Nature of the $C_7H_7^+$ Ions from Toluene Parent Ion Photodissociation

Robert C. Dunbar[1]

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received April 23, 1974

Abstract: The photochemistry of the gas-phase toluene cation has been examined using a time-resolved variation of the ion cyclotron resonance photodissociation technique. Using instrument conditions permitting trapping of ions for 5 min or more, the time dependent ion densities of the three species in the photochemical sequence $C_7H_8^+ \rightarrow C_7H_7^+ \rightarrow C_8H_9^+$ were observed directly. Two distinct populations of $C_7H_7^+$ were found, without interconversion at least for seconds, one of them being highly reactive and the other essentially unreactive in neutral toluene. A good fit to a kinetic model was obtained, yielding $K_1 = 4.0 \times 10^{-10}$ cm^3/(molecule sec) for the reactive $C_7H_7^+$ component. The reactive $C_7H_7^+$ probably has the benzyl structure, and the nonreactive component the tropylium structure. The relative amount of reactive (benzyl) ions formed decreased sharply with decreasing photon energy, extrapolating to zero near the photodissociation threshold. This energy dependence can be understood as being due to greater stability for the tropylium form of $C_7H_7^+$ relative to the benzyl form, and a quasi-equilibrium-theory calculation of the fragmentation of $C_7H_8^+$ reproduces the observed energy dependence under reasonable assumptions.

Although the $C_7H_7^+$ cation apparently normally exists in the tropylium form in condensed phase, recent evidence of several sorts has indicated the more than transitory existence in gas phase of at least two forms of this ion.[1-3] The results of Winkler and McLafferty[3] using the collisional activation mass spectrometry technique show convincingly that two or more different $C_7H_7^+$ species retain their identity for more than 10^{-5} sec. The correlation of the different species obtained in this work with the structure of the neutral precursor follows a coherent pattern, and there is no reason to question the supposition that ions of both benzyl and tropylium forms are observed.

Ion-molecule reaction patterns of $C_7H_7^+$ ions produced from isotopically labeled toluene were examined in this laboratory by Shen et al.,[4] and it was found that a $C_7H_7^+$ species was produced, with retention of identity for milliseconds, in which the hydrogens were not fully equivalent. On the basis of the reaction patterns observed, it was concluded that the $C_7H_7^+$ ion involved was the benzyl cation.

The $C_7H_7^+$ cation is produced in a very clean and controlled manner by the gas-phase photodissociation[5] of $C_7H_8^+$. We report here the results of a study of the $C_7H_7^+$ cations produced in this way using the techniques of ion cyclotron resonance (ICR) photodissociation. While this technique has been described,[5,6] new time-resolved methods were developed to meet the demands of the present work, and these will be described. A subsidiary goal of these experiments was the evaluation of these techniques for quantitative photochemical kinetic study in ion-molecule systems. The results show clearly the competitive production of two different $C_7H_7^+$ species, and the evidence and implications are discussed.

The initial photodissociation process occurring upon irradiation of $C_7H_8^+$ in toluene is the rapid and exclusive dissociation to $C_7H_7^+ + H$, with a rate whose wavelength dependence is known with confidence.[5] The subsequent ion-molecule reaction

$$C_7H_7^+ + C_7H_8 \xrightarrow{K_1} C_8H_9^+ + C_6H_6 \qquad (1)$$

is the only fast reaction process of the product ion.[4] Neither $C_7H_8^+$ nor $C_8H_9^+$ is known to react with toluene. Reaction 1 shows a wavelength dependence which was reported earlier without interpretation,[5] with the apparent rate constant rising sharply with increasing photon energy. For broadband irradiation, the rate constant for the appearance of $C_8H_9^+$ was measured by a flash photolysis method[7] as 7.7

$\times 10^{-10}$ cm^3/(molecule sec), but the rate of disappearance of $C_7H_7^+$ was not determined, and, as appears below, this photochemical system is more complex than was previously believed.

Methods and Results

The processes occurring in the toluene photochemical system are conveniently explored using ICR instrumental conditions under which ions are efficiently trapped;[5,6] the abundance of a particular ion species can be continuously monitored with the marginal oscillator detector, which does not significantly perturb the trapping process if the rf level is sufficiently low. Figure 1 shows the trapping of the non-reactive $C_7H_8^+$ ion under these conditions, and it is noteworthy that more than half the original ion signal is still present after 3 min. The ion-signal decay curve of Figure 1 was found to be reproducible and was used as a correction curve for other ionic species to account for the signal variation due to analyzer region ion density variations.

When the system is irradiated at 4200 Å, with irradiation commencing when the electron beam is turned off, the results shown in Figure 2 are obtained for the intensity of parent ion, $C_7H_7^+$, and $C_8H_9^+$ as a function of time. Qualitatively it is evident that $C_7H_8^+$ is rapidly dissociated to $C_7H_7^+$ and that a portion of the $C_7H_7^+$ reacts rapidly to give $C_8H_9^+$. The point of interest is that a major fraction of the $C_7H_7^+$ does not react, even after very long times. In fact, the $C_8H_9^+/C_7H_7^+$ ratio rises rapidly over the initial 20 sec, and then levels off, showing a slight slow decline at long times.[8] In order to determine whether this reflects two different kinds of $C_7H_7^+$ or alternatively a continuous range of reactivities, more detailed quantitative analysis of these curves is useful.

Several corrections are needed. (1) As noted above, all the signals were corrected for analyzer-region density variations. (2) The marginal oscillator was found to be less sensitive by a factor of 1.75 for operation at 130 kHz vs. operation at 150 kHz for observation of a given ion. Since the measurements were made at constant magnetic field, the signal at m/e 105 was corrected to account for this lower detection sensitivity. Moreover, the ICR signal is inversely proportional to ion mass,[9] and a correction of $105/91 = 1.15$ was applied to the m/e 105 signal. (3) The measured sum of the 91, 92, and 105 signals, which should remain constant, showed some variation, attributed to two factors: at short times, the 92 signal was 25% smaller than it should
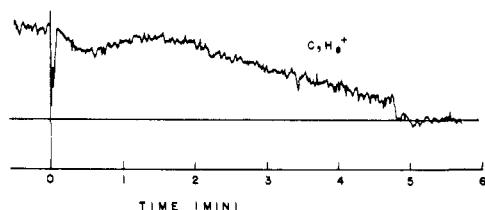
Figure 1. Trapping of $C_7H_8^+$ ions without light. At time zero the production of ions was terminated by turning off the electron beam (the electronic transient just after beam termination occurred sporadically), and the subsequent trapping and slow loss of ions were followed by continuously monitoring their ICR signal. The trapping was terminated at about 4.7 minutes in order to record the empty-cell baseline.

have been, due to marginal oscillator nonlinearity at high signal levels (this effect was not corrected, and is evident in Figure 3); at times between about 2 and 15 sec, the sum of the signals rose about 15% above its long-time steady value and then dropped back to a constant level. Inspection shows that the m/e 91 signal rises more rapidly than the drop of m/e 92 can account for. It was hypothesized (in accord with previous experience) that for the first few seconds after its formation, the cyclotron signal of an ion is larger than its long-term steady-state level, accounting for the anomalous signal increase during the period when m/e 91 and m/e 105 ions are being rapidly formed. A correction based on the excess total ion signal was applied to the m/e 91 and 105 signals.

The corrected curves, based on several scans of each ion, are shown as the dotted curves in Figure 3. If the proposed model of this photochemical system is correct, the results should fit a kinetic scheme involving two consecutive pseudo-first-order reactions, the first being $C_7H_8^+$ photodissociation and the second being reaction 1. The fit to these kinetics is shown in Figure 3, using a pseudo-first-order rate constant of 0.25 sec^{-1} for reaction 1 and assuming that 48% of the $C_7H_7^+$ produced in the photodissociation is totally unreactive. At the operating pressure of[10] 1.75×10^{-8} Torr, this corresponds to a bimolecular rate constant of $K_1 = 4.0 \times 10^{-10}$ cm^3/(molecule sec). The value of K_1 is not tightly constrained by the fit to the data of Figure 3, and this, along with the pressure uncertainty, probably limits the realistic accuracy to ±30%. No alternative model involving a smooth distribution of reactivities of the $C_7H_7^+$ cations can give any reasonable fit to the data; the good fit obtained gives strong support to the hypothesis of two distinct populations of $C_7H_7^+$ ions, one reacting with rate constant K_1, the other essentially nonreactive. This value of K_1 is in reasonable agreement with the earlier flash photolysis value.[7] The present measurement should be somewhat more reliable because of the lower background pressure achieved in these experiments.

At longer wavelengths the rapidly decreasing photodissociation rate makes a detailed analysis of this sort impractical, although a qualitative investigation at 4800 Å gave curves very similar to those of Figure 3 (but with a smaller fraction of reactive $C_7H_7^+$). In order to determine the wavelength dependence of the ratio of different $C_7H_7^+$ ions, the assumption was made that at all wavelengths the photodissociation of $C_7H_8^+$ yields two distinct $C_7H_7^+$ populations, one of which reacts with toluene at a rate which is rapid compared with the ion trapping time. It is straightforward to measure the steady-state concentrations of $C_7H_7^+$ and $C_8H_9^+$ under conditions where both the electron beam and the light are on and to use a steady-state kinetic analysis similar to that used previously.[5] Given the above assumptions, it is easily shown that the observed steady-state ratio of $C_8H_9^+$ to $C_7H_7^+$ is a good approximation to the
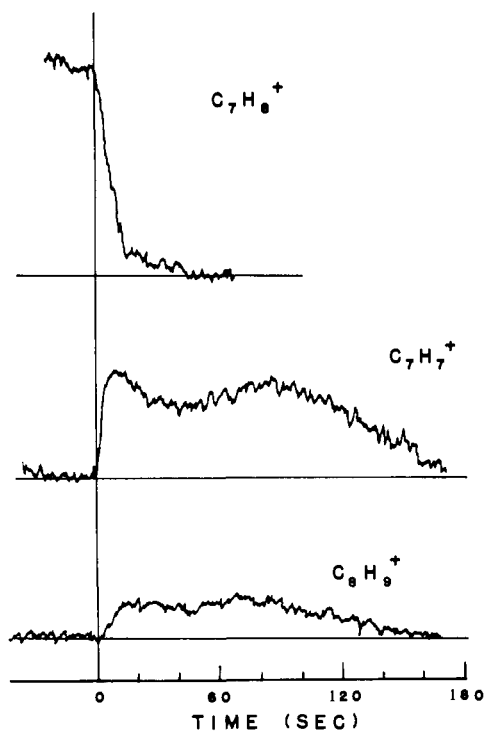

Figure 2. Time dependent behavior of the toluene cation photochemical system. At time zero the electron beam was turned off and the monochromatic irradiation (4200 Å) was initiated. The rapid photolysis of $C_7H_8^+$ and the rapid reaction of a fraction of the photoproduced $C_7H_7^+$ ions to give $C_8H_9^+$ are both evident.
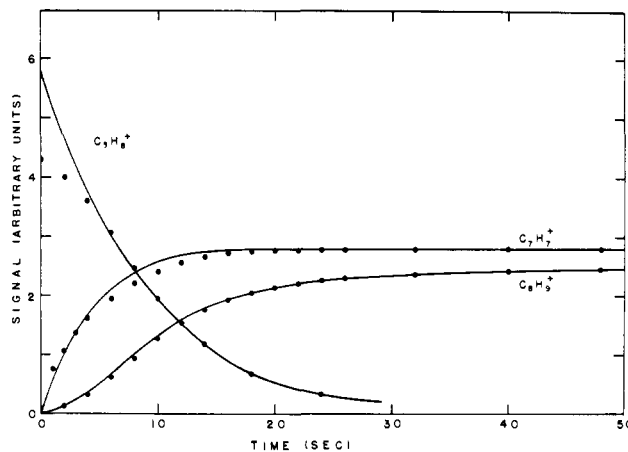

Figure 3. Fit of the data of Figure 2 to a consecutive reaction kinetic scheme, as detailed in the text.

ratio of production of reactive to nonreactive $C_7H_7^+$ ions. Table I indicates the fraction of reactive ions produced as a function of wavelength. An extrapolation of these results suggests that the production of reactive $C_7H_7^+$ reaches zero near 5800 Å, which corresponds closely to the dissociation threshold as calculated thermochemically and as determined from the extrapolated isotope effect.[5]

The possibility of conversion of one of the $C_7H_7^+$ populations to the other was further tested by experiments at increased pressure. Curves corresponding to those displayed in Figure 2, but obtained at 6×10^{-8} Torr, showed that the fraction of $C_7H_7^+$ which failed to react at long times was identical (within experimental error of ~10%) with the fraction at 2×10^{-8} Torr. At the lower pressure an ion collides with a toluene molecule roughly every 1.5 sec, while at the higher pressure a collision occurs every 0.5 sec, while

Table I. Wavelength Dependence of the Ratio of
Photodissociation-Produced $C_7H_7^+$ Ions Having the
Reactive (Benzyl) vs. Nonreactive (Tropylium) Forms

λ (Å)	Energy (eV)	Excess energy (eV)[16]	Benzyl/ tropylium
4000	3.10	1.0	1.07
4200	2.95	0.85	0.92
4400	2.82	0.72	0.82
4800	2.58	0.48	0.56
5000	2.48	0.38	0.41

the typical times for a reactive $C_7H_7^+$ ion to survive before reaction are, respectively, 3.5 and 1.2 sec. If the reactive toluene ions were isomerizing on a time scale of seconds, the pressure variation should give a large change in this ratio, while if isomerization took place much faster than this, little reaction would take place. Accordingly, interconversion of isomers or subsequent isomerization of the initially formed $C_7H_7^+$ ions are ruled out on a time scale of seconds. Similar experiments were performed with excess ethane gas used as a nonreactive buffer, at ethane pressures up to an (indicated) excess of about 5:1 of ethane pressure over toluene pressure. Little or no decrease was observed in the fraction of $C_7H_7^+$ ions which reacted to form $C_8H_9^+$. This indicates that collisional deexcitation or isomerization of the reactive $C_7H_7^+$ ions in ethane is sufficiently inefficient that several collisions of reactive $C_7H_7^+$ with ethane do not convert it to the nonreactive species. This provides a further indication that it is not vibrational excitation which distinguishes reactive from nonreactive $C_7H_7^+$, since it would be somewhat surprising for collisions with neutral ethane to be ineffective in reducing such excitation.

Discussion

These experiments demonstrate that following formation of $C_7H_7^+$ by $C_7H_8^+$ photodissociation, the $C_7H_7^+$ resolves itself within a fraction of a second into two separate populations, distinguished by their reactivity. It is of interest to consider what these populations might be and what mechanisms may reasonably explain their formation.

Since both populations are formed within a few tenths of an electron volt of the threshold for photoproduction of the most stable known $C_7H_7^+$ isomer, it is clear that the two forms differ at most by tenths of an electron volt in energy. Electronic excitation is therefore not a likely distinction between them. There are several reasons to believe that the different $C_7H_7^+$ reactivities are not an effect of vibrational excitation. First, the reaction rates are somewhat slower than anticipated rate of infrared radiative relaxation,[11] but no evidence was seen for radiative relaxation in competition with reaction. Second, the inert-buffer-gas results argue against vibrational energy effects. Third, vibrational excitation would be expected to give a range of reactivities as opposed to the observed definite twofold distinction of species.

Accordingly, it seems very likely that the two populations are in fact distinct isomers. Only three isomeric structures merit serious consideration, these being the benzyl, tolyl, and tropylium forms. The evidence of Shen et al.[4] strongly suggests on chemical grounds that the reactive component has the benzyl structure. The tolyl structure is probably less stable than the other structures and does not seem a likely product of photodissociation near threshold. Accordingly, we adopt the hypothesis that the reactive $C_7H_7^+$ component is benzyl and the nonreactive component is tropylium.

The accumulated evidence on $C_7H_7^+$ production provides the following features which a satisfactory model must pre-

dict: (1) before fragmentation, the $C_7H_8^+$ parent undergoes extensive randomization of its hydrogens, resulting in complete scrambling at low internal energies and partial scrambling at higher internal energies;[5,12] the carbon atoms are also extensively scrambled;[13,14] (2) within a very short time after formation of $C_7H_7^+$ from $C_7H_8^+$ parent ion, the $C_7H_7^+$ becomes frozen into one of two (or more) forms, one of which probably has the benzyl structure; the fraction of benzyl ion produced decreases sharply with decreasing internal energy of the parent ion, apparently reaching zero near the dissociation threshold. A reasonable model which appears compatible with all observations postulates that the excited $C_7H_8^+$ precursor exists in a dynamic equilibrium between the toluene and cycloheptatriene structures. At low internal energies, this equilibrium is fully achieved before dissociation, while at high internal energies, dissociation occurs before complete equilibrium is established. The increased tropylium ion production at low energies can then be accounted for by assuming that the tropylium ion is somewhat more stable than the benzyl ion, making the activation energy for dissociation somewhat lower for the cycloheptatrienyl form of $C_7H_8^+$ than for the toluene form.

Support for the interpretation of the energy dependence displayed in Table I as being due to the lower activation energy for tropylium ion formation is obtained from a quasi-equilibrium-theory calculation.[15] Using the neutral toluene vibrational frequencies as an approximation to the frequencies of $C_7H_8^+$ in either isomeric form, and assuming that the energy dependence of the tropylium ion/benzyl ion ratio is entirely determined by the relative rates of fragmentation to these two products,[16] an excellent fit (within a multiplicative constant ~ 2) to the data of Table I was obtained by setting ΔH_f° (benzyl) $- \Delta H_f^\circ$ (tropylium) $= 2.5 \pm 0.3$ kcal. The assumptions made in this calculation are undoubtedly an oversimplification of the actual situation, so that this number probably has limited quantitative significance, but support is provided for the proposed reaction model by the fact that the observed energy dependence can be satisfactorily reproduced with entirely reasonable assumptions and parameters.

References and Notes

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