Distribution of Rotational States in Half-Collisions: 193-nm Photolysis of Dichloroethylene Isomers

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The photodissociation of cis-, trans-, and 1,1-dichloroethylene (DCE) was studied by a pump-and-probe technique, using a 193-nm excimer laser to excite the parent molecule and time-of-flight resonance-enhanced multiphoton ionization to detect the products. We report here the nascent rotational state distributions of HCl(υ″=0,1,2) and also the relative yields and intensity dependencies of HCl, H, Cl(5P3/2), Cl(5P1/2), HCl+, and Cl+. Our finding that the rotational state distributions of HCl for all three isomers are very similar leads us to conclude that the nascent distribution is determined far along the reaction coordinate and is insensitive to the isomeric form of the parent molecule, regardless of whether photoelimination results from a three- or four-center transition state. We also observed qualitatively different behavior for HCl(υ″=0) and HCl(υ″=1,2). As in our previous study of vinyl chloride, we found that HCl(υ″=0) has a Boltzmann-like rotational state distribution, with temperatures in this case near 1400 K, whereas the distribution for υ″ = 0 is described by a biexponential function with a low J″ temperature around 300 K and a high J″ temperature around 10 000 K. We propose that the dichotomy between these two distributions is due to microscopic rather than chemical branching. The relative yields of HCl and Cl+ for trans-DCE are approximately double those of cis- and 1,1-DCE. This result is consistent with the interpretation that the yield-determining step is faster than cis–trans isomerization. The yields of all the other products are the same for cis and trans. For 1,1-DCE the yields of H, Cl(5P3/2), and HCl+ are much greater than for cis- and trans-DCE, while for Cl(5P1/2) the 1,1-DCE yield is somewhat smaller. The relative yields of H and Cl(5P3/2) can be explained by the stabilities of the organic fragments, while the HCl+ yields can be explained statistically. All of the neutral fragments were found to be produced by single-photon processes, while HCl+ and Cl+ require three and four photons, respectively. Ladder climbing mechanisms are proposed for the two ionic fragments.

Introduction

The close relationship between product state distributions in bimolecular collisions and photodissociation ("half-collisions") was pointed out by Dudley Herschbach nearly 20 years ago.1 As he noted, elucidation of the mechanism for bimolecular reactions is frequently complicated by the average over impact parameters and orientation of the reactants. In contrast, photodissociation reactions are initiated at a turning point where the geometry of the parent molecule is well-defined. Much can be learned about the reaction dynamics by measuring the energy and angular momentum distributions of the fragments for different initial states of the parent molecule.

An interesting opportunity arises when different isomers of the parent molecule are available. An example is the ultraviolet photoelimination of HCl from 1,1-, cis-, and trans-dichloroethylene (DCE)2

\[
\text{C}_2\text{H}_2\text{Cl}_2 + 193 \text{ nm} \rightarrow \text{C}_2\text{HCl} + \text{HCl},
\]

where ΔH is the total available energy. If we think of the elimination of HCl as a simple, concerted process, then very different product rotational states of HCl are expected for the three isomers. For the 1,1 isomer HCl is eliminated by a four-center (α,β) mechanism involving both carbon atoms. For the cis isomer a three-center (α,α) mechanism applies, with the H and Cl atoms departing from the same carbon atom, while for the trans compound both mechanisms may contribute. The different transition states leading to α,α and α,β elimination should produce different torques acting on the departing fragments, which would be reflected in the rotational state distribution of the HCl product. In reality, the mechanism need not be concerted. The 193-nm photon absorbed by the parent molecule provides sufficient energy for rotation about the C–C bond as well as for 1,2 migration of the hydrogen atoms. These processes may compete with the elimination reaction and thereby alter the product state distribution.

The present study is part of an ongoing investigation of the photodissociation dynamics of halogenated ethylenes. In an earlier paper Reilly et al.3 reported the rotational state distributions for HCl(υ″=0,1,2) produced in the 193-nm photodissociation of vinyl chloride (VCl). In that study they found strikingly different distributions for HCl(υ″=0) and HCl(υ″>0). The former displayed a non-Boltzmann distribution with a low-energy part (J″ ≤ 6) that could be described by a temperature of 340 K and a high-energy part (7 ≤ J″ ≤ 13) that is nearly flat with a "temperature" around 20 000 K. In contrast, the distributions for υ″ = 1 and 2 could be fit to a Boltzmann function with temperatures around 2000 K. It was tempting to assign the first distribution to α,α and the second to α,β elimination. A primary motivation for the present study was to see whether the two types of distributions also occur for the dichloroethylene compounds, with perhaps the different isomers showing a preference for one or the other.

In a second study Mo et al.4 explored a number of other dissociation pathways for various chlorinated ethylene compounds. One of the processes they characterized is a two-photon elimination of electronically excited HCl. This reaction path was apparent from a three-photon HCl+ signal which was observable with just the unfocused 193-nm laser. A further goal of the present study is to determine whether this process occurs also for the dichloro compounds and, if so, to discover how the reaction rate depends on isomeric structure of the molecule.

Although there are no published data on the rotational state distributions of HCl eliminated from DCE, there have been some studies of the vibrational and translational energy distributions of the fragments. Berry5 has used chemical laser techniques with flash lamp excitation of DCE to measure the relative populations...
of HCl(ν'',J''=0-3). He found the vibrational energy content of HCl to increase in the order trans < cis < 1,1. Donaldson and Leone⁶ used FTIR spectroscopy to measure the vibrational populations of HCl(ν''=1-4) produced from trans-DCE at 193 nm. The average vibrational energies obtained in the two studies are in good agreement, although the detailed distributions differ somewhat. Moss et al.⁷ observed infrared fluorescence from the organic fragments produced from all three isomers at 193 nm. Their data revealed considerable vibrational excitation of the fragments, with cis- and trans-DCE giving very similar spectra. Finally, Umemoto et al.⁸ measured the translational energy distributions of HCl from all three isomers. They found that the peak in the distribution is ≈6% of the total available energy, while the maximum fraction of kinetic energy is ≈35%.

Experimental Section

Since the experimental apparatus was described in detail previously, we will present here only a brief summary. Our apparatus is a pulsed molecular beam machine equipped with a standard Wiley-McLean time-of-flight (TOF) mass spectrometer. We performed two types of experiments with the apparatus. In the first set of experiments a pump-and-probe technique was used. An ArF (193 nm) excimer laser (Lambda Physik EMG150) was used to photodissociate the dichloroethylenes, while the product HCl was probed by 2 + 1 resonance-enhanced multiphoton ionization (REMPI), using a frequency-doubled excimer-pumped dye laser (Lambda Physik EMG102/FL2002). In the second set of experiments a single excimer laser was used both to dissociate the parent molecules and to ionize the fragments. In both experiments the ion signal was detected with a dual microchannel plate and averaged with a boxcar. The TOF detector was equipped with deflection plates which enabled us to shutter out all ions other than HCl⁺ and C1⁺. The gated integrator could readily distinguish between the arrival times of these remaining ions.

In the pump-and-probe experiments the two laser beams were counterpropagated along an axis that was perpendicular to both the molecular beam and the TOF detector, passing through a point midway between the repeller and extractor electrodes. The DCE molecular beam was introduced into the reaction chamber with a pulsed valve (Newport BV-100V) fitted with a Teflon tip located approximately 3 cm from the optical axis.

The HCl(ν'',J''=0,1,2) REMPI spectra were obtained using F/Δ as an intermediate Rydberg state. For all three isomers we scanned the fundamental wavelength from 481 to 486 nm to obtain the HCl F-X (0,0) and (1,1) bands and from 498 to 503 nm for the HCl F-X (0,1) and (1,2) bands, using Coumarin 480 and 500 dyes. In addition, we also detected H, Cl(2P1/2), and Cl(2P3/2), setting the fundamental of the probe laser at 486.02, 497.34, and 497.48 nm. In these experiments the pump laser fluence was typically 0.5-1 mJ/cm², while the probe laser energy was typically 10 mJ/cm², and the probe laser energy was varied continuously by passing the beam through an absorption cell containing a variable amount of ammonia gas. The ion signals and laser intensity were recorded on every shot, giving 1-2 orders of magnitude variation in laser intensity for a single run.

The purity of the DCE samples was checked by NMR spectroscopy, which confirmed the manufacturer’s (Aldrich) claimed purities (trans-DCE, 99%; cis-DCE, 97%; 1,1-DCE, 98%). The reagents were used without further purification. The neat DCE vapor was stored in a reservoir and admitted into the nozzle with a stagnation pressure of 200 Torr.

Results

The experimental results consist of (i) the rotational state distributions of HCl for vibrational levels ν''= 0, 1, and 2, (ii) the relative quantum yields of HCl, H, Cl(2P1/2), Cl(2P3/2), HC1⁺, and Cl⁺, and (iii) the intensity dependence of the products. These quantities were measured for all three DCE isomers.

The rotational state distributions were determined from the 2 + 1 REMPI spectrum of the F-X (ν''ν''') transitions. The spectrum for trans-DCE is shown in Figure 1. The vibrational bands that were assigned and calibrated are (0,0), (1,1), (0,1), and (1,2). Whenever possible, P, Q, and R branches were used. In Figure 2 the Q branch for the (0,0) transition is shown for each of the isomers.

The rotational state populations may be extracted from the spectrum using the well-known expression:¹²

\[ I(\nu''J''ν''',J''') = CP(\nu''ν''') q(\nu''ν'') S(J''J''')/(2J'' + 1) \]

where \( I(\nu''J''ν''',J''') \) is the signal intensity corresponding to the
This is especially evident in the Q branch of the rotational transition, C(0,0) of HCl produced from vinyl chloride and the three DCE isomers.

\[ F(v',J') \rightarrow X(v'',J'') \] transition, C is the population of the ground state, \( g(v'/J') \) is the Franck-Condon factor, and \( S(J',J'') \) is the rotational line strength. From the observed signals (peak heights) we can determine the relative rotational state distribution within a single vibrational band, providing that the line strength factor is known. If the upper state were unperturbed, this quantity would simply be the Boltzmann factor, but in fact the F state is strongly perturbed. This is especially evident in the Q branch of the (0,0) transition (see Figure 2), which has a peculiar bimodal appearance. This intensity anomaly is due in part to a predissociative process which depletes the population for \( J'' \). The effective rotational line strengths have been determined experimentally from a room temperature sample of HCl. Care was taken to ensure that the experimental conditions for obtaining the correction factors were as close as possible to those used in measuring the relative rotational populations of HCl produced from DCE. The resulting population distributions for \( v'' = 0, 1, \) and \( 2 \) are shown in Figures 3-5 in the form of Boltzmann plots.

In a second set of experiments we measured the relative yields of the atomic, molecular, and ionic products. These yields were measured relative to those of the 1,1 isomer for which they are defined as unity. The results are listed in Table I. The relative quantum yields for different fragments from the same parent molecule have been presented in the earlier paper by Mo et al. In the present study we remeasured the branching ratio of Cl(\( ^3P_{1/2} \)) to Cl(\( ^3P_{3/2} \)) for trans-DCE. The signal ratio was \( 0.074 \pm 0.007 \), in excellent agreement with the earlier value of \( 0.06 \pm 0.01 \). Applying the recently reported calibration factor of Tonukura et al., we obtain a product ratio of 0.19.

In order to compare the product yields for different isomers, we measured the absorption coefficients at 193 nm. The results, which are listed in Table II, are in good agreement with the synchrotron measurements of Berry. The relative yields listed in Table I for all the fragments except HCl+ and Cl+ (which require absorption of more than one photon) have been corrected for the different absorption cross sections.

\[ E(J'') \] (cm\(^{-1}\))

\[ P(J''/(2J''+1)) = a_1 \exp(-E(J'')/kT_1) + a_2 \exp(-E(J'')/kT_2) \]

(3)

is required. This dichotomy was observed previously for vinyl chloride. Second, the distributions are nearly the same for all three isomers. They are also similar to those found previously for vinyl chloride.
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for VCl, for which the available energy is only slightly greater (124 vs 120 kcal/mol).

A closer look shows some subtle differences both between DCE and VCl and also among the different DCE isomers. For \( \nu'' > 0 \) the fitted temperature for VCl is around 2000 K, while for all three DCE isomers it is near 1400 K. The temperatures for \( \nu'' = 0 \) are more difficult to establish since the data are of insufficient quality to fit four independent parameters accurately. All that we can say is that for VCl and all three isomers of DCE \( T_1 \) is approximately 300 K and \( T_2 \) is on the order of 10 000 K. The ratio of preexponential factors \( a_1/a_2 \), on the other hand, could be determined with an accuracy of about 20%, as is evident from just a visual inspection of the curvature in the Boltzmann plots (Figure 3). For VCl and cis-DCE \( a_1/a_2 = 1.5 \pm 0.3 \), while for trans- and 1,1-DCE the ratio is 0.9 \pm 0.2. Both effects—the variation in Boltzmann temperature for \( \nu'' > 0 \) and in \( a_1/a_2 \) for \( \nu'' = 0 \)—are significant at the confidence level of a single standard deviation. Finally, the vibrational distribution for trans-DCE appears to be slightly colder than for the other two isomers, as seen in Table I. While these differences between the state distributions for the three DCE isomers and VCl appear to be real, it is the overall similarity of the distributions that is most striking and which suggests a common mechanism.

Several experiments were performed to rule out possible artifacts. Since the \( F(\nu''=0) \) state of HCl has a \( J \)-dependent perturbation, we were concerned that the differences between the rotational state distributions for \( \nu'' = 0 \) and \( \nu'' > 0 \) might possibly be due to errors in the empirical line strength correction factors. We ruled out this possibility by three independent tests. First, for low values of \( J'(\nu''=0) \) we used also the \( E' \Xi' (\nu''=0) \to \Xi' \Sigma^+ (\nu''=0) \) transition, confirming that the curvature in the Boltzmann plot is real. Second, for \( \nu'' = 1 \) we used both the \( F(1,1) \) and the \( F(0,1) \) transitions. The results were identical within experimental scatter, even though perturbations of the upper states are very different. Third, in a companion study we photolyzed partially deuterated VCl (CH₂CDCl). The DCI and HCl Boltzmann plots were identical to the HCl distribution obtained with normal VCl, even though the perturbation in DCI occurs in a different part of the spectrum. In another study, variation of the time delay between the pump and probe lasers by an order of magnitude ruled out the possibility that the low \( J \) populations for \( \nu'' = 0 \) may be contaminated by rotational relaxation.

We consider next the possible origins of the dichotomy between the \( \nu'' = 0 \) and \( \nu'' > 0 \) distributions. A plausible explanation is that one distribution comes mainly from \( \alpha, \alpha \) elimination of HCl and the other from \( \alpha, \beta \) elimination. For this to be possible the
The insensitivity of the HCl state distribution to the electronic excitation. Lineberger and co-workers have determined that the energy of the organic fragment can be understood if we compare the time scales for HCl recoil and vinylidene-acetylene isomerization. The relative kinetic energy of the products, respectively, the prior distribution

\[ P(J''\nu'',JC,E_{in}) = C(2J''+1)\rho(E_{in})E_{i}^{-1/2} \]

where \( C \) is a normalization constant and \( \rho \) is the vibrational density of states of the organic fragment. The prior distribution of \( J'' \) and \( \nu'' \) is obtained by summing over \( JC \) and integrating over \( E_{in} \) using the Whitten–Rabinovich density of states and conserving energy.

For a total available energy of 120 kcal/mol, the model predicts a Boltzmann-like rotational state distribution with a temperature of 7900 K for \( \nu''=1 \) and 7400 K for \( \nu''=2 \) for all three isomers. For VCl the model predicts temperatures that are 8% higher. The experimental temperatures are considerably lower, with a ratio (VCl vs DCE) of 1.6 \( \pm \) 0.3 for \( \nu''=1 \) and 1.3 \( \pm \) 0.2 for \( \nu''=2 \). Better agreement is obtained with this simple model if not all of the exoergicity is available to HCl. The reverse reaction of HCl + HCCH has a barrier of approximately 45 kcal/mol, estimated from the thermal activation energy for photodissociation of VCl. If we think of this barrier as the energy needed to reorganize the H–Cl, C–Cl, and C–H bonds to form the transition state, then this value provides a rough estimate of the localized energy that is available to HCl in the forward direction.

In addition, some fraction of energy above the barrier might also be available. An empirical value for the localized energy proposed by Umemoto et al. is the maximum relative kinetic energy of the separating fragments, which they found to be 40 \( \pm \) 5, 45 \( \pm \) 5, and 45 \( \pm \) 5 kcal/mol for cis-, trans-, and 1,1-DCE, respectively. Adopting these values for the localized available energy, the phase space model predicts a Boltzmann distribution of rotational states with temperatures of 2400 K \( (\nu''=1) \) and 1900 K \( (\nu''=2) \) for cis-DCE and 2700 K \( (\nu''=1) \) and 2200 K \( (\nu''=2) \) for both trans- and 1,1-DCE. While these temperatures are still hotter than the observed ones, they are in qualitative agreement with the data. More importantly, the ratios of the predicted temperatures for VCl vs DCE are 1.5–1.6 for \( \nu''=1 \) and 1.3–1.5 for \( \nu''=2 \), which are in excellent agreement with experiment.

The phase space model greatly overestimates the vibrational energy of HCl, even when the full 120 kcal/mol is available. This is consistent with the finding of previous investigators that in order to fit the vibrational populations with a statistical model it was necessary to assume a lower vibrational frequency for HCl.

### Table III: Intensity Dependence of Photofragments

<table>
<thead>
<tr>
<th>Fragment</th>
<th>cis</th>
<th>trans</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.97 ( \pm ) 0.04</td>
<td>0.95 ( \pm ) 0.05</td>
</tr>
<tr>
<td>Cl(P1/2)</td>
<td>0.94 ( \pm ) 0.06</td>
<td>0.96 ( \pm ) 0.04</td>
</tr>
<tr>
<td>Cl(P1/2)</td>
<td>0.99 ( \pm ) 0.03</td>
<td>0.98 ( \pm ) 0.03</td>
</tr>
<tr>
<td>HC*</td>
<td>2.6 ( \pm ) 0.1</td>
<td>2.7 ( \pm ) 0.1</td>
</tr>
<tr>
<td>Cl*</td>
<td>3.4 ( \pm ) 0.2</td>
<td>3.8 ( \pm ) 0.2</td>
</tr>
</tbody>
</table>

* Uncertainties for \( n \) are either the standard deviations obtained from the least-squares fits of the intensity plots or the standard deviations in fitted values of \( n \) from multiple runs, whichever is larger.
The picture which emerges is that the vibrational population is determined much earlier along the reaction coordinate. At this stage of the reaction, the isomer of the parent molecule can affect the partitioning of internal energy of the fragments. Each vibrational state of HCl then evolves independently, with freezing of the rotational state distribution occurring only much later along the reaction path.

The biexponential rotational state distribution for \( v'' = 0 \) suggests the existence of a second mechanism. One possibility for microscopic branching is the competition between concerted and stepwise elimination of HCl. We might imagine the non-Boltzmann distribution for \( v'' = 0 \) coming from a concerted elimination (either three-center or four-center), while the quasi-statistical distribution for \( v'' > 0 \) arises from some sequential process.

It is instructive to compare HCl elimination from VCl with H\(_2\) elimination from ethylene. In the latter case, Popie and co-workers\(^{22} \) predicted that the lowest energy path is \( \alpha,\alpha \) elimination, with a barrier height of 74.2 kcal/mol. The second lowest energy path is a 1,2 hydrogen atom shift followed by threecenter elimination of H\(_2\), with a barrier height of 93.4 kcal/mol. The ethylidene intermediate was found to be an unstable structure along this energy path. A direct four-center elimination was ruled out since its barrier height is 109.3 kcal/mol. In contrast, for vinyl fluoride Kato and Morokuma\(^{23} \) found that direct \( \alpha,\alpha \) and \( \alpha,\beta \) elimination of HF have barriers of 79.8 and 81.0 kcal/mol, while a 1,2 shift occurs at the much higher energy of 111.5 kcal/mol. Morokuma et al.\(^{24} \) also found for formaldehyde that when the \( \alpha \) hydrogen is replaced by a fluorine atom the barrier for a 1,2 H atom shift is 25 kcal/mol higher than for direct elimination of HF. Similarly, for DCE we expect that a 1,2 shift of the H atom has a much higher barrier than direct HCl elimination. We accordingly rule out the migration of a hydrogen atom from one carbon to the other as the first part of a stepwise mechanism.

Without detailed knowledge about the potential energy surfaces, we can only speculate about the nature of the nonconcerted process. Further theoretical and experimental work is clearly needed. In particular, measurements of the relative kinetic energy distributions as a function of \( v'' \) and \( J'' \) would help to distinguish between concerted and stepwise mechanisms.\(^{25} \)

B. Product Yields. In Table I we show that the relative yields of HCl for the 1,1, cis, and trans isomers are in the approximate ratio of 1:1:2. The greater yield for trans-DCE might be a simple consequence of the availability of both \( \alpha,\alpha \) and \( \alpha,\beta \) pathways for this isomer, as compared with only \( \alpha,\beta \) elimination for 1,1-DCE and \( \alpha,\alpha \) elimination for cis-DCE. This argument works, however, only if elimination is rapid compared with rotation about the C–C bond. The barrier to cis–trans isomerization of DCE is only 57.4 kcal/mol,\(^{26} \) as compared with a total available energy of 120 kcal/mol. On the photoexcited \( \pi,\pi^* \) surface, one CH\(_2\) or CHCl group is twisted 90° with respect to the other.\(^{27} \) On both potential energy surfaces, therefore, rotation about the C–C bond should be facile.

Another possible explanation is that different electronic states of the isomers are simultaneously excited. For the trans compound 193 nm lies on the short wavelength side of the absorption maximum, while for 1,1 it lies near the peak and for cis it lies on the long wavelength side.\(^{28} \) This explanation can be tested by measuring the relative yields as a function of wavelength.\(^{29} \) We feel that this is an unlikely explanation since for all three isomers the very large oscillator strength (around 0.4 at the maximum) is carried by the same \( \pi \rightarrow \pi^* \) transition.

A third possibility is that the relative yields reflect different internal conversion rates of the isomers. Our hypothesis is that very rapid internal conversion to the ground electronic surface is followed by slow elimination (concerted or otherwise) on the lower surface.\(^{4} \) The matrix elements for surface crossing are likely to vary for the three isomers, resulting in different HCl yields.

A very different situation occurs for HCl\(^+ \). As is discussed in the following section, we previously established that this product is the result of two-photon elimination of electronically excited HCl followed by one-photon ionization.\(^{4} \) As shown in Table I, the yields in this case are 4:1:1 for 1,1, cis, and trans. The equal yields for cis and trans are plausible since we expect that two-photon absorption is slow compared with rotation about the C–C bond on an electronically excited surface. The greater yield for the 1,1, isomer can be understood in light of our recent study of VCl-d\(_1\), which showed that HCl\(^+ \) is produced mainly by an \( \alpha,\beta \) mechanism.\(^{14} \) Assuming that the excited state is twisted, we expect that for 1,1-DCE each CI atom can react with either of two H atoms, while for cis- and trans-DCE there is only one H atom available on the opposite carbon.

For all of the atomic fragments (H, Cl(\( ^{2}P_{3/2} \)), and Cl(\( ^{2}P_{1/2} \))) the cis and trans yields are equal. This would be the result if dissociation were slow compared with rotation about the C–C bond. Previously,\(^{4} \) we showed that H atoms recoil isotropically, indicating that dissociation is indeed slower than rotation of the molecule. On the other hand, a substantial fraction of the Cl atoms recoil anisotropically. If we suppose that the internal conversion rates in this case are the same for cis and trans, then the identical atomic yields for these two isomers may simply reflect the fact that the local environments of the Cl and H atoms are very similar. For both cis- and trans-DCE the H atoms share their C atom with a Cl atom, while for 1,1-DCE the H atoms are attached to the same carbon.

Since 1,1-DCE is topologically distinct, it is not surprising that its product yields are also different. It is intriguing to speculate why in some cases the yield for 1,1 is greater than for cis and trans (i.e., the 1,2 isomers), while in others it is smaller. For H atoms the 1,1 yield is 3–4 times greater. For 1,2-DCE the electron-withdrawing nature of \( \alpha,\beta \) atoms weakens the C–H bond. This is likely to be a small effect which would result in a larger yield for 1,2-DCE, contrary to what we observe. The correct explanation of the relative yields is more likely to lie with the relative stabilities of the organic fragments (structures 1 and 4 in Figure 7). Both radicals may have contributions from a zwitterionic structure\(^{30,32} \) having a positive charge on the \( \beta \) carbon atom (2 and 5). These zwitterions are stabilized by relocating the positive charge onto the CI atom (3 and 6). The key point is that the zwitterion produced from the 1,1 radical is doubly stabilized by the availability of two resonance structures (6a and 6b), accounting for the larger H atom yield for this isomer.
For Cl(2P,3P) atoms we observe the opposite trend, with the yield from 1,1-DCE being approximately 75% that of 1,2-DCE. In this case both zwitterions (structures 8 and 11 in Figure 8) are stabilized by only a single Cl atom. Here, however, the ionic structure produced from the 1 radical (10) is likely to be less stable because the unpaired electron resides on the positively charged carbon (11), leaving it with seven electrons in the resonant configuration (12). In the ion produced from the 1,2 radical (7) the unpaired electron lies on the negatively charged ion (8), and in the resonance structure (9) the stabilized carbon has a full octet.

Another interesting question is the branching fraction of Cl(2P,3P) atoms. While for ground-state atoms the yield from 1,1-DCE is approximately 75% that from 1,2-DCE, for Cl(2P,3P) it is approximately double. We know from past experience that the populations of the fine structure states are influenced by long-range forces.30 We conclude that the asymptotic forces are significantly different for CH2Cl and CHClCH2Cl, which have a large effect on the fine structure (i.e., electronic) state of the Cl atom. This is in contrast with the asymptotic forces in the molecular elimination channel, where isomeric differences have very little effect on rotational (i.e., nuclear) motion.

Finally, in the case of Cl+ the relative product yields depend somewhat on laser intensity. Qualitatively, the Cl+ yields resemble those of HCl, suggesting a common mechanism. This is discussed further in the following section.

C. Intensity Dependence of the Products. As in our study of VCI, we found that HCl, H, and Cl are all single-photon products. The only slightly surprising result is the H atom quantum yield. For ethylene Stokowit et al.31 found evidence of a two-photon mechanism, namely, slow photodissociation of ethylene followed by rapid photodissociation of the vinyl radical. For VCI and DCE, however, since the n → n* transition is shifted to longer wavelengths, detachment of the first H atom is the dominant process at 193 nm.

While HCl+ and Cl+ are only minor products under our experimental conditions, they are interesting because of the window they provide for viewing what happens on higher potential energy surfaces. Previously, we showed that HCl+ is the product of a 1 + 1 + 1 resonant mechanism. Rewriting this for DCE, the mechanism is

\[
\begin{align*}
\text{DCE} + h\nu &\rightarrow \text{DCE}^* \\
\text{DCE}^* + h\nu &\rightarrow \text{HCl}^* + \text{C}_2\text{HCl}
\end{align*}
\]  

and

\[
\text{HCl}^* + h\nu \rightarrow \text{HCl}^+ 
\]

Summarizing our earlier findings,4 the principal evidence for a three-photon resonant process is the observation of a cubic intensity dependence at a fluence as low as 2 mJ/cm².

Although we previously observed Cl+ in VCI photolysis, this is the first report of this reaction channel. Our observation of n = 3 indicates that at least four photons are involved. One possible mechanism is reactions 5a–5c to produce HCl+, followed by photodissociation of the ion. We can rule out this mechanism because of the very different relative yields of HCl+ and Cl+ for different isomers listed in Table I.

Another possibility is further "ladder climbing" in the DCE manifold followed by photodissociation to produce Cl+:

\[
\begin{align*}
\text{DCE} + h\nu &\rightarrow \text{DCE}^* \\
\text{DCE}^* + h\nu &\rightarrow \text{DCE}^* \\
\text{DCE}^{**} + h\nu &\rightarrow \text{Cl}^* + \text{C}_2\text{H}_2\text{Cl}
\end{align*}
\]

and

\[
\text{Cl}^* + h\nu \rightarrow \text{Cl}^+ 
\]

While this mechanism is not inconsistent with the data, it does not explain the similar relative yields for Cl+ and HCl. Since the latter is believed to result from internal conversion to the ground state of DCE, a comprehensive mechanism for both products might be

\[
\begin{align*}
\text{DCE} + h\nu &\rightarrow \text{DCE}^* \\
\text{DCE}^* &\rightarrow \text{DCE}^+ \\
\text{DCE}^+ &\rightarrow \text{HCl} + \text{CICCH} \\
\text{DCE}^+ + h\nu &\rightarrow \text{Cl}^* + \text{C}_2\text{H}_2\text{Cl}
\end{align*}
\]

and

\[
\text{Cl}^* + h\nu \rightarrow \text{Cl}^+ 
\]

In this mechanism (6d) DCE refers to vibrationally excited DCE on the ground electronic surface. The step which links the yields of HCl and Cl+ is (7b).

Conclusions

Most detailed studies of photodissociation dynamics have dealt with small molecules containing five or fewer atoms and only one chromophore. It is fascinating how the existence of two chromophores—in this case the carbon–carbon double bond and the chlorine lone pairs—can complicate the photodissociation dynamics, even for a molecule containing "only" six atoms. In this and our two preceding papers on the UV photodissociation of chloroethylenes, we have found abundant evidence for multiple reaction paths on both the ground and excited potential energy surfaces.

The main findings of the present study are summarized as follows:

1. The rotational state distributions of HCl produced from all three isomers of dichloroethylene are strikingly similar. All three have a biexponential distribution for v'' = 0 and a Boltzmann distribution for v'' = 1 and 2. These distributions are also very similar to those previously found for vinyl chloride. Since our recent work on partially deuterated VCI has shown that the state...
distributions are the same for three-center and four-center elimination, we attribute the differences between \( \phi'' > 0 \) and \( \phi'' = 0 \) to "microscopic" rather than "chemical" branching.

2. Close examination reveals some slight variations in the product distributions. For trans- and 1,1-DCE, the preexponential coefficients \( a \) and \( a_p \) for \( \phi'' = 0 \) are approximately equal, while for cis-DCE and VCI they have a ratio of 1.5. For all three isomers the Boltzmann temperatures for \( \phi'' > 0 \) are approximately 1400 K, as compared with 2000 K for VCl. In addition, the vibrational state distribution for trans-DCE is slightly colder than for the other two isomers.

3. We have measured the relative yields of HCl, H, Cl(2P3p), Cl(2P3p), HCl+, and Cl+ for 1,1-, cis-, and trans-DCE. For HCl and Cl+ the yield for trans-DCE is approximately double that of both the 1,1 and cis isomers. For the atomic fragments and HCl+ the yields for cis and trans are identical, with the 1,1 yield being smaller for Cl(2P3p) and greater for the other products. The relative yields of Cl and H can be explained by the stabilities of the organic fragments.

4. The yields of the neutral products were all found to vary linearly with laser intensity, indicating that they were produced by a single photon. In contrast, HCl+ requires three photons and Cl+ at least four photons, both resulting from ladder climbing mechanisms.

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References and Notes


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