5760 *J. Phys. Chem. A* **2006,** *110,* 5760−5771

Isomeric Effects in the Gas-Phase Reactions of Dichloroethene, $C_2H_2Cl_2$, with a Series of Cations

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Received: January 5, 2006; In Final Form: March 9, 2006

A study of the reactions of a series of gas-phase cations (NH_4^+, H_3O^+, SF_3^+, CF_3^+, CF^+, SF_5^+, SF_2^+, SF^+, CF_2^+, SF_4^+, O_2^+, Xe^+, N_2O^+, CO_2^+, Kr^+, CO^+, N^+, N_2^+, Ar^+, F^+, and Ne^+) with the three structural isomers of dichloroethene, i.e., 1,1-$C_2H_2Cl_2$, *cis*-1,2-$C_2H_2Cl_2$, and *trans*-1,2-$C_2H_2Cl_2$ is reported. The recombination energy (RE) of these ions spans the range of 4.7−21.6 eV. Reaction rate coefficients and product branching ratios have been measured at 298 K in a selected ion flow tube (SIFT). Collisional rate coefficients are calculated by modified average dipole orientation (MADO) theory and compared with experimental data. Thermochemistry and mass balance have been used to predict the most feasible neutral products. Threshold photoelectron−photoion coincidence spectra have also been obtained for the three isomers of $C_2H_2Cl_2$ with photon energies in the range of 10−23 eV. The fragment ion branching ratios have been compared with those of the flow tube study to determine the importance of long-range charge transfer. A strong influence of the isomeric structure of dichloroethene on the products of ion−molecule reactions has been observed for H_3O^+, CF_3^+, and CF^+. For 1,1-$C_2H_2Cl_2$ the reaction with H_3O^+ proceeds at the collisional rate with the only ionic product being 1,1-$C_2H_2Cl_2H^+$. However, the same reaction yields two more ionic products in the case of *cis*-1,2- and *trans*-1,2-$C_2H_2Cl_2$, but only proceeds with 14% and 18% efficiency, respectively. The CF_3^+ reaction proceeds with 56−80% efficiency, the only ionic product for 1,1-$C_2H_2Cl_2$ being $C_2H_2Cl^+$ formed via Cl^- abstraction, whereas the only ionic product for both 1,2-isomers is $CHCl_2^+$ corresponding to a breaking of the C═C double bond. Less profound isomeric effects, but still resulting in different products for 1,1- and 1,2-$C_2H_2Cl_2$ isomers, have been found in the reactions of SF^+, CO_2^+, CO^+, N_2^+, and Ar^+. Although these five ions have REs above the ionization energy (IE) of any of the $C_2H_2Cl_2$ isomers, and hence the threshold for long-range charge transfer, the results suggest that the formation of a collision complex at short range between these ions and $C_2H_2Cl_2$ is responsible for the observed effects.

1. Introduction

A study of isomeric effects in gas-phase ion−molecule reactions is an area of research which has received little attention, but such effects can dramatically influence the kinetics and hence provide useful insight into reaction mechanisms. This has been reported by us in a paper dealing with a series of anion reactions with the three structural isomers of dichloroethene: 1,1-$C_2H_2Cl_2$, *cis*-1,2-$C_2H_2Cl_2$, and *trans*-1,2-$C_2H_2Cl_2$.[1]

Dichloroethenes have attracted recent attention as environmental pollutants since they are toxic and potential human carcinogens. Several studies have been undertaken on the oxidation of various chloroethenes, including dichloroethenes, by neutral atmospheric radicals,[2−8] with some reporting the influence of the isomeric structure of dichloroethene on the reaction pathways. Reactions of the OH radical with these isomers were studied by laser photolysis/laser-induced fluorescence and by discharge−flow techniques.[2,3] At room temperature, the products from *trans*-1,2-$C_2H_2Cl_2$ are $C_2H_2Cl(OH) + Cl$, while for 1,1-$C_2H_2Cl_2$ the dominant product is the adduct $C(OH)H_2CCl_2$. The difference in behavior of the isomers was explained by the existence of a barrier to the addition of OH to the chlorine-containing carbon of 1,1-$C_2H_2Cl_2$.[2] The mechanism of the reaction between polychloroethenes and neutral radicals has been described as an electrophilic attack at the less-substituted carbon atom of the alkene.[2−4] An ab initio study of the reactions of the NO_3 radical with polychlorinated ethenes predicted that for the 1,2-$C_2H_2Cl_2$ isomers one of the possible pathways leads to the production of acid chlorides, whereas the 1,1-$C_2H_2Cl_2$ isomer leads to the formation of aldehydes.[8]

Reactions between different isomers of dichloroethenes and gas-phase positive ions have been investigated to a lesser extent. In the early work of Bowers and Laudenslager, reactions between rare gas ions and the three structural isomers of dichloroethene were studied in an ICR (ion cyclotron resonance) spectrometer.[9] The reaction proceeded via charge (electron) transfer for all three isomers. Rebrion et al.[10] investigated the reactions of N^+ and H_3^+ with the isomers of dichloroethene. For N^+ the reactions proceeded via charge transfer, H_3^+ reactions proceeded via proton transfer, but no significant influence of the isomeric structure on the reaction pathways was found in either case.

Reactions between several gas-phase negative ions (O_2^-, O^-, OH^-, CF_3^-, and F^-) and dichloroethene isomers have been investigated in our recent study.[1] A striking feature of these reactions is that the vinyl anion, $C_2HCl_2^-$, is observed only for *trans*-1,2-$C_2H_2Cl_2$, where it is the major product, while Cl^- is

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10.1021/jp060093s CCC: $33.50

the major product from the 1,1- and *cis*-1,2-isomers. The difference has been explained by the probable existence of a higher barrier to the loss of Cl^- from the initially formed vinyl anion in the case of *trans*-1,2-$C_2H_2Cl_2$. The gas-phase reaction between Cl^- and 1,2-dichloroethenes was studied experimentally and theoretically by Bagno et al.[11] The only possible product predicted was the addition complex $C_2H_2Cl_3^-$. However, only in the case of *cis*-1,2-$C_2H_2Cl_2$ could such a complex be observed experimentally due to the calculated lower energy of the binding site of Cl^- to this isomer.

Isomeric effects can be also observed in the reactions between ionized isomers and neutral molecules. Of relevance to our study is the work of Nixdorf and Grützmacher[12] on the reactions between dichloroethene cations and alcohols in an FT-ICR mass spectrometer. For methyl alcohol the reaction occurred with 1,1-$C_2H_2Cl_2^+$, protonated formaldehyde being the only ionic product. The reaction could not proceed via charge transfer, because of the higher ionization energy (IE) of CH_3OH (10.84 eV) than that of any isomer of $C_2H_2Cl_2$.

Though some effects of the isomeric structure of dichloroethene on its reactivity have been reported by different authors, there has been no systematic study of this subject which involves a large variety of reactant cations. Here we report a series of reactions at room temperature involving positive ions, with the range of recombination energies (REs) spanning 4.73−21.56 eV; namely, and in order of increasing RE, NH_4^+, H_3O^+, SF_3^+, CF_3^+, CF^+, SF_5^+, SF_2^+, SF^+, CF_2^+, SF_4^+, O_2^+, Xe^+, N_2O^+, CO_2^+, Kr^+, CO^+, N^+, N_2^+, Ar^+, F^+, and Ne^+. These ions subdivide into two categories: those with RE values less than, and those with RE values greater than, the adiabatic IE of the dichloroethene isomers. For the former category, charge-transfer reactions cannot take place under thermal conditions, and only chemical reactions involving formation of a short-range collision complex between the molecule and the attacking ion are possible. These reactions should therefore resemble the reactions between dichloroethene molecules and neutral free radicals. The main difference is that, in our study due to the strong charge−dipole forces between the ion and the molecule, the reaction rates are expected to be much higher.

For ions with RE > IE ($C_2H_2Cl_2$), charge transfer from the ion to the dichloroethene molecule is thermochemically possible. We have discussed in detail elsewhere two mechanisms for charge transfer, the long-range and short-range cases.[13] In the long-range mechanism, an ion, A^+, and a polar neutral molecule, BC, approach under the influence of their charge−dipole interaction, until at some critical distance (R_c) the A^+−BC and A−BC^+ potential energy curves cross. An electron transfer can then take place. R_c depends on the difference in energy between the RE of A^+ and the IE of BC; the smaller this difference, the larger R_c. Two further factors needed for an efficient long-range charge-transfer process are that there is a nonzero energy resonance connecting BC to an electronic state of BC^+ at the RE of A^+ and that the transferring electron comes from a molecular orbital of BC that is not shielded from the approaching cation. So long as there is some overlap of vibrational wave function between BC and BC^+ at the RE of A^+, the evidence from studies of both saturated and unsaturated perfluorocarbons (e.g., CF_4, C_2F_4, C_2F_6)[13] and less-symmetrical saturated molecules (e.g., CHF_3, $CHClF_2$, and $CHCl_2F$)[14,15] is that the magnitude of the photoionization Franck−Condon factor for BC is not as important as originally thought in determining the efficiency of such a reaction.

When long-range charge transfer is unfavorable, A^+ and BC move closer together. As their separation decreases, the potential energy surface, electron density, and energy levels of the BC molecule become distorted so that A^+ and BC lose their identity. Eventually, a curve crossing can occur through which efficient charge transfer takes place. This is called short-range charge transfer. As an intermediate complex has formed, a chemical reaction, defined as the breaking and making of bonds, may also occur, as for reactions of ions with RE(A^+) < IE(BC). This process can compete with short-range charge transfer. It is expected that the isomeric structure of BC should play a more important role for short-range ion−molecule reactions.

Long-range charge transfer can be followed by fragmentation of the ionized molecule (BC^+)*, where * donates the possibility of BC^+ being in an excited electronic state, and the neutral product will be a spectator to the process. The branching ratios for fragmentation of (BC^+)* should therefore be independent of how this state is produced. Hence, we would expect similar ion product branching ratios from ion−molecule and threshold photoelectron−photoion coincidence (TPEPICO) studies of BC, assuming the photon energy in the latter experiment matches the RE(A^+) in the former. For the short-range mechanism, it is unlikely that the product branching ratios from the two experiments will mimic each other. Thus, a comparison of the fragmentation patterns from the selected ion flow tube (SIFT) and TPEPICO experiments, together with an analysis of the threshold photoelectron spectrum (TPES) of BC at the energy of the RE of A^+, may indicate which mechanism, be it long-range or short-range, is dominant for the reaction of each cation. If the fragmentation patterns of the two studies differ, it indicates that all or part of the ion−molecule encounters follow the short-range route. There have been many studies of vacuum UV absorption and photoelectron spectra of dichloroethene isomers,[16−23] and the electronic states of their cations have been studied both experimentally and theoretically.[24−27] However, no study of the photodissociation products from ionized states of $C_2H_2Cl_2$ as a function of photon energy has been undertaken. In this paper we compare product yields from the ion−molecule and TPEPICO studies for the three isomers of $C_2H_2Cl_2$ in the range of ionizing energy of 10−23 eV.

2. Experimental Section

The ion−molecule reactions have been studied in a SIFT apparatus, and rate coefficients and percentage yields of cation products have been measured. The details of the apparatus, measurement technique, and data analysis have been extensively reviewed elsewhere,[28] and only a brief description is given here. All reagent cations were produced by electron impact ionization in a high-pressure ion source. The details of production of H_3O^+, O_2^+, N_2O^+, CO_2^+, CO^+, N^+, and N_2^+ have been described before.[14] For SF_n^+, $n = 1−5$, the precursor gas was SF_6, for CF_n^+, $n = 1−3$, and F^+ it was CF_4. Rare gas ions were generated directly from their neutral precursor. The mass-selected ions were injected via a Venturi inlet into a fast flowing (ca. 150 torr L s^{-1}) He (99.997% purity) buffer gas that was maintained at a temperature of ca. 298 K and a pressure of typically 0.5 torr. Collision-induced dissociation (CID) of polyatomic ions at the entrance to the flow tube was usually suppressed by adjusting the voltages at the coupling ion lenses. However, often to obtain a good parent ion signal we could not completely remove the fragment ions. Under such circumstances the intensity of the CID ions was always less than 5% of the parent ion signal. When it occurred allowances were made for the reactions of the CID ions when determining the product ion branching ratios. The only exception to this was SF_4^+ resulting from CID from SF_5^+, and this is described later. For some ions, which proved to be impossible to produce directly in the ion source, CID was used to form them at the entrance of the flow tube. The reagent ions were carried along the flow tube to react with the neutral reagent, where measured quantities were injected into the helium flow. Room temperature vapors of 1,1-, *cis*-1,2-, and *trans*-1,2-isomers of dichloroethene (Aldrich, 99%, 97%, and 98% purity, respectively) were supplied to the injecting facility. At the end of the flow tube the precursor and product cations were focused through a 1 mm orifice in a Faraday plate into a quadrupole mass filter and detected by a channeltron. Rate coefficients were obtained from the depletion of the signal of the reagent ions versus concentration of the neutral reagent under pseudo-first-order conditions. The accuracy of measured rate coefficients is estimated to be ±20%, and a measurable lower limit of ca. 10^{-13} cm^3 $molecule^{-1}$ s^{-1}. Branching ratios were derived from plots of the signals of the different product ions versus concentration of the neutral reagent. Extrapolation to zero concentration is performed routinely to exclude any secondary reactions. To eliminate as far as possible the effects of mass discrimination between ions of masses differing by more than 5 u, such measurements were taken with the lowest possible mass resolution. We estimate an error of 10% in our branching ratios, this error increasing for values below 10%.

TPEPICO studies were performed at the Daresbury synchrotron radiation source on beamline 3.2 using the 5m McPherson monochromator operating with a resolution of 0.3 nm. The monochromatic radiation is coupled into the reaction region via a capillary, and the flux is monitored by a photomultiplier tube through a sodium-salicylate-coated Pyrex window. Threshold photoelectrons and fragment cations are extracted in opposite directions by an electric field and are detected by a channeltron and a pair of microchannel plates, respectively. Both the threshold electron analyzer and the time-of-flight (TOF) mass spectrometer have been described elsewhere.[29] Raw data pulses are discriminated and then passed to a time-to-digital converter, from where the data is read by a dedicated personal computer. The electrons provide a “start” trigger while the ions provide a “stop” signal, allowing signals from the same ionization process to be detected in coincidence.

Different spectra can be recorded with the TPEPICO apparatus. At the start of measurements, the TPES is obtained by recording the threshold electron signal as a function of photon energy. Then the coincidence spectrum is recorded as a function of photon energy. Such TPEPICO spectra are recorded as a three-dimensional map of coincidence counts versus ion TOF versus photon energy. Sections from this map yield either the TOF mass spectrum at a selected photon energy or the yield of a particular ion. The product ion branching ratios as a function of photon energy are easily obtained. If the product ions are expected to cover a wide range of m/z values, the mass resolution is kept low for these scans. Finally, we fix the photon energy at defined values which range over the complete scan so that higher-resolution TOF spectra can be produced. This also allows us to check that no ion products have been missed in the low-resolution scans. Analysis of the TOF peak shape of a fragment ion can provide the kinetic energy release distribution (KERD) and the value for the mean kinetic energy release. Such data is reported elsewhere.[30]

The plots of photofragment ion yield versus photon energy can be used to obtain the appearance energies, AE_{298}, of the photofragment.[31] Appearance energies for fragment ions from vacuum UV photodissociation of the three dichloroethene isomers have been converted to upper limits for the enthalpies of the appropriate reaction, $\Delta_r H^0_{298}$, using the procedure described by Traeger and McLoughlin.[32] These values of $\Delta_r H^0_{298}$ can then be used to calculate an upper limit for the enthalpy of formation of the fragment ions, $\Delta_f H^0_{298}$.[14,31] Thus, we have determined an upper limit for $\Delta_f H^0_{298}$ of the 1,1-, *cis*-1,2-, and *trans*-1,2-isomers of $C_2H_2Cl^+$ to be 1051, 1053, and 1051 kJ mol^{-1}, respectively. We have used such data to predict thermochemically allowed neutral partners from photofragmentation and from ion−molecule reactions.

The use of 298 K thermochemical data to analyze our SIFT results requires some caution, because of the possibility of excited-state reactant ions being present in the flow tube. For example, we have previously demonstrated that about 40% of N_2^+ are found in the $v = 1$ vibrational state (0.27 eV above the ground level), while 20% of O_2^+ are found in the $v = 1$ and 2 vibrational states (0.23 and 0.46 eV above the ground level).[33] It is therefore highly likely that other molecular ions used in this investigation may have some vibrational excitation. No electronically excited reactant molecular ions have been detected in our previous measurements. The presence of excited vibrational states of the precursor ion may affect reactions which are slightly endothermic, and we discuss such possibilities later. It is also important to assess whether the presence of vibrationally excited states affects the measured rate coefficients. No curvature has been observed in any of the pseudo-first-order kinetic plots, however, implying that the ground state and any excited-state ions (if present) react with the same rate coefficient.

3. Results

3.1. Rate Coefficients. Experimental rate coefficients, k_{exp}, have been compared with the calculated values for collisional rate coefficients, k_c. The latter values are capture rate coefficients for ion−molecule reactions as predicted by the Langevin theory for molecules without a permanent dipole moment[34,35] or modified average dipole orientation (MADO) theory for molecules with a nonzero dipole moment.[36] The results for the experimental and calculated (collision) rate coefficients are given in the second columns of Tables 1−3. The values for the polarizabilities of 1,1-, *cis*-1,2-, and *trans*-1,2-dichloroethenes used in the calculations are 7.83, 8.15, and 8.03 × 10^{-30} m^3, respectively.[37] The dipole moments of 1,1- and *cis*-1,2-dichloroethene are 1.29 and 1.90 D, respectively,[38] but zero for *trans*-1,2-dichloroethene. The percentage difference between the dipole moments of the isomers is much larger than the difference between their polarizabilities, and it is this former difference which makes the major contribution to the difference of calculated rate coefficients of the isomers. Accordingly, MADO calculations predict the following relations between collisional rates: k_c(*cis*-1,2) > k_c(1,1) > k_c(*trans*-1,2).

In general, the efficiency of the reaction, defined as $(k_{exp}/k_c) \times 100\%$, is high for all ions with $RE_{ion} > IE(C_2H_2Cl_2)$, where $IE(C_2H_2Cl_2)$ is 9.65 eV for *cis*-1,2- and *trans*-1,2-$C_2H_2Cl_2$ and 9.83 eV for 1,1-$C_2H_2Cl_2$.[39] For reactions with experimental rate coefficients larger than the calculated values, experimental error in the SIFT measurements is the most likely cause, and we regard such reactions as being 100% efficient. With the use of this definition, the efficiency of reaction varies from 68% to 100% for the majority of ions with high REs. The reactions of SF_5^+ are slow, with efficiency less than 25% for all three isomers of $C_2H_2Cl_2$. This result mimics that of a previous study reporting the reactions of SF_5^+ with $CHCl_2F$, $CHClF_2$, and CH_2ClF.[15] We comment that MADO theory only predicts collisional rate coefficients and does not take into account the reaction probability per collision. If the reaction proceeds via

TABLE 1: Rate Coefficients at 298 K, Product Cations, Branching Ratios, and Suggested Neutral Products for the Reactions of 21 Cations with 1,1-$C_2H_2Cl_2$[a]

reagent ion [RE/eV]	rate coefficient $/10^{-9}$ cm^3 molecule^{-1} s^{-1}	productions [%]	proposed neutral products	$\Delta_rH^0_{298}$/kJ mol^{-1}
NH_4^+ [4.73]	no reaction	none	none	n/a
H_3O^+ [6.27]	2.0 [2.0]	$C_2H_2Cl_2H^+$ [100]	H_2O	$-808 + \Delta_fH^0_{298}$ ($C_2H_2Cl_2H^+$)
SF_3^+ [8.32]	no reaction[b]	association product	none	n/a
CF_3^+ [9.04]	1.2 [1.5]	$C_2H_2Cl^+$ [100]	CF_3Cl	-65[c]
CF^+ [9.11]	2.1 [2.0]	$CHCl_2^+$ [6] $CClFH^+$ [25] $C_2H_2Cl^+$ [69]	C_2HF C_2HCl CFCl	-142 -179 -54[d]
SF_5^+ [9.78]	0.3 [1.2]	$C_2H_2Cl_2F^+$ [71] $C_2H_2Cl_2^+$ [16] $C_2H_2Cl^+$ [13]	SF_4 SF_5 SF_5Cl	$-800 + \Delta_fH^0_{298}$ ($C_2H_2Cl_2F^+$)[e,f] 0[e,g] -19[e]
SF_2^+ [10.24]	1.4 [1.5]	$C_2H_2Cl_2^+$ [100]	SF_2	-45[h]
SF^+ [10.31]	1.6 [1.6]	$C_2H_2Cl_2^+$ [59] $C_2H_2ClSF^+$ [8] C_2HClSF^+ [8] $C_2H_2Cl^+$ [21] $CHCl_2^+$ [4]	SF Cl HCl SFCl CS + HF	-52[i] $-879 + \Delta_fH^0_{298}$ ($C_2H_2ClSF^+$)[i] $-1093 + \Delta_fH^0_{298}$ (C_2HClSF^+)[i] $51 + \Delta_fH^0_{298}$ (SFCl)[i] -106[i]
CF_2^+ [11.44]	1.9 [1.6]	$C_2H_2Cl_2^+$ [100]	CF_2	-160
SF_4^+ [11.99]	1.4 [1.3]	not measured	n/a	n/a
O_2^+ [12.07]	2.5 [1.9]	$C_2H_2Cl_2^+$ [77] $C_2H_2Cl^+$ [23]	O_2 OClO or ClOO	-221 -18 -17
Xe^+ $^2P_{3/2}$ [12.13]	1.3 [1.3]	$C_2H_2Cl_2^+$ [81] $C_2H_2Cl^+$ [19]	Xe Xe + Cl	-227 0
N_2O^+ [12.89]	1.7 [1.7]	$C_2H_2Cl_2^+$ [15] $C_2H_2Cl^+$ [85]	N_2O N_2OCl or N_2O + Cl	-300 -264 -73
CO_2^+ [13.76]	1.5 [1.7]	$C_2H_2Cl_2^+$ [13] $C_2H_2Cl^+$ [87]	CO_2 CO_2 + Cl	-385 -158
Kr^+ $^2P_{1/2}$ [14.00]	1.3 [1.4]	$C_2H_2Cl^+$ [93] C_2HCl^+ [7]	Kr + Cl Kr + HCl	-180 -209
CO^+ [14.01]	2.0 [2.0]	$C_2H_2Cl^+$ [100]	ClCO	-255
N^+ [14.53]	2.7 [2.7]	$C_2H_2Cl_2^+$ [40] $C_2H_2Cl^+$ [54] C_2HCl^+ [6]	N NCl N + HCl	-459 -512[j] -260
N_2^+ [15.58]	2.0 [2.0]	$C_2H_2Cl^+$ [83] C_2HCl^+ [17]	N_2 + Cl N_2 + HCl	-333 -361
Ar^+ [15.76]	1.5 [1.8]	$C_2H_2Cl^+$ [84] C_2HCl^+ [16]	Ar + Cl Ar + HCl	-351 -379
F^+ [17.42]	2.0 [2.3]	$C_2H_2Cl_2^+$ [14] $C_2H_2Cl^+$ [41] $C_2H_2^+$ [45]	F FCl F + Cl_2	-737 -761 -356
Ne^+ [21.56]	2.0 [2.3]	$C_2H_2Cl_2^+$ [5] $C_2H_2^+$ [50] C_2HCl^+ [35] CCl^+ [4] Cl^+ [6]	Ne Ne + Cl_2 Ne + HCl Ne + CH_2 + Cl or Ne+ CH + HCl Ne + C_2H_2Cl or Ne + Cl + C_2H_2	-1114 -755 -938 -331 -337 $-711 + \Delta_fH^0_{298}$ (C_2H_2Cl) -363

[a] The RE of the ion is shown in column 1 in square brackets. Experimental rate coefficients are shown in column 2; values in square brackets below the experimental data are MADO theoretical capture coefficients (see text). The product ions and their branching ratios are shown in column 3. The most likely accompanying neutral products are given in column 4, with the enthalpy of the proposed reaction given in column 5. These values are generally derived from the usual reference sources for neutrals (refs 39 and 40) and ions (refs 39 and 41), unless otherwise indicated. In the interests of brevity, only the proposed neutrals that give the most exothermic $\Delta_rH^0_{298}$ are listed, unless specifically discussed in the text. [b] Rate coefficient too small to measure, $k < 10^{-13}$ cm^3 s^{-1}. [c] $\Delta_fH^0_{298}$ (CF_3^+) = +406 kJ mol^{-1} (ref 42). [d] $\Delta_fH^0_{298}$ (CClF) = +31 kJ mol^{-1} (ref 43). [e] $\Delta_fH^0_{298}$ (SF_5^+) = +29 kJ mol^{-1} (ref 44). [f] $\Delta_fH^0_{298}$ (SF_4) = -768 kJ mol^{-1} (ref 45). [g] $\Delta_fH^0_{298}$ (SF_5) = -915 kJ mol^{-1} (ref 46). [h] $\Delta_fH^0_{298}$ (SF_2) = -295 kJ mol^{-1}, $\Delta_fH^0_{298}$ (SF_2^+) = +693 kJ mol^{-1} (ref 45). [i] $\Delta_fH^0_{298}$ (SF^+) = +998 kJ mol^{-1} (ref 45). [j] $\Delta_fH^0_{298}$ (NCl) = +314 kJ mol^{-1} (ref 47).

TABLE 2: Rate Coefficients at 298 K, Product Cations, Branching Ratios, and Suggested Neutral Products for the Reactions of 21 Cations with *cis*-1,2-$C_2H_2Cl_2$ (Adiabatic IE = 9.65 eV)[a]

reagent ion [RE/eV]	rate coefficient $/10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}	productions [%]	proposed neutral products	$\Delta_rH^0_{298}$/kJ mol^{-1}
NH_4^+	no reaction	none	none	n/a
[4.73]				
H_3O^+	0.4	$C_2H_2ClOH_2^+$ [62]	HCl	$-688 + \Delta_fH^0_{298}$ ($C_2H_2ClOH_2^+$)
[6.27]	[2.9]	$C_2H_2Cl_2H^+$ [32]	H_2O	$-837 + \Delta_fH^0_{298}$ ($C_2H_2Cl_2H^+$)
		$C_2H_2Cl_2{\cdot}H_3O^+$ [6]		n/a
SF_3^+	no reaction[b]	association product	none	n/a
[8.32]				
CF_3^+	1.0	$CHCl_2^+$ [100]	C_2HF_3	3[c]
[9.04]	[1.8]			
CF^+	2.0	$CHCl_2^+$ [41]	C_2HF	-144
[9.11]	[2.4]	$CClFH^+$ [59]	C_2HCl	-181
SF_5^+	0.2	$C_2H_2Cl_2F^+$ [69]	SF_4	$-802 + \Delta_fH^0_{298}$ ($C_2H_2Cl_2F^+$)[d,e]
[9.78]	[1.6]	$C_2H_2Cl_2^+$ [14]	SF_5	-15[d,f]
		$C_2H_2Cl^+$ [17]	SF_5Cl	-19[d]
SF_2^+	1.7	$C_2H_2Cl_2^+$ [100]	SF_2	-60[g]
[10.24]	[1.8]			
SF^+	1.5	$C_2H_2Cl_2^+$ [88]	SF	-67[h]
[10.31]	[2.0]	$C_2H_2ClSF^+$ [6]	Cl	$-881 + \Delta_fH^0_{298}$ ($C_2H_2ClSF^+$)[h]
		C_2HClSF^+ [6]	HCl	$-1095 + \Delta_fH^0_{298}$ (C_2HClSF^+)[h]
CF_2^+	1.6	$C_2H_2Cl_2^+$ [100]	CF_2	-175
[11.44]	[2.0]			
SF_4^+	1.4	not measured	n/a	n/a
[11.99]	[1.6]			
O_2^+	2.3	$C_2H_2Cl_2^+$ [78]	O_2	-236
[12.07]	[2.4]	$C_2H_2Cl^+$ [22]	OClO	-18
			or ClOO	-17
Xe^+ $^2P_{3/2}$	1.4	$C_2H_2Cl_2^+$ [82]	Xe	-242
[12.13]	[1.5]	$C_2H_2Cl^+$ [18]	Xe + Cl	0
N_2O^+	1.9	$C_2H_2Cl_2^+$ [15]	N_2O	-315
[12.89]	[2.1]	$C_2H_2Cl^+$ [85]	N_2O + Cl	-73
			or N_2 + OCl	-175
			or N_2OCl	-264
CO_2^+	1.9	$C_2H_2Cl_2^+$ [18]	CO_2	-400
[13.76]	[2.1]	$C_2H_2Cl^+$ [75]	CO_2 + Cl	-158
		C_2HCl^+ [7]	CO_2 + HCl	-188
Kr^+ $^2P_{1/2}$	1.6	$C_2H_2Cl^+$ [83]	Kr + Cl	-180
[14.00]	[1.7]	C_2HCl^+ [17]	Kr + HCl	-211
CO^+	1.7	$C_2H_2Cl_2^+$ [10]	CO	-423
[14.01]	[2.5]	$C_2H_2Cl^+$ [78]	CO + Cl	-181
			or COCl	-255
		C_2HCl^+ [12]	CO + HCl	-211
N^+	2.8	$C_2H_2Cl_2^+$ [56]	N	-474
[14.53]	[3.3]	$C_2H_2Cl^+$ [37]	NCl	-512[i]
		C_2HCl^+ [7]	N + HCl	-262
N_2^+	2.3	$C_2H_2Cl_2^+$ [10]	N_2	-574
[15.58]	[2.5]	$C_2HCl_2^+$ [6]	N_2 + H	$-1289 + \Delta_fH^0_{298}$ ($C_2HCl_2^+$)
		$C_2H_2Cl^+$ [68]	N_2 + Cl	-333
		C_2HCl^+ [16]	N_2 + HCl	-363
Ar^+	1.5	$C_2H_2Cl_2^+$ [4]	Ar	-592
[15.76]	[2.2]	$C_2HCl_2^+$ [4]	Ar + H	$-1307 + \Delta_fH^0_{298}$ ($C_2HCl_2^+$)
		$C_2H_2Cl^+$ [75]	Ar + Cl	-351
		C_2HCl^+ [17]	Ar + HCl	-381
F^+	2.4	$C_2H_2Cl_2^+$ [25]	F	-752
[17.42]	[2.9]	$C_2H_2Cl^+$ [29]	FCl	-761
		$C_2H_2^+$ [46]	F + Cl_2	-358
Ne^+	2.3	$C_2H_2Cl_2^+$ [11]	Ne	-1151
[21.56]	[2.8]	$C_2H_2^+$ [60]	Ne + Cl_2	-758
		C_2HCl^+ [21]	Ne + HCl	-940
		Cl^+ [8]	Ne + C_2H_2Cl	$-713 + \Delta_fH^0_{298}$ (C_2H_2Cl)

[a] The RE of the ion is shown in column 1 in square brackets. Experimental rate coefficients are shown in column 2; values in square brackets below the experimental data are MADO theoretical capture coefficients (see text). The product ions and their branching ratios are shown in column 3. The most likely accompanying neutral products are given in column 4, with the enthalpy of the proposed reaction given in column 5. These values are generally derived from the usual reference sources for neutrals (refs 39 and 40) and ions (refs 39 and 41), unless otherwise indicated. In the interests of brevity, only the proposed neutrals that give the most exothermic $\Delta_rH^0_{298}$ are listed, unless specifically discussed in the text.[b] Rate coefficient too small to measure, $k < 10^{-13}$ cm^3 s^{-1}. [c] $\Delta_fH^0_{298}$ (CF_3^+) = +406 kJ mol^{-1} (ref 42). [d] $\Delta_fH^0_{298}$ (SF_5^+) = +29 kJ mol^{-1} (ref 44). [e] $\Delta_fH^0_{298}$ (SF_4) = −768 kJ mol^{-1} (ref 45). [f] $\Delta_fH^0_{298}$ (SF_5) = −915 kJ mol^{-1} (ref 46). [g] $\Delta_fH^0_{298}$ (SF_2) = −295 kJ mol^{-1}, $\Delta_fH^0_{298}$ (SF_2^+) = +693 kJ mol^{-1} (ref 45). [h] $\Delta_fH^0_{298}$ (SF^+) = +998 kJ mol^{-1} (ref 45). [i] $\Delta_fH^0_{298}$ (NCl) = +314 kJ mol^{-1} (ref 47).

TABLE 3: Rate Coefficients at 298 K, Product Cations, Branching Ratios, and Suggested Neutral Products for the Reactions of 21 Cations with *trans*-1,2-$C_2H_2Cl_2$ (Adiabatic IE = 9.64 eV)[a]

reagent ion [RE/eV]	rate coefficient /10^{-9} cm^3 molecule^{-1} s^{-1}	productions [%]	proposed neutral products	$\Delta_r H^0_{298}$/kJ mol^{-1}
NH_4^+	no reaction	none	none	n/a
[4.73]				
H_3O^+	0.3	$C_2H_2ClOH_2^+$ [42]	HCl	$-685 + \Delta_f H^0_{298}$ ($C_2H_2ClOH_2^+$)
[6.27]	[1.7]	$C_2H_2Cl_2H^+$ [56]	H_2O	$-834 + \Delta_f H^0_{298}$ ($C_2H_2Cl_2H^+$)
		$C_2H_2Cl_2{\cdot}H_3O^+$ [2]		n/a
SF_3^+	no reaction[b]	association product	none	n/a
[8.32]				
CF_3^+	0.7	$CHCl_2^+$ [100]	C_2HF_3	5[c]
[9.04]	[1.0]			
CF^+	1.4	$CHCl_2^+$ [51]	C_2HF	−142
[9.11]	[1.4]	$CClFH^+$ [49]	C_2HCl	−179
SF_5^+	0.2	$C_2H_2Cl_2F^+$ [77]	SF_4	$-799 + \Delta_f H^0_{298}$ ($C_2H_2Cl_2F^+$)[d,e]
[9.78]	[0.9]	$C_2H_2Cl_2^+$ [16]	SF_5	−20[d,f]
		$C_2H_2Cl^+$ [7]	SF_5Cl	−19[f]
SF_2^+	1.4	$C_2H_2Cl_2^+$ [100]	SF_2	−64[g]
[10.24]	[1.0]			
SF^+	1.3	$C_2H_2Cl_2^+$ [89]	SF	−71[h]
[10.31]	[1.2]	$C_2H_2ClSF^+$ [6]	Cl	$-879 + \Delta_f H^0_{298}$ ($C_2H_2ClSF^+$)[h]
		C_2HClSF^+ [5]	HCl	$-1092 + \Delta_f H^0_{298}$ (C_2HClSF^+)[h]
CF_2^+	1.3	$C_2H_2Cl_2^+$ [100]	CF_2	−180
[11.44]	[1.2]			
SF_4^+	1.1	not measured	n/a	n/a
[11.99]	[0.93]			
O_2^+	1.2	$C_2H_2Cl_2^+$ [68]	O_2	−240
[12.07]	[1.4]	$C_2H_2Cl^+$ [32]	OClO	−18
			or ClOO	−17
Xe^+ $^2P_{3/2}$	0.9	$C_2H_2Cl_2^+$ [85]	Xe	−246
[12.13]	[0.9]	$C_2H_2Cl^+$ [15]	Xe + Cl	0
N_2O^+	0.9	$C_2H_2Cl_2^+$ [24]	N_2O	−319
[12.89]	[1.2]	$C_2H_2Cl^+$ [76]	N_2O + Cl	−73
			or N_2 + OCl	−175
			or N_2OCl	−264
CO_2^+	1.1	$C_2H_2Cl_2^+$ [15]	CO_2	−404
[13.76]	[1.2]	$C_2H_2Cl^+$ [74]	CO_2 + Cl	−158
		C_2HCl^+ [11]	CO_2 + HCl	−186
Kr^+ $^2P_{1/2}$	1.2	$C_2H_2Cl^+$ [80]	Kr + Cl	−180
[14.00]	[1.0]	C_2HCl^+ [20]	Kr + HCl	−208
CO^+	1.6	$C_2H_2Cl_2^+$ [11]	CO	−427
[14.01]	[1.4]	$C_2H_2Cl^+$ [74]	CO + Cl	−181
			or COCl	−255
		C_2HCl^+ [15]	CO + HCl	−209
N^+	2.0	$C_2H_2Cl_2^+$ [47]	N	−478
[14.53]	[1.9]	$C_2H_2Cl^+$ [42]	N + Cl	−232
			or NCl	−512[i]
		C_2HCl^+ [11]	N +HCl	−260
N_2^+	1.6	$C_2H_2Cl_2^+$ [9]	N_2	−579
[15.58]	[1.4]	$C_2HCl_2^+$ [4]	N_2 + H	$-1287 + \Delta_f H^0_{298}$ ($C_2HCl_2^+$)
		$C_2H_2Cl^+$ [66]	N_2 + Cl	−333
		C_2HCl^+ [21]	N_2 + HCl	−360
Ar^+	1.1	$C_2H_2Cl_2^+$ [5]	Ar	−597
[15.76]	[1.3]	$C_2HCl_2^+$ [7]	Ar + H	$-1305 + \Delta_f H^0_{298}$ ($C_2HCl_2^+$)
		$C_2H_2Cl^+$ [66]	Ar + Cl	−351
		C_2HCl^+ [22]	Ar + HCl	−378
F^+	1.4	$C_2H_2Cl_2^+$ [23]	F	−756
[17.42]	[1.7]	$C_2H_2Cl^+$ [32]	FCl	−761
		$C_2H_2^+$ [45]	F + Cl_2	−356
Ne^+	1.8	$C_2H_2Cl_2^+$ [5]	Ne	−1156
[21.56]	[1.6]	$C_2H_2^+$ [56]	Ne +Cl_2	−755
		C_2HCl^+ [34]	Ne + HCl	−937
		Cl^+ [5]	Ne + C_2H_2Cl	$-711 + \Delta_f H^0_{298}$ (C_2H_2Cl)

[a] The RE of the ion is shown in column 1 in square brackets. Experimental rate coefficients are shown in column 2; values in square brackets below the experimental data are MADO theoretical capture coefficients (see text). The product ions and their branching ratios are shown in column 3. The most likely accompanying neutral products are given in column 4, with the enthalpy of the proposed reaction given in column 5. These values are generally derived from the usual reference sources for neutrals (refs 39 and 40) and ions (refs 39 and 41), unless otherwise indicated. In the interests of brevity, only the proposed neutrals that give the most exothermic $\Delta_r H^0_{298}$ are listed, unless specifically discussed in the text. [b] Rate coefficient too small to measure, $k < 10^{-13}$ cm^3 s^{-1}. [c] $\Delta_f H^0_{298}$ (CF_3^+) = +406 kJ mol^{-1} (ref 42). [d] $\Delta_f H^0_{298}$ (SF_5^+) = +29 kJ mol^{-1} (ref 44). [e] $\Delta_f H^0_{298}$ (SF_4) = −768 kJ mol^{-1} (ref 45). [f] $\Delta_f H^0_{298}$ (SF_5) = −915 kJ mol^{-1} (ref 46). [g] $\Delta_f H^0_{298}$ (SF_2) = −295 kJ mol^{-1}, $\Delta_f H^0_{298}$ (SF_2^+) = +693 kJ mol^{-1} (ref 45). [h] $\Delta_f H^0_{298}$ (SF^+) = +998 kJ mol^{-1} (ref 45). [i] $\Delta_f H^0_{298}$ (NCl) = +314 kJ mol^{-1} (ref 47).

TABLE 4: Comparison of Rate Coefficients at 298 K, Product Cations, and Branching Ratios from the Reactions Where Different Products Are Observed for the 1,1- and 1,2-Isomers of $C_2H_2Cl_2$[a]

ion [RE/eV]	*k* (1,1) /10^{-9} cm^3 s^{-1}	*k* (*cis*-1,2) /10^{-9} cm^3 s^{-1}	*k* (*trans*-1,2) /10^{-9} cm^3 s^{-1}	products (1,1)	products (*cis*-1,2)	products (*trans*-1,2)
H_3O^+ [6.27]	2.0 [2.0] 100%	0.4 [2.9] 14%	0.3 [1.7] 18%	$C_2H_2Cl_2H^+$ [100] 18%	$C_2HClH_3O^+$ [62] $C_2H_2Cl_2H^+$ [32] $C_2H_2Cl_2{\cdot}H_3O^+$ [6]	$C_2HClH_3O^+$ [42] $C_2H_2Cl_2H^+$ [56] $C_2H_2Cl_2{\cdot}H_3O^+$ [2]
CF_3^+ [9.04]	1.2 [1.5] 80%	1.0 [1.8] 56%	0.7 [1.0] 70%	$C_2H_2Cl^+$ [100]	$CHCl_2^+$ [100]	$CHCl_2^+$ [100]
CF^+ [9.11]	2.1 [2.0] 100%	2.0 [2.4] 83%	1.4 [1.4] 100%	$CHCl_2^+$ [6] $CClFH^+$ [25] $C_2H_2Cl^+$ [69]	$CHCl_2^+$ [41] $CClFH^+$ [59]	$CHCl_2^+$ [51] $CClFH^+$ [49]
SF^+ [10.31]	1.6 [1.6] 100%	1.5 [2.0] 75%	1.3 [1.2] 100%	$C_2H_2ClSF^+$ [8] C_2HClSF^+ [8] $C_2H_2Cl_2^+$ [59] $CHCl_2^+$ [4] $C_2H_2Cl^+$ [21]	$C_2H_2ClSF^+$ [6] C_2HClSF^+ [6] $C_2H_2Cl_2^+$ [88]	$C_2H_2ClSF^+$ [6] C_2HClSF^+ [5] $C_2H_2Cl_2^+$ [89]
CO_2^+ [13.76]	1.5 [1.7] 88%	1.9 [2.1] 90%	1.1 [1.2] 92%	$C_2H_2Cl_2^+$ [13] $C_2H_2Cl^+$ [87]	$C_2H_2Cl_2^+$ [18] $C_2H_2Cl^+$ [75] C_2HCl^+ [7]	$C_2H_2Cl_2^+$ [15] $C_2H_2Cl^+$ [74] C_2HCl^+ [11]
CO^+ [14.01]	2.0 [2.0] 100%	1.7 [2.5] 68%	1.6 [1.4] 100%	$C_2H_2Cl^+$ [100]	$C_2H_2Cl_2^+$ [10] $C_2H_2Cl^+$ [78] C_2HCl^+ [12]	$C_2H_2Cl_2^+$ [11] $C_2H_2Cl^+$ [74] C_2HCl^+ [15]
N_2^+ [15.58]	2.0 [2.0] 100%	2.3 [2.5] 92%	1.6 [1.4] 100%	$C_2H_2Cl^+$ [83] C_2HCl^+ [17]	$C_2H_2Cl_2^+$ [10] $C_2HCl_2^+$ [6] $C_2H_2Cl^+$ [68] C_2HCl^+ [16]	$C_2H_2Cl_2^+$ [9] $C_2HCl_2^+$ [4] $C_2H_2Cl^+$ [66] C_2HCl^+ [21]
Ar^+ [15.76]	1.5 [1.8] 83%	1.5 [2.2] 68%	1.1 [1.3] 85%	$C_2H_2Cl^+$ [84] C_2HCl^+ [16]	$C_2H_2Cl_2^+$ [4] $C_2HCl_2^+$ [4] $C_2H_2Cl^+$ [75] C_2HCl^+ [17]	$C_2H_2Cl_2^+$ [5] $C_2HCl_2^+$ [7] $C_2H_2Cl^+$ [66] C_2HCl^+ [22]

[a] The values in squared brackets in columns 2−4 are the calculated rate coefficients. The values in squared brackets in columns 5−7 are percentage branching ratios.

formation of a transitional collision complex, the internal dynamics of such a complex can be responsible for the rate-determining steps.

For ions with $RE_{ion} < IE(C_2H_2Cl_2)$, long-range charge transfer cannot occur, and reactions can only proceed via a short-range encounter. For these ions variations in the efficiency of the reactions are larger than for ions with higher RE. The most prominent example of short-range effects in the reactions of different isomers is their reaction with H_3O^+. The rate coefficient for 1,1-$C_2H_2Cl_2$ is equal to the collisional value, while the *cis*-1,2- and *trans*-1,2-isomers react ca. 5 and 7 times slower with efficiencies of only 14% and 18%, respectively. Reactions of the $C_2H_2Cl_2$ isomers with CF_3^+ have a moderate efficiency between 56% and 80%; reactions with CF^+ are faster with a greater efficiency of 83−100%. NH_4^+ and SF_3^+ do not react with dichloroethene at a measurable rate in our apparatus, although a small amount of the association product was observed for the latter reaction with very high concentrations of $C_2H_2Cl_2$.

3.2. Branching Ratios. The product cations and their branching ratios for reactions of different isomers of $C_2H_2Cl_2$ are given in column 3 of Tables 1−3. The proposed neutral products (column 4) are the species giving the lowest values for the enthalpy of reaction at 298 K, $\Delta_r H^0_{298}$ (column 5), which are chemically reasonable. For some product cations, multiple possibilities for neutral partners are shown. First, we compare the product branching ratios for the reactions of the three isomers of $C_2H_2Cl_2$ with cations whose RE values are lower than the IE of the isomers. Second, we compare product branching ratios for ions with RE greater than the IE of the three isomers. Data on reactions showing significant isomeric effects have been extracted from Tables 1−3 and are summarized in Table 4.

3.2.1. Ions with REs Less than 10 eV. The ions with RE values less than the IE ($C_2H_2Cl_2$) for which reaction is observed are H_3O^+, CF_3^+, CF^+, and SF_5^+. The first three ions show the greatest isomeric effects. The reaction of H_3O^+ with 1,1-$C_2H_2Cl_2$ proceeds only via nondissociative proton transfer, whereas this channel is one of three products for both 1,2-isomers (Table 4). Thus, the proton affinity (PA) of all isomers exceeds that of H_2O, and we determine upper limits of 808, 837, and 834 kJ mol^{-1} for $\Delta_f H^0_{298}$ of 1,1-, *cis*-1,2, and *trans*-1,2-$C_2H_2Cl_2H^+$, respectively. In the reaction of H_3O^+ with the two 1,2-isomers, the other products are $C_2HClH_3O^+$ and the adduct $C_2H_2Cl_2{\cdot}H_3O^+$. The latter is formed with a very small branching ratio. The most feasible neutral companion for the former product is HCl, giving an upper limit for $\Delta_f H^0_{298}$ of $C_2HClH_3O^+$ to be 688 and 685 kJ mol^{-1} from the reactions with the *cis*-1,2- and *trans*-1,2-isomers, respectively. Although the PAs of $C_2H_2Cl_2$ isomers are not known, from our measurements with NH_4^+ and H_3O^+ we conclude that $696 < PA(C_2H_2Cl_2) < 854$ kJ mol^{-1}.

The most dramatic difference in the behavior of 1,1- and 1,2-isomers of dichloroethene is found in the reaction involving CF_3^+. For 1,1-$C_2H_2Cl_2$ the reaction proceeds via a single channel with Cl^- abstraction from the dichloroethene, with the most feasible neutral product assumed to be CF_3Cl:

$$CF_3^+ + C_2H_2Cl_2 \rightarrow C_2H_2Cl^+ + CF_3Cl \qquad (I)$$

For both 1,2-isomers, the reaction products are different:

$$CF_3^+ + C_2H_2Cl_2 \rightarrow CHCl_2^+ + C_2HF_3 \qquad (II)$$

Whereas reaction I involves the simple mechanism of Cl^-

transfer, reaction II requires cleavage of the C═C double bond in dichloroethene and transfer of a chlorine atom from one carbon to the other. This reaction would be highly endothermic if a new C═C double bond did not exist in the neutral product. Assuming production of C_2HF_3, thermochemistry predicts a slightly endothermic reaction with $\Delta_rH^0_{298}$ values of +3 and +5 kJ mol^{-1} for the *cis*-1,2- and *trans*-1,2-isomers, respectively. However, the uncertainty in the value of $\Delta_fH^0_{298}$ (C_2HF_3) is ±8 kJ mol^{-1},[39] and reaction II is observed with high efficiency, 56−70%. Therefore, this reaction is probably exothermic. We cannot exclude the possibility, however, that some CF_3^+ ions in the flow tube were vibrationally excited and facilitated the production of C_2HF_3.

A breaking of the C═C double bond in dichloroethene and formation of $CHCl_2^+$ also takes place in the reactions of CF^+ with all isomers of $C_2H_2Cl_2$, but here it is not the only ionic product. Only a small branching ratio of $CHCl_2^+$ (6%) is detected from the reaction with the 1,1-isomer, and the main product is $C_2H_2Cl^+$ with a branching ratio of 69%. For reactions with both 1,2-isomers $C_2H_2Cl^+$ is not produced, while larger branching ratios of $CHCl_2^+$, 41% and 51%, are observed for the reactions of *cis*-1,2- and *trans*-1,2-isomers, respectively. Another ionic product from the reactions of the 1,2-isomers with CF^+ is $CClFH^+$ (59% for the *cis*-1,2- and 49% for the *trans*-1,2-isomer). We have also observed trace amounts of parent ion $C_2H_2Cl_2^+$, not shown in Tables 1−3, for each isomer in the reaction with CF^+. This charge-transfer reaction should be energetically forbidden because the RE of CF^+, 9.11 eV, is less than the IE of all isomers of $C_2H_2Cl_2$. The effect may be due to the presence of a small amount of excited CF^+ ions and/or other ions with higher RE, e.g., CF_2^+, in the flow tube; CF^+, which could not be produced in sufficient quantities directly from the ion source, was produced by CID of CF_2^+, a small amount of which remained in the helium flow (less than a few percent of the CF^+ intensity).

The last in the series of ions, SF_5^+, has an RE value close to that of the IE ($C_2H_2Cl_2$). The IE of the SF_5 radical has been the subject of much controversy, with literature values in the broad range of 9.2−10.0 eV. Using experimental values for the enthalpy of formation of neutral and cation of −915 and +29 kJ mol^{-1}, respectively,[44,46] we use an RE value for SF_5^+ of 9.78 eV. This value is slightly greater than the IE of the two 1,2-isomers of $C_2H_2Cl_2$ (9.65 eV), while within experimental error the same as the IE of the 1,1-isomer (9.83 eV). It explains why $C_2H_2Cl_2^+$ can be observed as a charge-transfer product, with branching ratios of 16%, 14%, and 16% for the 1,1-, *cis*-1,2-, and *trans*-1,2-isomers, respectively. We note, however, that the presence of vibrationally excited precursor ions can also give rise to the charge-transfer product. Other products formed from the SF_5^+ reactions are $C_2H_2Cl_2F^+$ (by F^+ transfer), ca. 70%, and $C_2H_2Cl^+$ (by Cl^- abstraction), ca. 15%. The neutral partners are assumed to be SF_4 and SF_5Cl, respectively. The branching ratios of these products are similar for all three isomers of $C_2H_2Cl_2$.

3.2.2. Ions with REs Greater than 10 eV. The second group of reactant cations have RE values significantly greater than the IE values of the dichloroethene isomers. SF_4^+ (RE = 11.99 eV) provides a special case in that no measurements of branching ratios from the reaction of $C_2H_2Cl_2$ with this ion were possible. The reason for this is that SF_4^+ cannot be produced in the ion source. The major fragment in the ion source resulting from electron impact on SF_6 was SF_5^+. While a large signal of SF_5^+ could be obtained, a small amount of SF_4^+, ca. 2%, was always produced by CID of SF_5^+ at the entrance to the flow tube. At such a low percentage, this ion will have a negligible effect on the branching ratios we quote for the SF_5^+ reactions. The SF_4^+ signal was of sufficient intensity to provide rate coefficients, but not branching ratios, given in Tables 1−3.

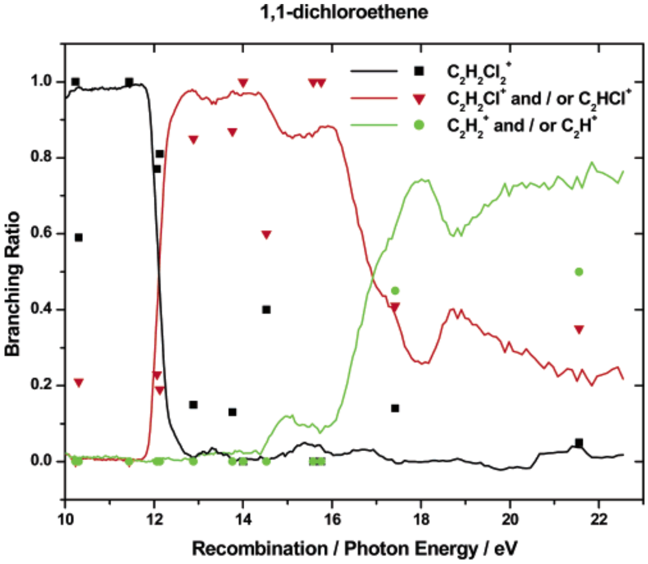


Figure 1. Comparison of the ionic products from ion−molecule studies of 1,1- $C_2H_2Cl_2$ with TPEPICO photoionization branching ratios over the energy range of 10−23 eV.

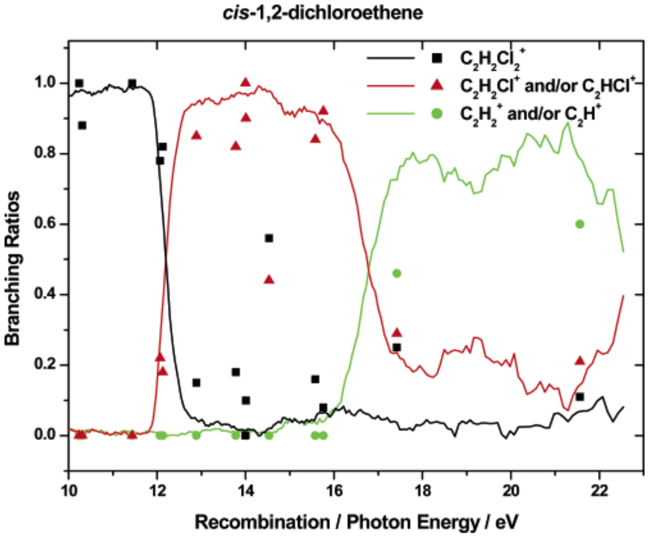


Figure 2. Comparison of the ionic products from ion−molecule studies of *cis*-1,2-$C_2H_2Cl_2$ with TPEPICO photoionization branching ratios over the energy range of 10−23 eV.

Given that charge-transfer reaction is now energetically possible, we present the results of these reactions by comparison of product branching ratios with photon-induced TPEPICO data on fragmentation of photoionized 1,1-, *cis*-1,2-, and *trans*-1,2-$C_2H_2Cl_2$. Figures 1−3 show branching ratios from both experiments versus photon energy (TPEPICO) or RE of the ion (SIFT). The former appear as continuous graphs, the latter as data points at defined values of the RE$_{ion}$. The ionic products from the TPEPICO spectra over the photon range of 10−23 eV are $C_2H_2Cl_2^+$, $C_2H_2Cl^+$, and $C_2H_2^+$ for all three isomers. We measured the branching ratios with a higher mass resolution at several selected photon energies within this range and did not observe $C_2HCl_2^+$, C_2HCl^+, or C_2H^+. However, we cannot completely exclude the possibility that a small fraction of these ions could be present at other photon energies. To make an appro-

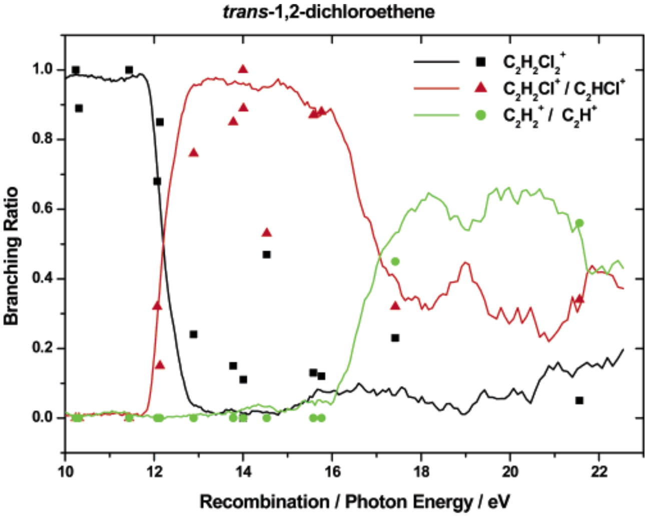


Figure 3. Comparison of the ionic products from ion−molecule studies of *trans*-1,2-$C_2H_2Cl_2$ with TPEPICO photoionization branching ratios over the energy range of 10−23 eV.

priate comparison with branching ratios from the SIFT data, the sum of the branching ratios of $C_2H_2Cl_2^+$ and $C_2HCl_2^+$, and of $C_2H_2Cl^+$ and C_2HCl^+ from the SIFT experiment are plotted in Figures 1−3.

The appearance of new fragmentation channels in the TPEPICO experiment can be observed as the photon energy increases. At an energy of ca. 12 eV there is a switch in the major product channel from $C_2H_2Cl_2^+$ to $C_2H_2Cl^+$. Another less sharp change in the product branching ratios takes place between 16 and 18 eV, where $C_2H_2^+$ starts to appear. No significant differences between the branching ratios as a function of photon energy can be observed for the different isomers of $C_2H_2Cl_2$. The small differences for energies larger than 18 eV are probably due to the low signal-to-noise ratio of the spectra in this range. In general, the product branching ratios from the two experiments are fairly similar. As explained earlier, this is the expected result if long-range charge transfer is the dominant reaction mechanism for the ions with $RE_{ion} > IE(C_2H_2Cl_2)$. However, there are some significant differences between data from these two experiments which we now highlight. These differences arise from chemical reactions, the breaking and making of bonds following formation of an ion−molecule complex.

For reactions of SF^+ (RE = 10.31 eV), there are small branching ratios for production of $C_2H_2ClSF^+$ and C_2HClSF^+ for all three isomers. $C_2H_2Cl^+$ (21%) is observed only for the reaction with the 1,1-isomer, and we note that this ion is not observed at a photon energy of 10.31 eV in any of the TPEPICO spectra. The branching ratio for parent ion production is significantly less for the 1,1-isomer (59%) than for either of the 1,2-isomers (88%). Thus, the evidence shows that, despite having an RE at least 0.5 eV greater than the IE of all isomers of $C_2H_2Cl_2$, the reactions of SF^+ are not exclusively dominated by long-range charge transfer, but a short-range mechanism contributes to a significant extent. For reactions of SF_2^+, CF_2^+, O_2^+, and Xe^+ (RE spanning 10.24−12.13 eV), the product branching ratios agree reasonably well with the TPEPICO branching ratios; $C_2H_2Cl_2^+$ is the major product, and long-range charge transfer is probably dominant. For ions with RE spanning 12.89−15.76 eV, the major product is $C_2H_2Cl^+$. For most ions there is good agreement between the product branching ratios from the two experiments, with the exception of N^+ (RE = 14.53 eV), where the yield of this ion is ca. 50% lower than from the TPEPICO experiment and the parent ion is correspondingly higher. We note, however, that our branching ratios for the N^+ reaction agree well with the earlier data of Rebrion et al.[10] We note also the significant difference in the parent ion branching ratio for the reaction of the 1,2-isomer of $C_2H_2Cl_2$ with Kr^+ (RE = 14.00 eV) and CO^+ (RE = 14.01 eV), values taking 0% and 10%, respectively. For reactions of F^+ and Ne^+, $C_2H_2^+$ is the strongest product ion with a branching ratio of ca. 45−60%. The agreement of the branching ratios for F^+ (RE = 17.42 eV) is poor. In particular, the parent ion, $C_2H_2Cl_2^+$, is observed at ca. 15−25% for all isomers reacting with F^+, whereas this ion is absent at $h\nu = 17.42$ eV in the TPEPICO spectra. For Ne^+ (RE = 21.56 eV), the agreement between branching ratios is good for the two 1,2-isomers but poor for the 1,1-isomer. In general, we note that the intensity of the parent ion is greater in the SIFT experiment for ions with RE > 13 eV than for photon energies over this same range.

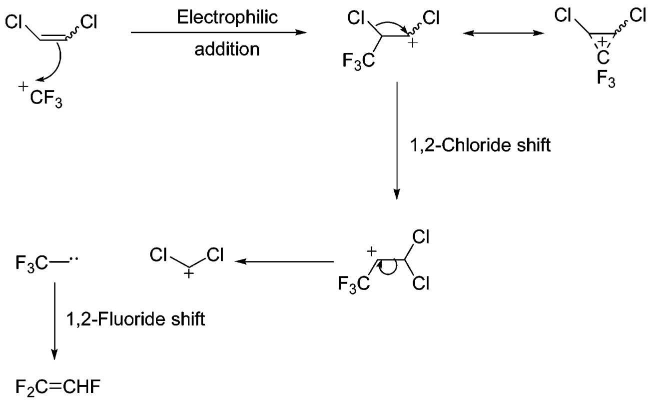
In contrast to the reactions of H_3O^+, CF_3^+, and CF^+, where the $RE_{ion} < IE(C_2H_2Cl_2)$, the influence of isomeric structure of $C_2H_2Cl_2$ on the reaction pathways does not appear so pronounced for ions with $RE > IE(C_2H_2Cl_2)$. For ion REs spanning 10−13 eV the branching ratios are similar for all three isomers and suggest similar reaction routes. However, some products only form in reactions with either 1,1- or 1,2-isomers. For example, $CHCl_2^+$ (4%) and $C_2H_2Cl^+$ (21%) are only formed from the reaction of SF^+ with the 1,1-isomer. Likewise, CCl^+ (4%) only forms from the reaction of the 1,1-isomer with Ne^+. C_2HCl^+ only forms in the reaction of CO_2^+ with either 1,2-isomer. Likewise, $C_2H_2Cl_2^+$ and C_2HCl^+ are only formed from the reaction of the 1,2-isomers with CO^+, and $C_2H_2Cl_2^+$ and $C_2HCl_2^+$ only from the reactions with N_2^+ and Ar^+.

4. Discussion

A major aim of this study is to investigate the effects of isomeric structure on the reaction dynamics and kinetics of ion−molecule reactions. The reactions of $C_2H_2Cl_2$ which show the most significant isomeric effects are those with H_3O^+, CF_3^+, and CF^+, and the predominant difference is between the 1,1- and 1,2-isomers. We shall therefore discuss these reactions first. These ions have REs below the barrier to charge transfer; thus, only chemical reactions with $C_2H_2Cl_2$ are possible. This means that a collision ion−molecule complex must form. We can therefore expect that the various reaction pathways will depend on the details of the potential energy surfaces associated with this complex, which in turn depends on the properties of the $C_2H_2Cl_2$ isomer and the reagent ion. It is not only the reaction pathways which show isomeric effects. Differences are also observed in the reaction rate coefficients.

In terms of reaction efficiencies, the most noticeable effects involve the reactions with protonated water. H_3O^+ reacts with the 1,1-isomer with unit efficiency producing $C_2H_2Cl_2H^+$ (100%), whereas its reaction with either 1,2-isomer is substantially less efficient. For these 1,2-isomers three types of reaction occur, namely, proton transfer, hydrogen halide ejection, and association. The observation that nondissociative proton transfer occurs for reactions of H_3O^+ with all three isomers implies that the PAs of these isomers are greater than that of H_2O but not so great that sufficient energy is liberated to promote fragmentation of the protonated molecule. Although proton transfer from H_3O^+ to the 1,2-isomers must be exothermic, the small rate coefficients imply that the presence of atomic hydrogen on either side of the C═C double bond results in a potential energy barrier to reaction. This not only reduces the efficiency of the reaction but also allows the reagent ion to sample other potential energy pathways which can result in the formation of different products, e.g., $C_2H_2Cl{\cdot}H_2O^+ + HCl$. We have attempted to repeat these experiments with D_3O^+ to determine which hydrogen atom takes part in HCl elimination. The results were inconclusive due to rapid interchange between H^+ and D^+ in the reagent ion. When the bimolecular reaction pathways are inefficient, it is not unusual to observe association products, i.e., the ion–molecule complex will be stabilized and cooled by collisions with He in the flow tube. The complex will then have insufficient internal energy to overcome the barrier for further reaction. We observe such an association complex only for the two 1,2-isomers. No attempt has been made to investigate the dependence of the association rate on the helium pressure. Hence, the rate coefficients presented for the 1,2-isomers represent an effective two-body value. Interestingly, in the reactions of C_2HCl_3 and C_2Cl_4 with H_3O^+, the main ionic products are protonated parent ions for both chloroethenes, but only 5% of $C_2Cl_3^+$ formed in the case of C_2Cl_4.[48] The reaction of C_2HCl_3 proceeds at almost the collisional rate, while it is 3 times slower than the collisional rate for C_2Cl_4. It is difficult to correlate such variations of the rate coefficient either with the total number of chlorine atoms in the polychloroethene or with the number of geminal chlorine atoms in it.

The reactions with CF_3^+ are fairly efficient, but all are below the collisional expectation (56–80%), and only one product ion is observed for each isomer. It is well-known that reactions between alkenes and cations preferentially occur via electrophilic attack on the π orbital of the C=C double bond.[49] This is our starting assumption to interpret these reactions. For the 1,2-isomers, the products are $CHCl_2^+$ and C_2HF_3. This result implies that Cl atom transfer from carbon atom 1 to carbon atom 2, the cleavage of the C=C double bond, and the formation of a new C=C bond in C_2HF_3 involves no barrier:



However, to form the same products from the 1,1-isomer, H atom transfers from carbon atom 2 to carbon atom 1, and a similar formation of a new C=C double bond, would be needed. It appears that this latter process involves an energy barrier and is not observed. For the 1,1-isomer, the products are completely different, $C_2H_2Cl^+$ and CF_3Cl, formed by simple Cl^- transfer. The reasons why this reaction is not observed for either 1,2-isomer are not clear. We comment that the presence of two chlorine atoms at the same end of $C_2H_2Cl_2$ molecule, as it is the case for the 1,1-isomer, appears to make Cl^- abstraction facile. We are attempting to explain this dramatic isomeric effect using ab initio methods.

For reactions of CF^+, the products $CHCl_2^+$ and C_2HF are observed for all three isomers but with much higher branching ratios for the two 1,2-isomers. We assume that this reaction follows similar mechanisms described above for CF_3^+. The dominant product from the 1,1-isomer is $C_2H_2Cl^+$ caused by Cl^- transfer, but this product is not observed for either 1,2-isomer. The reaction of CF^+ with all three isomers also results in the product ion $CClFH^+$ and, presumably, the corresponding neutral C_2HCl. This product has no direct analogue in the reactions of CF_3^+.

The RE of SF_5^+, 9.78 eV, lies very close to the IE of all isomers of $C_2H_2Cl_2$. The main products are formed by F^+ transfer, Cl^- abstraction, and charge transfer. Being closed shell, SF_5^+ also exhibits low reaction rates with all three $C_2H_2Cl_2$ isomers, and an intermediate complex is probably formed. SF_5^+ shows only small isomeric effects with $C_2H_2Cl_2$, with similar branching ratios being observed in the reactions of all its isomers. This similarity can be a result of the high symmetry of SF_5^+ and the large number of fluorine atoms available for reaction in the transition complex.

For ions with RE > IE($C_2H_2Cl_2$), charge transfer is expected to take place. If it proceeds via the long-range mechanism, ionization of $C_2H_2Cl_2$ will occur to a particular vibronic level with vertical IE equal to the RE_{ion}. The final products of the reaction will depend on the dissociation properties of the vibronic state of $C_2H_2Cl_2^+$, and TPEPICO data can provide this information. With the exception of reactions of SF^+ (RE = 10.31 eV), the reactions of ions with RE < 13 eV have branching ratios similar for all three $C_2H_2Cl_2$ isomers. The ionizing energy between 10 and 13 eV corresponds to formation of the $\tilde{X}$, $\tilde{A}$, $\tilde{B}$, and $\tilde{C}$ electronic states of $C_2H_2Cl_2^+$.[24–27] The character of these states is similar for all isomers of $C_2H_2Cl_2$, and the similarity between the branching ratios for different isomers in this energy range indicates domination of the long-range mechanism.

In the range of ca. 13–16 eV, the main product from the ion–molecule reactions is $C_2H_2Cl^+$. This ion can form by dissociation of an excited vibronic state of $C_2H_2Cl_2^+$ which has been produced by long-range charge transfer. With the exception of N^+ (RE = 14.53 eV), there is relatively good agreement between the TPEPICO and SIFT branching ratios over this energy range, which suggests that this indeed is the mechanism for production of $C_2H_2Cl^+$. Dissociative charge transfer is the only mechanism for the production of this ion in reactions with rare gas ions. However, for more chemical atomic and molecular ions, $C_2H_2Cl^+$ can also form by Cl^- transfer within a transitional collision complex. Thermochemical analysis predicts that for CO^+, N^+, and F^+, the production of $C_2H_2Cl^+$ together with COCl, NCl, and FCl, respectively, makes these reactions more exothermic than the products of dissociative charge transfer (Tables 1–3). The same point can also be made for the reaction with N_2O^+. This possibility does not mean that a long-range charge transfer does not occur for these ions but that the alternative short-range mechanism of Cl^- abstraction from dichloroethene can also play a significant role.

For most ions with RE > 12.5 eV, the yield of the parent ion $C_2H_2Cl_2^+$ from the ion–molecule reaction exceeds that from TPEPICO measurements. This effect is more pronounced for the two 1,2-isomers. The percentage yield of parent ion, ca. 15%, can result from thermal stabilization of $C_2H_2Cl_2^+$ by collisions with helium buffer gas in the flow tube. This effect, however, cannot explain the very large yield of $C_2H_2Cl_2^+$, 40–56%, for the N^+ reactions. Such a large difference between TPEPICO and SIFT branching ratios indicates that the long-range charge-transfer mechanism is not favored in this reaction. Our results are in agreement with those of Rebrion et al. for this reaction,[10] and we note that the nondissociative charge-transfer products with high branching ratios of 25% were also observed in the reaction of N^+ with C_2H_4 (IE = 10.51 eV) in a SIFT.[50] Both theory[49] and molecular beam studies[51] indicated that the major products should be $C_2H_3^+$ and NH, and the yield of parent ion should be zero. We note that a relatively high percentage yield of the charge-transfer ions reported in such SIFT measurements can result from collisional cooling, if the transitional collision complex has a sufficiently long lifetime.

For some ions in the range of 13−16 eV, namely, CO_2^+, CO^+, N_2^+, and Ar^+, more exit channels are observed from the reactions with either 1,2-isomer than the 1,1-isomer of $C_2H_2Cl_2$. If reaction for these ions proceeds via the long-range mechanism, then this difference in reaction pathways should be attributed to the different characters of the corresponding excited states of the isomers of $C_2H_2Cl_2^+$. The characters of the relevant excited states of $C_2H_2Cl_2^+$, i.e., the $\tilde{D}$, $\tilde{E}$, $\tilde{F}$, and $\tilde{G}$ states, have been studied by ab initio methods at the restricted Hartree−Fock/6-31++G** level of theory by Leung and coworkers.[25−27] At this level of theory, isomeric differences in electronic structure could be found only for the $\tilde{F}$ and $\tilde{G}$ states, which correspond to vertical IEs above 15.7 eV. Therefore, only in the charge-transfer reaction with Ar^+ (RE = 15.76 eV) should the isomer-specific character of the relevant ($\tilde{F}$) electronic state of $C_2H_2Cl_2^+$ make any difference to the reaction pathways. Indeed, such differences in the product branching ratios do exist for the reaction of Ar^+ with the three isomers of $C_2H_2Cl_2$ (Table 4). However, these effects are not observed in the TPEPICO branching ratios in the range of 13−16 eV. We conclude that the reactions of CO_2^+, CO^+, N_2^+, and Ar^+ do not proceed by long-range charge transfer but via an intermediate complex. Interestingly, there is no significant difference in branching ratios for the reactions of N^+ with different isomers of $C_2H_2Cl_2$, although differences from the TPEPICO branching ratios imply a close-range reaction. We believe, therefore, that the collision complex between N^+ and $C_2H_2Cl_2$ has a similar character for all three isomers.

Within the accuracy of our experiment, the isomeric effects in $C_2H_2Cl_2$ are small for reactions with Kr^+ (RE = 14.00 eV), F^+ (17.42 eV), and Ne^+ (21.56 eV), and the branching ratios are not too dissimilar to those from the TPEPICO studies. These results imply that these reactions probably occur by long-range charge transfer. At energies of 17.4 and 21.6 eV, the ab initio calculations predict slightly different character for the corresponding electronic states of the isomers of $C_2H_2Cl_2^+$,[25−27] with a stronger s-type component in the "ionized" molecular orbital of the 1,1-isomer and a stronger p-type component for the 1,2-isomers. However, for photon energies >18 eV, ionization processes involve inner-valence orbitals of $C_2H_2Cl_2$, and many-body features are observed in both photoelectron and ionization (e, 2e) spectra.[25−27] Because several molecular orbitals are involved in ionization processes, the higher-lying electronic states of $C_2H_2Cl_2^+$ isomers should be mixed and hence have similar character. The dissociation pathways from these states, as our TPEPICO data demonstrate, should then show only small isomeric effects.

5. Concluding Remarks

There are compelling reasons to study the ion chemistry of chlorocarbons, one reason being the trace gas analysis of these molecules in the atmosphere, and another one being the chemistry of industrial plasmas. When the chlorocarbon has structural isomers, the chemistry of ion−molecule reactions can be strongly affected by their isomeric form. In this paper we have presented a detailed study of the reactions of several monatomic and molecular cations with 1,1-, *cis*-1,2-, and *trans*-1,2-$C_2H_2Cl_2$. Most of these reactions have not been studied before. Strong isomeric effects have been found in the product branching ratios for reactions with H_3O^+, CF_3^+, and CF^+, where ion REs are below the barrier to the charge-transfer reaction. The H_3O^+ reaction proceeds at the collisional rate for 1,1-$C_2H_2Cl_2$, while it is much slower for *cis*-1,2- and *trans*-1,2-$C_2H_2Cl_2$. The product ions from H_3O^+ reactions with 1,1- and 1,2-isomers are also different. This finding is of interest to the application of proton-transfer reaction mass spectrometry to trace gas analysis. We also comment that the CF_3^+ ion can be used as a probe ion for distinguishing between the 1,1- and 1,2-isomers of dichloroethene. The reactions with this ion proceed with 56−80% efficiency, the only ionic product for 1,1-$C_2H_2Cl_2$ being $C_2H_2Cl^+$, while the only ionic product for the 1,2-isomers is $CHCl_2^+$.

Smaller isomeric effects resulting in the appearance of different products have been found in the reactions of SF^+, CO_2^+, CO^+, N_2^+, and Ar^+. These reactions take place above the barrier to charge transfer. As for ions with lower RE, the differences have been found between the reactions of the 1,1- and 1,2-isomers, while the difference between *cis*-1,2- and *trans*-1,2-$C_2H_2Cl_2$ reactions is not significant. The same products of photoionization have been observed for all three isomers of dichloroethene in TPEPICO measurements, with only small differences in the branching ratios. We propose that these reactions with SF^+, CO_2^+, CO^+, N_2^+, and Ar^+ proceed via formation of an intimate collision complex. This conclusion does not mean that long-range charge transfer does not occur at all for these ions, but competition between the two mechanisms occurs.

Finally, our work has demonstrated the importance to acknowledge and study isomeric effects in ion−molecule reactions. The most profound influence of the isomeric structure can be expected in reactions of ions with REs below the barrier to charge transfer. In this case, the reaction can proceed only via formation of a transitional collision complex between the ion and the molecule. However, some isomeric effects may also take place above the barrier to charge transfer if formation of the collision complex can compete with long-range charge transfer. We plan to extend this study not only with other neutral isomers, but also with different isomeric forms of molecular ions.

Acknowledgment. We thank Dr. Chris Howle and Mr. Sahanghir Ali for help with collection of data and Drs. Liam Cox and John Snaith for discussions about electrophilic attack. We are grateful to EPSRC for Grants (GR/M42974 and GR/S21557) and for the help of the staff of the Daresbury Laboratory, especially Dr. Andrew Malins. Michael Parkes wishes to thank the University of Birmingham for a Studentship.

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