119. The Infrared Multiphoton-Dissociation Spectra of Bromopropene Isomeric Cations

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The infrared quasi-resonance stepwise-multiphoton-dissociation spectra of the molecular ions of 1-bromopropene, 2-bromopropene, 3-bromopropene, and bromocyclopropane have been obtained at selected wavelengths between 9.2 and 10.7 μm in a *Fourier*-transform mass spectrometer. The resulting spectra and the photofragmentation kinetics suggest that these molecular ions retain their identity upon ionization, and can, thus, provide fingerprint spectral identifications for the ions.

Introduction. – The spectroscopic characterization of gas-phase ions remains among the most challenging subjects in the present-day chemical physics. Several experimental techniques have been developed in recent years to observe the rotational, vibrational, and electronic spectra of a growing number of mostly diatomic and triatomic ions [1]. The spectroscopic parameters, thus, determined have provided direct insight on the structural changes induced by the removal or addition of an electron.

One approach to ion spectroscopy is the use of photodissociation techniques in an ion trap [2]. This method is particularly suitable for dissociative electronic states of polyatomic ions. In favorable cases, the vibrational spectra of ions can also be inferred by quasi-resonant stepwise IR multiphoton dissociation (MPD) as demonstrated by *Beauchamp* and coworkers [3] [4].

An important aspect of ion spectroscopy is the potential ability to distinguish different isomers. While mass spectrometric techniques can often provide indirect evidence about isomeric ions, it is not always possible to establish unequivocally, whether a given molecular or fragment ion undergoes rapid rearrangement to its most stable configuration or retains the structure of the precursor molecule. An impressive example of the ability of photodissociation (VIS-UV) to identify different isomeric chloropropene cations produced by ion/molecule reactions was first reported by *Orth* and *Dunbar* [5].

The present report describes the IR-MPD spectra in the 9.2 to 10.7 μm region of molecular ions $C_3H_5Br^{+\cdot}$ obtained from 1-bromopropene, 2-bromopropene, 3-bromopropene, and bromocyclopropane. These spectra provide a fingerprint identification for the recognition of isomeric ions much like the distinct IR spectra of their precursors. An earlier study [6] had already explored successfully the ability to distinguish complex isomeric ions, like $C_7H_{14}^{+\cdot}$, by the wavelength dependence of the IR-MPD. Isomeric ions have also been identified on the basis of differences in photofragmentation patterns [7] or photofragmentation rate constants [8] at a given wavelength.

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Experimental. – The studies were carried out in a *Nicolet FTMS*-1000 *Fourier Transform* mass spectrometer coupled to a tunable *CW* CO_2 laser as described in [6]. Photodissociation spectra were obtained typically at power densities of 25 W/cm^2 (measured outside the *ICR* cell) corresponding to a laser beam diameter of *ca.* 6 mm. General procedure for these experiments as well as some of the inherent uncertainties associated them have been carefully explained in [6].

The $C_3H_5Br^{+\cdot}$ ions were generated by electron impact from samples (purified by GC) of 1-bromopropene and 2-bromopropene, 3-bromopropene, and bromocyclopropane. While most of the experiments were carried out at 70-eV electron energy, no significant differences were observed at lower energies (25 eV and 14 eV). The pressure of the neutral was maintained constant in the vicinity of $4.5 \cdot 10^{-9}$ mbar. The actual experiments involved the selective isolation of the molecular ions, $C_3H_5{}^{79}Br^{+\cdot}$ and $C_3H_5{}^{81}Br^{+\cdot}$, ejection of all other primary ions by the *SWIFT* technique [9], and observation of the photofragmentation as a function of variable laser irradiation times. Acquisition of the transient signals under computer control was carried out with a 5-s delay time between successive laser pulses to insure that no heating effects interfere with the measurements. The signals were averaged over 75 scans.

Results and Discussion. – The IR-MPD of the $C_3H_5Br^{+\cdot}$ ions yields exclusively $C_3H_5^+$ as an ionic product,

$$C_3H_5Br^{+\cdot} + nh\nu \rightarrow C_3H_5{}^+ + Br\cdot$$

The time-resolved experiments as outlined above provide a measurement of the kinetics of the photofragmentation under collision-free conditions. For a given ionic species, photofragmentation is a unimolecular process characterized by a photodissociation rate constant that depends on the photon flux and on the absorption coefficient [2]. While the chemical process bears similarities to a mass-spectral fragmentation, the photofragmentation process is considerably slower at typical photon fluxes. Furthermore, the sequential nature of the absorption of IR photons leading to dissociation frequently results in an induction time of hundreds of milliseconds for the onset of photofragmentation [3] [6]. The data obtained from typical experiments are shown in *Fig. 1*. While the molecular ions obtained from 1-bromopropene display a typical induc-

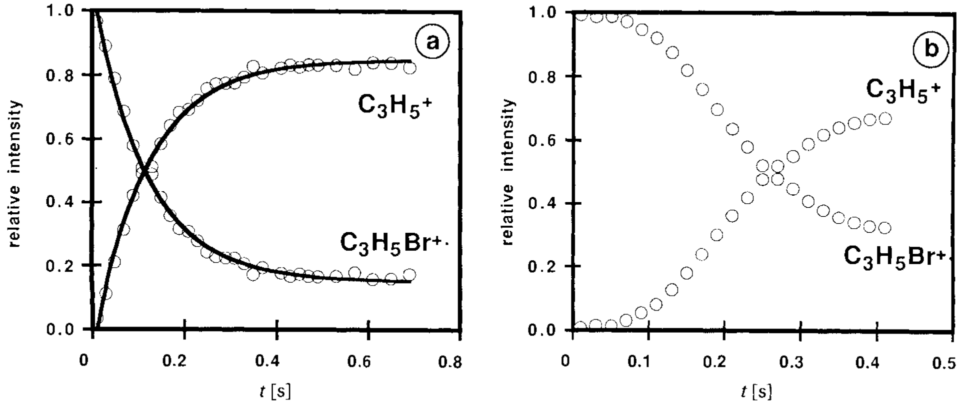

Fig. 1. a) *Normalized photofragmentation plot of the molecular and fragment ions of 3-bromopropene at 10.248 µm.* The experimental points for the primary ion are shown for convenience as the sum of the two isotopic species of $C_3H_5{}^{79}Br^{+\cdot}$ (m/z = 120) and $C_3H_5{}^{81}Br^{+\cdot}$ (m/z = 122). The full curve represents the calculated fitting for a photodissociation constant of 8.50 s^{-1} and a plateau value $a_2 = 0$ 0.15 for the molecular ions and $b_1 = 0.85$ for $m/z = 41$. b) *Typical normalized photofragmentation plot of the molecular ions of 1-bromopropene at 10.59 µm showing an induction time.*

tion time τ of *ca.* 50–100 ms *(Fig. 1, b)*, all other species reported here display induction times less than 15 ms at all wavelengths *(Fig. 1, a)*.

The ion intensity I for the disappearance of the molecular ions and the growth of the fragment ion of m/z 41 can be adequately described in all cases by a simple first-order process:

$$I(\text{molecular ions}) = a_1 \cdot \exp(-k(t - \tau_1)) + a_2$$

$$I(41^+) = b_1(1 - \exp(-k(t - \tau_2)))$$

The simplex optimization method [10] was used to obtain the photodissociation rate constant k and the parameters a_i, b_i, and τ_i for each ion at a given wavelength. A comparison between the experimental points and the calculated curve is shown in *Fig. 1, a*. The fact that good fittings are obtained by a simple exponential function strongly suggests that only one isomeric species is present upon ionization. However, it is noticeable that the photofragmentation kinetics reveals in some cases a non-zero plateau value (a_2). This observation may imply the presence of an isomeric molecular ion that does not undergo photofragmentation. Further experiments are presently underway to establish the nature of the process leading to this result.

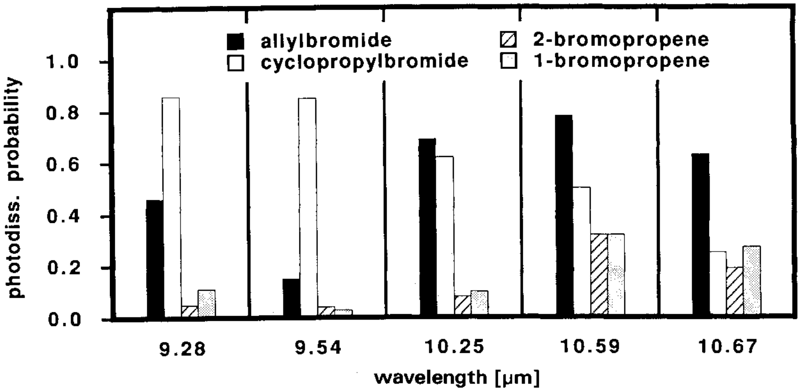

Fig. 2. *IR-MPD histogram of the $C_3H_5Br^{+\cdot}$ isomers measured as the photodissociation probability* (PD) *as a function of wavelength at a constant irradiation time of 200 ms and power densities of 25 W/cm^2*

The actual IR-MPD spectra for each isomer is shown in *Fig. 2* as a plot of ion fractional dissociation as a function of a few selected wavelengths at a fixed laser irradiation time of 200 ms. The observed spectra are very distinct indeed, if one also takes into account the differences in induction time between the 1- and 2-bromopropene generated ions which undergo slower photodissociation than the other isomers. Thus, it seems clear that the molecular ions retain a characteristic structure related presumably to the precursor neutral. While these spectra reveal similarities with the IR spectra of the corresponding neutrals [11], a quantitative comparison is not trivial. The photodissociation probability in these cases is related to two different factors: *1)* the one-photon absorption coefficient for the different isomers at a given wavelength and the rate constants for pumping the ion up the vibrational manifold, and *2)* the fragmentation threshold energies for each isomer. Unfortunately, no reliable appearance-potential measurements are available for these systems to assess the possible effect of the latter quantity on the overall photodissociation efficiency.

The photofragmentation process for these isomers is in itself an interesting process. While the present results suggest that the barrier for interconversion among the different $C_3H_5Br^{+\cdot}$ isomers is higher than for fragmentation to $C_3H_5^+$, the nature of the latter ions is open to question and is presently under investigation. Collision-induced dissociation experiments for $C_3H_5^+$ ions generated by electron impact suggest that 3-bromopropene and bromocyclopropane yield the allyl cation, 2-bromopropene the propenyl cation, and 1-bromopropene probably a mixture of the two forms [12] [13].

The present case represents another example of the ability to establish the identity of isomeric ions by their IR-MPD, spectra as first illustrated in [6]. Furthermore, it supports the idea previously advanced [8] that meaningful data for this type of experiment can only be obtained from the full photofragmentation kinetics. Thus, such a technique can be particularly useful to identify these isomers under conditions where their reactivity may be very similar [4].

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