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A catalyzed rearrangement of gaseous 1,1-dichloroethene radical cations

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Dedicated to Prof. Yannik Hoppilliard as a salute to her important contribution to gas phase ion chemistry and organic mass spectrometry.

Abstract

The reaction of the radical cation of 1,1-dichloroethene **1** with methanol has been investigated by FT-ICR spectrometry and compared with that of the radical cations of 1,2-dichloroethene **2** and of the 1,1- and 1,2-dibromoethenes **3** and **4** with methanol and ethanol, respectively. The 1,1-dichloro derivative $\mathbf{1}^{\bullet +}$ is special because it exhibits besides a slow hydride transfer also a slow isomerization into an unreactive isomer, which was proven by separate experiments to be the 1,2-disubstituted isomer $\mathbf{2}^{\bullet +}$. This unprecedented isomerization of a radical cation by a reciprocal 1,2-shift of Cl and H is catalyzed by methanol. The mechanism of this isomerization and the competing reactions of $\mathbf{1}^{\bullet +}$ with methanol have been modeled by ab initio calculation of the corresponding minimum energy reaction pathway (MERP). The results show that the isomerization takes place by a 1,2-Cl shift in a β-distonic onium ion $\mathbf{1}\text{distb}^{\bullet +}$ which is formed by a fast addition of methanol to the ionized C=C double bond. The resulting α-distonic ion $\mathbf{1}\alpha\text{distb}^{\bullet +}$ displays the structure of the addition product of methanol to the carbene center of chloromethyl chlorocarbene $\mathbf{5}^{\bullet +}$. However, the 1,2-H shift within $\mathbf{1}\alpha\text{distb}^{\bullet +}$, which completes the exothermic isomerization $\mathbf{1}^{\bullet +} \rightarrow \mathbf{2}^{\bullet +}$, requires a very large critical energy and blocks this reaction pathway. This large barrier is encompassed by a reaction route on which $\mathbf{1}\alpha\text{distb}^{\bullet +}$ starts to dissociate into methanol and $\mathbf{5}^{\bullet +}$, and the incipient chloromethyl chlorocarbene radical cation $\mathbf{5}^{\bullet +}$ isomerizes with the aid of methanol by some kind of an internal proton shuttle. Thus, the catalyst methanol acts in this system in two different modes. Firstly, it is covalently bonded to the 1,1-dichloroethene radical cation and enables an easy 1,2-Cl shift within the resulting β-distonic ion. Secondly, during the process of reconstituting methanol it lowers the energy of the transition state of the 1,2-H shift in the incipient chloromethyl chlorocarbene radical cation $\mathbf{5}^{\bullet +}$ to the 1,2-dichloroethene radical cation $\mathbf{2}^{\bullet +}$. (Int J Mass Spectrom 219 (2002) 409–427)

Keywords: Alkene radical cation; Ion/molecule reaction; Isomerization; Catalysis; FT-ICR spectrometry; Ab initio calculation

1. Introduction

The reactions of the radical cations of alkenes, alkadienes and arenes with electron-rich reactants (nucleophiles) are outstanding examples of the acceleration of the rate of an organic reaction by the so-called "electron hole catalysis" [1], achieved by the conversion of one of the reactants into a radical cation. These reactions have been studied extensively during the last 20 years, and have found in the meantime many interesting synthetic applications [2]. To get more insight into the salient features of the mechanism of "electron hole catalysis" we have studied these reactions

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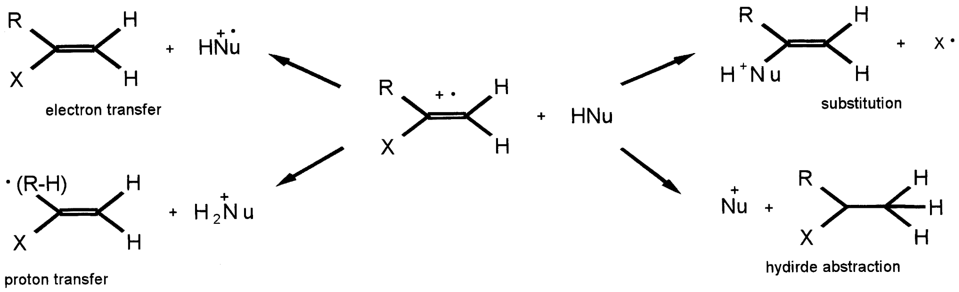


Scheme 1.

in the gas phase by Fourier transform ion cyclotron resonance (FT-ICR) spectrometry. During the last years the focus of our work has been on the reactions of radical cations of simple alkenes with a variety of nucleophiles [3]. Generally, the four reaction pathways depicted in Scheme 1 have been observed.

Electron-rich nucleophiles have a low ionization energy (IE) and are also bases of a considerable gas phase basicity (GB). Therefore, the first two reactions that may be observed are electron transfer and proton transfer. The third reaction corresponds to a substitution of a suitable group X, mostly a halogen atom in the reactants used, by the attacking nucleophile, and the last reaction is formally a hydride abstraction from the nucleophile by the alkene radical cation with large rate constants only exothermic reactions are observed in the diluted gas phase of an FT-ICR spectrometer, and any critical barrier along the minimum energy reaction pathway (MERP) must be located below the energy level defined by the heats of formation of the reactants. Otherwise the rate constant k_{bi} of the reaction is small compared to the rate constant k_{coll} of the collisions of the reactants. This is conveniently expressed by the reaction efficiency eff $= 100k_{\mathrm{exp}}/k_{\mathrm{coll}}$ (%) indicating the percentage of reactive collisions. Usually exothermic electron transfer and proton transfer do not involve a critical barrier and proceed with eff $> 50\%$. Therefore, the observation [3c] that substitution and hydride abstraction, which may include critical barriers, compete successfully with exothermic electron transfer and proton transfer is significant for the mechanism of "electron hole catalysis". Ab initio calculations of the MERPs reveal that the first reaction step of substitution and hydride abstraction is an exothermic addition of the nucleophile to the ionized C–C carbon bond which proceeds without a critical barrier [3b–e]. As a consequence the collision complex of an ionized alkene and a nucleophile collapses spontaneously into the β-distonic onium ion of the addition product. This barrier-less collapse of the collision complex of a radical cation of an alkene with an electron-rich reactant followed by fast secondary reactions is the very heart of the phenomenon of the "electron hole catalysis" [3,4]. In the diluted gas phase an exothermic addition gives rise to an energetically excited β-distonic ion which decomposes unimolecularly. Thus, substitution corresponds to fragmentation of the excited β-distonic adduct ion by simple bond cleavage at a β-position to the radical site, and formal hydride abstraction is actually a rearrangement of the β-distonic adduct ion by a 1,4-H shift.

It has been shown previously [3f], that the radical cation of vinyl chloride $H_2C{=}CHCl^{\bullet+}$ reacts with aliphatic alcohols by oxidation of the alcohol via formal hydride abstraction, yielding protonated aldehydes or ketones, while that of vinyl bromide $H_2C{=}CHBr^{\bullet+}$ yields substitution with methanol and hydride abstraction with ethanol. This switching between the main reactions channel is clearly a manifestation of a change of the reaction energy by the structural changes of the reactants. Further, radical cations of various dihalogenoethenes react with ethanol although with different reaction efficiencies and yielding different products [3f]. In this paper we discuss in detail the reactions of the radical cation of 1,1-dichloroethene $\mathbf{1}^{\bullet+}$ with methanol. Using methanol as the reactant, the 1,2-dichloroethene radical cation $\mathbf{2}^{\bullet+}$ is completely unreactive. In contrast, $\mathbf{1}^{\bullet+}$ undergoes a slow and obviously endothermic hydride abstraction. However, parallel to hydride abstraction an isomerization of $\mathbf{1}^{\bullet+}$ into an unreactive isomer is observed. It will be shown that this unreactive isomer is the 1,2-isomer $\mathbf{2}^{\bullet+}$ which arises from $\mathbf{1}^{\bullet+}$ by a hitherto unknown reaction corresponding to reciprocal 1,2-shifts of a Cl-atom and a H-atom catalyzed by a molecule of methanol. The isomerization of gaseous cations and radical cations catalyzed by collision with a neutral molecule has been studied extensively [5]. Usually, isomerization proceeds by reciprocal proton or H-atom transfer between the partners of a collision complex. It will be shown that here the isomerization $\mathbf{1}^{\bullet+} \rightarrow \mathbf{2}^{\bullet+}$ occurs by a different mechanism which includes covalent bonding of the catalyst and rearrangements within the intermediate distonic ion.

2. Experimental

2.1. Compounds

The dichloroethenes **1**, *cis*-**2**, *trans*-**2**, and 1,2-dibromoethene **4** (mixture of *cis*- and *trans*-isomer) as well as methanol and its deuterated derivatives CD_3OH and CD_3OD are commercially available. The 1,1-dibromoethene **3** decomposes on standing and prior to analysis fresh samples were prepared using methods described before [3b,c].

2.2. FT-ICR spectrometry

A Bruker CMS 47× FT-ICR spectrometer equipped with a 4.7 T superconducting magnet, an Infinity® ICR cell, and an external EI- and CI-ion source [6] has been used to measure the kinetics of the reactions of the radical cations of **1**–**4** with methanol and ethanol. The procedure used has been described in detail before [3b,e]. In brief, the radical cations were generated in the external ion source by electron impact ionization with 30 eV electrons, if not stated otherwise, and transferred into the ICR cell (trapping voltage < 1 V). After cooling the ions by collisions with argon atoms, introduced by a pressure pulse, the dihaloethene ions containing only the isotopes ^{35}Cl or ^{79}Br were selected by the appropriate ejection technique. Subsequently, the ions reacted with the alcohol present in the ICR cell at a constant background pressure between 2×10^{-8} and 5×10^{-7} mbar. The pressure within the ICR cell was measured with an ionization gauge positioned between the ICR cell and the turbo pump. The reading of the ionization gauge was calibrated by measuring the rate constants of the reactions $CH_4^{\bullet+} + CH_4 \rightarrow CH_5^+ + CH_3^{\bullet}$ and $NH_3^{\bullet+} + NH_3 \rightarrow NH_4^+ + NH_2^{\bullet}$ [7] and using the compound specific sensitivities listed by Bartmess and Georgiadis [8].

The kinetics of the reactions were followed by taking mass spectra at variable reaction times and constructing therefrom kinetic plots showing the time dependence of the relative intensity of the ionized reactant and products by using the Origin program [9]. With the exception of the reaction of **1** with methanol, which exhibits bimodal kinetics, excellent first-order kinetics were observed. The first-order rate constants k_{exp} of the reactions were obtained from the kinetic plots by curve fitting using the Origin program and were converted into the bimolecular rate constants k_{bi} by taking into account the number density of the neutral reactant. The reproducibility of k_{exp} (s^{-1}) and k_{bi} ($cm^3\,s^{-1}\,molecule^{-1}$), respectively, is excellent, and the main source of the error of k_{bi} of 30% is the determination of the pressure within the ICR cell. The rate constant of collision k_{coll} was calculated according to Su and Bowers [10].

2.3. Theoretical calculations

The MERPs of the reactions of the radical cation of **1** with methanol were modeled by calculating the energy of the relevant species at the minima and maxima of the energy hypersurface using the Gaussian 98 program [11]. Both unrestricted Hartree–Fock (UHF) methods and density functional theory (DFT) with the hybrid method B3LYP have been used. It is known that UHF methods may not give reliable results in the case of radicals and radical ions, in particular in the case of halogen containing species, unless a very high level of theory is used. This is out of reach for the present work with quite large molecules and ions. In a recent review Radom and coworkers have shown [12] that a DFT-calculation of the relative energies of radicals and radical ions using geometry optimization at the B3LYP/6-31G(d) level of theory and further refinement by single point calculation at a higher level of theory reproduces experimental values very well. Consequently, B3LYP/6-31G(d) has been used for geometry optimization followed by a single point calculation of the electronic energy E_{el} by B3LYP/6-311+G(3df,2p). All stationary points were characterized by calculation of the frequencies at B3LYP/6-31G(d) to exhibit either no imaginary frequency (minima) for stable species and one imaginary frequency (maxima) for transition states (if not stated otherwise). The zero-point energy (ZPE) correction was taken from the B3LYP/6-31G(d) frequency calculation which was used without scaling to obtain the zero-point energy E_0 from B3LYP/6-311+G(3df,2p). Spin contamination was not a problem, since the values of $\langle S^2\rangle$ were always below 0.770 and mostly close to the theoretical value 0.750.

3. Results and discussion

3.1. Mass spectrometry

For comparison the bimolecular rate constants k_{bi} of the reactions of the dihalogenoethene radical cations $\mathbf{1}^{\bullet+}$– $\mathbf{4}^{\bullet+}$ with methanol and ethanol are shown in Table 1. The reactions of the 1,1- and 1,2-dichloroethene radical cations $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ with ethanol occur by hydride abstraction with high reaction efficiencies of 41 and 22%, respectively, as expected for exothermic reactions. The stereoisomers *cis*-$\mathbf{2}^{\bullet+}$ and *trans*-$\mathbf{2}^{\bullet+}$ exhibit identical reactivities and the increased reaction efficiency for the reaction of $\mathbf{1}^{\bullet+}$ can be attributed to the somewhat larger exothermicity owing to the decreased stability of the isomer $\mathbf{1}^{\bullet+}$.

The 1,1-dibromoethene radical cation $\mathbf{3}^{\bullet+}$ reacts with ethanol also exclusively by hydride abstraction with 40% efficiency while the 1,2-dibromoethene radical cation $\mathbf{4}^{\bullet+}$ gives mainly substitution and formation of an O-protonated bromovinyl ethyl ether CH_3OH^+–C_2H_2Br. However, the efficiency of this reaction is only 4% indicating a moderately endothermic process, evidently because of the increased stability of the 1,2-isomer $\mathbf{4}^{\bullet+}$. In none of these reactions bimodal kinetics are observed but instead excellent agreement with pseudo-first-order kinetics. Changing the neutral reagent into methanol considerably reduces the reaction efficiencies of the reactions of all dihalogeno-ethene radical cations $\mathbf{1}^{\bullet+}$– $\mathbf{4}^{\bullet+}$. The more stable 1,2-substituted isomers $\mathbf{2}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$ do not react at all with methanol. Obviously, all of the four reaction pathways correspond either to strongly endothermic processes or are blocked by considerable critical barriers. The less stable 1,1-disubstituted isomers $\mathbf{1}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$ react slowly with methanol exhibiting efficiencies of only 8 and 6%, respectively. The kinetic plots of these two reactions are shown in Figs. 1 and 2.

Table 1
Bimolecular rate constants k_{bi} and efficiencies eff of the reactions of dihalogenoethene radical cations $\mathbf{1}^{\bullet+}$–$\mathbf{4}^{\bullet+}$ with methanol or ethanol

Ion	Neutral reactant			
	Methanol		Ethanol	
	k_{bi} ($\times 10^{-10}$ cm^3 s^{-1} molecule^{-1})	Eff (%)	k_{bi} ($\times 10^{-10}$ cm^3 s^{-1} molecule^{-1})	Eff (%)
1,1-Dichloroethene $\mathbf{1}^{\bullet+}$	1.5	8	7.2	41
1,2-Dichloroethene $\mathbf{2}^{\bullet+}$	No reaction	–	3.8	22
1,1-Dibromoethene $\mathbf{3}^{\bullet+}$	1.0	6	6.5	40
1,2-Dibromoethene $\mathbf{4}^{\bullet+}$	No reaction	–	0.7	4

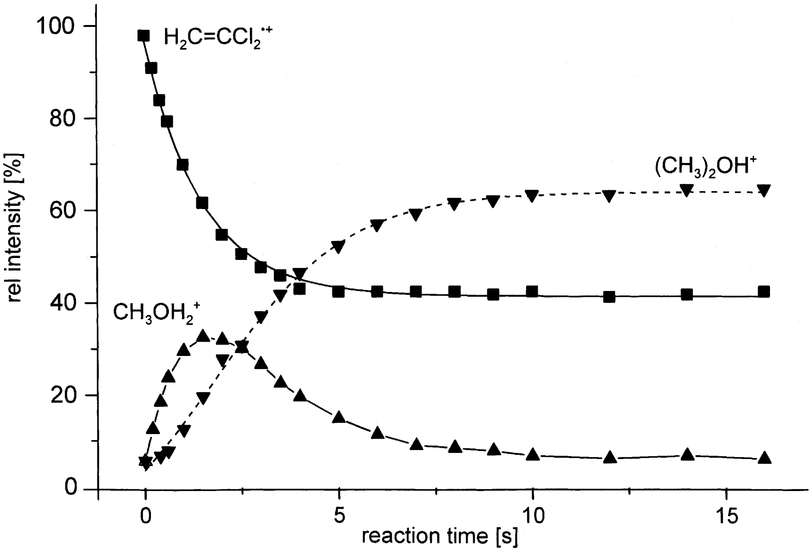


Fig. 1. Kinetic plot of the reaction of 1,1-dichloroethene radical cations **1**$^{\bullet+}$ and methanol.

The main reaction of the dibromo derivative **3**$^{\bullet+}$ is substitution of one bromine atom to yield O-protonated bromovinyl methyl ether, *m*/*z* 137, but formation of protonated methanol, *m*/*z* 33, followed by condensation to protonated dimethyl ether, *m*/*z* 47, is also abundant. It is a priori not obvious from the kinetic plot that protonated methanol is already a secondary product generated by proton transfer from protonated formaldehyde which is the true primary product generated by hydride abstraction. This can

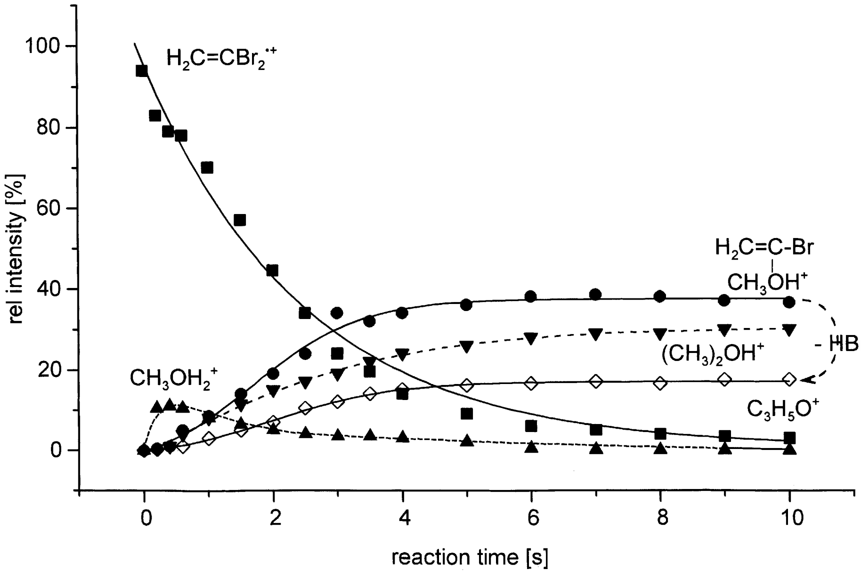


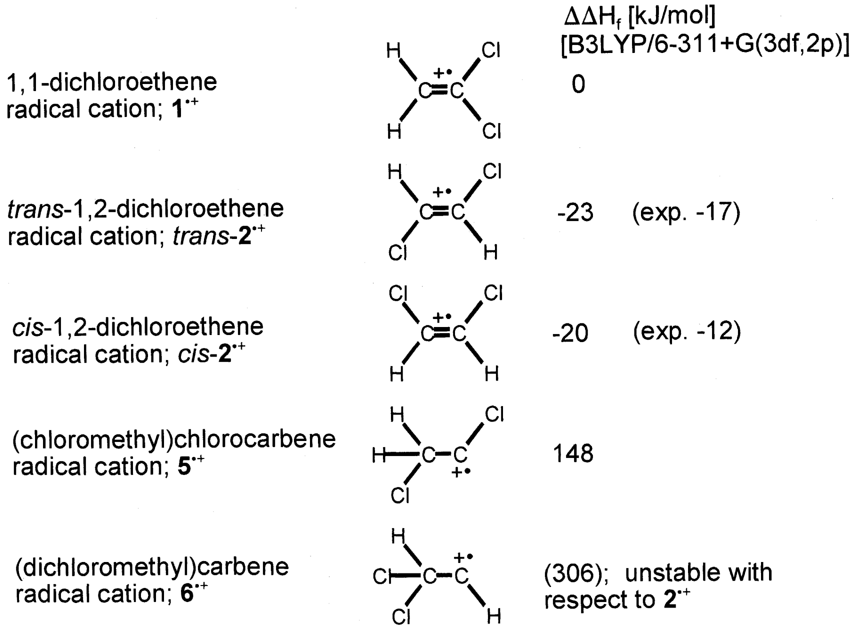
Fig. 2. Kinetic plot of the reaction of 1,1-dibromoethene radical cations **1**$^{\bullet+}$ and methanol.

be proven by separate experiments, although the relative intensity of protonated formaldehyde remains always below 1.5% because its is formed by a slow endothermic process and transfers a proton quickly to methanol which is present in large excess in the gas phase of the ICR cell. The only observable reaction of the dichloro derivative $\mathbf{1}^{\bullet+}$ is formation of protonated methanol, *m*/*z* 33 and of its condensation product protonated dimethyl ether, *m*/*z* 47. In particular, a substitution of a chlorine atom of $\mathbf{1}^{\bullet+}$ by CH_3OH is not observed. Also in this reaction system a specific search for protonated formaldehyde shows that this is the true primary product generated by hydride abstraction. The special feature of the reaction of $\mathbf{1}^{\bullet+}$ with methanol is the observation of bimodal kinetics, and the reactions stops at 60–75% conversion. Thus, the $C_2H_2Cl_2{}^{\bullet+}$ ions generated in the external ion source by electron impact ionization of **1** display in the ICR cell the kinetic behavior of a mixture of isomers which are reactive and unreactive, respectively, towards methanol.

It is possible that a mixture of isomers is generated from **1** by the electron impact ionization with 30 eV electrons. To test this possibility radical cations $\mathbf{1}^{\bullet+}$ of 1,1-dichloroethene were produced by impact with electrons of different energy and by charge exchange with primary ions of Ar (IE = 15.7 eV [13]) and of CO_2 (IE = 12.2 eV [13]) and reacted with methanol. The results are shown in Table 2. In all cases a significant amount of unreactive $C_2H_2Cl_2{}^{\bullet+}$ ions was observed which varied between 25 and 37%. The $C_2H_2Cl_2{}^{\bullet+}$ ions generated by charge exchange from **1** appear to contain a lesser amount of unreactive ions. However, the experimental conditions using electron impact ionization and chemical ionization with charge exchange have a different delay time between the transfer of the ions into the ICR cell and the starting point the kinetic experiment. Hence, this systematic effect on the composition of the mixture of $C_2H_2Cl_2{}^{\bullet+}$ ions is likely instrumental. Further, all other reactions of $\mathbf{1}^{\bullet+}$ with various nucleophiles do not display bimodal behavior. Therefore, the unreactive isomer present in the mixture of $C_2H_2Cl_2{}^{\bullet+}$ ions derived from **1** is very likely generated after the ionization event by reaction of $\mathbf{1}^{\bullet+}$ with methanol. The reactive fraction of the $C_2H_2Cl_2{}^{\bullet+}$ ions corresponds clearly to 1,1-dichloroethene radical cations $\mathbf{1}^{\bullet+}$. The analogous dibromo substituted ions $\mathbf{3}^{\bullet+}$ exhibit a similar reactivity towards methanol, and both $\mathbf{1}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$ undergo a slow hydride abstraction from this substrate. In fact, the reactions of $\mathbf{1}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$ with methanol differ mainly in that the former ion shows isomerization whereas the latter undergoes substitution of one bromine atom besides hydride abstraction. A priori the structure of the unreactive isomer of $\mathbf{1}^{\bullet+}$ not known. The 1,2-dichloroethene radical cation $\mathbf{2}^{\bullet+}$ is an obvious candidate since $\mathbf{2}^{\bullet+}$ is more stable than $\mathbf{1}^{\bullet+}$ and has been shown not to react with methanol [3d]. However, other possible structures of $C_2H_2Cl_2$ besides **1** and **2** are the chloromethyl chlorocarbene (**5**) and the dichlormethyl carbene (**6**) (Scheme 2). Of these two carbenic structures the chlorocarbene radical cation $\mathbf{5}^{\bullet+}$ should be the more stable one because of a stabilization of the carbene center by π-back donation from the electron lone pairs of the chlorine substituent, but both carbene radical cations are certainly less stable

Table 2
Effect of ionization method on the reaction of 1,1-dichloroethene radical cation $\mathbf{1}^{\bullet+}$ with methanol

Ionization	k_{bi} ($\times 10^{-10}$ cm^3 s^{-1} molecule^{-1})	Eff (%)	% of ions $C_2H_2Cl_2{}^{\bullet+}$	
			Unreactive	Reactive
IE = 50 eV	1.4	8	37	63
IE = 28 eV	1.5	8	39	61
IE = 18 eV	1.5	8	37	63
CE(Ar)	1.6	8	25	75
CE(CO_2)	1.7	8	29	71



Scheme 2.

than the isomeric ethene ions. This has been confirmed by ab initio calculation, and the calculated ΔE_0 of the radical cations relative to $\mathbf{1}^{\bullet+}$ are included in Scheme 2 together with the experimental values for the relative heats of formation of $\mathbf{1}^{\bullet+}$ and the stereoisomers of $\mathbf{2}^{\bullet+}$ [13]. The experimental differences in the stability of the isomers are reasonably reproduced by B3LYP/6-311+(3df,2p)//B3LYP/6-31G(d) chosen for the calculation. However, $\mathbf{6}^{\bullet+}$ is found to be unstable by calculation at any level of molecular orbital theory and is transformed into $\mathbf{1}^{\bullet+}$ or $\mathbf{2}^{\bullet+}$ during geometry optimization. The ΔE_0 value of 306 kJ mol^{-1} shown in Scheme 2 was obtained by "freezing" the angles of the dichloromethyl group at the AM1 geometry to prevent a rearrangement. The chloro-carbene radical cation $\mathbf{5}^{\bullet+}$ is a minimum on the energy hypersurface at $\Delta E_0 = 148$ kJ mol^{-1}, but is only separated from the global minimum (represented by $\mathbf{2}^{\bullet+}$) by a small critical barrier of ≈10 kJ mol^{-1}. From these data it is very unlikely that $\mathbf{5}^{\bullet+}$ or $\mathbf{6}^{\bullet+}$ corresponds to the unreactive isomer formed during the reaction of $\mathbf{1}^{\bullet+}$ with methanol. Rather, the calculated relative energies of isomers of $C_2H_2Cl_2{}^{\bullet+}$ radical cations substantiate the assumption that the unreactive isomer is the 1,2-dichloroethene radical cation $\mathbf{2}^{\bullet+}$.

To obtain experimental evidence for the generation of $\mathbf{2}^{\bullet+}$ during the reaction of $\mathbf{1}^{\bullet+}$ with methanol we have made use of the different reactions of $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ with ammonia [3d]. First, $\mathbf{2}^{\bullet+}$ reacts with ammonia by substitution of only one halogen giving rise to the substitution product H_3N^+–HC=CHCl, *m*/*z* 78, while the 1,1-dihalogenoethene radical cation $1^{\bullet+}$ $Cl_2C{=}CH_2{}^{\bullet+}$ undergoes sequential substitution of both halogens in a series of reactions and generates eventually the proton bound dimers $[CH_3CN\cdots H^+\cdots NH_3]$, *m*/*z* 59, and $[H_3N\cdots H^+\cdots NH_3]$, *m*/*z* 35 [3d]. The efficiency of the reaction of $\mathbf{1}^{\bullet+}$ with methanol is much smaller than that of the reaction with ammonia, and the rate of the reaction with methanol can be further reduced by using a low partial pressure of methanol in the ICR cell. Then, by introducing ammonia into the ICR as a pressure pulse by a pulsed magnetic valve it is possible to quench the reaction with methanol and to identify the remaining $C_2H_2Cl_2{}^{\bullet+}$ by their reaction products with ammonia. The sequence of pulses used for this experiment and mass spectra obtained at an early and at an late stage of the reaction of $\mathbf{1}^{\bullet+}$ with methanol are shown in Fig. 3.

A partial pressure of 2×10^{-7} mbar was used in this experiment, and following the isolation of surviving $C_2H_2Cl_2{}^{\bullet+}$ ions after a variable reaction time, ammonia was introduced by three subsequent pressure pulses of 4 ms duration and allowed to react with the $C_2H_2Cl_2{}^{\bullet+}$ ions for 1.5 s. Separate experiments had shown that this reaction time is sufficient to remove all surviving $C_2H_2Cl_2{}^{\bullet+}$ ions form the ICR cell. This cycle of measurement was repeated for several times, using a adequately long pumping time between each cycle to get rid of the ammonia introduced during the previous cycle. All mass spectra obtained in this way at the early stages of the reaction of $\mathbf{1}^{\bullet+}$ with methanol contain signals of $[CH_3CN\cdots H^+\cdots NH_3]$, *m*/*z* 59, and $[H_3N\cdots H^+\cdots NH_3]$, *m*/*z* 35, as the characteristic reaction products of $\mathbf{1}^{\bullet+}$ with ammonia besides a peak of the $C_2H_5NCl^+$ ion, *m*/*z* 78. However, we could not find experimental conditions which resulted in a complete consumption of the ion *m*/*z* 78. In the mass spectra taken at the end of the reaction of $\mathbf{1}^{\bullet+}$ with methanol the signals of the proton bound dimers are absent and the only relevant peak observed corresponds to the $C_2H_5NCl^+$ ion, *m*/*z* 78, which is the final reaction product of $\mathbf{2}^{\bullet+}$ with ammonia. Thus, the outcome of these experiments clearly proves that the 1,1-dichloroethene radical cation $\mathbf{1}^{\bullet+}$ is absent when the reaction with methanol stops and agrees with the assumption that the 1,2-dichloroethene radical cation $\mathbf{2}^{\bullet+}$ is the product of the isomerization, but we cannot exclude completely the presence of $\mathbf{2}^{\bullet+}$ already at the beginning of the reaction. This is, however, unlikely regarding the experiments varying the ionization conditions, so that the whole set of the experiments give convincing evidence for an isomerization of 1,1-dichloroethene radical cations $\mathbf{1}^{\bullet+}$ into 1,2-dichloroethene radical cations $\mathbf{2}^{\bullet+}$ catalyzed by methanol.

The isomerization $\mathbf{1}^{\bullet+} \rightarrow \mathbf{2}^{\bullet+}$ corresponds formally to a reciprocal 1,2-shift of a H atom and a Cl atom. A possible mechanism for this rearrangement under the action of a methanol molecule could involve proton or hydrogen atom transfer between $\mathbf{1}^{\bullet+}$ and methanol in a long lived collision complex, in analogy to other catalyzed isomerizations [5]. To test this possibility $\mathbf{1}^{\bullet+}$ was reacted with CD_3OH and CD_3OD. The kinetic plot of the reaction system $\mathbf{1}^{\bullet+}/CD_3OH$ is shown in Fig. 4. Some H/D exchange between $\mathbf{1}^{\bullet+}$ and CD_3OH is observed which produces mono- and dideuterated $\mathbf{1}^{\bullet+}$, but these ions disappear at longer reaction time. No H/D-exchange is observed for the unreactive $C_2H_2Cl_2{}^{\bullet+}$ ions. The same result is obtained for the reaction of $1^{\bullet+}$ with CD_3OD, but the main primary reaction product is again $CD_3OH_2{}^+$ indicating that the mobile D atom of the hydroxyl group of CD_3OD was mostly exchanged by H in the FT-ICR instrument before the reaction. In any case a D incorporation into the unreactive $C_2H_2Cl_2{}^{\bullet+}$ ions was not observed in both experiments showing that the isomerization $\mathbf{1}^{\bullet+} \rightarrow \mathbf{2}^{\bullet+}$ catalyzed by methanol takes place without H/D-transfer between the reactants. Summarizing the experimental results it is shown that the 1,1-dichloroethene radical cation $\mathbf{1}^{\bullet+}$ isomerizes in the gas phase by reaction with methanol into the 1,2-dichloroethene radical cation $\mathbf{2}^{\bullet+}$ by a slow process competing with a formal hydride abstraction of $\mathbf{1}^{\bullet+}$ from methanol. This isomerization is specific for the reaction system $\mathbf{1}^{\bullet+}$/methanol and is neither observed in the reaction of $\mathbf{1}^{\bullet+}$ with other alcohols or with ammonia nor in the reactions of the 1,1-dibromoethene radical cation $\mathbf{3}^{\bullet+}$. Finally, the methanol catalyzes this isomerization as a “spectator” molecule and no hydrogen exchange between the reactants or any other modification of the methanol is detected.

3.2. Theoretical calculations

To understand the mechanism of the isomerization $\mathbf{1}^{\bullet+} \rightarrow \mathbf{2}^{\bullet+}$ catalyzed by methanol the potential energy hypersurface of the reaction system $\mathbf{1}^{\bullet+}$ was explored by ab initio calculations. The results for the relevant species are compiled in Table 3 and some of the structures are displayed in Scheme 3. As a first step the reaction energies ΔE_{r0} of the different reaction pathways usually found for the reaction of alkene radical cations with nucleophiles besides

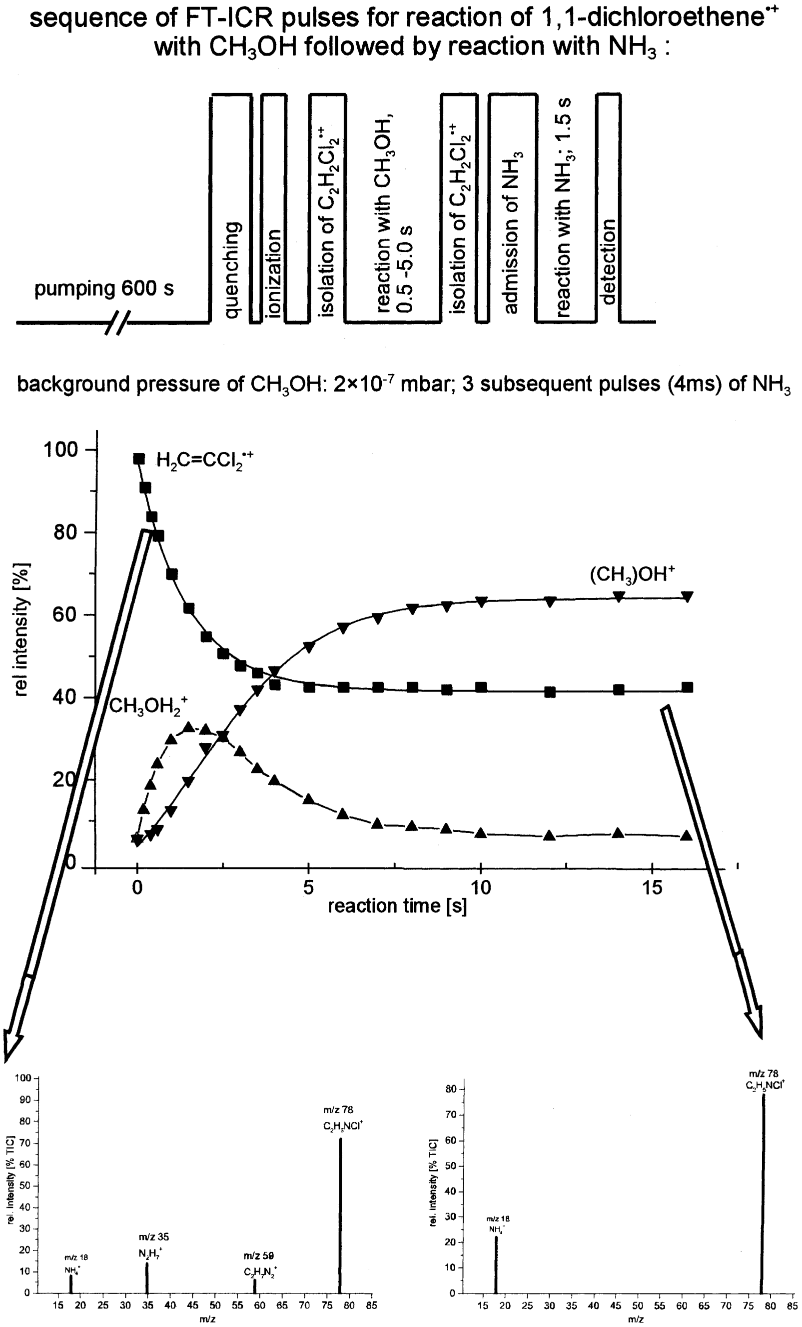


Fig. 3. Experiment of consecutive reactions of 1,1-dichloroethene radical cations $\mathbf{1}^{\bullet+}$ with CH_3OH and NH_3 (see text).

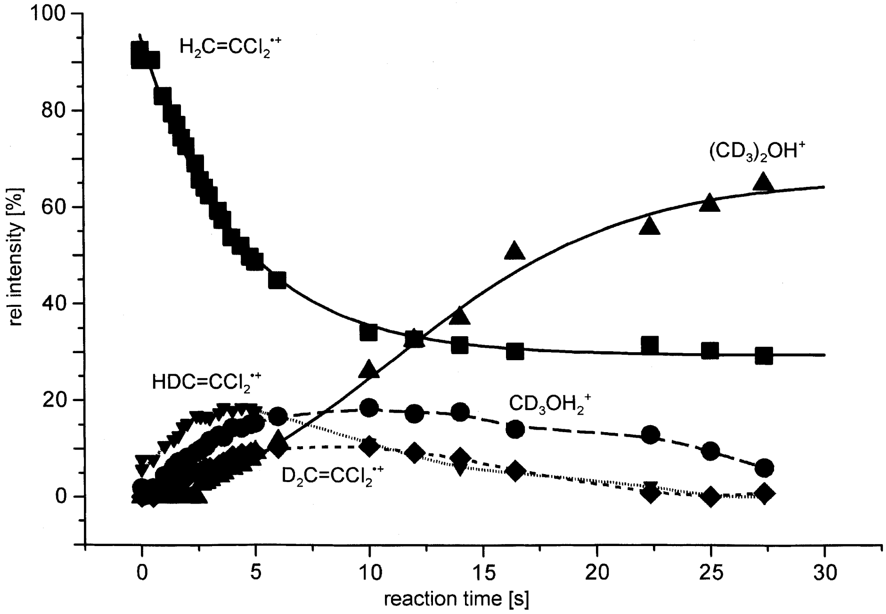
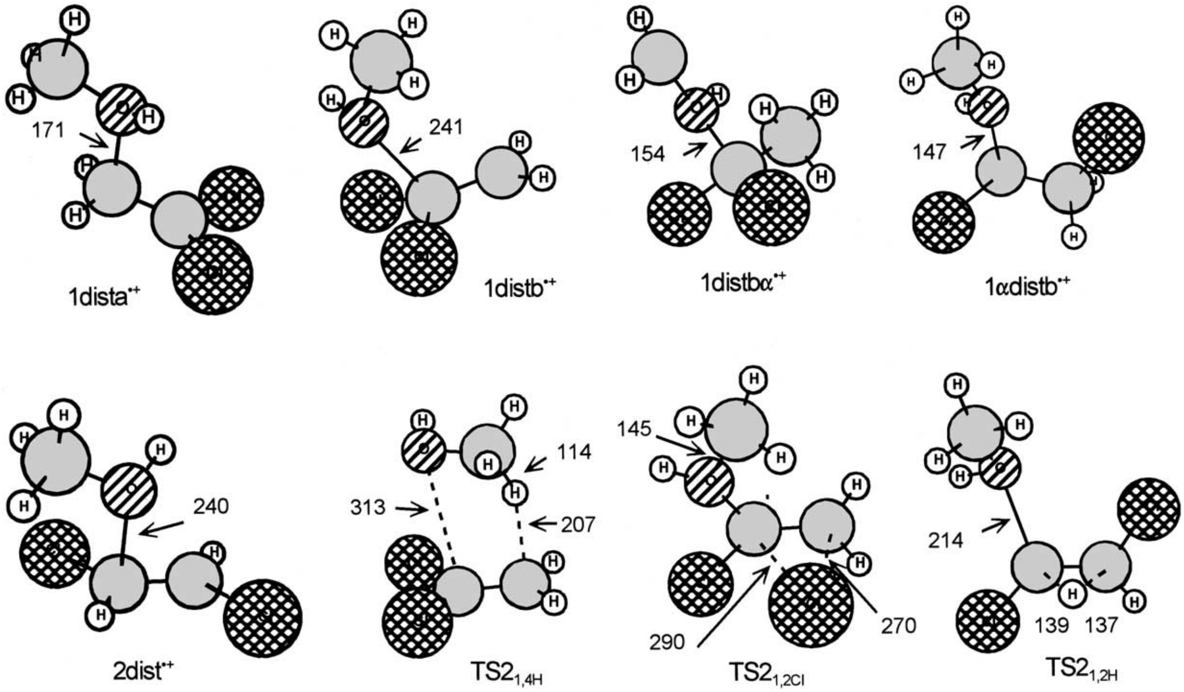


Fig. 4. Kinetic plot of the reaction of 1,1-dichloroethene radical cations **1**$^{\bullet+}$ and CD_3OH.

Table 3
Electronic energy E_{el} and zero-point energy E_0 of relevant species of the reaction of dichloroethenes **1**$^{\bullet+}$ and **2**$^{\bullet+}$ with methanol by ab initio calculation

Species	B3LYP/6-31G(d)		B3LYP/6-311+G(3df,2p)
	E_{el} (hartree)	ZPE (hartree)	E_{el} (hartree)
1$^{\bullet+}$ $CH_2{=}CCl_2^{\bullet+}$	−997.427553	0.033077	−997.522794
1 $CH_2{=}CCl_2$	−997.775291	0.033730	−997.873606
trans-**2**$^{\bullet+}$ CHCl=CHCl	−997.437737	0.033977	−997.532539
cis-**2**$^{\bullet+}$ CHCl=CHCl	−997.436436	0.034169	−997.531325
CH_3OH	−115.714440	0.051476	−115.772615
$CH_3OH^{\bullet+}$	−115.329192	0.046867	−115.377221
$CH_3OH_2^+$	−116.015744	0.064390	−116.070159
2,2-$C_2HCl_2^\bullet$	−997.086228	0.020070	−997.183487
1,2-$C_2HCl_2^\bullet$	−997.094129	0.021926	−997.191301
1,1-$C_2H_2Cl_2^\bullet$	−998.357554	0.044273	−998.454492
2,2-$C_2H_2Cl_2^\bullet$	−998.343809	0.042853	−998.440067
1,2-$C_2H_2Cl_2^\bullet$	−998.355795	0.044451	−998.452080
$CH_2{=}OH^+$	−114.782500	0.040669	−114.830956
CH_3OH^+–CCl=CH_2	−653.000234	0.088039	−653.109062
CH_3OH^+–CH=CHCl	−652.997129	0.088111	−653.106223
$Cl^\bullet$	−460.136242	–	−460.168403
5$^{\bullet+}$ CH_2Cl–$CCl^{\bullet+}$	−997.370208	0.032937	−997.466468
6$^{\bullet+}$ $CHCl_2$–$CH^{\bullet+}$	−997.306700	0.028869	−997.401515



Scheme 3.

isomerization were determined using different levels of theory. These pathways can be electron transfer, proton transfer, substitution, and hydride abstraction [3]. The corresponding reaction energies ΔE_{r0} derived from the data of Table 3 are shown in Table 4 and for comparison are included in Scheme 4 together with values obtained by UHF/6-31G(d) calculation.

Using UHF/6-31G(d), substitution as well as hydride transfer is calculated to be exothermic for the reaction of $\mathbf{1}^{\bullet+}$ and of $\mathbf{2}^{\bullet+}$. Further, in the case of $\mathbf{1}^{\bullet+}$ substitution is found to be even more exothermic than the isomerization $\mathbf{1}^{\bullet+} \rightarrow \mathbf{2}^{\bullet+}$. However, experimentally substitution is not observed in both cases, although this pathway is known to exhibit no extra critical barrier besides the reaction energy and should effectively compete with other pathways if it is exothermic. This shows that UHF/6-31G(d) is not reliable in the present case. More correct results are obtained by a calculation using B3LYP/6-31G(d) and B3LYP/6-311+G(3df,2p). At these levels of theory all reaction pathways of $\mathbf{2}^{\bullet+}$ with methanol are calculated to be endothermic by at least 34 kJ mol^{-1} (B3LYP/6-31G(d)) or 57 kJ mol^{-1} (B3LYP/6-311+G(3df,2p)), in agreement with the absence of any reaction of $\mathbf{2}^{\bullet+}$ with methanol. For the reactions of $\mathbf{1}^{\bullet+}$ the isomerization $\mathbf{1}^{\bullet+} \rightarrow \mathbf{2}^{\bullet+}$ is distinctly exothermic by 23 kJ mol^{-1} (B3LYP/6-31G(d) and B3LYP/6-311+G(3df,2p)) while hydride abstraction yielding protonated formaldehyde and the 1,1-dichloroethyl radical is only moderately endothermic (6 kJ mol^{-1} (B3LYP/6-31G(d)) or 27 kJ mol^{-1} (B3LYP/6-311+G(3df,2p))), again in agreement with the observation of a slow reaction of $\mathbf{1}^{\bullet+}$ along this pathway. Further, the calculated value for ΔE_{r0} for electron transfer of 106 kJ mol^{-1} agrees reasonably with the experimental value of 99 kJ mol^{-1} [13]. Therefore, B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) has been used to calculate the stationary points along the MERPs of substitution, of hydride abstraction, and of isomerization. These results are

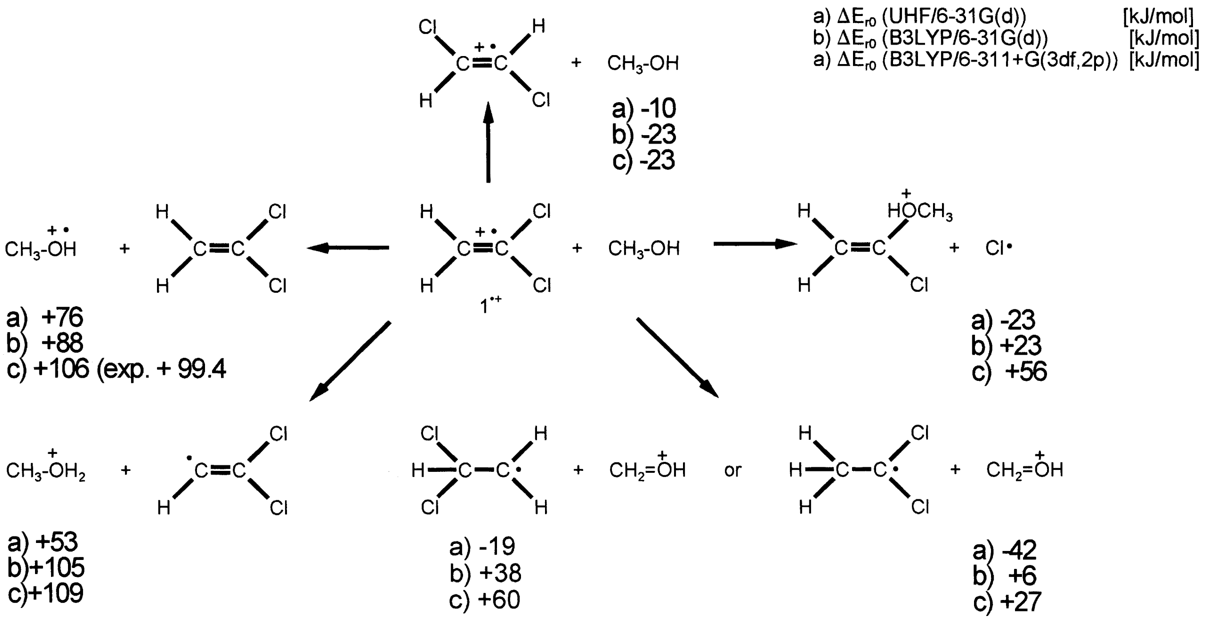
Table 4
Zero-point energy E_0 at stationary point along the reaction pathways and reaction energy ΔE_{r0} of $\mathbf{1}^{\bullet+}$ with methanol

Stationary point	B3LYP/6-31G(d), E_0 (hartree)	ΔE_0 (kJ mol^{-1})	B3LYP/6-311+G(3df,2p), E_{el} (hartree)[a]	ΔE_0[b] (kJ mol^{-1})
$\mathbf{2}^{\bullet+}$ + CH_3OH	−1113.066325	**0**	−1113.219701	**0**
2dist$^{\bullet+}$	−1113.092388	−68	−1113.236478	−73
$CH_3OH_2^+$ + 1,2-$C_2HCl_2^\bullet$	−1113.024458	110	−1113.176045	115
CH_3OH^+–CH=CHCl + $Cl^\bullet$	−1113.045261	53	−1113.186515	87
$CH_2{=}OH^+$ + 1,2-$C_2H_2Cl_2^\bullet$	−1113.053175	35	−1113.197916	57
$\mathbf{1}^{\bullet+}$ + CH_3OH	−1113.057405	**0**	−1113.210856	**0**
1 + $CH_3OH^{\bullet+}$	−1113.023885	88	−1113.170230	107
$CH_3OH_2^+$ + 2,2-$C_2HCl_2^\bullet$	−1113.017513	105	−1113.169186	109
CH_3OH^+–CCl=CH_2 + $Cl^\bullet$	−1113.048437	24	−1113.189426	56
$CH_2{=}OH^+$ + 1,1-$C_2H_2Cl_2^\bullet$	−1113.055112	6	−1113.200506	27
$CH_2{=}OH^+$ + 2,2-$C_2H_2Cl_2^\bullet$	−1113.053175	11	−1113.188104	60
$\mathbf{1}^{\bullet+} \rightarrow \mathbf{2}^{\bullet+}$	–	−23	–	−23
1dista$^{\bullet+}$	−1113.309203	−91	−1113.234776	−63
$TS1_{1,4\text{-}H}$	−1113.035094	59	−1113.178453	85
1dista$\alpha^{\bullet+}$	−1113.061453	−11	−1113.204783	16
$TS1_{1,2\text{-}H}$	−1113.000337	150	−1113.146352	169
1αdista$^{\bullet+}$	−1113.066089	−23	−1113.209279	4
$TS1_{1,2\text{-}Cl}$	−1113.021908	93	−1113.167358	114
1distb$^{\bullet+}$[c]	−1113.081349	−63	−1113.218858	−21
$TS2_{1,4\text{-}H}$	−1113.079106	−57	−1113.227107	−43
1distb$\alpha^{\bullet+}$	−1113.093586	−95	−1113.239142	−74
$TS2_{1,2\text{-}Cl}$	−1113.049962	20	−1113.191465	50
1αdistb$^{\bullet+}$	−1113.072306	−39	−1113.243790	−9
$TS2_{1,2\text{-}H}$	−1113.006437	134	−1113.154803	147
$\mathbf{5}^{\bullet+}$ + CH_3OH	−1113.001101	148	−1113.155570	145
$[CH_3OH_2^+;\ 1,2\text{-}C_2HCl_2^\bullet]_{compl}$	−1113.038385	50	−1113.186142	31

[a] ZPE from B3LYP/6-31G(d).
[b] Relative to reactants.
[c] Geometry not fully optimized, see text.

included in Table 4. In the following discussion only values calculated by this level of theory will be used, if not stated otherwise.

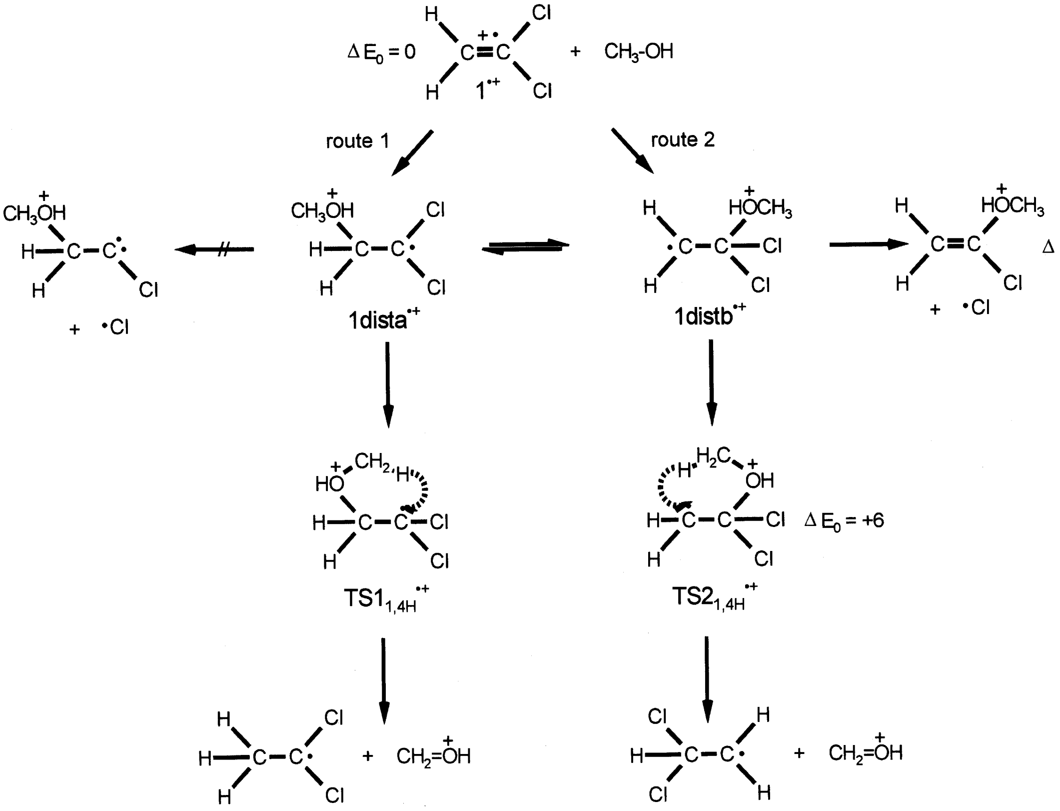
First, substitution and hydride abstraction are examined as the typical reaction pathways. The initial step of a reaction of $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ with methanol is the addition of the nucleophile methanol to the ionized C=C double bond (Scheme 5 and Fig. 5). As has been shown for other reactions of this type [3], the addition is quite exothermic and proceeds without a critical barrier. The symmetrically substituted 1,2-dichloroethene radical cation $\mathbf{2}^{\bullet+}$ forms only one β-distonic addition product **2**dist$^{\bullet+}$ by addition at either end of the double bond, and the addition is exothermic by 56 kJ mol^{-1}. However, since all reaction channels besides back dissociation into reactants are distinctly endothermic, no reaction is observed. The unsymmetrically substituted 1,1-dichloroethene radical cation $\mathbf{1}^{\bullet+}$ generates two different β-distonic ions **1**dista$^{\bullet+}$ and **1**distb$^{\bullet+}$ (Scheme 5) by addition of methanol to the C=C double bond. Of these two species **1**dista$^{\bullet+}$, which is formed in analogy to the Markovnikov rule by addition to the less substituted C atom of the double bond, is more stable with $\Delta E_0 = -63$ kJ mol^{-1}. The β-distonic ion **1**distb$^{\bullet+}$ arising by a “anti-Markovnikov” mode of addition, turns out to be not a minimum on the ab initio hypersurface at any level of theory, but is transformed into **1**dista$^{\bullet+}$during geometry optimization. An ab initio calculation keeping the AM1-optimized angle C_{methyl}–O–C frozen to prevent isomerization locates this species at $\Delta E_0 = -21$ kJ mol^{-1}. Nonetheless, **1**distb$^{\bullet+}$ has to be a



Scheme 4.

transient structure of the MERP for substitution and hydride abstraction. The structure of **1**dista$^{\bullet+}$ is not appropriate for the direct loss of a Cl atom, because both Cl atoms are situated at the radical site, while within **1**distb$^{\bullet+}$ a simple β-C–Cl bond cleavage is possible to complete the substitution process. Substitution is calculated to be significantly endothermic by $\Delta E_{\mathrm{r}0} = 56\,\mathrm{kJ\,mol^{-1}}$, however. Since substitution is not observed experimentally, this $\Delta E_{\mathrm{r}0}$ sets the “limiting energy level”, and exit channels and critical energies of all actually observed reaction pathways have to be positioned below this limit.

The hydride abstraction includes a 1,4-hydrogen shift within the β-distonic onium ions **1**dista$^{\bullet+}$ or **1**distb$^{\bullet+}$ from the O-methyl group to the radical site which gives rise to α-distonic onium ions **1**distaα$^{\bullet+}$ or **1**distbα$^{\bullet+}$ and eventually by dissociation to protonated formaldehyde and a dichloroethyl radical (Scheme 5 and Fig. 5) [3f]. On route 1 starting with **1**dista$^{\bullet+}$, the critical energy of the 1,4-H shift is rather large and the transition state TS$1_{1,4\text{-H}}$ as well as the exit channel is located above the energy limit of $\Delta E_0 = 56\,\mathrm{kJ\,mol^{-1}}$. Consequently, route 1 of the hydride abstraction process does not occur. One reason for this result is the formation of the energetically unfavorable 2,2-dichloroethyl radical. On route 2, the transient structure **1**distb$^{\bullet+}$ is the intermediate and the more stable 1,1-dichloroethyl radical is produced. As a consequence the reaction energy $\Delta E_{\mathrm{r}0}$ is only $27\,\mathrm{kJ\,mol^{-1}}$, well below the limiting energy level. A transition state TS$2_{1,4\text{-H}}$ for the 1,4-H shift from **1**distb$^{\bullet+}$ to the corresponding α-distonic onium ion is found at $\Delta E_{\mathrm{r}0} = -43\,\mathrm{kJ\,mol^{-1}}$. This is below ΔE_0 of **1**distb$^{\bullet+}$, but this is very likely not significant, since the geometry of **1**distb$^{\bullet+}$ is not fully optimized. The structure of the transition state TS$2_{1,4\text{-H}}$ displays a very long C–O bond and resembles actually an ion/neutral complex of $\mathbf{1}^{\bullet+}$ and methanol with a contact between one of the H atoms of the O-methyl group and the radical site at the unsubstituted C atom of **1** concurrently with a slight elongation of this C–H bond (see Scheme 3). Thus, it appears possible that TS$2_{1,4\text{-H}}$ can be realized directly from a collision complex of $\mathbf{1}^{\bullet+}$ and methanol. In any case, these results shows that hydride abstraction on route 2 is not obstructed by a large critical energy.



Scheme 5.

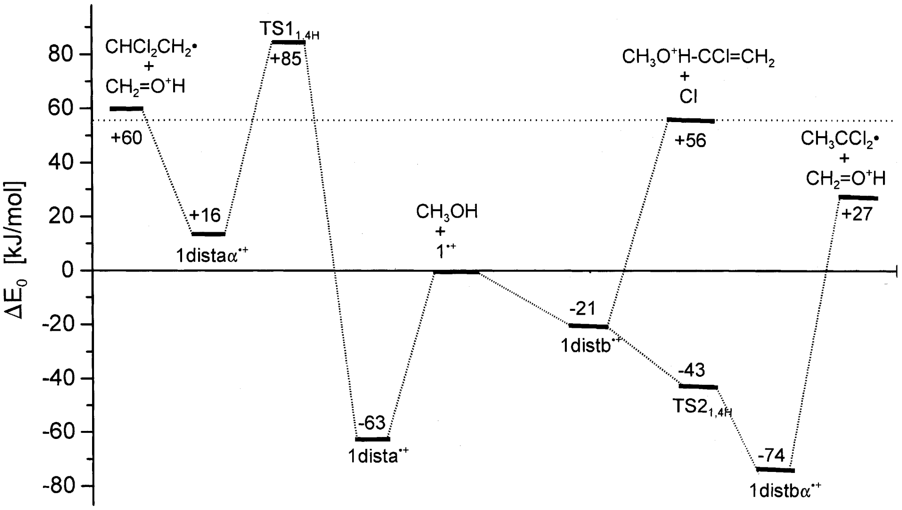
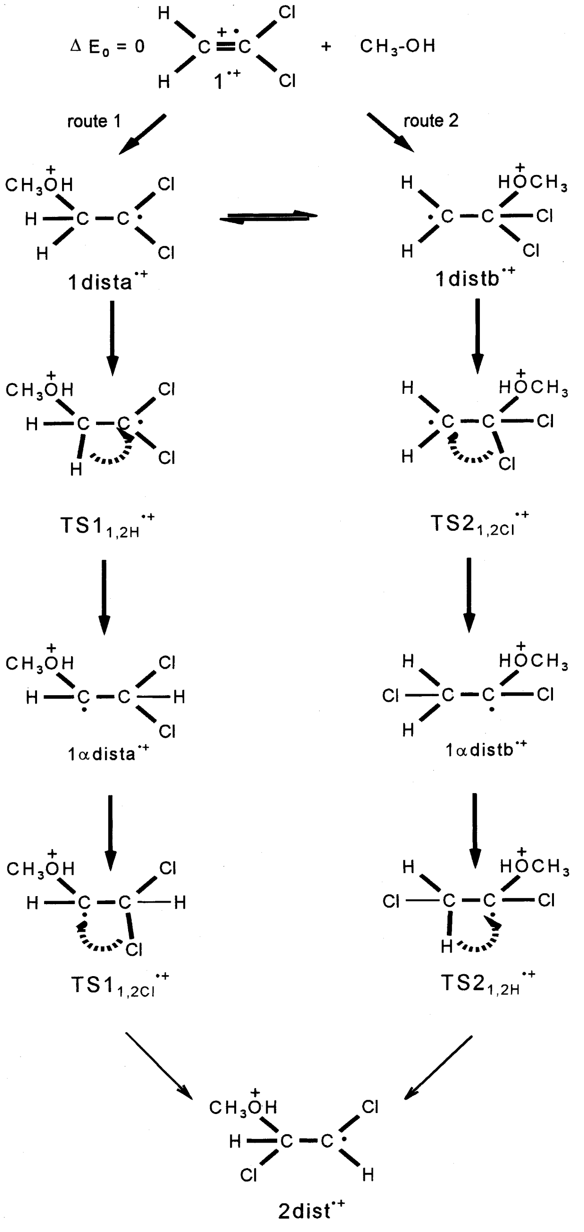


Fig. 5. MERP for substitution and hydride abstraction reaction of $\mathbf{1}^{\bullet +}$ and CH_3OH (values of ΔE_0 from B3LYP/6311+G(3df,2p (//B3LYP/6-31G(d)))).



Scheme 6.

Next, the mechanism of the isomerization $\mathbf{1}^{\bullet+} \rightarrow \mathbf{2}^{\bullet+}$ is explored by ab initio calculation (Scheme 6 and Fig. 6). Since isomerization requires the presence of a molecule of methanol, the rearrangements by a H-shift and a Cl-shift certainly takes place in the β-distonic addition products **1dista**$^{\bullet+}$ and **1distb**$^{\bullet+}$, but involve only the atoms of the dichloroethene part of these species. There are two routes to generate the β-distonic addition product **2dist**$^{\bullet+}$ of $\mathbf{2}^{\bullet+}$ and methanol and eventually, by subsequent dissociation, $\mathbf{2}^{\bullet+}$ and methanol. Route 1 starts from **1dista**$^{\bullet+}$, while route 2 uses **1distb**$^{\bullet+}$ as an intermediate. Starting on route 1 with **1dista**$^{\bullet+}$, the first step is a 1,2-H shift which gives rise to the α-distonic ion **1αdista**$^{\bullet+}$. This is followed by a 1,2-Cl-shift to generate **2dist**$^{\bullet+}$. On route 2 starting with **1distb**$^{\bullet+}$, the rearrangement steps are exchanged and the 1,2-Cl shift comes first forming the α-distonic ion **1αdistb**$^{\bullet+}$ which subsequently rearranges to **2dist**$^{\bullet+}$.

Hydrogen atom migrations in radical cations and distonic ions are ubiquitous in organic mass spectrometry, but 1,2-shifts usually require a large critical energy [14]. A “ring walk” of F and Cl atoms in the radical cations of halogenated arenes has been proposed [15], but to our knowledge a rearrangement of an aliphatic radical cation by migration of a chlorine atom in the gas phase has not been reported in the literature. In solution a fast rearrangement of β-chloro- and β-bromoalkyl radicals by a 1,2-halogen shift has been observed by ESR spectrometry [16], and even radicals bridged by Cl or Br have been suggested to explain the kinetics during radical halogenation of alkanes in solution [17]. Further, Squires and coworkers [18] and Kenttämaa and coworkers [19] have shown that distonic onium ions do exhibit radical reactivity in the gas phase. Therefore, 1,2-shifts of Cl atoms in appropriate distonic onium ions should be feasible. Concerning the distonic ions of route 1, the 1,2-Cl-shift within the α-distonic intermediate **1αdista**$^{\bullet+}$ (generated by the initial 1,2-H shift) requires a substantial critical energy of 110 kJ mol^{-1} which locates this transition state TS1$_{1,2\text{-Cl}}$ at $\Delta E_0 = 114$ kJ mol^{-1}, well above the energy limit of $\Delta E_0 = 56$ kJ mol^{-1} set by the substitution process. In addition, the preceding 1,2-H shift transforming **1dista**$^{\bullet+}$ into **1αdista**$^{\bullet+}$ requires a very large critical energy of 232 kJ mol^{-1}, and the corresponding transition state TS1$_{1,2\text{-H}}$ is located at $\Delta E_0 = 169$ kJ mol^{-1}. This makes route 1 inaccessible for the isomerization $\mathbf{1}^{\bullet+} \rightarrow \mathbf{2}^{\bullet+}$. On route 2, the

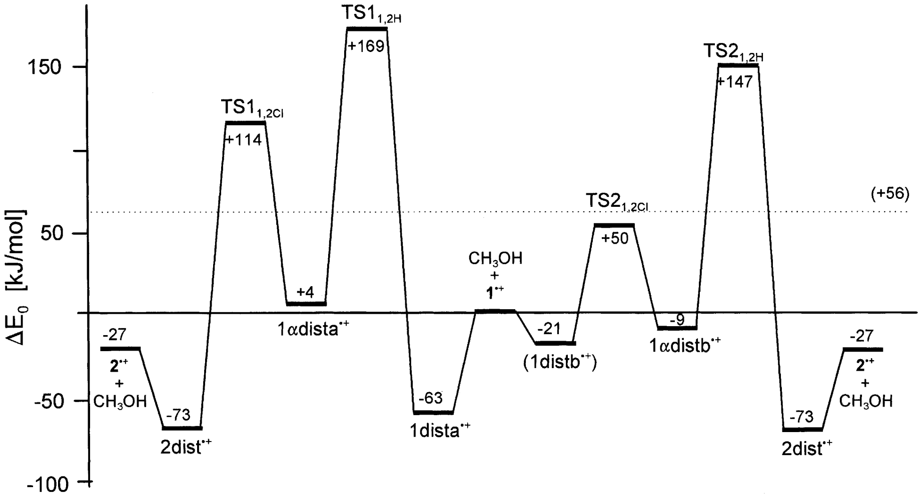


Fig. 6. MERP for isomerization reaction of $\mathbf{1}^{\bullet+}$ + CH_3OH → $\mathbf{2}^{\bullet+}$ + CH_3OH (values of ΔE_0 from B3LYP/6311+G(3df,2p (//B3LYP/6-31G(d))).

1,2-Cl shift occurs in the β-distonic ion **1**distb$^{\bullet+}$, and this requires a critical energy of only 71 kJ mol^{-1}, distinctly less than the Cl-shift in **1**αdista$^{\bullet+}$, and the corresponding transition state TS2$_{1,2\text{-Cl}}$ is positioned at $\Delta E_0 = 50$ kJ mol^{-1}, below the energy limit of $\Delta E_0 = 5$ kJ mol^{-1}. Thus, a rearrangement of a collision complex of $\mathbf{1}^{\bullet+}$ and methanol via the addition product **1**distb$^{\bullet+}$ into the α-distonic ion **1**αdistb$^{\bullet+}$ is energetically possible as a slow reaction. It is of interest to analyze the structural changes during this 1,2-Cl shift **1**distb$^{\bullet+}$ → TS2$_{1,2\text{-Cl}}$ → **1**αdistb$^{\bullet+}$ (see Scheme 3) in more detail. The migrating Cl atom bridges C(1) and C(2) in the transition state TS2$_{1,2\text{-Cl}}$ but the bonds to both C atoms are rather long with 290 and 270 pm, respectively. Noteworthy, the Cl atom is already closer to the end point C(2) than to the starting point C(1) of the Cl shift. Further, the initial structure of **1**distb$^{\bullet+}$ is characterized by a long C–O bond of C(1) to the O-atom of the CH_3OH moiety, and this bond is shortened considerably in TS2$_{1,2\text{-Cl}}$. This gives the 1,2-Cl shift some analogy to a nucleophilic S_N2 substitution of a Cl atom at C(1) of $\mathbf{1}^{\bullet+}$ by methanol since the C–Cl bond increases synchronously with the approach of the O-atom of CH_3OH to C(1). But instead of leaving the complex the Cl atom is captured by the neighboring C(2) atom of the radical cation $\mathbf{1}^{\bullet+}$. These considerations help to understand the Cl-shift in **1**distb$^{\bullet+}$ as an energetically feasible reaction step. However, the subsequent 1,2-H shift within **1**αdistb$^{\bullet+}$, which should complete the isomerization, still exhibits a large critical barrier of 156 kJ mol^{-1} and a transition state TS2$_{1,2\text{-H}}$ placed at $\Delta E_0 = 147$ kJ mol^{-1}, distinctly above the energy limit of $\Delta E_0 = 56$ kJ mol^{-1}. Hence, route 2 also has to be abandoned as the mechanism for the isomerization $\mathbf{1}^{\bullet+}$ → $\mathbf{2}^{\bullet+}$ because of the large barrier of the 1,2-H shift.

A way out of this dilemma arises from the fact, that the α-distonic ion **1**αdistb$^{\bullet+}$ corresponds to the addition product of methanol to the carbene center of the chlorocarbene radical cation $\mathbf{5}^{\bullet+}$. In fact, the dissociation of **1**αdistb$^{\bullet+}$ into these products as free species results in $\Delta E_0 = 145$ kJ mol^{-1}, about the same ΔE_0 as the critical energy of the 1,2-H shift. On dissociation $\mathbf{5}^{\bullet+}$ and methanol form initially an ion/neutral complex which is energetically stabilized compared to the free products, so that formation of this complex from **1**αdistb$^{\bullet+}$ should be energetically even more favored than the 1,2-H shift. Further, $\mathbf{5}^{\bullet+}$ is a very acidic radical cation, and proton transfer from the C(2) of the chloromethyl group to methanol and formation of protonated methanol and the 1,2-dichloroethenyl radical is calculated to be actually exothermic by $54\,\mathrm{kJ\,mol^{-1}}$. Thus, the $\mathbf{5}^{\bullet+}$/methanol complex should be converted spontanously into a complex of protonated methanol and the 1,2-dichlorethenyl radical. However, in this complex a proton transfer from the protonated methanol now to C(1) of the 1,2-dichloroethenyl radical is strongly exothermic by $114\,\mathrm{kJ\,mol^{-1}}$. The reason for this behavior is the very different *local* proton affinity (PA) at C(1) and C(2) of the 1,2-dichloroethenyl radical. This is already clearly reflected by the large difference of $\Delta E_0 = 168\,\mathrm{kJ\,mol^{-1}}$ between isomers $\mathbf{5}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$. The PA of methanol is in between the local PAs of the 1,2-dichloroethenyl radical, and this results in the situation typical of a rearrangement catalyzed by a proton shuttle [5,20]. Therefore, methanol coming into contact with the chloromethylchloro-carbene radical cation $\mathbf{5}^{\bullet+}$ should induce the isomerization into the much more stable 1,2-dichloroethene radical cation $\mathbf{2}^{\bullet+}$. Combining these findings it appears feasible that the very exothermic rearrangement $\mathbf{5}^{\bullet+}$ + methanol → $\mathbf{2}^{\bullet+}$ + methanol occurs already in an incipient carbene radical cation $\mathbf{5}^{\bullet+}$during the dissociation of **1**αdistb$^{\bullet+}$ by some kind of an "internal proton shuttle". Such a reaction pathway should be considerably lower energy than either that of a complete dissociation of **1**αdistb$^{\bullet+}$ or that of an isomerization of **1**αdistb$^{\bullet+}$ by a 1,2-H shift and a "classical" transition state.

It was tried to model the steps of such an isomerization mechanism via ion/neutral complexes by ab initio calculation, but it was not possible to explore the complete potential energy hypersurface in the neighborhood of **1**αdistb$^{\bullet+}$ and **2**dist$^{\bullet+}$. As expected, stretching of only the C(1)–O bond of **1**αdistb$^{\bullet+}$ sends the system back to **1**distb$^{\bullet+}$ by a 1,2-Cl shift. However, if at the same time one of the C(2)–H bonds of **1**αdistb$^{\bullet+}$ is stretched, a "*syn*-β elimination" of protonated methanol occurs. In this way a structure $[\mathrm{CH_3OH_2}^+;\ 1,2\text{-}\mathrm{C_2HCl_2}\bullet]_{\mathrm{compl}}$ is generated which formally corresponds to a hydrogen bonded ion/neutral complex of protonated methanol and the 1,2-dichlorethenyl radical located at $\Delta E_0 = 31\,\mathrm{kJ\,mol^{-1}}$. The frequency analysis showed that this structure represents a minimum on the potential hypersurface at B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d), but we were not able to find a transition state for the rearrangement of this complex into **2**dist$^{\bullet+}$. Instead the complex was transformed into **2**dist$^{\bullet+}$ (or $\mathbf{2}^{\bullet+}$ and methanol) by transferring the proton from methanol to C(1). Apparently, the complex is separated from **2**dist$^{\bullet+}$ by only a small energy barrier. Nonetheless, the results indicate that there is indeed a low energy pathway for the 1,2-H-shift of **1**αdistb$^{\bullet+}$ to generate **2**dist$^{\bullet+}$ mediated by hydrogen-bonded ion/molecule complexes and circumventing the "classical" transition state. The importance of hydrogen bonded ion/neutral complexes for the isomerization of ions by migration of H atoms has been reported before [21], and Radom and coworkers have shown [22], that the association of a neutral atom or molecule to the migrating H atom significantly lowers the critical energy of a 1,2-H shift. The rearrangement **1**αdistb$^{\bullet+}$ → **2**dist$^{\bullet+}$ suggested in the present case as the final step of the isomerization of the radical cations of 1,1-dichloroethene $\mathbf{1}^{\bullet+}$ into those of 1,2-dichloroethene $\mathbf{2}^{\bullet+}$ is clearly another example of this proton transport catalysis.

4. Conclusion

There is convincing experimental evidence that the radical cations of 1,1-dichloroethene $\mathbf{1}^{\bullet+}$ isomerize into those of 1,2-dichloroethene $\mathbf{2}^{\bullet+}$ during the reaction with methanol. Although this isomerization is exothermic, it is a slow reaction which implies that notable critical energy barriers are present on the reaction pathway between $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$. Since this isomerization corresponds to reciprocal 1,2-shifts of a Cl- and a H-atom, a multi-step reaction mechanism involving considerable activation barriers is indeed likely. D-labeling experiments exclude that the isomerization $\mathbf{1}^{\bullet+}$ → $\mathbf{2}^{\bullet+}$ is induced by reciprocal H-shifts between $\mathbf{1}^{\bullet+}$ and methanol. Finally, if either substitution or hydride transfer is promoted by corresponding structural changes of the reactants, the isomerization $\mathbf{1}^{\bullet+} \rightarrow \mathbf{2}^{\bullet+}$ is not observed anymore. This is a further indication of a complicated and not very favorable mechanism of the isomerization.

The analysis of the reactions of $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ with methanol by ab initio calculation reveals that the isomerization takes place in energetically excited addition products **1**dista$^{\bullet+}$ and **1**distb$^{\bullet+}$. The distonic onium ion **1**distb$^{\bullet+}$ contains the structural element of a β-chloroalkyl radical. In solution these radicals are known to isomerize easily by a 1,2-Cl shift. A corresponding 1,2-Cl shift within **1**distb$^{\bullet+}$ is exothermic and exhibits only a moderate critical energy of 72 kJ mol^{-1}. If this is a typical critical energy of 1,2-Cl shifts in distonic ions one can expect a hitherto undetected family of isomerization reactions by Cl migration in excited chloro-organic radical ions. In the present case of **1**distb$^{\bullet+}$, the 1,2-Cl shift is driven by the excess energy originating from the initial addition step.

The α-distonic isomer **1**αdistb$^{\bullet+}$ created by an exothermic 1,2-Cl shift can be viewed as the addition product of methanol to the radical cation of chloromethyl-chlorocarbene $\mathbf{5}^{\bullet+}$. The further reactions of **1**αdistb$^{\bullet+}$ which eventually yield $\mathbf{2}^{\bullet+}$ and methanol, are still not firmly established. The most simple reaction step, a 1,2-H shift of **1**αdistb$^{\bullet+}$, is excluded by the prohibitively large critical energy. A dissociation of **1**αdistb$^{\bullet+}$ into $\mathbf{5}^{\bullet+}$ and methanol and a subsequent facile isomerization $\mathbf{5}^{\bullet+} \rightarrow \mathbf{2}^{\bullet+}$ includes a large dissociation energy for the first step and is not likely to occur. However, a dissociation of **1**αdistb$^{\bullet+}$ by transferring a proton from C(2) of the incipient chlorocarbene radical cation $\mathbf{5}^{\bullet+}$ to the leaving methanol molecule and generating instead the 1,2-dichloroethenyl radical and protonated methanol is energetically much more favorable. Then, proton transfer from the protonated methanol to C(1) of the 1,2-dichloroethenyl radical is exothermic and produces $\mathbf{2}^{\bullet+}$ and methanol (or the addition product of these reactants) in a direct fashion. An amalgamation of these two steps would afford a low energy pathway for the isomerization **1**αdistb$^{\bullet+} \rightarrow 2^{\bullet+} +$ methanol. Ab initio calculations of selected points along the reaction path corroborate this mechanism, which in fact corresponds to a special variant of an "internal" proton transport catalysis.

In conclusion, the gas-phase isomerization of the 1,1-dichloroethene radical cation $\mathbf{1}^{\bullet+}$ into the 1,2-dichloroethene radical cation $\mathbf{2}^{\bullet+}$, which is catalyzed by methanol, proceeds by a mechanism including at least three steps: the first step is the addition of the catalyst methanol to the double bond of the ionized ethene which activates $\mathbf{1}^{\bullet+}$ and transforms it into a distonic onium ion **1**distb$^{\bullet+}$ with a β-chloroalkyl structure. The second step is the 1,2-Cl shift in this charged β-chloroalkyl radical which requires only a moderate activation energy. In spite of this such a rearrangement has not been reported before. The third and final step is an isomerization during the dissociation of the α-distonic ion **1**αdistb$^{\bullet+}$ to $\mathbf{2}^{\bullet+}$ through a proton transport catalysis by the leaving catalyst methanol.

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