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THE PHOTOIONIZATION OF ALLYL CHLORIDE FROM ONSET TO 20 eV

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ABSTRACT

Photoionization efficiency data have been obtained for the parent ion and two fragment ions ($C_3H_5^+$ and $C_3H_3^+$) of allyl chloride. Onset energies are determined for these ions and heats of formation calculated for the fragment ions. The structures of the fragment ions are discussed in relation to their heats of formation.

INTRODUCTION

The photoionization efficiency curves for the $C_3H_5Cl^+$, $C_3H_5^+$, and $C_3H_3^+$ ions from allyl chloride are shown in Fig. 1. Onset energies were determined for these ions and heats of formation calculated for the fragment ions. The $C_3H_5^+$ ion is found to have the allyl structure while no definite structure is determined for the $C_3H_3^+$ ion.

A review of the current literature reveals no other photoionization experiments on allyl chloride. However, the photoelectron spectrum of allyl chloride from 5 through 20 eV is given by Worrell [1]. The results for the photoionization efficiency curve of the parent ion are in general agreement with the photoelectron spectrum given by Worrell.

EXPERIMENTAL

The experimental work reported here was performed using a photoionization mass spectrometer, a conventionally designed, 60°-sector, three-inch radius magnetic instrument coupled with a one-meter focal length Seya—Namioka monochromator. The light sources utilized were the hydrogen many-lined spectrum and the helium molecular spectrum. The hydrogen spectrum was obtained by a high-voltage d.c. discharge in hydrogen gas, whereas the helium molecular spectrum (Hopfield continuum) was produced

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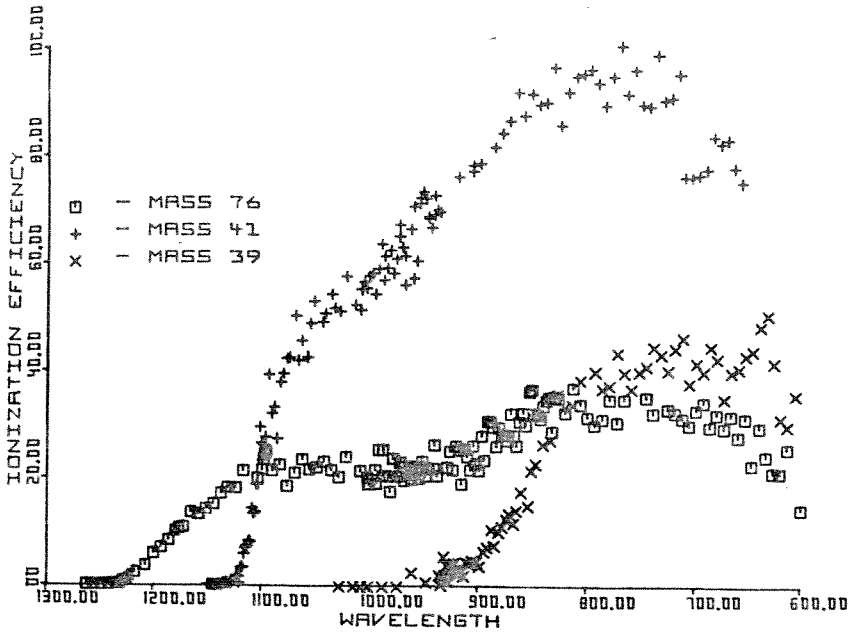

Fig. 1. Photoionization efficiency curves for allyl chloride and its fragment ions between threshold and 600 Å. The ordinate is the photoionization efficiency (arbitrary units), the abscissa the wavelength (Å). The curves have been corrected to give the proper relative intensities of the parent and fragment ions. Masses 76, 41, and 39 refer to the $C_3H_5Cl^+$, $C_3H_5^+$, and $C_3H_3^+$ ions, respectively. The conversion used to obtain the equivalent photon energy is $E(\text{eV}) = 12398.51/\lambda(\text{Å})$.

by a pulsed high-voltage (8-kV) discharge in helium gas. Differential pumping and use of the hydrogen and helium molecular light-sources gave radiation from 600 Å to beyond 2000 Å with a bandpass of ~1 Å. A photomultiplier was used to monitor the photon flux while a continuous-channel electron multiplier was used to monitor the ion countrate. The direct current from the photomultiplier was measured using a dynamic capacitor electrometer, and the individual ions detected by the electron multiplier were counted with an electronic scaling system. The phosphor used in the photomultiplier was sodium salicylate. It was assumed that the quantum efficiency of sodium salicylate remains constant over the range of radiation wavelengths reported here [2].

Analysis by the method of electron impact showed impurities in the allyl chloride to be less than 1%.

RESULTS AND DISCUSSION

The photoionization efficiency curves for the parent ion $C_3H_5Cl^+$ and the fragment ions $C_3H_5^+$ and $C_3H_3^+$ are shown in Fig. 1. In these curves the abscissa is linear
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Parent ion: $C_3H_5Cl^+$

The onset for the parent ion is taken to be the first rise from background in the photoionization efficiency curve. This is found to be at 10.04 ±0.01 eV and is taken to be the adiabatic onset energy. Above this onset the photoionization curve rises from background through a series of incompletely resolved steps until ~11.2 eV, where the curve levels off. The photoionization efficiency shows a large increase in value at ~13.4 eV.

The features of the parent-ion curve agree fairly well with the results of Worrell [1].

$C_3H_5^+$

The $C_3H_5^+$ ion has an appearance energy measured to be 11.05 ±0.04 eV, where the larger error is due to uncertainty in determining the onset. The photoionization curve for this ion shows an unexpected rapid rise in ionization efficiency with increase in energy just after onset. A rapidly rising fragment curve such as this may imply that this fragment is the result of a direct dissociative ionization process or is occurring by pre-dissociation.

In the discussion of the parent-ion curve, it was stated that a leveling-off in the photoionization efficiency occurred at ~11.2 eV. The rapid rise in photoionization efficiency for the $C_3H_5^+$ ion at this point suggests that the parent ion is being formed in a manner such that the excess energy remains in the parent ion which fragments to form the $C_3H_5^+$ ion. Thus the formation of the $C_3H_5^+$ ion is a process which competes with the existence of the parent ion at higher energies. The $C_3H_5^+$ ionization efficiency curve is linear after ~0.1 eV and remains so for ~1 eV. This is the region in the parent ionization efficiency curve that exhibits the first leveling-off.

Using the appearance potential for the heat of the reaction

$$C_3H_5Cl + h\nu \rightarrow C_3H_5^+ + Cl + e^- + KE$$

the calculated value for the heat of formation of the $C_3H_5^+$ ion is found to be 225 kcal mol^{-1} at 298 K. This agrees well with the value of 226 kcal mol^{-1} given by Lossing [3] who determined this ion to have the allyl structure. Thus it can be assumed that the $C_3H_5^+$ ion observed here also has the allyl structure.

$C_3H_3^+$

The $C_3H_3^+$ ion was found to have an appearance energy of 13.37 ±0.08 eV. The photoionization efficiency curve rises slowly and then levels off at

~15.5 eV. The fragment ion $C_3H_5^+$ has a leveling off in its ionization efficiency curve at ~14 eV. This is in the region where the $C_3H_3^+$ ion intensity has reached an appreciable value. This suggests that the $C_3H_3^+$ ion is formed by a process competing with the formation of the $C_3H_5^+$ ion. The leveling-off for both fragment ions at ~15 eV could be due to competition with another process not observed in this study.

Using the appearance energy for the heat of the reaction

$$C_3H_5Cl + h\nu \rightarrow C_3H_3^+ + H_2 + e^- + KE$$

the calculated value for the heat of formation of the $C_3H_3^+$ ion is found to be 279 ±2 kcal mol^{-1} at 298 K. This value lies between other values listed [4] as 257 and 281 kcal mol^{-1}, making identification of the ion's structure doubtful at this time.

SUMMARY

Photoionization studies have been made of allyl chloride, in which three ions were detected with significant rates of ionization. The adiabatic onset energy for the parent ion is found to be 10.04 ±0.01 eV. The fragment ions detected were the $C_3H_5^+$ and the $C_3H_3^+$ ions with onset energies of 11.05 ±0.04 and 13.37 ±0.08 eV, respectively. The onset energies for the fragment ions give related heats of formation computed to be 226 and 279 kcal mol^{-1}, respectively. This indicates that the $C_3H_5^+$ ion probably has the allyl structure. No determination of the structure of the $C_3H_3^+$ ion has been made.

The onset energies reported here may be useful for other experiments in which a sample is synthesized from allyl chloride [5] or where a sample may contain trace impurities due to allyl chloride. The results of this work may enable such impurities to be accounted for.

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ABSTRACT

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