Dye Laser-Induced Photodissociation of $C_7H_8^+$ Ions in Gaseous Toluene

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Abstract: The photodissociation process $C_7H_8^+ + h\nu \rightarrow C_7H_7^+ + H\cdot$ has been studied in the wavelength region 540–490 nm using a flashlamp-pumped organic dye laser with a pulsed ion cyclotron resonance analyzer cell located inside the laser cavity. A smoothly rising curve with an apparent onset at 538 ± 2 nm (2.31 ± 0.01 eV) and no significant fine structure has been observed. The onset and general shape of the observed curve agree quite well with an earlier study. By comparison with the photodetachment of SH^- ($SH^- + h\nu \rightarrow SH\cdot + e^-$), a value of $\sigma(490) = 1.01 \pm 0.24 \times 10^{-18}$ cm^2 has been obtained for the absolute cross-section for $C_7H_8^+$ photodissociation at 490 nm.

The photodissociation of various positively charged gaseous ions ($A^+ + h\nu \rightarrow B^+ + C$)has recently been studied by a number of investigators,[2-5] and valuable information about the structures and excited states of the parent ions (A^+ above) as well as the subsequent reactions of the photoproduced daughter ions (B^+ above) has been obtained. In particular, the investigations of Dunbar and co-workers[4,5] have strongly suggested that the photodissociation process must proceed via an (usually electronically) excited state of the A^+ ion, A^{+*}. If thermochemically allowed dissociation pathways exist between the state A^{+*} excited at a particular wavelength and $B^+ + C$, then photodissociation will be observed. If such pathways do not exist, no photodissociation is seen until the energy of the exciting light, $h\nu$, is sufficiently energetic to produce a state $A^{+*\prime}$, from which dissociation to $B^+ + C$ is energetically favorable. Conversely, even if the energy of photoexcitation, $h\nu$, is greater than the endoergicity of the reaction $A^+ \rightarrow B^+ + C$, *no photodissociation is observed* if there is no state A^{+*} accessible from A^+ upon excitation by photons of energy $h\nu$.[6] In this latter case, photodissociation is then observed only when the energy of the incident photons is sufficient to excite A^+ to an excited state A^{+*}. Using the photodissociation process as a monitor, one can then obtain "spectroscopic" information about the relative energies of A^+ and A^{+*}. In systems studied to date, A^{+*} has been an electronically excited state, and the results obtained from these studies have been in quite good agreement with those obtained from photoelectron spectroscopy,[7] which also provides direct information about the electronic (and sometimes vibrational) energy level spacing in gaseous ions.

A survey of recently published photodissociation spectra reveals, in general, rather broad and featureless curves. This has been primarily due to the low resolution (75–100 Å) employed in wavelength selection of the exciting light,[2,5] although certainly the possibility that a number of vibrational and rotational levels are populated in the ground state (A^+) ion and that many rotational and vibrational levels in A^{+*} exist from which dissociation to $B^+ + C$ can occur also may cause decided broadening in the observed curves. Hints of some structure in photodissociation spectra have appeared,[3,5] although no detailed comment upon, or analysis of, this structure has been made. Recently the use of a flashlamp-pumped dye laser to induce photodissociation has been reported as one part of a more comprehensive study,[4b] but to our knowledge no work dealing solely with tunable laser-induced positive ion photodissociation has yet been published.

We have recently initiated a series of investigations[8,9] which involve coupling a flashlamp-pumped organic dye laser[10] with a pulsed ion cyclotron resonance (ICR) mass spectrometer.[11] The pulsed ICR spectrometer affords a convenient means of producing gaseous ions by several mechanisms and trapping them for time periods seconds in duration, if necessary. During this time there is ample opportunity for irradiation of the trapped ions by the intense, monochromatic (3–5 Å bandwidth) radiation of the grating-tuned flashlamp-pumped dye laser. Our initial study[8] involved the photodetachment of SH^- ions ($SH^- + h\nu \rightarrow SH\cdot + e^-$), and fine structure observed in the photodetachment spectrum was related to the spin–orbit coupling in $SH\cdot$. Such fine structure had not been observed in earlier studies[12] of SH photodetachment using lower resolution light sources. It was hoped that application of the pulsed ICR-pulsed dye laser technique to photodissociation studies might allow fine structure, possibly related to different vibrational levels of the electronic states involved in the photodissociation process, to be observed.

To aid in studying photoinduced processes of low cross-section, an intracavity technique which places the ICR cell *inside* the laser cavity has recently been developed.[9] This modification allows the ions in the ICR cell to interact with numerous passes of the laser photons, thus producing a higher probability of interaction between photons and ions, and giving rise to significant enhancement of the desired effect. This technique was applied[9] to the photodetachment of OH^- ($OH^- + h\nu \rightarrow OH\cdot + e^-$) as a test case, but no detailed study was carried out to determine its general applicability to photoinduced ionic processes. Thus a second objective of the work reported here was to test the intracavity technique on a detailed high-resolution study of positive ion photodissociation. Cross-sections for photodissociation have been estimated[2,3,13] to be no greater than, and often somewhat lower than, those measured for photodetachment of negative ions,[12,14] so the intracavity technique was expected to be especially useful in these investigations.

Photodissociation of parent ions in gaseous toluene was chosen as an initial system for study

$$C_7H_8^+ + h\nu \rightarrow C_7H_7^+ + H\cdot \qquad (1)$$

using the intracavity ICR-laser technique. Low-resolution photodissociation spectra for this system have been reported by Dunbar and co-workers,[5,15,16] showing an onset at wavelengths near 540 nm and the first of two maxima near 400 nm. This wavelength range, particularly that near the onset, is easily accessible to tunable dye laser output. Also, since suggestions of structure appeared in photodissociation spectra for certain alkylbenzenes,[15] it was hoped that even more pronounced structure might be seen in the spectrum of the simple alkylbenzene toluene, using the narrow bandwidth irradiation from a tunable dye laser.

The third objective of the work reported here was to obtain a value of the absolute cross-section for $C_7H_8^+$ photodissociation. Although various estimates for similar cross-sections have been given,[2,3,13] our earlier work with SH^-, for which a

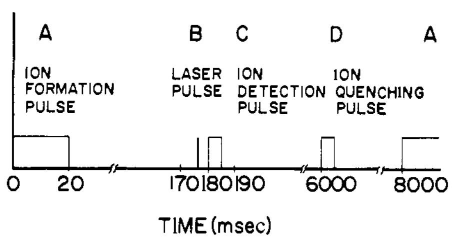

Figure 1. Pulse sequence used in laser photodissociation experiments.

cross-section of 1.9 ± 0.4 × 10^{-17} cm^2 has been obtained by Steiner,[12] suggested that a comparison of $C_7H_8^+$ photodissociation with SH^- photodetachment might lead to a reliable value for the photodissociation cross-section.

This paper reports the successful application of the intracavity ICR-dye laser technique to a high-resolution study of the photodissociation process 1. In addition, comparison of $C_7H_8^+$ photodissociation with SH^- photodetachment under nearly identical experimental conditions has permitted a determination of the absolute cross-section for process 1.

Experimental Section[17]

All experiments were performed using a pulsed ICR spectrometer constructed at the National Bureau of Standards, whose salient operating features have been reported previously.[18] Modifications to the ICR cell and vacuum chamber necessary to utilize the intracavity technique have also been described.[9] In addition, the 7056 glass/stainless steel viewing port used to permit laser light to enter the vacuum chamber was antireflectivity coated on both sides to minimize reflective losses. The output mirror (M2 in ref 9) of the laser was also replaced with a diffraction grating (1800 lines/mm, blazed at 500 nm in first order) to permit wavelength selection of the laser output which is coupled onto the ions in the intracavity technique.

In all experiments $C_7H_8^+$ ions were produced by an electron beam of nominal energy 10 eV (filament-to-trapping plate), to ensure that only the ground electronic state of $C_7H_8^+$ was formed. Figure 1 shows the pulse sequence ued for all experiments. Ions were formed by allowing the electron beam to pass through the cell for 20 ms and then were trapped for an additional 156 ms before laser irradiation. Since parent ions formed at ~10 eV do not react with toluene neutrals,[15] the approximately 30 collisions between each $C_7H_8^+$ ion and the parent neutral during this "trapping" time served to remove some of the excess vibrational and rotational energy from the ions and to bring about a more nearly thermal distribution of internal energies. Four milliseconds after laser irradiation at a given wavelength, the number of $C_7H_7^+$ ions formed in process 1 was detected. After approximately 6 s all remaining ions were swept from the cell by a "quenching" pulse, and the entire cycle was repeated every 8 s. The relatively slow repetition rate was dictated by the capacitor charging characteristics of the laser system and the necessity of not overheating the (uncooled) flash lamp.

Other details of the laser system used have been published previously.[8] The same three dyes (Coumarins 6, 30, and 102) used in our earlier study[8] of SH^- photodetachment were used in this work since the relevant range of laser photon energies was the same in both cases. To determine the wavelength of laser irradiation a small fraction of the beam was reflected by a beam splitter and passed into a spectrograph, where the wavelength-analyzed laser output was recorded on a photographic plate. Comparison with lines of known wavelength from a low-pressure mercury-neon lamp by using a travelling microscope allowed determination of laser wavelength to within approximately ±0.5 nm to be made. Determination of the laser energy per pulse was made by using a fast-response joulemeter.[19] Peak response of this instrument was sampled and held with a peak detection circuit, and the peak value (directly proportional to the laser pulse energy) was then sampled by the data collection system (see below). The peak detector was reset to zero 76 ms before each laser pulse.

Outputs from the pulsed marginal oscillator[18] (directly proportional to the number of $C_7H_7^+$ ions produced upon laser irradiation) and from the joulemeter peak detector circuit were multiplexed in an analog multiplexer, and their values were converted by an analog-to-digital converter, then printed on a teletype and punched on paper tape.[20] Thus, for *each* pulse repetition cycle, *both* the ion signal intensity ($C_7H_8^+$ or $C_7H_7^+$) *and* the energy per laser pulse (or the "background" level if the laser did not fire) were recorded. Complete details of the data analysis and averaging used to obtain the final values of relative cross-section vs. wavelength may be obtained from the author.

Reagent grade (ACS certified) toluene was used for all experiments and was purified only by repetitive freeze-pump-thaw cycles to remove noncondensable gases. During experiments, pressure of the gas was maintained at 5.0 ± 0.3 × 10^{-6} Torr as monitored by an ionization gauge located downstream from the main ICR vacuum chamber.

Results

Figure 2 shows the photodissociation spectrum obtained for process 1 as a function of wavelength in the threshold region between 490 and 550 nm (closed circles). The appearance of the photoproduced $C_7H_7^+$ ion, rather than the disappearance of the $C_7H_8^+$ ion, was monitored to obtain the results in Figure 2. As a comparison, points obtained in an earlier, low-resolution study[15] are plotted as open circles. Error bars represent ±1 standard deviation about the mean relative cross-section calculated using all results in a given 1.0 nm wavelength interval.

Although some possible structure in the cross-section vs. wavelength curve is suggested by fluctuations in the mean values shown in Figure 2, the relatively large error bars dictate that these fluctuations cannot be considered statistically significant. Thus, given the signal-to-noise ratio of these experiments, the curve in Figure 2 must be described as a smoothly rising one with no sharply defined onset. This, of course, makes exact determination of the onset quite difficult, if not impossible. The wavelength at which the error bars for the relative cross-section begin to regularly contain the zero line has been chosen as the best estimate for the observed onset of photodissociation. This occurs at 538 ± 2 nm, corresponding to a photon energy of 2.31 ± 0.01 eV.

To obtain a value for the absolute cross-section for process (1), as monitored by $C_7H_7^+$ appearance, the relative cross-section for SH^- photodetachment was determined under conditions identical with those given in the Experimental Section (except that all cell voltages were reversed since negative, rather than positive ions were being trapped and irradiated). These studies were carried out at a wavelength of 490.0 ± 0.5 nm. This point was chosen because it coincides with the maximum in the SH^- photodetachment process, determined by Steiner[12] to be 1.9 ± 0.4 × 10^{-17} cm^2. The ratio of $\sigma(SH^-$ photodetachment$)/\sigma(C_7H_8^+$ photodissociation$)$ at 490 nm was found to be 1.88 ± 0.20 × 10. This leads to a value of $\sigma(490$ nm$) = 1.01 \pm 0.24 \times 10^{-18}$ cm^2 as the absolute cross-section for process 1 as determined by monitoring appearance of the $C_7H_7^+$ ion.

Discussion

The general shape of the photodissociation spectrum shown in Figure 2 agrees quite well with the (few) points reported in an earlier study[15] for the threshold region. This suggests that the intracavity laser ICR technique can be used to study photoinduced ionic processes of this sort. However, contrary to one of the initial expectations before beginning these studies, no statistically significant fine structure is evident in Figure 2.

The onset for photodissociation chosen in this study, 538 ± 2 nm (2.31 ± 0.01 eV), agrees well with an earlier study,[15] where the onset was reported at "about 540 nm". This value is also in quite good agreement with photoelectron spectroscopic results[21] which show an excited state of the cation lying about 2.2–2.3 eV above the ground state of the cation. However, given the lack of a sharply defined onset, the value of 538 ± 2 nm reported here must be considered as merely a lower

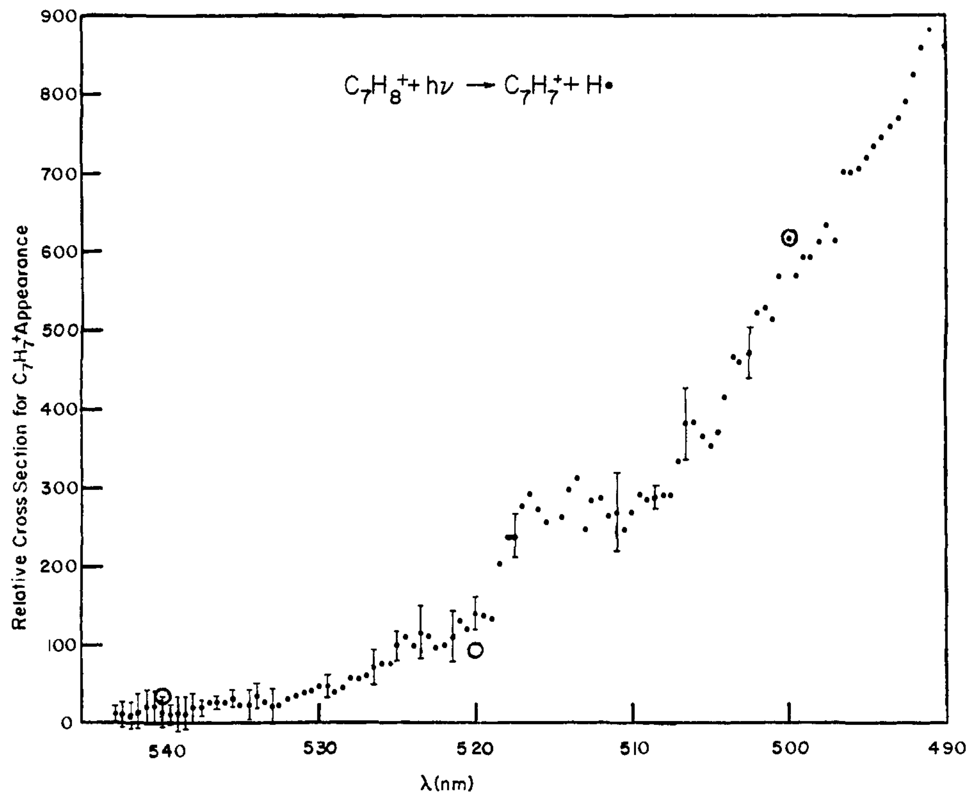

Figure 2. Relative cross-section for the appearance of $C_7H_7^+$ via the process $C_7H_8^+ + h\nu \rightarrow C_7H_7^+ + H\cdot$ as a function of wavelength (closed circles). Results from ref 14 are plotted as open circles.

wavelength limit to the true onset. An onset at longer wavelengths would most probably be found in experiments with higher sensitivity.

Certain difficulties arise in assessing the accuracy of the value $\sigma(490\ \mathrm{nm}) = 1.01 \pm 0.24 \times 10^{-18}\ \mathrm{cm}^2$ for process 1. The number is obtained in a comparative way, and while no experimental parameters were changed in the SH^- and $C_7H_8^+$ determinations, an absolute measurement would still be preferable. Difficulties in determining accurately the exact volume of interaction between the intracavity laser photons and the trapped ions make an absolute cross-section determination somewhat suspect. It should also be pointed out that the comparative method reported here is dependent on a second relative cross-section comparison. The value of $\sigma = 1.9 \pm 0.4 \times 10^{-17}\ \mathrm{cm}^2$ reported by Steiner[12] for the maximum SH^- photodetachment cross-section and used in these calculations was itself determined by comparison of SH^- photodetachment with H^- photodetachment, since the cross-section for the latter has been reliably determined by a number of experimental and theoretical techniques.[22]

As mentioned in the introductory section, the full photodissociation spectrum for process 1 rises steadily from onset to a maximum near 400 nm. From the relation $\sigma(400\ \mathrm{nm})/\sigma(490\ \mathrm{nm}) = 5.0 \pm 1.0$[23] and the value $\sigma(490\ \mathrm{nm}) = 1.01 \pm 0.24 \times 10^{-18}\ \mathrm{cm}^2$ determined in this work, one can obtain $\sigma(400\ \mathrm{nm}) = 5.1 \pm 1.6 \times 10^{-18}\ \mathrm{cm}^2$ for process 1 at its first (lower energy) maximum. This number is of the same general magnitude as others reported for photodissociation cross-sections: $7.8 \times 10^{-18}\ \mathrm{cm}^2$ [13] and $2.3 \times 10^{-18}\ \mathrm{cm}^2$ [3] for the process $CH_3Cl^+ + h\nu \rightarrow CH_3^+ + Cl$; $6.6 \times 10^{-18}\ \mathrm{cm}^2$ [3] for the process $CH_3Br^+ + h\nu \rightarrow CH_3^+ + Br$; and $2.0 \times 10^{-17}\ \mathrm{cm}^2$ [2] for the process $C_3F_5^+ + h\nu \rightarrow CF_3^+ + C_2F_2$. For the limited data available, the conclusion that photodissociation cross-sections are generally a factor of 2 to 10 lower than the photodetachment cross-sections of atomic and small molecular negative ions (which range from ~1.0 to $5.0 \times 10^{17}\ \mathrm{cm}^2$ [22]) seems justified.

Acknowledgments. The author is indebted to Drs. L. W. Sieck, P. J. Ausloos, S. G. Lias, and R. A. Keller for support and encouragement and to the NBS Laser Chemistry Program for the loan of several items of equipment. Experimental work was performed in the Physical Chemistry Division, National Bureau of Standards, Gaithersburg, Md. Research was supported in part by the U.S. Atomic Energy Commission.

References and Notes

(1) NRC-NBS Postdoctoral Associate, 1972–1974.
(2) B. S. Freiser and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 6260 (1974).
(3) M. L. Vestal and J. H. Futrell, *Chem. Phys. Lett.*, **28** (**4**), 559 (1974), and references contained therein.
(4) (a) R. C. Dunbar, *J. Am. Chem. Soc.*, **97**, 1382 (1975); (b) E. W. Fu, P. P. Dymerski, and R. C. Dunbar, *ibid.*, **98**, 337 (1976).
(5) R. C. Dunbar, *J. Am. Chem. Soc.*, **95**, 6191 (1973), and references contained therein.
(6) The occurrence of two-photon processes may complicate these conclusions. See, for example, B. S. Freiser and J. L. Beauchamp, *Chem. Phys. Lett.*, **35**, 35 (1975).
(7) See, for instance, D. W. Turner et al., "Molecular Photoelectron Spectroscopy", Wiley-Interscience, London, 1970.
(8) J. R. Eyler and G. H. Atkinson, *Chem. Phys. Lett.*, **28** (**2**), 217 (1974).
(9) J. R. Eyler, *Rev. Sci. Instrum.*, **45**, 1154 (1974).
(10) F. P. Schafer, Ed., "Topics in Applied Physics 1", Springer-Verlag, Berlin, 1973.
(11) R. T. McIver, Jr., and R. C. Dunbar, *Int. J. Mass Spectrom. Ion Phys.*, **7**, 471 (1971).
(12) B. Steiner, *J. Chem. Phys.*, **49**, 5097 (1968)(1974).
(13) R. C. Dunbar, *J. Am. Chem. Soc.*, **93**, 4354 (1971).
(14) L. M. Branscomb, *Phys. Rev.*, **148**, 11 (1966).
(15) R. C. Dunbar, *J. Am. Chem. Soc.*, **95**, 472 (1973).
(16) P. P. Dymerski, E. Fu, and R. C. Dunbar, *J. Am. Chem. Soc.*, **96**, 4109 (1974).
(17) Certain commercial instruments and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the instruments or materials are necessarily the best available for the purpose.
(18) S. G. Lias, J. R. Eyler, and P. Ausloos, *Int. J. Mass Spectrom. Ion Phys.*, **19**, 219 (1976).

(19) Gen-Tec Inc. (Quebec, Canada) Model ED-200.
(20) Data collection was carried out using a Princeton Applied Research (Princeton, N.J.) Model 131/SSA data acquisition system.
(21) D. W. Turner et al., ref 7, Chapter 11.
(22) B. Steiner, "Case Studies in Atomic Collision Physics 2", E. W. McDaniel and M. R. C. McDowell, Ed., North-Holland Publishing Co., Amsterdam, 1972, p 483.
(23) R. C. Dunbar, personal communication.

Isomerization of Protonated Cyclopropane Cations[1]

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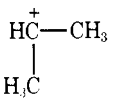
Received October 15, 1975

Abstract: The collisional activation (CA) spectra of gaseous ions formed by the protonation of cyclopropane and propene are identical, indicating that the isomerization c-$C_3H_7^+$ → *sec*-$C_3H_7^+$ occurs in $<10^{-5}$ s. However, ion-molecule reactions of $C_3H_7^+$ at $\sim 10^{-2}$ Torr indicate that c-$C_3H_7^+$ ions can have lifetimes of 10^{-7} s, supporting the results of equilibrium constant measurements by Chong and Franklin.[5] They derived $\Delta H_f(\text{c-}C_3H_7^+) - \Delta H_f(sec\text{-}C_3H_7^+) = 8$ kcal/mol, consistent with the prediction of MINDO/3 calculations;[3] however, the apparent low activation energy for c-$C_3H_7^+$ → *sec*-$C_3H_7^+$ indicated by the CA results is not consistent with the MINDO/3 value[3] of $\Delta H_f(n\text{-}C_3H_7^+) - \Delta H_f(\text{c-}C_3H_7^+)$ if the transition state for this reaction is similar to the structure of the *n*-$C_3H_7^+$ ion.

The isomeric $C_3H_7^+$ ions I-IV have been the object of extensive experimental and theoretical studies; a number of these studies have resulted in conflicting conclusions.[2-6] Molecular orbital calculations of several types now predict[3,4] (Table I), in agreement with experiment,[5,6] that *sec*-propyl (I) is the most stable ion structure. Gaseous *n*-$C_3H_7^+$ ions have been shown experimentally to be unstable, isomerizing without hydrogen scrambling to *sec*-$C_3H_7^+$.[6] MINDO/3 calculations[3] predict the most stable form of the cyclic isomer to be the edge-protonated (IIa) cyclopropane structure, deriving a heat of formation value in close agreement with the experimental value determined by Chong and Franklin[5] (Table I) from equilibrium constant measurements of reactions 1 and 2 (Scheme I, A = HCOOH or CH_3OH) at 0.2-0.4 Torr total pressure, assuming the intrinsic entropy changes of these reactions to be zero.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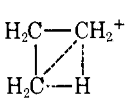
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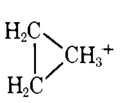
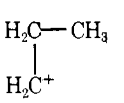
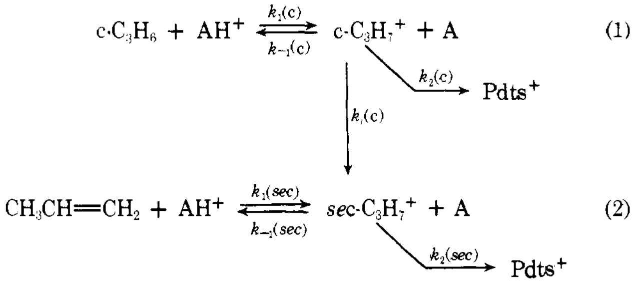

IIb


III

Scheme I



These theoretical calculations[3] also predict the lowest energy form of the cyclic $C_3H_7^+$ ion (IIa) to be 11 kcal/mol more stable than the *n*-propyl ion (III); if the latter structure resembles closely the transition state[7] for the rearrangement II → I, this reaction should exhibit a relatively high activation energy. However, interpretations of the experimental results[5,6] differ markedly in the stability indicated for the cyclic ion. In ion cyclotron resonance (ICR) experiments[6] (ion lifetimes of $\sim 10^{-3}$ s) ions formed by the protonation of cyclopropane were found to react with methanol in the same manner as *sec*-$C_3H_7^+$ ions react; it was concluded that either c-C_3H_6 and $CH_3CH{=}CH_2$ have nearly identical proton affinities, as postulated by Chong and Franklin, or that the c-$C_3H_7^+$ ions have isomerized to the *sec*-$C_3H_7^+$ structure before reacting (Scheme I). We report here evidence on the structures of these ions obtained from collisional activation (CA) spectra[8] (ion lifetimes of $\sim 10^{-5}$ s) utilizing a revised instrument with a higher pressure ion source, and from ion-molecule reaction studies at pressures $\sim 10^{-2}$ Torr with variation of the ion source residence time.

Experimental Section

Measurements were made on a Hitachi RMU-7 double-focusing mass spectrometer of reversed geometry,[9] with 7.8 kV ion accelerating potential and 70 eV ionizing electron energy. The instrument was modified with restricted electron entrance and ion exit slits on the ion source and a 1200 l./s diffusion pump on the source housing. Propene or cyclopropane was introduced at low pressure (10^{-6} Torr), and the ion source pressure was increased with CH_3OH, HCOOH, orH_2S, as well as with the C_3H_6 isomer itself, until the contribution of $C_3H_7^+$ to the *m/e* 43 peak in the normal mass spectrum was a factor of ~16 greater than that of $C_2{}^{13}CH_6^+$ ($\sim 10^{-2}$ Torr, source housing pressure $\sim 1 \times 10^{-4}$ Torr; higher pressures seriously degrade instrument performance). Helium was introduced into the collision chamber between the magnetic and electrostatic (ESA) analyzers at a pressure ($\sim 5 \times 10^{-3}$ Torr) selected so that the abundance of *m/e* 43 ions reaching the collector would be reduced to approximately 25% of its original value. The ionic products resulting from collisional activation (the CA spectrum) were then determined by multiple scanning of the ESA potential and averaging of the data under computer control; only the ions resulting from higher energy processes (those other than unimolecular metastable decompositions) were included.[8] Contributions from the CA spectrum of $C_2{}^{13}CH_6^+$ were subtracted, correcting for the experimental observation that the cross-section for the CA decomposition of $C_3H_7^+$ is 0.82 times that of $C_2{}^{13}CH_6^+$. The ion source repeller controls were modified (voltages adjustable from +90 to −90 V) to give limited ion trapping capabilities, both by direct trapping with the negative voltages and by the negative space charge in the electron beam with positive repeller voltages.[10] Changing the repeller potential to more positive as well as more negative values increases the ion residence time in the source,[11] as shown by the increase in *m/e* 103 and 121 ion abundances produced by ion-molecule reactions of acetic acid at $\sim 10^{-2}$ Torr.

Results and Discussion

The CA spectra of the $C_3H_7^+$ ions obtained by protonation of propene and cyclopropane by methanol are given in Table