

Photodissociation of Isomeric Chloropropene Cations and Structure of Reactively Produced Chloropropene Ions

Robert G. Orth[†] and Robert C. Dunbar*

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received November 16, 1981

Abstract: The photodissociation spectrum of the isomers of chloropropene cations have been obtained in the visible and ultraviolet regions of the light spectrum. The observed spectrum in the UV region has two maxima that were assigned to the $\pi \leftarrow n_z$ transition (3.5-eV peak maximum) and $\pi^* \leftarrow \pi$ transition (5.0-eV peak maximum). The observed photodissociation spectrum in the visible region from 640 to 580 nm is believed to arise from the $\pi \leftarrow n_{xy}$ transition and shows a vibrational progression for 1-chloropropene cation of 500 cm^{-1} and for 2-chloropropene cation of 320 cm^{-1} . This progression has been tentatively assigned to the skeletal vibration involving the chlorine atom. The 0-0 transition of the cis isomer was observed to be red-shifted by 8 nm with respect to the 0-0 transition of the trans isomer at 611 nm. The 2-chloropropene cation is further red shifted to 630 nm. The allyl chloride cation is distinctly different having a lower extent of dissociation and lacking resolved vibrational structure. These spectra were then compared with the spectra obtained for $\text{C}_3\text{H}_5\text{Cl}^+$ cations formed in the ion-molecule reaction of C_3H_6^+ with 1-chloropropene cation present. The photodissociation spectra of the $\text{C}_3\text{H}_5\text{Cl}^+$ originating from the reaction involving 1-chloropropene indicates that the $\text{C}_3\text{H}_5\text{Cl}^+$ cations are probably composed of a mixture of *cis*- and *trans*-1-chloropropene cations.

In ion-molecule reactions of gas-phase cations, there is frequently the possibility of different isomeric structures of the ionic reaction products. The application of photodissociation (PD) spectroscopy as a means of optical spectroscopic characterization of gas-phase ions has opened the possibility of unambiguous identification of isomeric ions from their distinct spectra.¹⁻⁹ Particularly promising is the highly specific and characteristic structural information obtained when vibrational fine structure can be resolved in the ion photodissociation spectra, usually by laser photodissociation techniques.⁵⁻⁹ We have reported the successful application of these ideas to identifying the isomeric $\text{C}_3\text{H}_5\text{Cl}^+$ product ions of ion-molecule reactions in chloropropene systems,¹⁰ and we give here a full description of this work. Detailed knowledge of the product-ion structure, normally not available in mass spectrometer or ion cyclotron resonance spectrometer studies of ion-molecule chemistry, is an important part of the information required to construct a reliable mechanistic picture of an ionic reaction.

The chemistry of interest here is the reaction of C_3H_6^+ with 1-chloropropane or 2-chloropropane to form $\text{C}_3\text{H}_5\text{Cl}^+$, which has four reasonable structures besides cyclic forms, namely *trans*- and *cis*-1-chloropropene, 2-chloropropene, and 3-chloropropene (allyl chloride). This ion-molecule reaction has apparently not been previously reported, although the homologous reaction between C_2H_4^+ and $\text{C}_2\text{H}_5\text{Cl}$ has been noted in the ion chemistry of ethyl chloride.¹¹

The needed spectroscopic information was obtained by forming the $\text{C}_3\text{H}_5\text{Cl}^+$ ions from the appropriate isomeric neutral at electron energies that would minimize interconversion and determining the photodissociation spectrum in the UV and visible regions of the optical spectrum by utilizing an ion cyclotron resonance instrument. The vibrational structure in the visible region was determined by use of a CW tunable dye laser that permits the measurements of the photodissociation spectrum with a resolution of 1 nm. With the vibrationally resolved spectra of the isomers available for comparison, the photodissociation spectrum of the $\text{C}_3\text{H}_5\text{Cl}^+$ ionic product was measured for each of the reactions. Comparison of the resulting photodissociation spectra with those obtained for the various authentic isomers gave a satisfactory picture of product-ion structures.

Experimental Section

The photodissociation spectra were obtained by using a Varian ICR-9 spectrometer modified by replacing the drift cell by a trapped-ion square cell and by operating the trapping cell in a pulse mode.¹² The light

source for determination of the photodissociation (PD) spectrum in the UV-visible region was a 2.5-kW Hg-Xe arc lamp, with the wavelength selected by a Schoeffel GM-250 monochromator with a grating blazed at 300 nm and a bandwidth of 14 nm. Where increased light intensity was needed, as in the 600-400-nm region, interference filters with band-pass of 100 Å were utilized. The absolute cross sections for PD were determined by using the absolute cross sections of toluene cation as the reference, which in previous results has yielded cross sections believed accurate to within a factor of 2.¹³

The high-resolution photodissociation spectra were determined by using a Coherent Radiation Model 490 CW tunable dye laser pumped by a CR-12 argon ion laser. Dyes used included sodium fluorescein (with a lasing output between 530-580 nm) and rhodamine 6G (with a lasing output between 570 and 645 nm). The data were collected at a constant power output from the dye laser as the wavelength was varied. For accurate determination of relative photodissociation cross sections, the laser beam was expanded in such a way as to uniformly illuminate the ion trap. The wavelength dial on the pump dye laser head was calibrated against the Schoeffel monochromator with 1-mm slits, and the dial reading was believed to be accurate to within 1 nm.

The ion trap was operated in a dynamic pulsed mode.^{12,14} In this mode of operation, the ions are formed by a pulse of electrons that lasts for 50 ms. The energy of the electrons was 1-2 eV above the ionization potential of the compounds as determined from photoelectron spectra in order to minimize olefin ion isomerizations. After the ions are formed, they are trapped for a reaction period of up to 5 s, at the end of which they are rapidly detected to determine to what extent they have undergone change due to reactions or interactions with light. At the end of the detection period, the ions are cleared from the ion trap and the experiment repeated. The photodissociation process was observed by monitoring the change in the ion intensity when the ions were illuminated as compared to the intensity without light.

All samples were reagent grade and were checked for purity by using the ICR as an EI mass spectrometer. The reaction pathways were de-

- (1) J. M. Kramer and R. C. Dunbar, *J. Chem. Phys.*, **59**, 3092 (1973).
- (2) R. C. Dunbar and E. Fu, *J. Am. Chem. Soc.*, **95**, 2716 (1973).
- (3) R. C. Dunbar, *Anal. Chem.*, **48**, 723 (1976).
- (4) E. W. Fu and R. C. Dunbar, *J. Am. Chem. Soc.*, **100**, 2283 (1978).
- (5) R. C. Dunbar and H. H. Teng, *J. Am. Chem. Soc.*, **100**, 2283 (1978).
- (6) T. F. Thomas, F. Dale, and J. F. Paulson, *J. Chem. Phys.*, **67**, 793 (1977).
- (7) D. C. McGilvery and J. D. Morrison, *J. Chem. Phys.*, **67**, 368 (1977).
- (8) R. C. Dunbar in "Ion Photodissociation in Gas Phase Ion Chemistry", Vol. 11, M. T. Bowers, Ed., Academic Press, New York, 1979.
- (9) R. C. Dunbar, *Mass Spectrom.*, **6**, in press.
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- (11) J. L. Beauchamp, D. Holtz, S. D. Woodgate, and S. L. Patt, *J. Am. Chem. Soc.*, **94**, 2798 (1972).
- (12) R. G. Orth and R. C. Dunbar, *Chem. Phys.*, **45**, 195 (1980).
- (13) R. G. Orth and R. C. Dunbar, *J. Chem. Phys.*, **66**, 1616 (1977).
- (14) B. S. Freiser and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 6260 (1974).

[†] Present address: Department of Chemistry, Montana State University, Bozeman, MT 59717.

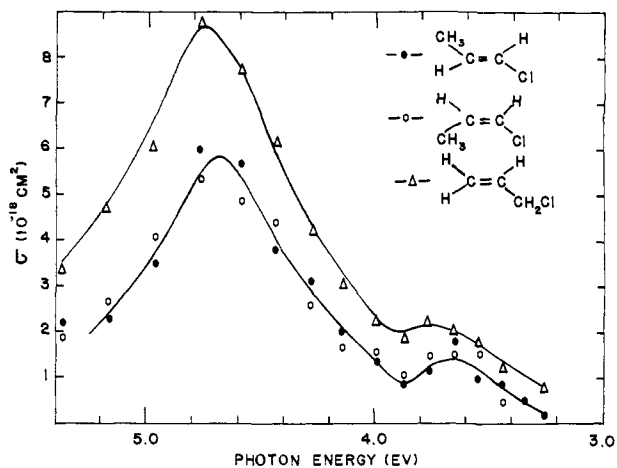
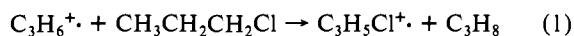


Figure 1. Photodissociation curves for allyl chloride, *cis*-1-chloropropene, and *trans*-1-chloropropene cation. The data were obtained with resolution of 14 nm.

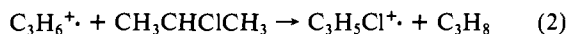
terminated by double-resonance technique that have been described elsewhere.¹⁵

Results

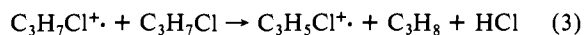
Ion-Molecule Reactions. The double-resonance capability of the ICR spectrometer was used to identify the reactions leading to $C_3H_5Cl^+$ formation in 2-chloropropane and 1-chloropropane at a pressure of $(1-2) \times 10^{-7}$ torr. For both systems, $C_3H_6^+$ (abundant from electron impact on C_3H_7Cl) was found to be the precursor of more than 75% of the $C_3H_5Cl^+$ formed, the reactions presumably being



and

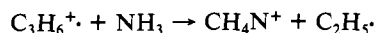
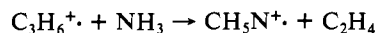


In both systems the remainder of the $C_3H_5Cl^+$ was found to originate from the $C_3H_7Cl^+$ parent ion. This suggests the reaction



although the neutral products $C_3H_7Cl + H_2$ are also plausible (being about 11 kcal less stable¹⁶ than the products indicated in reaction 3).

The photodissociation results described below address the question of the product ion of reactions 1 and 2 but have nothing to say about the structure of the $C_3H_6^+$ reactant ion. It has been observed that the $C_3H_6^+$ ion formed from cyclopropane undergoes the following reactions:¹⁷



The $C_3H_6^+$ ion that is formed by electron impact on propane, however, does not react with NH_3 . The results of labeling studies carried out with labeled tetrahydrofuran¹⁵ as the source of $C_3H_5D^+$ ions further supported the belief that the reactive $C_3H_6^+$ was indeed cyclic in structure. To determine if $C_3H_6^+$ ions in reactions 1 and 2 have cyclic or linear structure, we examined reactions of the $C_3H_6^+$ ions with NH_3 in a tandem ion cyclotron resonance instrument.¹⁸ The $C_3H_6^+$ was formed from 1-chloropropane and 2-chloropropane in the source of a Dempster mass spectrometer and then injected into an ICR cell that contained NH_3 . No reaction products were observed, indicating that

(15) T. A. Lehman and M. M. Bursey, "Ion Cyclotron Resonance Spectrometry", Wiley, New York, 1976, 13-14 and references therein.

(16) H. M. Rosenstock et al., *J. Phys. Chem. Ref. Data, Suppl.*, **1**, 6, (1977).

(17) M. L. Gross, *J. Am. Chem. Soc.*, **94**, 3744 (1972).

(18) For a complete description of this instrument, see D. L. Smith and J. H. Futrell, *Int. J. Mass Spectrom. Ion Phys.*, **14**, 171 (1974).

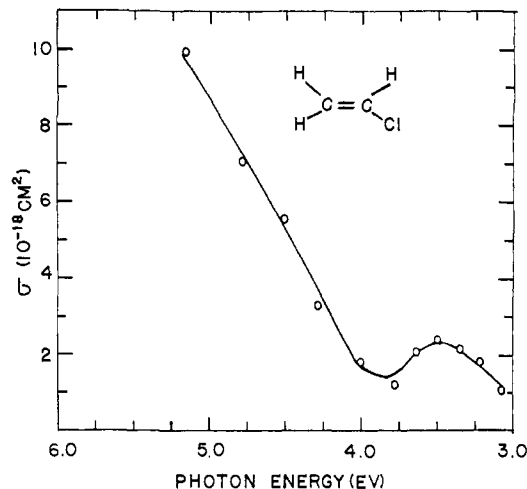


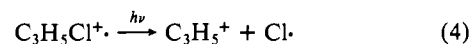
Figure 2. Photodissociation curve for vinyl chloride cation.

the $C_3H_6^+$ formed from 1-chloropropane and 2-chloropropane has a structure that is not cyclic.

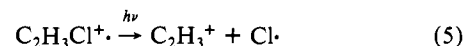
Photodissociation Spectra. Low-resolution photodissociation spectra of $C_3H_5Cl^+$ parent ions from isomeric neutrals are shown in Figure 1 over the range 3.0-5.4 eV. A spectrum is not shown for the 2-chloropropene parent ion, whose relatively high reactivity limited the ion's lifetime in the ion trap; only at the intense Hg lines at 3.38 (366 nm) and 4.0 eV (310 nm) was photodissociation measurable, giving cross sections at these wavelengths of 1.0×10^{-18} and 1.5×10^{-18} cm², respectively, which are similar to the cross sections of the other ions at these wavelengths. The spectra of figure 1 are clearly very similar, differing evidently only in absolute cross section. A peak is seen in each case at 3.65 eV, and a much more intense peak at 4.7 eV.

For comparison, a spectrum of vinyl chloride was also taken in this region, as shown in Figure 2. A peak with cross section 2.5×10^{-18} cm² is seen at 3.3 eV. At energies above 4.0 eV, the curve increases steadily with no maximum observed out to 5.1 eV.

For all four of these isomers, double resonance showed that the photoinduced increase in $C_3H_5^+$ arose from $C_3H_5Cl^+$ throughout the UV and visible photodissociation regions, indicating the photodissociation process



Vinyl chloride ion also dissociated via loss of Cl:



The spectra of Figure 1 are of little value for product isomer identification in reactions 1 and 2: the relatively small cross-section differences would be difficult to exploit, and added complications arise because the reactant $C_3H_6^+$ is itself photodissociated at short wavelengths. More useful is the weak photodissociation of $C_3H_5Cl^+$ in the red, which was initially observed by using the strong Hg line at 579 nm, with a cross section of about 5×10^{-20} cm². This red photodissociation feature was examined in detail with the dye laser, and laser spectra are shown in Figure 3. The high intensity and narrow bandwidth of the laser make the resolution of vibrational structure possible in these weak photodissociation features. The first maximum in the PD curve of 2-chloropropene cation occurs at 630 nm and shows a vibrational progression of 350 ± 30 cm⁻¹ (0.042 eV). The *cis*-1-chloropropene cation has a vibrational progression of 500 ± 30 cm⁻¹ (0.060 eV) and a first maximum, which is blue shifted with respect to 2-chloropropene cation, at 618 nm. The 2-chloropropene PD spectrum differs from *cis*-1-chloropropene, indicating that there is little or no structural interconversion after electron impact. The PD spectrum for *trans*-1-chloropropene cation is blue shifted with respect to *cis*-1-chloropropene cation by 8-610 nm, and the vibrational progression is observed at 420 ± 20 cm⁻¹ (0.051 eV)

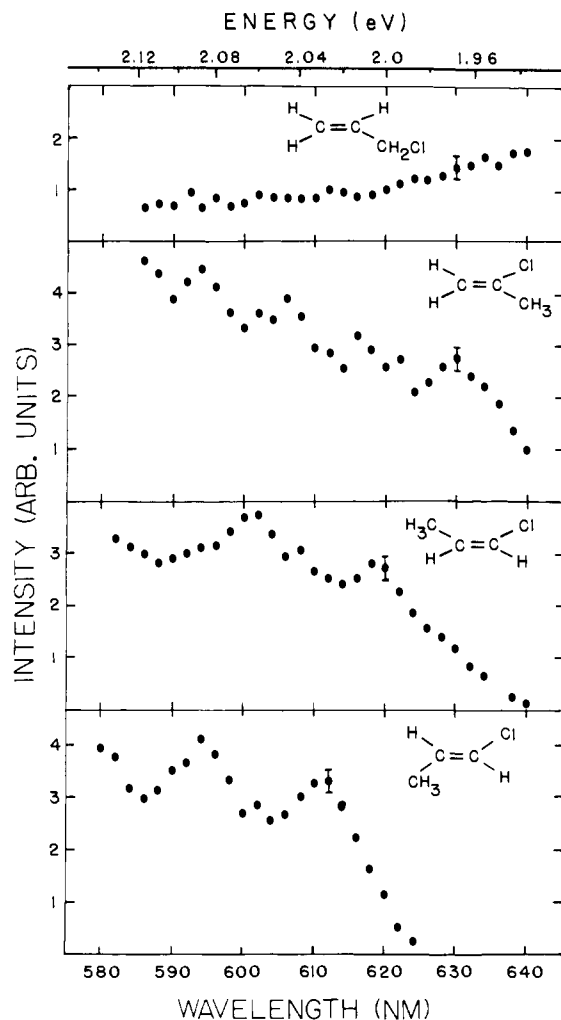


Figure 3. The high-resolution photodissociation spectra for the $C_3H_5Cl^+$ isomers are shown at a resolution of 1 nm. The data were obtained with the CW tunable dye laser.

Table I. Radical Cation Excited States Derived from PES Spectra

allyl chloride, ^{23,25} eV	1-chloropropene, ²⁴ eV	vinyl chloride, ^{23,25} eV
(A) 1.2	2.0	1.66
(B) 3.0	3.5	3.13
(C) 3.9	4.5	3.55
(D) 5.0	5.25	5.29

(in contrast to 500 cm^{-1} observed for the cis isomer). The allyl chloride cation on the other hand showed no vibrational structure, and the relative intensity was found to increase to higher wavelengths, showing no clear photodissociation onset.

Discussion

Photodissociation Spectra: Electronic Transitions. A valuable point of reference in assigning PD spectra has been comparison with photoelectron spectra of the corresponding neutrals.¹⁹⁻²² Shown in Table I are low-lying ion excited states derived from PES spectra of vinyl chloride, 1-chloropropene, and allyl chloride.²³⁻²⁵ For comparison with ion optical transitions, these are

(19) P. P. Dymerski, E. W. Fu, and R. C. Dunbar, *J. Am. Chem. Soc.*, **96**, 4109 (1974).

(20) R. C. Dunbar, *Anal. Chem.*, **48**, 723 (1976).

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(22) R. C. Dunbar, *Chem. Phys. Lett.*, **32**, 508 (1975).

(23) C. W. Worrell, *J. Electron Spectrosc. Relat. Phenom.*, **3**, 359 (1974).

(24) A. Katrib, T. P. Debies, R. J. Colton, T. H. Lee, and J. W. Rabalais, *Chem. Phys. Lett.*, **23**, 196 (1973).

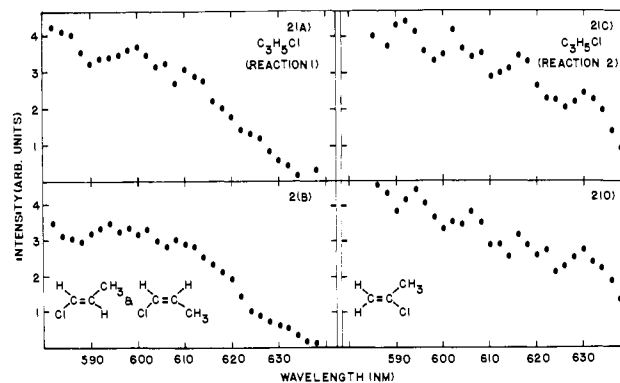


Figure 4. (A) Relative photodissociation curve for $C_3H_5Cl^+$ formed in reaction 1. (B) The photodissociation curve for mixture of *trans*- and *cis*-chloropropene cation is shown for comparison and was calculated from the results in Figure 3. (C) The relative photodissociation spectrum of $C_3H_5Cl^+$ formed in reaction 2 is shown. (D) Photodissociation spectrum of 2-chloropropene (reproduced from Figure 3).

tabulated as the energy of the (vertical) PES peak position above the (adiabatic) lowest PES ionization potential, which, it has been argued,^{4,26} should be the quantity most nearly comparable to optical absorption peak energies.

1-Chloropropene. The photodissociation feature near 2 eV clearly corresponds to the PES peak²⁴ at 2.0 eV. This orbital is the out-of-plane chlorine lone-pair orbital (A'). Optical transition from the ion ground state ($A''\pi$) to this ($A'n_{xy}$) state is not symmetry forbidden but has a very unfavorable transition dipole as a result of the poor overlap of the in-plane n_{xy} orbital with the π system. Thus it is not surprising that this $n_{xy} \rightarrow \pi$ transition has a low observed cross section ($5 \times 10^{-20}\text{ cm}^2$ at 579 nm).

The PDS peak at 3.65 eV in the 1-chloropropene ion evidently corresponds to the PES peak at 3.5 eV that arises from removal of an electron from the out-of-plane nonbonding chlorine orbital: in fact, the "nonbonding" designation is inaccurate, as the ($A'n_z$) orbital is believed to include substantial participation of the π system. There are accordingly no critical symmetry or spatial-overlap restrictions on this $n_z \rightarrow \pi$ optical transition, and the moderate observed cross section, although considerably smaller than that observed in strong $\pi \rightarrow \pi$ transitions,³ still seems reasonable.

In alkene radical ions studied by photodissociation spectroscopy, a universal feature has been a very strong peak in the far UV, in the vicinity of 5 eV, which is understood to arise from $\pi \rightarrow \pi^*$ excitation of an electron into the empty antibonding π^* orbital.³ This ion-excited state corresponds to a double-excitation process in the PES spectrum and is therefore expected to be weak or absent in PES; it is shifted substantially to lower energy relative to the corresponding π^* state in the neutral. Although the PES spectrum of 1-chloropropene does show an orbital at 4.5 eV that could conceivably correspond to the intense 4.7-eV PDS peak in 1-chloropropene ion, it seems most unlikely that such a $\sigma \rightarrow \pi$ excitation could be responsible, and it is entirely likely that this UV peak in the PD spectrum is the usual alkene $\pi \rightarrow \pi^*$ transition.

2-Chloropropene. While a PES spectrum was not found for this compound, there is no reason to expect material differences from 1-chloropropene, and the arguments and assignments made above for the 1-chloropropene PD spectrum should be equally valid for this ion.

Vinyl Chloride. The out-of-plane n_{xy} orbital lies near 1.66 eV,^{23,25} which, unfortunately, is not readily accessible to our laser, so that photodissociation in this region was not attempted. The dissociation observed in the 5-eV region most likely reflects $\pi \rightarrow \pi^*$ excitation, as in the 1-chloropropene case. The PD peak at 3.3 eV presumably arises from $n_z \rightarrow \pi$ excitation involving the

(25) G. W. Mines and H. W. Thompson, *Spectrochim. Acta, Part A* **29A**, 1377 (1973).

(26) R. C. Benz, P. C. Claspy, and R. C. Dunbar, *J. Am. Chem. Soc.*, **103**, 1799.

chlorine out-of-plane lone-pair electrons, in analogy with the chloropropene spectra. The PES spectrum is actually not helpful in assigning this peak, since PES peaks are reported at both 3.13 and 3.55 eV; although Mines and Thompson²⁵ assign the 3.13-eV peak to the chlorine n_z lone pair, this assignment does not seem very secure, and the correct correspondence between PES and PDS peaks in this case is not clear.

Allyl Chloride. The PES spectrum^{23,25} shows no orbital in the 2-eV region, and the weak photodissociation observed with the red laser is likely to be the short-wavelength tail of a broad absorption corresponding to the (nearly degenerate) chlorine lone-pair orbitals at 1.2 eV.

The PD feature at 3.7 eV lies close to the PES peak at 3.9 eV. Mines and Thompson²⁵ assign this orbital (on unexplained grounds) as having C-Cl bond character. In contrast to the other ions, the interaction between chlorine and the π system is weak in allyl chloride, so that the chlorine lone-pair orbitals both lie near 1.2 eV, and the 3.7-eV PDS peak cannot be an $n \rightarrow \pi$ excitation.

As in the other cases, it seems reasonable to assign the intense 4.7-eV peak in allyl chloride as a $\pi \rightarrow \pi^*$ excitation.

Vibrational Spectral Structure and Isomeric Ions. The high-resolution spectra in Figure 3 show a remarkable contrast between the allyl chloride, the *cis*- and *trans*-1-chloropropene, and the 2-chloropropene cations. Figure 3 clearly shows that it is possible to distinguish all of the isomers. The allyl chloride cation photodissociation lacks vibrational structure and shows a slow increase in relative photodissociation cross section as 640 nm is approached. This increase suggests that a maximum in the photodissociation may occur at longer wavelengths, which is in agreement with the placement of the first excited state of the ion at 1.2 eV (Table I).

The PD spectra of the *cis*- and *trans*-1-chloropropene cations and the 2-chloropropene cation shown in Figure 3 have clearly defined onsets for photodissociation as well as vibrational structure. The vibrational progressions observed in the PD curves cannot unambiguously be assigned at this point. However, in vinyl chloride cation, the peak that arises from loss of an electron from the in-plane chloride n_{xy} orbitals shows a progression that has tentatively been assigned to C-Cl stretching.²⁷ This progression has a frequency of ~ 500 cm^{-1} , which corresponds well with the progressions noted here. The neutral chloropropenes have been examined extensively with regard to the vibrational frequencies.²⁸⁻³² The modes having the correct symmetry and frequencies all arise from C-Cl stretching or C-C-Cl rocking motions. Thus it would seem reasonable at this point to say that the progressions observed in $\text{C}_3\text{H}_5\text{Cl}^+$ belong to skeletal vibrations involving the chlorine atom, very possibly in a C-Cl stretching motion.

It is clear from the photodissociation curves in Figure 3 that the four isomeric cations have independent and noninterconverting structures. This stands to point out the usefulness of PD curves in the identification of isomeric cations. The observed differences in photodissociation onsets and the vibrational frequencies are somewhat surprising considering the common observation in mass spectrometry of the interconversion of olefinic ions. However, this is not the first case where olefinic isomeric structures have been differentiated by photodissociation,^{1,26} as for instance the results reported by Kramer and Dunbar¹ for isomeric butenes 1-butene, *cis*- and *trans*-2-butene, and isobutene, where the 1-butene cation was clearly differentiated from the *cis*-2-butene cation both in photodissociation onset and in the shape of the curve. These observed differences were further supported by photoionization mass spectrometry results³³ that indicated that at pho-

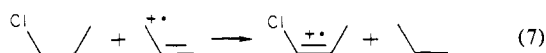
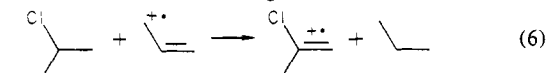
tonizing energies near the ionization potential of 1-butene, little or no ion rearrangement occurred, but that 2.0-2.2 eV above the IP for 1-butene, rearrangement was the predominant pathway.

It is notable that the *cis* and *trans* isomers of 1-chloropropene cation are readily identified and that no interconversion occurs. Although 1-chloropropene is distinguished from simple olefins both by the intersection between the chlorine atomic orbitals and the double-bond π system, and also by the relatively massive chlorine substituent, it is nevertheless notable that this is the closest test case yet available on the question of whether rotation about the double bond occurs in olefin radical ions. (The removal of one of the two bonding π electrons makes free rotation a much more plausible process than in the corresponding neutral olefin). There is, on the other hand, substantial evidence for hindered rotation in diene radical cations.²⁶

Identification of $\text{C}_3\text{H}_5\text{Cl}^+$ Products. Laser PD spectra were taken of the product $\text{C}_3\text{H}_5\text{Cl}^+$ ions from reactions 1 and 2, as displayed in Figure 4. These spectra can be compared with the corresponding authentic-isomer spectra of Figure 3. As Figures 4C and 4D indicate, the $\text{C}_3\text{H}_5\text{Cl}^+$ formed in reaction 2 show good agreement in curve shape and structure with the 2-chloropropene cation in the region of PD onset. As shorter wavelengths are approached, there are differences that are outside of the experimental uncertainties. This comparison indicates that the bulk of the $\text{C}_3\text{H}_5\text{Cl}^+$ ions formed in reaction 2 have the 2-chloropropene structure, while the differences seen at shorter wavelengths may suggest that some 1-chloropropene is present as well.

As can be seen in Figure 4A, the photodissociation curve for the $\text{C}_3\text{H}_5\text{Cl}^+$ formed in reaction 1 shows little or no vibrational structure, with a slowly rising photodissociation onset. The low extent of photodissociation observed at 630 nm, the substantial PD cross section at shorter wavelengths, and the lack of PD at longer wavelengths rule out both allyl chloride cations and 2-chloropropene cations as major product-ion components. This would leave the 1-chloropropene as the major component, but the lack of the expected vibrational structure casts some doubt on this conclusion. The loss in vibrational structure can, however, be attributed to the product being composed of a mixture of *cis*- and *trans*-1-chloropropene cations. This is supported by Figure 4B, where the calculated photodissociation curve is shown for equal mixtures of the *cis*- and *trans*-1-chloropropene cations. As is evident from the comparison of parts A and B of Figure 4, there is satisfactory agreement, supporting the contention that the $\text{C}_3\text{H}_5\text{Cl}^+$ is composed of a mixture of 1-chloropropene cations.

The definite nonidentity of the products of reactions 1 and 2 carries a strong implication that the $\text{C}_3\text{H}_5\text{Cl}^+$ skeleton is derived from the neutral reactant by formal H_2^- abstraction. The reactions can be summarized in the following:



While not an obviously favorable reaction, H_2^- abstraction is not unprecedented, and there is evidence for its occurrence in olefin ion-molecule reaction chemistry.³⁴⁻³⁶ The failure of reaction 7 to form allyl chloride product ion suggests further that the abstraction of H_2^- is derived from hydrogens at the 1 and 2 positions, since 2,3 elimination would yield allyl chloride product ions. These mechanistic conclusions can usefully be confirmed by complementary deuterium-labeling studies, but the present results point up the mechanistic utility of reliable spectroscopic product-ion structure information.

(27) J. W. Rabalais in "Principles of Ultraviolet Photoelectron Spectroscopy," Wiley, New York, 1977, p 319.

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Acknowledgment. The support of the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the U.S. Air Force Geophysical Laboratory is gratefully acknowledged. We also acknowledge with thanks the kindness of Professor J. H. Futrell in providing the use of the tandem ICR instrument at Utah

and in supporting R.G.O.'s work on it.

Registry No. Allyl chloride radical cation, 82880-45-3; *cis*-1-chloropropene radical cation, 82916-36-7; *trans*-1-chloropropene radical cation, 82916-37-8; vinyl chloride radical cation, 50910-56-0; 2-chloropropene radical cation, 82880-46-4; propene radical cation, 34504-10-4; 1-chloropropane, 540-54-5; 2-chloropropane, 75-29-6.

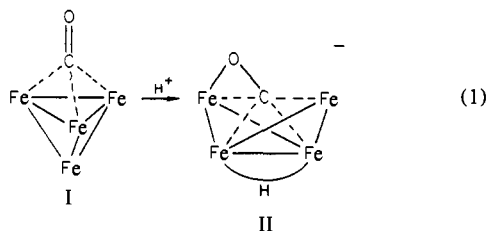
Nucleophilic Attack and Structural Rearrangements in Some Iron Carbonyl Cluster Carbides. Syntheses, Structures, and Reactions of the Tetrahedral Four-Iron Clusters $[\text{Fe}_4(\text{CO})_{12}(\mu_3\text{-COCH}_3)]^-$ and $[\text{Fe}_4(\text{CO})_{12}(\text{CCH}_3)]^-$

E. M. Holt,*^{1a} K. H. Whitmire,^{1b} and D. F. Shriver*^{1b}

Contribution from the Departments of Chemistry, Northwestern University, Evanston, Illinois 60201, and Oklahoma State University, Stillwater, Oklahoma 74078. Received January 19, 1982

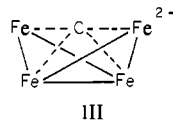
Abstract: The reaction of the four-iron butterfly compound $[\text{Fe}_4(\text{CO})_{12}\text{C}]^{2-}$ with the strong carbocation reagent $\text{CH}_3\text{SO}_3\text{CF}_3$ leads to alkylation of the carbide carbon and structural rearrangement of the metal framework to produce a tetrahedral ethyne compound, $[\text{Fe}_4(\text{CO})_{12}(\mu_3\text{-CCH}_3)]^-$. The rearrangement is readily explained by the cluster valence electron count. The tetrahedral carbonyl anion $[\text{Fe}_4(\text{CO})_{12}(\mu_3\text{-CO})]^{2-}$ in the presence of $\text{CH}_3\text{SO}_3\text{CF}_3$ is alkylated on the oxygen of a trihapto carbonyl to produce $[\text{Fe}_4(\text{CO})_{12}(\mu_3\text{-COCH}_3)]^-$, in which the tetrahedral iron array is retained. In this case, alkylation does not change the formal count of electrons available for cluster bonding and therefore does not change the geometry of the four-iron array. There is, however, an inductive electron demand imposed on the cluster by O-alkylation, and this appears to be responsible for the shift of ancillary semibridging CO ligands into terminal positions.

The four-iron carbonyl cluster compounds such as $[\text{Fe}_4(\text{CO})_{12}(\mu_3\text{-CO})]^{2-}$ (I) display novel chemistry and structural transformations. The first indication of this unusual chemistry was the discovery that protonation of I leads to a rearrangement of the four-iron skeleton from a tetrahedral to a butterfly array (eq 1).² More recently, four-iron butterfly carbides have been



Fe = iron with three attached CO ligands

discovered in which the carbide exhibits significant reactivity, e.g., III,³⁻⁵ and the conversion of the $\eta^2\text{-CO}$ in II to the exposed carbide in III has been achieved.⁶



In this paper we explore further the structural consequences of electrophilic attack on these four-iron systems. We find that the carbide in III is attacked by the methyl carbocation, yielding a product containing a tetrahedral four-iron skeleton. Protonation of III has been previously shown to occur in the metal framework, leaving the four-iron butterfly intact.

The tetrahedral cluster $[\text{Fe}_4(\text{CO})_{12}(\mu_3\text{-CO})]^{2-}$ (I) contains a $\mu^3\text{-CO}$ bridging one face and three semibridging CO ligands between the iron atoms of this unique face, V.⁷ In contrast to the protonation reaction, which occurs on the iron framework and transforms the tetrahedron into a butterfly array (eq 1) alkylation occurs on the oxygen of the face-bridging CO and leaves the tetrahedral array of iron atoms intact. The sites of attack and structural rearrangements provide valuable insight into the reactivity patterns of metal carbonyl and carbide cluster compounds.⁸

Experimental Section

General Procedures. Inert atmosphere Schlenk and dry-box techniques were used in handling all of the iron cluster compounds. Solvents were rigorously dried and degassed prior to use. $[\text{PPN}]_2[\text{Fe}_4(\text{CO})_{12}(\mu_3\text{-CO})]$ was synthesized by modifications of the procedure of Hieber and Werner for the synthesis of other salts of this polynuclear iron-carbonyl anion.^{9,10} (PPN = bis(triphenylphosphine)nitrogen cation). $[\text{PPN}]_2[\text{Fe}_4(\text{CO})_{12}\text{C}]$ was prepared by addition of methanolic KOH to a methanol solution of $\text{HFe}_4(\text{CO})_{12}(\text{CH})$,⁴ addition of a slight excess of $[\text{PPN}]\text{Cl}$ in methanol, and collection of the precipitate, which was washed with methanol. The infrared spectrum of this compound in CH_2Cl_2 solution agreed with the published infrared spectrum for the anion.⁴ Triflic acid (HSO_3CF_3) and methyl fluorosulfate ($\text{CH}_3\text{SO}_3\text{F}$) were distilled in an all-glass apparatus and stored in containers in which they were exposed to glass and Teflon surfaces only.¹¹

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