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V. Mikhailov, M.A. Parkes, R.P. Tuckett and C.A. Mayhew *

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Isomeric effects in the gas-phase reactions of dichloroethene, $C_2H_2Cl_2$, with a series of cations

Victor A. Mikhailov,¹ Michael A. Parkes,² Richard P. Tuckett,² and Chris A. Mayhew^{*1}

¹School of Physics and Astronomy and ²School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

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*Corresponding author: E-mail : c.mayhew@bham.ac.uk. Tel. : 0044 121 414 4592. Fax : 0044 121 414 4577

Abstract : 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- $\text{C}_2\text{H}_2\text{Cl}_2$, *cis*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$ and *trans*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$ is reported. The recombination energy of these ions spans the range 4.7–21.6 eV. Reaction rate coefficients and product branching ratios have been measured at 298 K in a selected ion flow tube. Collisional rate coefficients are calculated by modified average dipole orientation 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 $\text{C}_2\text{H}_2\text{Cl}_2$ with photon energies in the range 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- $\text{C}_2\text{H}_2\text{Cl}_2$ the reaction with H_3O^+ proceeds at the collisional rate with the only ionic product being 1,1- $\text{C}_2\text{H}_2\text{Cl}_2\text{H}^+$. However, the same reaction yields two more ionic products in the case of *cis*-1,2- and *trans*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$, 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- $\text{C}_2\text{H}_2\text{Cl}_2$ being $\text{C}_2\text{H}_2\text{Cl}^+$ 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- $\text{C}_2\text{H}_2\text{Cl}_2$ isomers, have been found in the reactions of SF^+ , CO_2^+ , CO^+ , N_2^+ , and Ar^+ . Although these five ions have recombination energies above the ionization energy of any of the $\text{C}_2\text{H}_2\text{Cl}_2$ 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 $\text{C}_2\text{H}_2\text{Cl}_2$ is responsible for the observed effects.

Keywords: Ion-Molecule Reactions, Selected Ion Flow Tube, TPEPICO, Charge Transfer

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-C₂H₂Cl₂, *cis*-1,2-C₂H₂Cl₂ and *trans*-1,2-C₂H₂Cl₂.¹

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-C₂H₂Cl₂ are C₂H₂Cl(OH) + Cl, whilst for 1,1-C₂H₂Cl₂ the dominant product is the adduct C(OH)H₂CCl₂. The difference in behaviour of the isomers was explained by the existence of a barrier to the addition of OH to the chlorine-containing carbon of 1,1-C₂H₂Cl₂.² 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 NO₃ radical with polychlorinated ethenes predicted that for the 1,2-C₂H₂Cl₂ isomers one of the possible pathways leads to the production of acid chlorides, whereas the 1,1-C₂H₂Cl₂ 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 spectrometer.⁹ The reaction proceeded *via* charge (electron) transfer for all three isomers. Rebrion *et al.*¹⁰ investigated the reactions of N⁺ and H₃⁺ with the isomers of dichloroethene. For N⁺ the reactions proceeded *via* charge transfer, H₃⁺ 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 (O₂⁻, O⁻, OH⁻, CF₃⁻ and F⁻) and dichloroethene isomers have been investigated in our recent study.¹ A striking feature of these reactions is that the vinyl anion, C₂HCl₂⁻ is observed only for *trans*-1,2-C₂H₂Cl₂ where it is the major product, whilst Cl⁻ is 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-C₂H₂Cl₂. 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 ionised isomers and neutral molecules. Of relevance to our study is the work of Nixdorf and Grützmacher¹² 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 ionisation energy 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 (RE) spanning 4.73 eV to 21.56 eV ; namely, and in order of increasing recombination energy, 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 sub-divide into two categories: those with RE values less than, and those with RE values greater than the adiabatic ionisation energies (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 a non-zero energy resonance connecting BC to an electronic state of BC^+ at the RE of A^+ , and 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 wavefunction 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 photoionisation 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 unfavourable, 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 ionised molecule $(BC^+)^*$, where * denotes 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-ultraviolet 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 ionised 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 ionising energy 10–23 eV.

2. Experiment

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 ionisation 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 SF₆, for CF_n⁺, n=1-3, and F⁺ it was CF₄. 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 1 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 SF₄⁺ resulting from CID from SF₅⁺, 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 vapours 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 *vs.* 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 cm³ molecule⁻¹ s⁻¹. Branching ratios were derived from plots of the signals of the different product ions *vs.* 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 analyser and the time-of-flight 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 ionisation process to be detected in coincidence.

Different spectra can be recorded with the TPEPICO apparatus. At the start of measurements, the threshold photoelectron spectrum (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 3-dimensional map of coincidence counts *vs.* ion time of flight *vs.* photon energy. Sections from this map yield either the time-of-flight 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 *vs.* photon energy can be used to obtain the appearance energies, AE_{298} , of the photofragment.³¹ Appearance energies for fragment ions from vacuum-ultraviolet photodissociation of the three dichloroethene isomers have been converted to upper limits for the enthalpies of the appropriate reaction, $\Delta_r H^{\circ}_{298}$, using the procedure described by Traeger and McLoughlin.³² These values of $\Delta_r H^{\circ}_{298}$ can then be used to calculate an upper limit for the enthalpy of formation of the fragment ions, $\Delta_f H^{\circ}_{298}$.^{14,31} Thus, we have determined an upper limit for $\Delta_f H^{\circ}_{298}$ 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 analyse 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 $\nu=1$ vibrational state (0.27 eV above the ground level), whilst 20 % of O_2^+ are found in the $\nu=1$ 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 non-zero 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 polarisabilities of 1,1-, *cis*-1,2-, and *trans*-1,2-dichloroethenes used in the calculations are 7.83, 8.15, and $8.03 \times 10^{-30} \text{ m}^3$, 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 polarisabilities, 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: $k_c(\textit{cis}\text{-}1,2) > k_c(1,1) > k_c(\textit{trans}\text{-}1,2)$.

In general, the efficiency of the reaction, defined as $(k_{\text{exp}} / k_c) \times 100 \%$, is high for all ions with $\text{RE}_{\text{ion}} > \text{IE}(\text{C}_2\text{H}_2\text{Cl}_2)$, where $\text{IE}(\text{C}_2\text{H}_2\text{Cl}_2)$ is 9.65 eV for *cis*-1,2- and *trans*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$, and 9.83 eV for 1,1- $\text{C}_2\text{H}_2\text{Cl}_2$.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. Using 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 $\text{C}_2\text{H}_2\text{Cl}_2$. 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* formation of a transitional collision complex, the internal dynamics of such a complex can be responsible for the rate-determining steps.

For ions with $\text{RE}_{\text{ion}} < \text{IE}(\text{C}_2\text{H}_2\text{Cl}_2)$, 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- $\text{C}_2\text{H}_2\text{Cl}_2$ is equal to the collisional value, whilst the *cis*-1,2- and *trans*-1,2- isomers react *ca.* five and seven times slower with efficiencies of only 14% and 18%, respectively. Reactions of the $\text{C}_2\text{H}_2\text{Cl}_2$ 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 $\text{C}_2\text{H}_2\text{Cl}_2$.

3.2. Branching Ratios. The product cations and their branching ratios for reactions of different isomers of C₂H₂Cl₂ 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, $\Delta_r H^\circ_{298}$ (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 C₂H₂Cl₂ 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 summarised in Table 4.

3.2.1 Ions with recombination energies less than 10 eV. The ions with RE values less than the IE (C₂H₂Cl₂) for which reaction is observed are H₃O⁺, CF₃⁺, CF⁺ and SF₅⁺. The first three ions show the greatest isomeric effects. The reaction of H₃O⁺ with 1,1-C₂H₂Cl₂ proceeds only *via* non-dissociative proton transfer, whereas this channel is one of three products for both 1,2-isomers (Table 4). Thus, the proton affinity of all isomers exceeds that of H₂O, and we determine upper limits of 808, 837 and 834 kJ mol⁻¹ for $\Delta_r H^\circ_{298}$ of 1,1-, *cis*-1,2 and *trans*-1,2-C₂H₂Cl₂H⁺, respectively. In the reaction of H₃O⁺ with the two 1,2-isomers, the other products are C₂HClH₃O⁺ and the adduct C₂H₂Cl₂·H₃O⁺. 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 $\Delta_r H^\circ_{298}$ of C₂HClH₃O⁺ to be 688 and 685 kJ mol⁻¹ from the reactions with the *cis*-1,2- and *trans*-1,2- isomers, respectively. Although the proton affinities (PA) of C₂H₂Cl₂ isomers are not known, from our measurements with NH₄⁺ and H₃O⁺ we conclude that 696 < PA (C₂H₂Cl₂) < 854 kJ mol⁻¹.

The most dramatic difference in the behaviour of 1,1- and 1,2-isomers of dichloroethene is found in the reaction involving CF₃⁺. For 1,1-C₂H₂Cl₂ the reaction proceeds *via* a single channel with Cl⁻ abstraction from the dichloroethene, with the most feasible neutral product assumed to be CF₃Cl :



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



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 C₂HF₃, thermochemistry predicts a slightly endothermic reaction with $\Delta_r H^\circ_{298}$ 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 $\Delta_f H^\circ_{298}(\text{C}_2\text{HF}_3)$ is $\pm 8 \text{ kJ mol}^{-1}$,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 $\text{C}_2\text{H}_2\text{Cl}_2$, 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 $\text{C}_2\text{H}_2\text{Cl}^+$ with a branching ratio of 69%. For reactions with both 1,2-isomers $\text{C}_2\text{H}_2\text{Cl}^+$ is not produced, whilst 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 *cis*-1,2- and 49% for *trans*-1,2- isomer). We have also observed trace amounts of parent ion $\text{C}_2\text{H}_2\text{Cl}_2^+$, 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 $\text{C}_2\text{H}_2\text{Cl}_2$. 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 ($\text{C}_2\text{H}_2\text{Cl}_2$). The ionisation energy of the SF_5 radical has been the subject of much controversy, with literature values in the broad range 9.2 to 10.0 eV. Using experimental values for the enthalpy of formation of neutral and cation of -915 and $+29 \text{ kJ mol}^{-1}$, respectively,^{46,44} 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 $\text{C}_2\text{H}_2\text{Cl}_2$ (9.65 eV), whilst within experimental error the same as the IE of the 1,1- isomer (9.83 eV). It explains why $\text{C}_2\text{H}_2\text{Cl}_2^+$ 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 $\text{C}_2\text{H}_2\text{Cl}_2\text{F}^+$ (by F^+ transfer), *ca.* 70%, and $\text{C}_2\text{H}_2\text{Cl}^+$ (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 $\text{C}_2\text{H}_2\text{Cl}_2$.

3.2.2 Ions with recombination energies 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 $\text{C}_2\text{H}_2\text{Cl}_2$ 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 SF₆ was SF₅⁺. Whilst a large signal of SF₅⁺ could be obtained, a small amount of SF₄⁺, *ca.* 2 %, was always produced by CID of SF₅⁺ 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 SF₅⁺ reactions. The SF₄⁺ signal was of sufficient intensity to provide rate coefficients, but not branching ratios, given in Tables 1-3.

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 photoionised 1,1-, *cis*-1,2- and *trans*-1,2-C₂H₂Cl₂. Figures 1-3 show branching ratios from both experiments *vs.* 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 10–23 eV are C₂H₂Cl₂⁺, C₂H₂Cl⁺ and C₂H₂⁺ 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 C₂HCl₂⁺, C₂HCl⁺, or C₂H⁺. However, we cannot completely exclude the possibility that a small fraction of these ions could be present at other photon energies. In order to make an appropriate comparison with branching ratios from the SIFT data, the sum of the branching ratios of C₂H₂Cl₂⁺ and C₂HCl₂⁺, and of C₂H₂Cl⁺ and C₂HCl⁺ 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 C₂H₂Cl₂⁺ to C₂H₂Cl⁺. Another less sharp change in the product branching ratios takes place between 16 and 18 eV, where C₂H₂⁺ starts to appear. No significant differences between the branching ratios as a function of photon energy can be observed for the different isomers of C₂H₂Cl₂. 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(C₂H₂Cl₂). 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 C₂H₂ClSF⁺ and C₂HClSF⁺ for all three isomers. C₂H₂Cl⁺ (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 C₂H₂Cl₂, 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; $\text{C}_2\text{H}_2\text{Cl}_2^+$ 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 $\text{C}_2\text{H}_2\text{Cl}^+$. 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 $\text{C}_2\text{H}_2\text{Cl}_2$ 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, $\text{C}_2\text{H}_2\text{Cl}_2^+$, 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 $\text{RE}_{\text{ion}} < \text{IE}(\text{C}_2\text{H}_2\text{Cl}_2)$, the influence of isomeric structure of $\text{C}_2\text{H}_2\text{Cl}_2$ on the reaction pathways does not appear so pronounced for ions with $\text{RE} > \text{IE}(\text{C}_2\text{H}_2\text{Cl}_2)$. For ion recombination energies 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 $\text{C}_2\text{H}_2\text{Cl}^+$ (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 with CO_2^+ with either 1,2- isomer. Likewise, $\text{C}_2\text{H}_2\text{Cl}_2^+$ and C_2HCl^+ are only formed from the reaction of the 1,2- isomers with CO^+ , and $\text{C}_2\text{H}_2\text{Cl}_2^+$ and C_2HCl_2^+ only from the reactions with N_2^+ and Ar^+ .

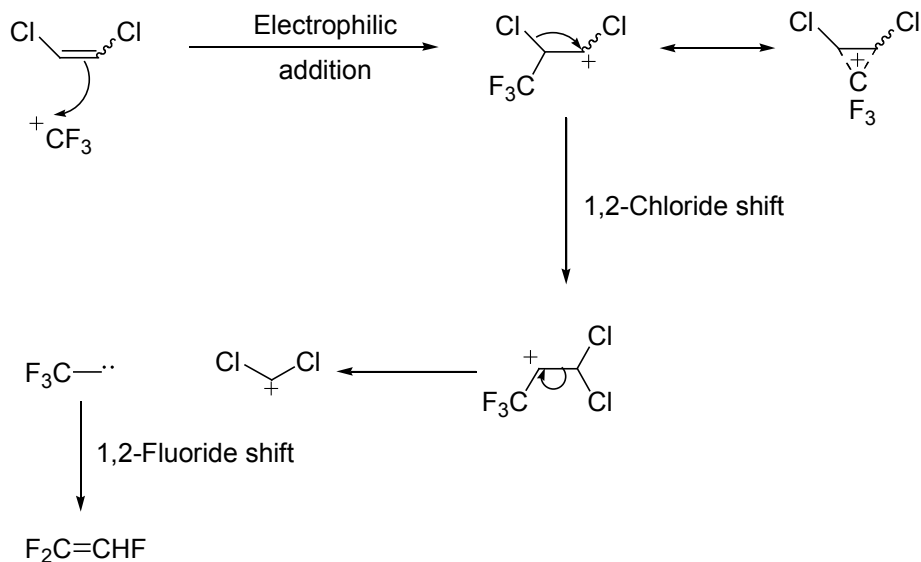
4. Discussion

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 $\text{C}_2\text{H}_2\text{Cl}_2$ 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 recombination energies below the barrier to charge transfer, thus only chemical reactions with $\text{C}_2\text{H}_2\text{Cl}_2$ 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 $\text{C}_2\text{H}_2\text{Cl}_2$ isomer and the reagent ion. It is not only the observed reaction

pathways which show observable 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 $\text{C}_2\text{H}_2\text{Cl}_2\text{H}^+$ (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 non-dissociative proton transfer occurs for reactions of H_3O^+ with all three isomers implies that the proton affinities 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 $\text{C}=\text{C}$ 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.* $\text{C}_2\text{H}_2\text{Cl.H}_2\text{O}^+ + \text{HCl}$. 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 stabilised 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, whilst it is three 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 $\text{C}=\text{C}$ 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 $\text{C}=\text{C}$ double bond, and the formation of a new $\text{C}=\text{C}$ 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, $\text{C}_2\text{H}_2\text{Cl}^+$ 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 $\text{C}_2\text{H}_2\text{Cl}_2$ 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 $\text{C}_2\text{H}_2\text{Cl}^+$ 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 $\text{C}_2\text{H}_2\text{Cl}_2$. 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 $\text{C}_2\text{H}_2\text{Cl}_2$ isomers, and an intermediate complex is probably formed. SF_5^+ shows only small isomeric effects with $\text{C}_2\text{H}_2\text{Cl}_2$, 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 $\text{RE} > \text{IE}(\text{C}_2\text{H}_2\text{Cl}_2)$, charge transfer is expected to take place. If it proceeds *via* the long-range mechanism, ionisation of $\text{C}_2\text{H}_2\text{Cl}_2$ will occur to a particular vibronic level with vertical ionisation

energy 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 ionising 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 *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 stabilisation 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 favoured in this reaction. Our results are in agreement with those of Rebrion *et al.* for this reaction,¹⁰ and we note that the non-dissociative 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 theory⁴⁹ and molecular beam studies⁵¹ 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 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 co-workers.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 ionisation energies 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 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 ‘ionised’ molecular orbital of the 1,1 isomer and a stronger *p*-type component for the 1,2 isomers. However, for photon energies > 18 eV, ionisation processes involve inner-valence orbitals of $C_2H_2Cl_2$, and many-body features are observed in both photoelectron and ionisation (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 have both more complex and more 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 recombination energies are below the barrier to the charge transfer reaction. The H_3O^+ reaction proceeds at the collisional rate for 1,1- $\text{C}_2\text{H}_2\text{Cl}_2$, whilst it is much slower for *cis*-1,2- and *trans*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$. The product ions from H_3O^+ reactions with 1,1 and 1,2 isomers are also different. This finding presents certain interests for 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- $\text{C}_2\text{H}_2\text{Cl}_2$ being $\text{C}_2\text{H}_2\text{Cl}^+$, whilst the only ionic product for the 1,2 isomers is CHCl_2^+ .

Smaller isomeric effects resulting in 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, whilst the difference between *cis*-1,2- and *trans*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$ reactions is not significant. The same products of photoionisation 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 recombination energies 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.

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Table 1. Rate coefficients at 298 K, product cations, branching ratios, and suggested neutral products for the reactions of twenty-one cations with 1,1-C₂H₂Cl₂. The recombination energy (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 MADDO 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^{39, 40} and ions,^{39, 41} unless otherwise indicated. In the interests of brevity, only the proposed neutrals that give the most exothermic $\Delta_r H^\circ_{298}$ are listed, unless specifically discussed in the text.

Reagent ion [RE / eV]	Rate coefficient / 10 ⁻⁹ cm ³ molecule ⁻¹ s ⁻¹	Product ions (%)	Proposed neutral Products	$\Delta_r H^\circ_{298}$ / kJ mol ⁻¹
NH ₄ ⁺ [4.73]	No reaction	None	None	n/a
H ₃ O ⁺ [6.27]	2.0 [2.0]	C ₂ H ₂ Cl ₂ H ⁺ [100]	H ₂ O	-808 + $\Delta_r H^\circ_{298}$ (C ₂ H ₂ Cl ₂ H ⁺)
SF ₃ ⁺ [8.32]	No reaction ^t	association product	None	n/a
CF ₃ ⁺ [9.04]	1.2 [1.5]	C ₂ H ₂ Cl ⁺ [100]	CF ₃ Cl	-65 ^a
CF ⁺ [9.11]	2.1 [2.0]	CHCl ₂ ⁺ [6] CClFH ⁺ [25] C ₂ H ₂ Cl ⁺ [69]	C ₂ HF C ₂ HCl CFCl	-142 -179 -54 ^b
SF ₅ ⁺ [9.78]	0.3 [1.2]	C ₂ H ₂ Cl ₂ F ⁺ [71] C ₂ H ₂ Cl ₂ ⁺ [16] C ₂ H ₂ Cl ⁺ [13]	SF ₄ SF ₅ SF ₃ Cl	-800 + $\Delta_r H^\circ_{298}$ (C ₂ H ₂ Cl ₂ F ⁺) ^{c,d} 0 ^{c,e} -19 ^c
SF ₂ ⁺ [10.24]	1.4 [1.5]	C ₂ H ₂ Cl ₂ ⁺ [100]	SF ₂	-45 ^g
SF ⁺ [10.31]	1.6 [1.6]	C ₂ H ₂ Cl ₂ ⁺ [59] C ₂ H ₂ ClSF ⁺ [8] C ₂ HClSF ⁺ [8] C ₂ H ₂ Cl ⁺ [21] CHCl ₂ ⁺ [4]	SF Cl HCl SFCl CS + HF	-52 ^f -879 + $\Delta_r H^\circ_{298}$ (C ₂ H ₂ ClSF ⁺) ^f -1093 + $\Delta_r H^\circ_{298}$ (C ₂ H ₂ ClSF ⁺) ^f 51 + $\Delta_r H^\circ_{298}$ (SFCl) ^f -106 ^f
CF ₂ ⁺ [11.44]	1.9 [1.6]	C ₂ H ₂ Cl 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 ₂ H ₂ Cl ₂ ⁺ [77] C ₂ H ₂ Cl ⁺ [23]	O ₂ OCIO or ClOO	-221 -18 -17
Xe ⁺ ² P _{3/2} [12.13]	1.3 [1.3]	C ₂ H ₂ Cl ₂ ⁺ [81] C ₂ H ₂ Cl ⁺ [19]	Xe Xe + Cl	-227 0
N ₂ O ⁺ [12.89]	1.7 [1.7]	C ₂ H ₂ Cl ₂ ⁺ [15] C ₂ H ₂ Cl ⁺ [85]	N ₂ O N ₂ OCl or N ₂ O + Cl	-300 -264 -73
CO ₂ ⁺ [13.76]	1.5 [1.7]	C ₂ H ₂ Cl ₂ ⁺ [13] C ₂ H ₂ Cl ⁺ [87]	CO ₂ CO ₂ + Cl	-385 -158

Kr ⁺ ² P _{1/2} [14.00]	1.3 [1.4]	C ₂ H ₂ Cl ⁺ [93] C ₂ HCl ⁺ [7]	Kr + Cl Kr + HCl	-180 -209
CO ⁺ [14.01]	2.0 [2.0]	C ₂ H ₂ Cl ⁺ [100]	ClCO	-255
N ⁺ [14.53]	2.7 [2.7]	C ₂ H ₂ Cl ₂ ⁺ [40] C ₂ H ₂ Cl ⁺ [54] C ₂ HCl ⁺ [6]	N NCl N + HCl	-459 -512 ^h -260
N ₂ ⁺ [15.58]	2.0 [2.0]	C ₂ H ₂ Cl ⁺ [83] C ₂ HCl ⁺ [17]	N ₂ + Cl N ₂ + HCl	-333 -361
Ar ⁺ [15.76]	1.5 [1.8]	C ₂ H ₂ Cl ⁺ [84] C ₂ HCl ⁺ [16]	Ar + Cl Ar + HCl	-351 -379
F ⁺ [17.42]	2.0 [2.3]	C ₂ H ₂ Cl ₂ ⁺ [14] C ₂ H ₂ Cl ⁺ [41] C ₂ H ₂ ⁺ [45]	F FCl F+Cl ₂	-737 -761 -356
Ne ⁺ [21.56]	2.0 [2.3]	C ₂ H ₂ Cl ₂ ⁺ [5] C ₂ H ₂ ⁺ [50] C ₂ HCl ⁺ [35] CCl ⁺ [4] Cl ⁺ [6]	Ne Ne + Cl ₂ Ne + HCl Ne + CH ₂ + Cl or Ne + CH + HCl Ne + C ₂ H ₂ Cl or Ne + Cl + C ₂ H ₂	-1114 -755 -938 -331 -337 -711 + Δ _f H ^o ₂₉₈ (C ₂ H ₂ Cl) -363

^a Δ_fH^o₂₉₈ (CF₃⁺) = +406 kJ mol⁻¹.⁴²

^b Δ_fH^o₂₉₈ (CClF) = +31 kJ mol⁻¹.⁴³

^c Δ_fH^o₂₉₈ (SF₅⁺) = +29 kJ mol⁻¹.⁴⁴

^d Δ_fH^o₂₉₈ (SF₄) = -768 kJ mol⁻¹.⁴⁵

^e Δ_fH^o₂₉₈ (SF₅) = -915 kJ mol⁻¹.⁴⁶

^f Δ_fH^o₂₉₈ (SF⁺) = +998 kJ mol⁻¹.⁴⁵

^g Δ_fH^o₂₉₈ (SF₂) = -295 kJ mol⁻¹, Δ_fH^o₂₉₈ (SF₂⁺) = +693 kJ mol⁻¹.⁴⁵

^h Δ_fH^o₂₉₈ (NCl) = +314 kJ mol⁻¹.⁴⁷

ⁱ Rate coefficient too small to measure, $k < 10^{-13}$ cm³ s⁻¹

Table 2. Rate coefficients at 298 K, product cations, branching ratios, and suggested neutral products for the reactions of twenty-one cations with *cis*-1,2-C₂H₂Cl₂ (adiabatic IE=9.65 eV). The recombination energy (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 MADDO 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^{39,40} and ions,^{39,41} unless otherwise indicated. In the interests of brevity, only the proposed neutrals that give the most exothermic $\Delta_r H^\circ_{298}$ are listed, unless specifically discussed in the text.

Reagent ion [RE / eV]	Rate coefficient / 10 ⁻⁹ cm ³ molecule ⁻¹ s ⁻¹	Product ions (%)	Proposed neutral products	$\Delta_r H^\circ_{298}$ / kJ mol ⁻¹
NH ₄ ⁺ [4.73]	No reaction	none	none	n/a
H ₃ O ⁺ [6.27]	0.4 [2.9]	C ₂ H ₂ ClOH ₂ ⁺ [62] C ₂ H ₂ Cl ₂ H ⁺ [32] C ₂ H ₂ Cl ₂ ·H ₃ O ⁺ [6]	HCl H ₂ O –	–688 + $\Delta_r H^\circ_{298}$ (C ₂ H ₂ ClOH ₂ ⁺) –837 + $\Delta_r H^\circ_{298}$ (C ₂ H ₂ Cl ₂ H ⁺) n/a
SF ₃ ⁺ [8.32]	No reaction ^h	association product	none	n/a
CF ₃ ⁺ [9.04]	1.0 [1.8]	CHCl ₂ ⁺ [100]	C ₂ HF ₃	3 ^a
CF ⁺ [9.11]	2.0 [2.4]	CHCl ₂ ⁺ [41] CClFH ⁺ [59]	C ₂ HF C ₂ HCl	–144 –181
SF ₅ ⁺ [9.78]	0.2 [1.6]	C ₂ H ₂ Cl ₂ F ⁺ [69] C ₂ H ₂ Cl ₂ ⁺ [14] C ₂ H ₂ Cl ⁺ [17]	SF ₄ SF ₅ SF ₅ Cl	–802 + $\Delta_r H^\circ_{298}$ (C ₂ H ₂ Cl ₂ F ⁺) ^{b,c} –15 ^{b,d} –19 ^b
SF ₂ ⁺ [10.24]	1.7 [1.8]	C ₂ H ₂ Cl ₂ ⁺ [100]	SF ₂	–60 ^f
SF ⁺ [10.31]	1.5 [2.0]	C ₂ H ₂ Cl ₂ ⁺ [88] C ₂ H ₂ ClSF ⁺ [6] C ₂ HClSF ⁺ [6]	SF Cl HCl	–67 ^e –881 + $\Delta_r H^\circ_{298}$ (C ₂ H ₂ ClSF ⁺) ^e –1095 + $\Delta_r H^\circ_{298}$ (C ₂ HClSF ⁺) ^e
CF ₂ ⁺ [11.44]	1.6 [2.0]	C ₂ H ₂ Cl ₂ ⁺ [100]	CF ₂	–175
SF ₄ ⁺ [11.99]	1.4 [1.6]	Not measured	n/a	n/a
O ₂ ⁺ [12.07]	2.3 [2.4]	C ₂ H ₂ Cl ₂ ⁺ [78] C ₂ H ₂ Cl ⁺ [22]	O ₂ OCIO or ClOO	–236 –18 –17
Xe ⁺ ² P _{3/2} [12.13]	1.4 [1.5]	C ₂ H ₂ Cl ₂ ⁺ [82] C ₂ H ₂ Cl ⁺ [18]	Xe Xe + Cl	–242 0
N ₂ O ⁺ [12.89]	1.9 [2.1]	C ₂ H ₂ Cl ₂ ⁺ [15] C ₂ H ₂ Cl ⁺ [85]	N ₂ O N ₂ O + Cl or N ₂ + OCl or N ₂ OCl	–315 –73 –175 –264
CO ₂ ⁺ [13.76]	1.9 [2.1]	C ₂ H ₂ Cl ₂ ⁺ [18] C ₂ H ₂ Cl ⁺ [75] C ₂ HCl ⁺ [7]	CO ₂ CO ₂ + Cl CO ₂ + HCl	–400 –158 –188

Kr ⁺ ² P _{1/2} [14.00]	1.6 [1.7]	C ₂ H ₂ Cl ⁺ [83] C ₂ HCl ⁺ [17]	Kr + Cl Kr + HCl	-180 -211
CO ⁺ [14.01]	1.7 [2.5]	C ₂ H ₂ Cl ₂ ⁺ [10] C ₂ H ₂ Cl ⁺ [78] C ₂ HCl ⁺ [12]	CO CO + Cl or COCl CO + HCl	-423 -181 -255 -211
N ⁺ [14.53]	2.8 [3.3]	C ₂ H ₂ Cl ₂ ⁺ [56] C ₂ H ₂ Cl ⁺ [37] C ₂ HCl ⁺ [7]	N NCl N + HCl	-474 -512 ^g -262
N ₂ ⁺ [15.58]	2.3 [2.5]	C ₂ H ₂ Cl ₂ ⁺ [10] C ₂ HCl ₂ ⁺ [6] C ₂ H ₂ Cl ⁺ [68] C ₂ HCl ⁺ [16]	N ₂ N ₂ + H N ₂ + Cl N ₂ + HCl	-574 -1289 + Δ _f H ^o ₂₉₈ (C ₂ HCl ₂ ⁺) -333 -363
Ar ⁺ [15.76]	1.5 [2.2]	C ₂ H ₂ Cl ₂ ⁺ [4] C ₂ HCl ₂ ⁺ [4] C ₂ H ₂ Cl ⁺ [75] C ₂ HCl ⁺ [17]	Ar Ar + H Ar + Cl Ar + HCl	-592 -1307 + Δ _f H ^o ₂₉₈ (C ₂ HCl ₂ ⁺) -351 -381
F ⁺ [17.42]	2.4 [2.9]	C ₂ H ₂ Cl ₂ ⁺ [25] C ₂ H ₂ Cl ⁺ [29] C ₂ H ₂ ⁺ [46]	F FCl F + Cl ₂	-752 -761 -358
Ne ⁺ [21.56]	2.3 [2.8]	C ₂ H ₂ Cl ₂ ⁺ [11] C ₂ H ₂ ⁺ [60] C ₂ HCl ⁺ [21] Cl ⁺ [8]	Ne Ne + Cl ₂ Ne + HCl Ne + C ₂ H ₂ Cl	-1151 -758 -940 -713 + Δ _f H ^o ₂₉₈ (C ₂ H ₂ Cl)

^a Δ_fH^o₂₉₈ (CF₃⁺) = +406 kJ mol⁻¹.⁴²

^b Δ_fH^o₂₉₈ (SF₅⁺) = +29 kJ mol⁻¹.⁴⁴

^c Δ_fH^o₂₉₈ (SF₄) = -768 kJ mol⁻¹.⁴⁵

^d Δ_fH^o₂₉₈ (SF₅) = -915 kJ mol⁻¹.⁴⁶

^e Δ_fH^o₂₉₈ (SF⁺) = +998 kJ mol⁻¹.⁴⁵

^f Δ_fH^o₂₉₈ (SF₂) = -295 kJ mol⁻¹, Δ_fH^o₂₉₈ (SF₂⁺) = +693 kJ mol⁻¹.⁴⁵

^g Δ_fH^o₂₉₈ (NCl) = +314 kJ mol⁻¹.⁴⁷

^h Rate coefficient too small to measure, $k < 10^{-13}$ cm³ s⁻¹

Table 3. Rate coefficients at 298 K, product cations, branching ratios, and suggested neutral products for the reactions of twenty-one cations with *trans*-1,2-C₂H₂Cl₂ (adiabatic IE=9.64 eV). The recombination energy (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^{39,40} and ions,^{39,41} unless otherwise indicated. In the interests of brevity, only the proposed neutrals that give the most exothermic $\Delta_r H^\circ_{298}$ are listed, unless specifically discussed in the text.

Reagent ion [RE / eV]	Rate coefficient / 10 ⁻⁹ cm ³ molecule ⁻¹ s ⁻¹	Product ions (%)	Proposed neutral products	$\Delta_r H^\circ_{298}$ / kJ mol ⁻¹
NH ₄ ⁺ [4.73]	No reaction	none	none	n/a
H ₃ O ⁺ [6.27]	0.3 [1.7]	C ₂ H ₂ ClOH ₂ ⁺ [42] C ₂ H ₂ Cl ₂ H ⁺ [56] C ₂ H ₂ Cl ₂ ·H ₃ O ⁺ [2]	HCl H ₂ O –	–685 + $\Delta_r H^\circ_{298}$ (C ₂ H ₂ ClOH ₂ ⁺) –834 + $\Delta_r H^\circ_{298}$ (C ₂ H ₂ Cl ₂ H ⁺) n/a
SF ₃ ⁺ [8.32]	No reaction ^h	association product	none	n/a
CF ₃ ⁺ [9.04]	0.7 [1.0]	CHCl ₂ ⁺ [100]	C ₂ HF ₃	5 ^a
CF ⁺ [9.11]	1.4 [1.4]	CHCl ₂ ⁺ [51] CClFH ⁺ [49]	C ₂ HF C ₂ HCl	–142 –179
SF ₅ ⁺ [9.78]	0.2 [0.9]	C ₂ H ₂ Cl ₂ F ⁺ [77] C ₂ H ₂ Cl ₂ ⁺ [16] C ₂ H ₂ Cl ⁺ [7]	SF ₄ SF ₅ SF ₅ Cl	–799 + $\Delta_r H^\circ_{298}$ (C ₂ H ₂ Cl ₂ F ⁺) ^{b,c} –20 ^{b,d} –19 ^d
SF ₂ ⁺ [10.24]	1.4 [1.0]	C ₂ H ₂ Cl ₂ ⁺ [100]	SF ₂	–64 ^f
SF ⁺ [10.31]	1.3 [1.2]	C ₂ H ₂ Cl ₂ ⁺ [89] C ₂ H ₂ ClSF ⁺ [6] C ₂ HClSF ⁺ [5]	SF Cl HCl	–71 ^e –879 + $\Delta_r H^\circ_{298}$ (C ₂ H ₂ ClSF ⁺) ^e –1092 + $\Delta_r H^\circ_{298}$ (C ₂ HClSF ⁺) ^e
CF ₂ ⁺ [11.44]	1.3 [1.2]	C ₂ H ₂ Cl ₂ ⁺ [100]	CF ₂	–180
SF ₄ ⁺ [11.99]	1.1 [0.93]	not measured	n/a	n/a
O ₂ ⁺ [12.07]	1.2 [1.4]	C ₂ H ₂ Cl ₂ ⁺ [68] C ₂ H ₂ Cl ⁺ [32]	O ₂ OCIO or ClOO	–240 –18 –17
Xe ⁺² P _{3/2} [12.13]	0.9 [0.9]	C ₂ H ₂ Cl ₂ ⁺ [85] C ₂ H ₂ Cl ⁺ [15]	Xe Xe + Cl	–246 0
N ₂ O ⁺ [12.89]	0.9 [1.2]	C ₂ H ₂ Cl ₂ ⁺ [24] C ₂ H ₂ Cl ⁺ [76]	N ₂ O N ₂ O + Cl or N ₂ + OCl or N ₂ OCl	–319 –73 –175 –264
CO ₂ ⁺ [13.76]	1.1 [1.2]	C ₂ H ₂ Cl ₂ ⁺ [15] C ₂ H ₂ Cl ⁺ [74] C ₂ HCl ⁺ [11]	CO ₂ CO ₂ + Cl CO ₂ + HCl	–404 –158 –186

Kr ⁺ ² P _{1/2} [14.00]	1.2 [1.0]	C ₂ H ₂ Cl ⁺ [80] C ₂ HCl ⁺ [20]	Kr + Cl Kr + HCl	-180 -208
CO ⁺ [14.01]	1.6 [1.4]	C ₂ H ₂ Cl ₂ ⁺ [11] C ₂ H ₂ Cl ⁺ [74] C ₂ HCl ⁺ [15]	CO CO + Cl or COCl CO + HCl	-427 -181 -255 -209
N ⁺ [14.53]	2.0 [1.9]	C ₂ H ₂ Cl ₂ ⁺ [47] C ₂ H ₂ Cl ⁺ [42] C ₂ HCl ⁺ [11]	N N + Cl or NCl N + HCl	-478 -232 -512 ^g -260
N ₂ ⁺ [15.58]	1.6 [1.4]	C ₂ H ₂ Cl ₂ ⁺ [9] C ₂ HCl ₂ ⁺ [4] C ₂ H ₂ Cl ⁺ [66] C ₂ HCl ⁺ [21]	N ₂ N ₂ + H N ₂ + Cl N ₂ + HCl	-579 -1287 + Δ _f H ^o ₂₉₈ (C ₂ HCl ₂ ⁺) -333 -360
Ar ⁺ [15.76]	1.1 [1.3]	C ₂ H ₂ Cl ₂ ⁺ [5] C ₂ HCl ₂ ⁺ [7] C ₂ H ₂ Cl ⁺ [66] C ₂ HCl ⁺ [22]	Ar Ar + H Ar + Cl Ar + HCl	-597 -1305 + Δ _f H ^o ₂₉₈ (C ₂ HCl ₂ ⁺) -351 -378
F ⁺ [17.42]	1.4 [1.7]	C ₂ H ₂ Cl ₂ ⁺ [23] C ₂ H ₂ Cl ⁺ [32] C ₂ H ₂ ⁺ [45]	F FCl F + Cl ₂	-756 -761 -356
Ne ⁺ [21.56]	1.8 [1.6]	C ₂ H ₂ Cl ₂ ⁺ [5] C ₂ H ₂ ⁺ [56] C ₂ HCl ⁺ [34] Cl ⁺ [5]	Ne Ne + Cl ₂ Ne + HCl Ne + C ₂ H ₂ Cl	-1156 -755 -937 -711 + Δ _f H ^o ₂₉₈ (C ₂ H ₂ Cl)

^a Δ_fH^o₂₉₈ (CF₃⁺) = +406 kJ mol⁻¹.⁴²

^b Δ_fH^o₂₉₈ (SF₅⁺) = +29 kJ mol⁻¹.⁴⁴

^c Δ_fH^o₂₉₈ (SF₄) = -768 kJ mol⁻¹.⁴⁵

^d Δ_fH^o₂₉₈ (SF₅) = -915 kJ mol⁻¹.⁴⁶

^e Δ_fH^o₂₉₈ (SF⁺) = +998 kJ mol⁻¹.⁴⁵

^f Δ_fH^o₂₉₈ (SF₂) = -295 kJ mol⁻¹, Δ_fH^o₂₉₈ (SF₂⁺) = +693 kJ mol⁻¹.⁴⁵

^g Δ_fH^o₂₉₈ (NCl) = +314 kJ mol⁻¹.⁴⁷

^h Rate coefficient too small to measure, $k < 10^{-13}$ cm³ s⁻¹.

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 C₂H₂Cl₂. 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.

Ion [RE / eV]	$k(1,1)/$ $10^{-9} \text{ cm}^3 \text{ s}^{-1}$	$k(\text{cis-1,2})/$ $10^{-9} \text{ cm}^3 \text{ s}^{-1}$	$k(\text{trans-1,2})/$ $10^{-9} \text{ cm}^3 \text{ s}^{-1}$	Products (1,1)	Products (<i>cis</i> -1,2)	Products (<i>trans</i> -1,2)
H ₃ O ⁺ [6.27]	2.0 [2.0] 100 %	0.4 [2.9] 14 %	0.3 [1.7] 18 %	C ₂ H ₂ Cl ₂ H ⁺ [100]	C ₂ HClH ₃ O ⁺ [62] C ₂ H ₂ Cl ₂ H ⁺ [32] C ₂ H ₂ Cl ₂ ·H ₃ O ⁺ [6]	C ₂ HClH ₃ O ⁺ [42] C ₂ H ₂ Cl ₂ H ⁺ [56] C ₂ H ₂ Cl ₂ ·H ₃ O ⁺ [2]
CF ₃ ⁺ [9.04]	1.2 [1.5] 80 %	1.0 [1.8] 56 %	0.7 [1.0] 70 %	C ₂ H ₂ Cl ⁺ [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 ₂ H ₂ Cl ⁺ [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 ₂ H ₂ ClSF ⁺ [8] C ₂ HClSF ⁺ [8] C ₂ H ₂ Cl ₂ ⁺ [59] CHCl ₂ ⁺ [4] C ₂ H ₂ Cl ⁺ [21]	C ₂ H ₂ ClSF ⁺ [6] C ₂ HClSF ⁺ [6] C ₂ H ₂ Cl ₂ ⁺ [88]	C ₂ H ₂ ClSF ⁺ [6] C ₂ HClSF ⁺ [5] C ₂ H ₂ Cl ₂ ⁺ [89]
CO ₂ ⁺ [13.76]	1.5 [1.7] 88 %	1.9 [2.1] 90 %	1.1 [1.2] 92 %	C ₂ H ₂ Cl ₂ ⁺ [13] C ₂ H ₂ Cl ⁺ [87]	C ₂ H ₂ Cl ₂ ⁺ [18] C ₂ H ₂ Cl ⁺ [75] C ₂ HCl ⁺ [7]	C ₂ H ₂ Cl ₂ ⁺ [15] C ₂ H ₂ Cl ⁺ [74] C ₂ HCl ⁺ [11]
CO ⁺ [14.01]	2.0 [2.0] 100 %	1.7 [2.5] 68 %	1.6 [1.4] 100 %	C ₂ H ₂ Cl ⁺ [100]	C ₂ H ₂ Cl ₂ ⁺ [10] C ₂ H ₂ Cl ⁺ [78] C ₂ HCl ⁺ [12]	C ₂ H ₂ Cl ₂ ⁺ [11] C ₂ H ₂ Cl ⁺ [74] C ₂ HCl ⁺ [15]
N ₂ ⁺ [15.58]	2.0 [2.0] 100 %	2.3 [2.5] 92 %	1.6 [1.4] 100 %	C ₂ H ₂ Cl ⁺ [83] C ₂ HCl ⁺ [17]	C ₂ H ₂ Cl ₂ ⁺ [10] C ₂ HCl ₂ ⁺ [6] C ₂ H ₂ Cl ⁺ [68] C ₂ HCl ⁺ [16]	C ₂ H ₂ Cl ₂ ⁺ [9] C ₂ HCl ₂ ⁺ [4] C ₂ H ₂ Cl ⁺ [66] C ₂ HCl ⁺ [21]
Ar ⁺ [15.76]	1.5 [1.8] 83 %	1.5 [2.2] 68 %	1.1 [1.3] 85 %	C ₂ H ₂ Cl ⁺ [84] C ₂ HCl ⁺ [16]	C ₂ H ₂ Cl ₂ ⁺ [4] C ₂ HCl ₂ ⁺ [4] C ₂ H ₂ Cl ⁺ [75] C ₂ HCl ⁺ [17]	C ₂ H ₂ Cl ₂ ⁺ [5] C ₂ HCl ₂ ⁺ [7] C ₂ H ₂ Cl ⁺ [66] C ₂ HCl ⁺ [22]

Figure Captions

Figure 1. Comparison of the ionic products from ion-molecule studies of 1,1- $\text{C}_2\text{H}_2\text{Cl}_2$ with TPEPICO photoionization branching ratios over the energy range 10–23 eV.

Figure 2. Comparison of the ionic products from ion-molecule studies of *cis*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$ with TPEPICO photoionization branching ratios over the energy range 10–23 eV.

Figure 3. Comparison of the ionic products from ion-molecule studies of *trans*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$ with TPEPICO photoionization branching ratios over the energy range 10–23 eV.

Figure 1.

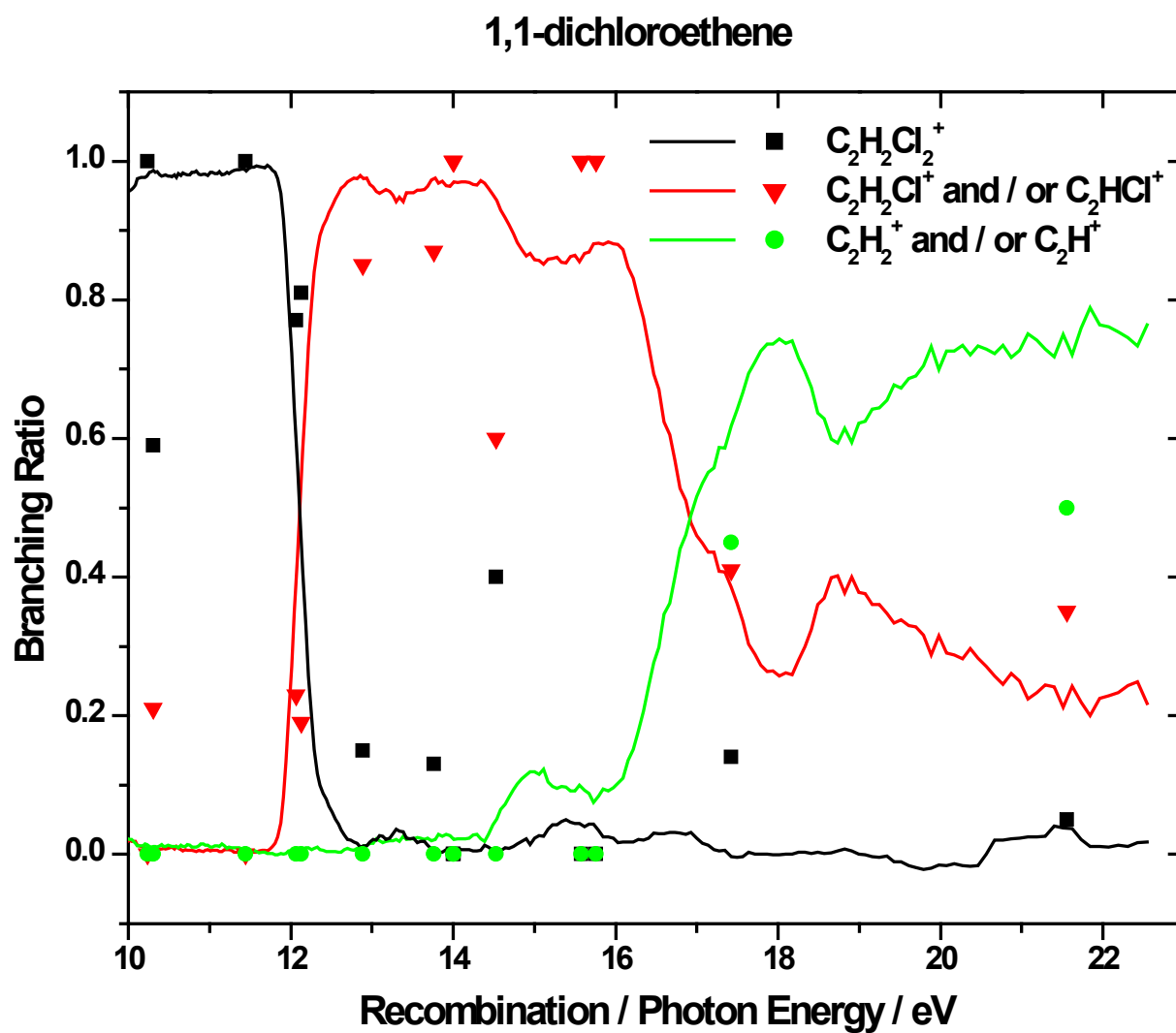


Figure 2.

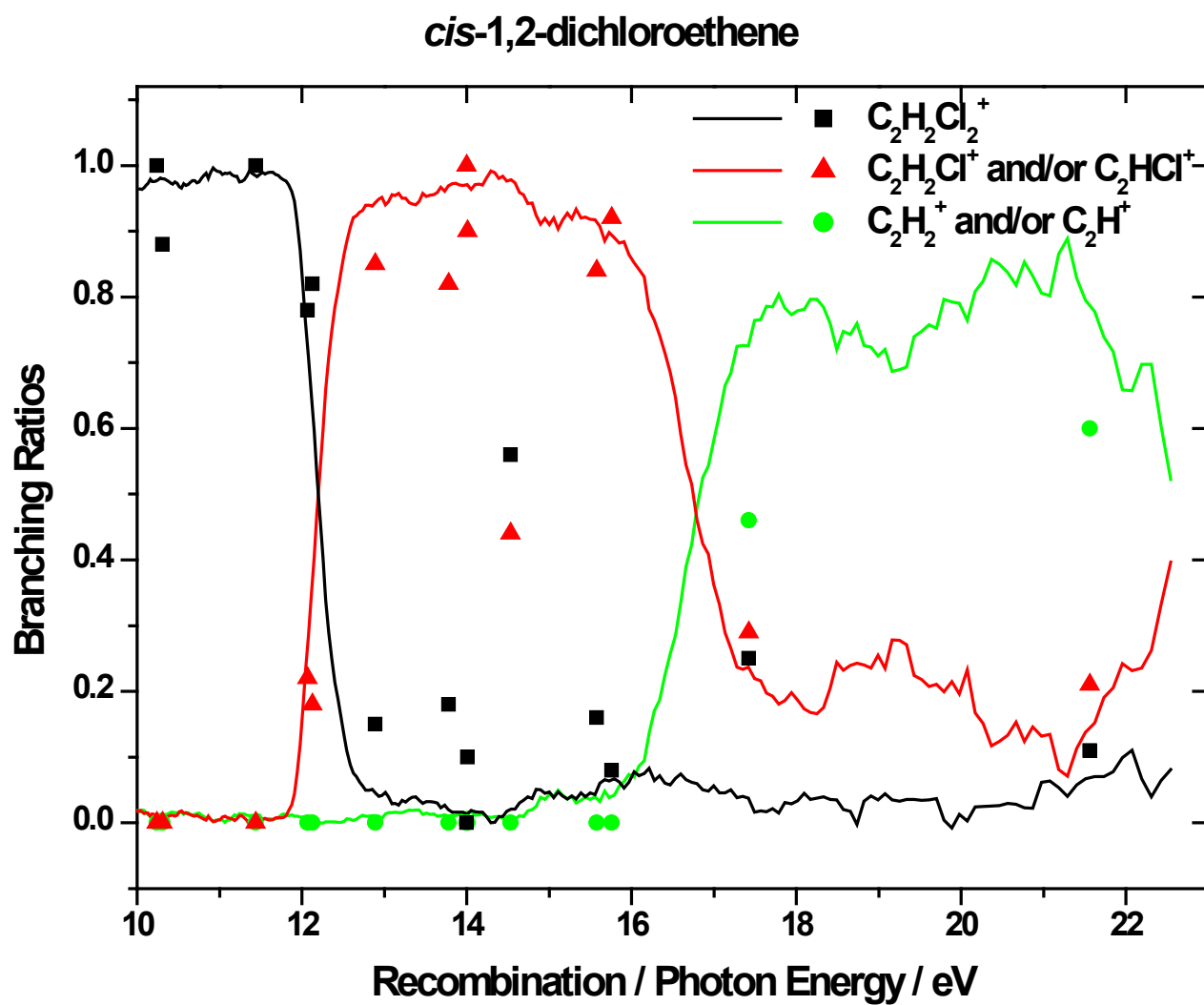


Figure 3.

