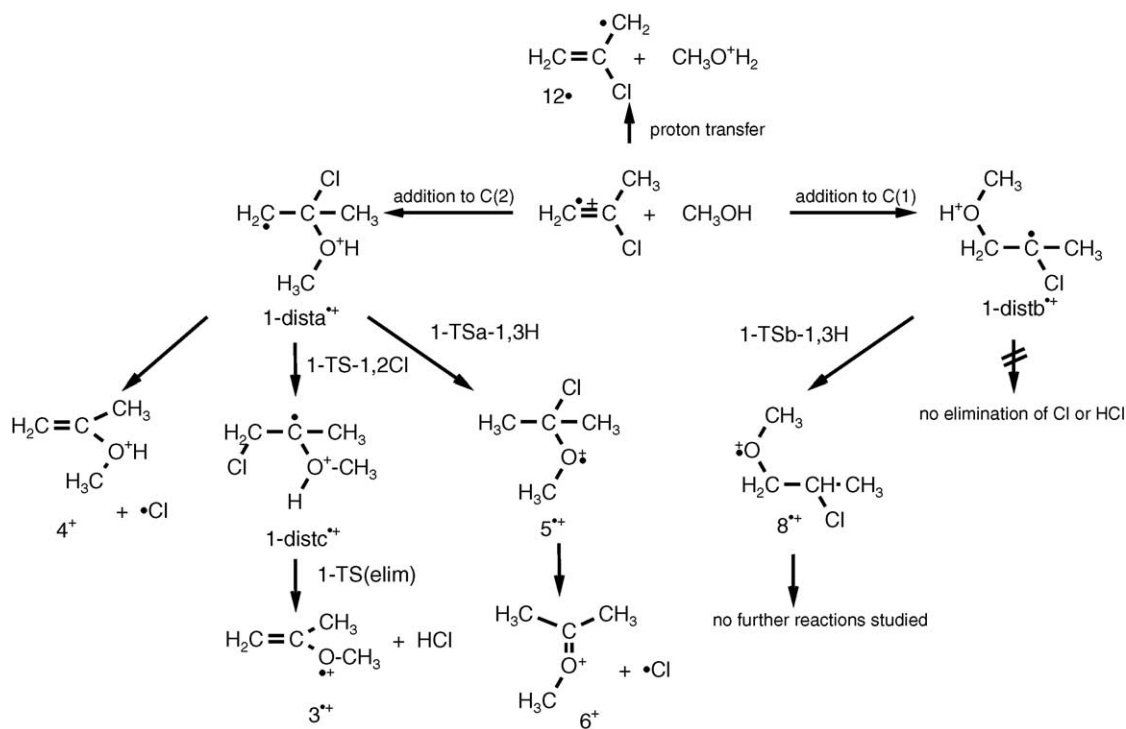
Fig. 5. Calculated MERP of the ion/molecule reactions of 2-bromopropene radical cation $2^{\bullet+}$ and methanol.

Scheme 3. Stationary points calculated for the MERP of $1^{\bullet+}$ and methanol.

homolysis in $5^{\bullet+}$ would yield the Cl atom and the tertiary 2-methoxypropyl cation 6^+, which is a more stable tautomer of 4^+. Therefore, this step is exothermic by $-96.6\,\text{kJ} \times \text{mol}^{-1}$, but the total process does not occur because this reaction sequence requires the unfavorable 1,3-H shift of $1\text{-dista}^{\bullet+}$. In principle, the same products 6^+ and $\text{Cl}^{\bullet}$ could also be obtained through hydrogen atom transfer between HCl and the enol ether radical cation $3^{\bullet+}$, but this process is endothermic

and not expected to occur. Finally, starting from the more stable β-distonic radical cation $1\text{-distb}^{\bullet+}$, elimination of Cl or HCl would result in carbenic structures of high energy and is excluded. Intramolecular 1,3-hydrogen migration in $1\text{-distb}^{\bullet+}$ leads through transition state 1-TSb-1,3H to the rearranged radical cation $8^{\bullet+}$ (Fig. 3). The reaction product $8^{\bullet+}$ is thermochemically quite favorable at $-25.3\,\text{kJ} \times \text{mol}^{-1}$, but the activation barrier for this process is again large at

$+75.9 \, \text{kJ} \times \text{mol}^{-1}$. Therefore, the only possible reaction of **1-distb•+** appears to be oxidation according to Scheme 2 besides isomerization to **1-dista•+**.

The oxidation of methanol by a format hydrid shift to **1•+** is initiated by 1,4-shifts in the addition products **1-dista•+** and **1-distb•+**, and eventually produces protonated formaldehyd and either the tertiäry 2-chloro-prop-2-yl radical **7•** $(\Delta H_{298}^{\circ}) + 55.9 \, \text{kJ} \times \text{mol}^{-1}$ or the primary 2-chloro-prop-1-yl radical **10•** $\Delta H_{298}^{\circ} + 76.0 \, \text{kJ} \times \text{mol}^{-1}$; see Scheme 2 and Fig. 4. A 1,4-H-shift in **1-distb•+** was identified which generates the α-distonic ion **9•+**. Subsequent decomposition of **9•+**, which is located slightly below the entry channel at $-8.3 \, \text{kJ} \times \text{mol}^{-1}$, would afford protonated formaldehyde $H_2C=O^+H$ and **10•**, but the corresponding transition state **1-TSb-1,4H** is very unfavorable at $+80.7 \, \text{kJ} \times \text{mol}^{-1}$. Thus, this route of the oxidation is not expected to occur experimentally. All efforts to locate a transition state **1-TSa-1,4H** for a 1,4-H shift in the less stable isomer **1-dista•+** have converged to transition state **1-TS-1,4H** which is surprisingly favorable at $-21.7 \, \text{kJ} \times \text{mol}^{-1}$ but which exhibits some unusual properties. Its structure resembles a complex between **1•+** and methanol, in which an H transfer between the *O*-methyl group of methanol and the chloropropene component occurs. Unexpectedly, IRC calculations unambiguously prove that **1-TS-1,4H** is connected to the more stable β-distonic radical cation **1-distb•+** (and not to **1-dista•+**) at one side and to a weakly bonded complex of the products at the other side. This product complex is located at $-18.5 \, \text{kJ} \times \text{mol}^{-1}$, and both components are arranged almost parallel to each other with the H atom of the *O*-methyl group, which was transferred to **1•+**, still pointing to its origin. This complex dissociates not to $H_2C=O^+H$ and **7•** but to the 2-chloropropyl cation **11+** and the hydroxymethyl radical $^{\bullet}CH_2OH$. This outcome corresponds to the expected products of the oxidation process but with inverse charge distribution. The free products **11+** and $^{\bullet}CH_2OH$ are located $+27.6 \, \text{kJ} \times \text{mol}^{-1}$ relative to reactants. This is distinctly more favorable than the dissociation to $H_2C=O^+H$ and **7•**.

A ΔH_{298}° of $+27.6 \, \text{kJ} \times \text{mol}^{-1}$ for the formation of **11+** and $^{\bullet}CH_2OH$ is slightly less than those calculated for PT $(+28.2 \, \text{kJ} \times \text{mol}^{-1})$ and substitution with loss of Cl• $(+32.8 \, \text{kJ} \times \text{mol}^{-1})$. Therefore, this process is able to compete with the other reactions, but the carbenium ion **11+** cannot be observed experimentally. The acidic cabenium ion **11+** is quickly deprotonated by the excess of methanol in the FT-ICR cell, so that protonated methanol is the final reaction product also of this route. It should be noted that the complex $(\mathbf{11^+} + {}^{\bullet}CH_2OH)_{\text{complex}}$ is more stable than the reactants, and a reversible route $\mathbf{1^{\bullet+}} + CH_3OH \rightleftharpoons \mathbf{1\text{-}TS(1,4H)} \rightleftharpoons (\mathbf{11^+} + {}^{\bullet}CH_2OH)_{\text{complex}}$ gives a better explanation for the fast H/D exchange observed in the system **1•+**/CD₃OH than H-shifts in the distonic adduct ions, which include considerable activation barriers.

Summarizing the results of these calculations for **1•+**/methanol it turns out that all reaction pathways are either endothermic or blocked by a substantial activa-

tion barrier. The two least endothermic reaction pathways, devoid of an extra activation barrier, are PT $(\Delta H_{298}^{\circ} = +28.2 \, \text{kJ} \times \text{mol}^{-1})$ and substitution by loss of Cl atom $(\Delta H_{298}^{\circ} = +32.8 \, \text{kJ} \times \text{mol}^{-1})$, and these reactions are indeed observed experimentally as slow reactions. It appears possible that protonated methanol is also formed by deprotonation of 2-chloroprop-2-yl carbenium ion **11+** which results in a special process by H transfer from methanol to **1•+** and which exhibits a reaction enthalpy of $+27.6 \, \text{kJ} \times \text{mol}^{-1}$. Finally, the further process observed is substitution by loss of HCl and formation of the enol radical cation **3•+**, which is the most exothermic reaction pathway, but which may be slow because of two tight transition states along this route.

In the case of reactions of the bromo derivative **2•+** with methanol, major changes are expected only for those reactions which involve the weaker C−Br bond [21]. This is corroborated by the values of the reaction enthalpy ΔH_{298}° collected in Table 3. The corresponding MERP is shown in Fig. 4, and the numbering of the species is as in Scheme 3 with a subscript Br, if the Cl substituent of a fragment is changed to Br. The addition of methanol to **2•+** is somewhat less exothermic than in the case of **1•+** and generates the distonic ions **2-dista•+** and **2-distb•+** at -24.8 and $-46.5 \, \text{kJ} \times \text{mol}^{-1}$, respectively. The reason for this is certainly a reduced stabilization of a neighboring radical site by a Br substituent. This effect is also seen for the processes which produce the Br-substituted radicals **7Br•** and **15Br•**. Further, both PT and oxidation by formal hydride transfer are more endothermic than for **1•+**/methanol. A transition state **2-TS(1,4H)** is found in analogy with the chloro derivative, which leads to a complex of the products at $-9.6 \, \text{kJ} \times \text{mol}^{-1}$ with a structure similar to that arising from **1•+** and methanol. Dissociation of the product complex yields 2-bromo-prop-2-yl cation **11Br+** and hydroxymethyl radical $^{\bullet}CH_2OH$ at $+32.1 \, \text{kJ} \times \text{mol}^{-1}$, which is much less than the products of oxidation by formal hydride transfer. Nonetheless, both processes are too endothermic to be observed experimentally. In contrast, the reaction enthalpy of substitution by loss of a Br atom is distinctly diminished, and this process is now exothermic with $-13.5 \, \text{kJ} \times \text{mol}^{-1}$. These results agree with experiment, in which substitution and loss of $^{\bullet}Br$ is the only reaction observed. Furthermore, according to DFT calculations the activation barriers for the 1,2-Br shift in **2-dista•+** and the elimination of HBr are distinctly smaller than in the case of the chloro derivative. Nonetheless, HBr elimination is not observed experimentally, which is in line with the rule that substitution accompanied by HX elimination is not observed if substitution and loss of X• is exothermic.

The computational analysis of the reaction of the halogenoalkene radical cations **1•+** and **2•+** with ethanol was focused on reactions relevant for the oxidation process, since oxidation is the only (for **1•+**) or dominating reaction (for **2•+**) observed by experiment [22]. The results are presented in the supplement material, and the respective data have been used to calculate the reaction enthalpies ΔH_{298}° which are presented in Table 4. Comparison of the reaction

systems $\mathbf{1}^{\bullet+}$/methanol (Table 2) and $\mathbf{1}^{\bullet+}$/ethanol (Table 4) shows, on the one side, that in the latter case the oxidation process by a formal hydride transfer, which produces protonated acetaldehyde $H_3C-HC=O^+H$ and 2-chloroprop-2-yl radical $\mathbf{7}^{\bullet}$ or 2-chloroprop-1-yl radical $\mathbf{10}^{\bullet}$, becomes exothermic by -31.0 and $-10.8\,kJ \times mol^{-1}$, respectively, relative to reactants. Both pathways are endothermic in the methanol case. On the other side, PT and substitution are at most thermoneutral or still endothermic. This agrees very well with the experimental observation of an efficient oxidation process. However, the mechanism of oxidation of ethanol by $\mathbf{1}^{\bullet+}$ does again not correspond to Scheme 2, but bypasses the energy rich transition states of the 1,4-H shifts in the distonic adduct ions by a loose and complex-like transition state $\mathbf{1_{Et}}$-$\mathbf{TS(1,4H)}$, which is located at $-32.4\,kJ \times mol^{-1}$. Although this transition state is structurally similar to $\mathbf{1}$-$\mathbf{TS(1,4H)}$ of the system $\mathbf{1}^{\bullet+}$/methanol, it corresponds to a hydride transfer yielding $H_3C-HC=O^+H$ and $\mathbf{7}^{\bullet}$. This is seen by the structure of the rather stable product complex at $-98.2\,kJ \times mol^{-1}$. Its structure is characteristically different from that of the complex resulting from $\mathbf{1}$-$\mathbf{TS(1,4H)}$, and both components are now oriented almost perpendicular to each other and form a hydrogen bridge between the HO group and the Cl atom.

The results of the calculations for the reactions of $\mathbf{2}^{\bullet+}$ and ethanol are somewhat more complicated. Here, not only the oxidation pathway is exothermic by -24.6 or $-15.0\,kJ \times mol^{-1}$, depending on the bromoalkyl radical formed, but substitution and loss of Br atom is even more exothermic by $-30.6\,kJ \times mol^{-1}$. In spite of this, the predominant reaction pathway experimentally observed is oxidation while substitution is rather inefficient. The origin for this apparent discrepancy must be the reaction dynamics of both routes, and the key to an understanding of the competition between the two exothermic routes are the essential intermediates and transition states. An obligatory intermediate for substitution and loss of $Br^{\bullet}$ is the β-distonic ion $\mathbf{2_{Et}}$-$\mathbf{dista}^{\bullet+}$, which is the less stable one of the two addition products. In

contrast, the oxidation process may, in principle, start from each of the intermediates $\mathbf{2_{Et}}$-$\mathbf{dista}^{\bullet+}$ and $\mathbf{2_{Et}}$-$\mathbf{distb}^{\bullet+}$ to generate $CH_3CH=O^+H$ and 2-bromo-prop-2-yl radical $\mathbf{7_{Br}}^{\bullet}$ after passing the loose transition state $\mathbf{2_{Et}}$-$\mathbf{TSb(1,4H)}$. Note that the transition state for a 1,4-H shift in the more stable isomer $\mathbf{2_{Et}}$-$\mathbf{distb}^{\bullet+}$ is much too high in enthalpy ($+57.7\,kJ \times mol^{-1}$) to make this route competitive, while ΔH°_{298} of -32.1 of transition state $\mathbf{2_{Et}}$-$\mathbf{TSb(1,4H)}$ is comparable to that of $\mathbf{2_{Et}}$-$\mathbf{dista}^{\bullet+}$, which is needed for substitution.

This result emphasizes the importance of the loose transition state $\mathbf{1}$-$\mathbf{TS(1,4H)}$, $\mathbf{2}$-$\mathbf{TS(1,4H)}$, $\mathbf{1_{Et}}$-$\mathbf{TS(1,2H)}$, and $\mathbf{2_{Et}}$-$\mathbf{TS(1,2H)}$, respectively, for favoring hydrogen or hydride transfer between the reactants 2-halogeno-propene radical cation and alcohol. These transition states are properly characterized by one imaginary frequency which in every case conforms to a motion of a hydrogen atom at the α-C atom of the alcohol towards the C(1) atom of the 2-halogenopropene radical cation. However, the structures of these transition states resemble a complex of the reactants ($\mathbf{1}^{\bullet+}$ or $\mathbf{2}^{\bullet+}$ and methoanl or ethanol) with a hydrogen bridge between the C atoms involved in the H-transfer. In particular, the C–O bond of the β-distonic adduct ion is completely cleaved (C–O-distance $\mathbf{1}$-$\mathbf{TS(1,4H)}$: 302 pm, $\mathbf{2}$-$\mathbf{TS(1,4H)}$: 297 pm, $\mathbf{1_{Et}}$-$\mathbf{TS(1,2H)}$: 407 pm, $\mathbf{2_{Et}}$-$\mathbf{TS(1,2H)}$: 308 pm). This structure explains, why IRC calculation on reformation of the C–O bond ends at the most stable β-distonic adduct ion, even if the search for the transition state was originally started from the other isomer. Likely, these complex-like transition state structures are not only connecting the β-distonic adduct ions and the product complex of the haydrogen or hydride transfer, but can be achieved also directly from the collision complex of the radical cation with the alcohol as shown in Scheme 4. In this case, the β-distonic adduct ions are not obligatory intermediates for the oxidation process as assumed in Scheme 2, but addition of the alcohol to the ionized double bond and hydrogen or hydride transfer as the key step of oxidation compete with each other already in the initial collision complex of
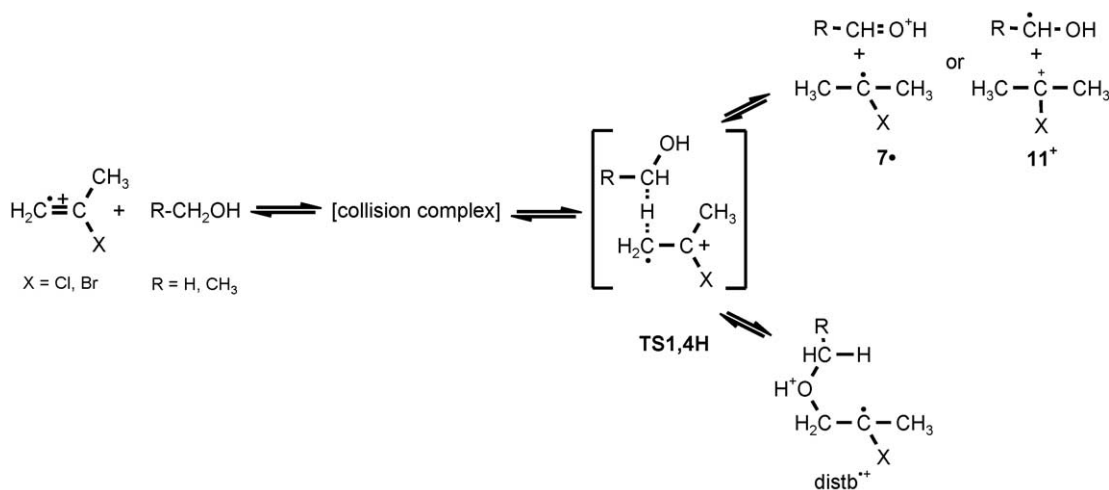
Scheme 4. Mechanism of oxidation of alcohol by halogenoalkene radical cation via transition state **TS-1,4H**.

the reactants. It is feasible, that the oxidation process which results in a loose complex of products wins this competition because of favorable entropy effects.

Although all four transition states **1-TS(1,4H)**, **2-TS(1,4H)**, **1$_{Et}$-TS(1,2H)**, and **2$_{Et}$-TS(1,2H)** exhibit similar structures, in the case of methanol as the nucleophil the transition states **1-TS(1,4H)** and **2-TS(1,4H)** lead eventually to 2-halogenoprop-2-yl cation and hydroxymethyl radical, while in the case of ethanol as the neutral reactant **1$_{Et}$-TS(1,4H)** and **2$_{Et}$-TS(1,4H)** result in 2-halogenoprop-2-yl radical and $H_3C–HC=O^+H$. The reason for this reversed charge distribution between the products is the low ionization energy of the radical $CH_3–C^•HOH$, in accordance with Stevensons rule. This different charge distribution is reflected in different structures of the product complexes. In the product complex $(11^+ + {}^•CH_2OH)_{complex}$ and $(11_{Br}{}^+ + {}^•CH_2OH)_{complex}$, respectively, which are arise from methanol as neutral reactant, the two components are coordinated in a more or less parallel fashion, while in $(7^• + CH_3CH=O^+H)_{complex}$ and $(7_{Br}{}^• + CH_3CH=O^+H)_{complex}$, which are derived from ethanol, both components are arranged perpendicular to each other with a proton bridge between the OH group and the halogen atom. However, it is not obvious whether one type of the transition state involves transfer of an H atom and the other transfer of a hydride. It may be possible that electron transfer actually follows H atom transfer as a separate reaction step within the complex if such a charge distribution is energetically more favorable.

4. Conclusion

In principle, the ion/molecule reactions of the 2-halogenopropene radical cations with methanol and ethanol as *O*-nucleophiles, which were investigated in this study, follow the reaction scheme developed earlier for halogenoethenes [4]. Proton transfer (PT) from the halogenopropene radical cation to the alcohol, which was expected to interfere severely with other reactions and which is an efficient reaction between propene radical cation itself and methanol, was observed only as a very inefficient reaction of the 2-chloropropene radical cation **1$^{•+}$** and not at all for the bromo derivative **2$^{•+}$**. In fact, **1$^{•+}$** is almost unreactive towards methanol (total eff = 0.09%), exhibiting substitution accompanied by loss of HCl and Cl$^•$, respectively, besides slow PT. The bromo derivative **2$^{•+}$** is somewhat more reactive (total eff = 0.9%) and displays substitution and loss of Br$^•$ as the only reaction. The modeling of these ion/molecule reactions by extensive DFT calculations revealed new and unexpected features of the reaction mechanisms. According to these calculations, the usual pathways observed for the reactions of halogenoalkene radical cations with nucleophiles (see Schemes 1 and 2) are all endothermic or blocked by large activation barriers if methanol is used as the neutral reactant. The loss of HCl and HBr, respectively, which may follow the addition of the alcohol to the ionized double bond of **1$^{•+}$** and

2$^{•+}$ and which is strongly exothermic, turns out to proceed by a quite complicated multi-step mechanism. The crucial step of this mechanism is an isomerization of the β-distonic addition product by a 1,2-shift of the halogen which yields an isomeric distonic ion enabling a 1,3-elimination of HCl or HBr. This isomerization requires an additional activation energy. The chloro- and bromopropene radical cations **1$^{•+}$** and **2$^{•+}$** react efficiently with ethanol by a formal hydride abstraction from ethanol. This generates protonated acetaldehyde $H_3C–HC=O^+H$ as the primary oxidation product, a reaction known from the interaction of ionized halogenoethenes with ethanol [4]. However, from the previous studies it was not clear why the oxidation reaction is preferred over an exothermic substitution pathway if both processes are of comparable exothermicity. The present computational study shows that the reason is a loose transition state for the transfer of a H atom between the reactants, which circumvents the "classical" transition states of a 1,4-H-shift in the β-distonic addition products and which is comparable to a direct H transfer in the collision complex of the alkene radical cation and the alcohol.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2004.10.012.

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[21] Products which are structurally analogous to those of the reactions of $1^{\bullet+}$ with methanol but containing the Br atom of $2^{\bullet+}$ are marked by a subscript "Br".

[22] Products which are structurally analogous to those of the reactions of $1^{\bullet+}$ and $2^{\bullet+}$ with methanol but containing the ethyl group are marked by a subscript "Et".