Photodissociation of Toluene Parent Cations

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Abstract: Ion cyclotron resonance photodissociation techniques were used to investigate the events following photoexcitation of toluene parent cations. Photodissociation to produce $C_7H_7^+$ proceeded readily. The threshold behavior was discussed both in terms of the thermochemistry of the reaction and the optical absorption properties of the cation, and it appeared that both influences were likely to be involved. Examination of deuterated toluenes showed that photodissociation occurred with complete hydrogen scrambling and a strong isotope effect. The energy dependence of the isotope effect was studied in detail and was found to agree with that determined for dissociative electron-impact ionization, and also with quasi-equilibrium theory calculations. Determination of the C–D bond dissociation energy by extrapolation to infinite isotope effect gave close agreement with the best available thermochemical data. The photoproduced $C_7H_7^+$ cations reacted with parent neutrals to give $C_8H_9^+$. The dependence of the reaction rate on photon energy was determined and suggested the presence of an activation energy for the reaction.

Study of fragmentation and reaction processes of gaseous cations as a function of internal energy has been retarded by the difficulty of preparing cations of known internal energy. Photoexcitation of cations offers the possibility of depositing a precisely known amount of energy in an isolated cation, and the recent use of the ion cyclotron resonance (icr) spectrometer for the study of photodissociation[1] and photon induced reaction[2] processes of gaseous cations has made such studies possible. We report here the study by such techniques of the events following photoexcitation of toluene parent cations.

The mass spectral fragmentation patterns of selectively deuterium labeled toluene cations is characterized by extensive scrambling of ring and side chain hydrogens, and by loss of positional identity of both hydrogen and carbon atoms.[3,4] This evidence has led several investigators to postulate that the $C_7H_8^+$ cation formed from toluene rearranges to a more symmetrical, possibly cycloheptatriene-like structure.[5,6] However, using icr techniques, Hoffman and Bursey showed[7] that for those $C_7H_8^+$ cations not possessing sufficient energy to dissociate, there was no rearrangement of the cations to a cycloheptatriene cation structure. Recent icr chemical reactivity results of Shen[8] with $C_6H_5CD_3$, $C_6D_5CH_3$, and c-C_7H_8 also suggest that the toluene $C_7H_7^+$ fragment ion may have a benzyl cation structure. Howe and McLafferty[9] have made a careful study of the hydrogen–deuterium isotope effect in loss of hydrogen from toluene parent cations, reaction 1, and they find that the isotope effect, which is identical for all of the various deuterium labeled toluenes which they studied, is in excellent agreement with the quasi-equilibrium theory calculations of Vestal and Lerner.[10] The question of whether the $C_7H_7^+$ product of reaction 1 has the benzyl cation or the tropylium cation structure is unsettled; apparently careful electron impact and photoionization studies of the ionization of benzyl radicals, which might shed light on this question, give ambiguous and contradictory results.[11,12]

$$C_6H_5CH_3 \xrightarrow[-2e^-]{e^-} C_7H_8^+ \longrightarrow C_7H_7^+ + H\cdot \qquad (1)$$

Experimental Section

These photodissociation studies were carried out with a Varian ICR-9 spectrometer with a standard cell 2.54 cm × 2.54 cm × 13 cm. The cell conditions of high trapping voltage and low drift voltages appropriate for the trapping of ions have been described.[1] Ion lifetimes were measured by the usual procedure[1] under various conditions and were found to range from about 3 to 70 sec, depending chiefly on neutral gas pressure. Ionizing electron energies were kept as low as consistent with sufficient ion production, normally between 10 and 11 eV (filament-to-trapping plate). Since the second ionization potential of toluene is at about 11.0 eV, production of $C_7H_8^+$ ions in excited electronic states would not be expected to be significant. Except as discussed below, the toluene neutral gas pressure was 1×10^{-7} Torr (measured, as were all pressures, from the VacIon pump current). The marginal oscillator frequency was 153 kHz at about 10 mV, except that in the comparative reactivity studies, the frequency was varied so that the different isotopically labeled systems could be examined at the same magnetic field.

Reagent grade toluene and ethane were used without further purification, and no extraneous peaks were observed. $C_6H_5CD_3$ was found by nmr to contain 3.0% $C_6H_5CD_2H$ and no other detectable impurities.[13] The small available sample of $C_6D_5CH_3$ was not analyzed, but showed no unexpected peaks in the icr spectra, except small peaks attributable to a deuterated xylene impurity.

Light was provided by a 2500-W Hanovia Xenon arc, and wavelength selection was accomplished with Baird–Atomic interference

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(13) The author is indebted to Dr. Jacob Shen for supplying samples of $C_6H_5CD_3$ and $C_6D_5CH_3$.

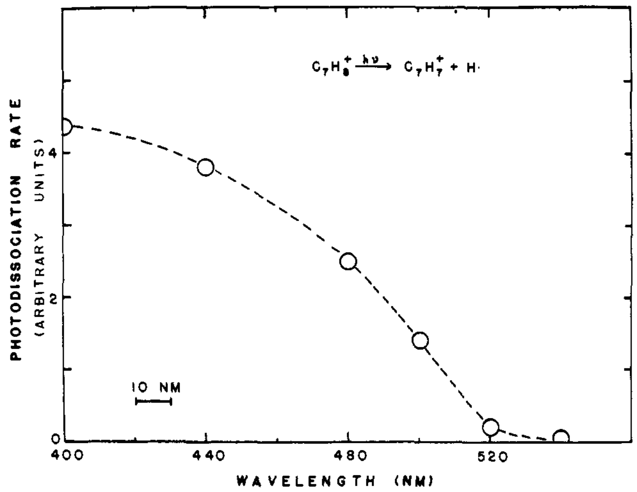

Figure 1. Relative photodissociation rate for $C_7H_8^+$, obtained by comparing the parent ion signal with the sum of the $C_7H_7^+$ and $C_8H_9^+$ signals. Most of the photons lie within the nominal bandpass of 10 nm.

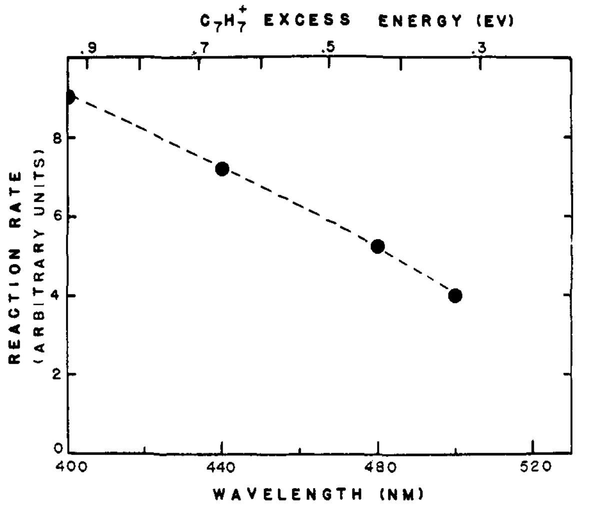

Figure 2. Relative pseudo-first-order rate constants for reaction 1 as a function of photodissociation wavelength. Also shown is the calculated excess internal energy deposited in the reactant ion following its photoproduction.

filters having a 10-nm bandpass. Where appropriate, corrections were made to the light output using the manufacturer's figures for the arc spectrum and measured transmission coefficients for the filters. No pressure increase was observed with the light source illuminating the cell.

Results

Reaction of $C_7H_7^+$ with Toluene. At the toluene pressures used, the $C_7H_8^+$ cation (the only primary cation produced at 11 eV) is nonreactive toward toluene neutral. However, at higher electron energy, Shen[8] has observed a reaction of $C_7H_7^+$ cations with toluene neutral to give a $C_8H_9^+$ product (reaction 2). When

$$C_7H_7^+ + C_7H_8 \longrightarrow C_8H_9^+ + C_6H_6 \qquad (2)$$

$C_7H_7^+$ cations are photoproduced (reaction 3) they also

$$C_7H_8^+ \xrightarrow{h\nu} C_7H_7^+ + H\cdot \qquad (3)$$

undergo reaction 2, so that when the icr cell is irradiated, the spectrum goes from a single peak at *m/e* 92 to a spectrum with peaks at 91, 92, and 105. No other photodissociation or reaction products have been observed in the toluene system for irradiating wavelengths of 400 nm and longer. Further confirmation of reaction 3 was obtained by cyclotron ejection of $C_7H_8^+$ ions,[2] which resulted in the disappearance of $C_7H_7^+$.

The extent of photodissociation of the parent cation is indicated by the sum of the peaks at 91 and 105, and the relative photodissociation rates as a function of wavelength for the toluene parent cation are shown in Figure 1. The rate of reaction 2, as indicated by the relative peak heights of the peaks at 91 and 105, is strongly dependent on the wavelength of the photodissociating light. Assuming that reaction 2 obeys simple bimolecular kinetics, the rate constant for the reaction can be calculated as a function of wavelength, as shown in Figure 2. If it is assumed that the excess energy of the photon in reaction 3 is retained in the $C_7H_7^+$ product, and no significant energy is carried off as kinetic energy of the hydrogen atom (this is a reasonable assumption if the dissociation event occurs in a quasi-equilibrium process, as is suggested in the following discussion), then the rate constant for reaction 2 may be plotted against the internal energy in excess of thermal energy which remains in the $C_7H_7^+$ reactant cation, and this has also been indicated in Figure 2.

The possibility that some of the $C_8H_9^+$ was being produced by a photon-induced reaction of $C_7H_8^+$ was tested by a cyclotron ejection experiment.[1] The $C_8H_9^+$ peak was monitored with irradiation at 400 nm while the $C_7H_8^+$ and $C_7H_7^+$ ions were successively ejected from the cell. If there were a photon-induced reaction of $C_7H_8^+$, one would expect that the $C_8H_9^+$ peak would be more effectively suppressed by ejection of $C_7H_8^+$ than by ejection of $C_7H_7^+$. This was not the case, and, if anything, the ejection of $C_7H_7^+$ was slightly more effective in suppressing the reaction. This indicates that virtually all of the $C_8H_9^+$ observed is actually produced from $C_7H_7^+$, as assumed above.

Hydrogen Scrambling. In order to approach the question of hydrogen scrambling in the photodissociation reaction, reaction 3 was investigated using $C_6H_5CD_3$ and $C_6D_5CH_3$. Figure 3 shows typical icr photodissociation spectra for these two compounds under irradiation with light at 400 nm. In both cases it is seen that hydrogen is lost from the parent cation more readily than deuterium; in $C_6H_5CD_3$, the ratio of hydrogen loss to deuterium loss is 1.3, while in $C_6D_5CH_3$, the ratio is 3.9. These ratios may be multiplied by $^5/_3$ and $^3/_5$, respectively, to correct these numbers for the statistical ratios of hydrogen to deuterium in the parent cations, and when this is done, statistically corrected ratios of hydrogen loss to deuterium loss of 2.2 and 2.3 are obtained for these two deuterium labeled cations at 400 nm. Within experimental error, these two numbers are the same, indicating that the relative rates of hydrogen and deuterium loss were independent of the original location of the atoms in the neutral molecule. In similar fashion, it is found that hydrogen/deuterium loss occurs with complete loss of positional identity for photodissociation at all wavelengths between 520 and 400 nm.

Isotope Effect. When the relative rates of hydrogen loss and deuterium loss are calculated, with a statistical correction applied to allow for the numbers of hydrogen and deuterium atoms in the parent cation as in the

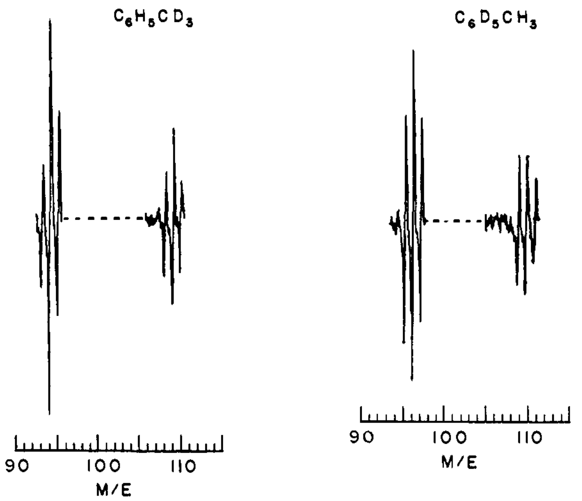

Figure 3. Field-sweep, field-modulation icr spectra for the C_6H_5-CD_3 and $C_6D_5CH_3$ systems under irradiation at 400 nm. Complete hydrogen scrambling is indicated by the equality of the statistically corrected ratios of the (parent-minus-hydrogen) to (parent-minus-deuterium) peaks for the two systems. The peaks in the region of *m/e* 110 are products of reaction 2, with some contribution from impurities.

previous section, the number obtained is a measure of the relative probability of breaking a C–H or C–D bond, and this number may be termed the isotope effect for the dissociation.[9] At all dissociating wavelengths, the isotope effect is found to be substantially greater than unity, and, as expected from the results of Howe and McLafferty,[9] increases sharply with decreasing photon energy. The isotope effect can, in principle, be determined directly from spectra such as those in Figure 3, but there are several points to be considered.

(1) The obvious corrections must be made for the carbon-13 isotopic satellites lying one mass unit above each of the peaks, and a similar correction for the 3% (as determined by nmr) of $C_7H_6D_2$ contained in the $C_7H_5D_3$ deuterated toluene sample.

(2) In some of the experiments where the ion lifetimes were extremely long, a small, but not negligible, parent minus hydrogen peak was observed even with the light off, thought to arise from stray room light entering the cell, and an appropriate correction was made for this peak.

(3) The possibility was considered that an error was being introduced by slow photodissociation of ions in the C_8 region, arising either as products of reaction 2, or as primary ions and charge transfer products from small deuterated xylene impurities in the deuterated samples. This possibility was tested by using the trapping ejection technique of Armstrong and Beauchamp,[14] from which the ions in a given region of the spectrum may be ejected from the cell by superimposing an appropriate rf field on the electrostatic trapping potential in the cell. For the present purpose, this technique has the advantage over cyclotron ejection techniques in that it was possible to simultaneously eject all of the different ions in the C_8 region while leaving essentially undisturbed the ions in the C_7 region of the spectrum. This was done in the case of the $C_6D_5CH_3$ photodissociation spectra, and it was found that ejection of the ions in the C_8 region increased the isotope effect at all wavelengths used by about 0.1. The quality of the data obtained for $C_6H_5CD_3$ did not seem to warrant elimination of such a small error, and no attempt was made to perform ejection experiments in that case.

(4) Since reaction 2 is relatively fast and results in a substantial depletion of $C_7H_7^+$ photodissociation product ions, especially at shorter wavelengths, it is possible that even a relatively small kinetic isotope effect in this reaction would result in selective depletion of the two possible photodissociation product ions, resulting in an error in the apparent isotope effect calculated from the remaining peaks. No definitive way was found to rule out this possibility, but the results of the following experiment seem to indicate that such an isotope effect is probably not great enough to affect the results in a significant way. The rate of reaction 2 in pure toluene with toluene parent ions was compared with the rate of the same reaction in $C_6H_5CD_3$ with $C_6H_5CD_3^+$ cations. By comparing the relative amounts of conversion of reactant to product for the two systems under conditions of identical magnetic field, electrostatic field, ionizing beam characteristics, and other operating parameters of the spectrometer with 400-nm irradiating light, the difference in reaction rates for toluene and toluene-d_3 was no more than about 10% (with the reaction apparently slightly faster for the deuterated toluene), while at 480-nm irradiating wavelength, the difference in reactivities was no more than 20%. Since it seems reasonable to suppose that in the case of interest, namely the relative rates of reaction of parent ion minus H and parent ion minus D with the same parent neutral, the kinetic isotope effect would be considerably smaller than in this model system, and considering the extent of conversion of $C_7H_7^+$ to $C_8H_9^+$ products at various wavelengths, it was concluded that the effect of such a kinetic isotope effect on the apparent photodissociation isotope effect should be negligible.

(5) Since photoexcitation provides such high precision in the amount of energy deposited in the cation, it becomes of considerable importance to determine whether the parent cations being photodissociated are formed at the electron beam with significant internal vibrational energy. This possibility was tested by comparing the results of photodissociation under the normal conditions (toluene without added gas at 10^{-7} Torr) with photodissociation using an added pressure of 1×10^{-6} Torr of ethane as an inert buffer gas. With the added ethane, satisfactory reproducibility and stability of the results could not be obtained by sweeping the spectra as was normally done under the lower pressure conditions, but good reproducible results were obtained in a steady-state experiment in which the observing oscillator was fixed at the frequency of each of the ions of interest for a time long enough for steady state to be reached. No significant difference in photodissociation wavelength dependence or isotope effects was observed with or without the buffer gas. It is of course not possible to be certain that under these conditions the toluene parent ions were completely vibrationally deexcited. With the added buffer gas, the ion lifetimes were measured at

(14) J. L. Beauchamp and J. T. Armstrong, *Rev. Sci. Instrum.*, 40, 123 (1969).

approximately 10 sec, and assuming an elastic ion–molecule collision rate constant of 10^{-9} cc/(molecule sec), a toluene parent ion probably undergoes on the order of 500 collisions during its lifetime in the cell. Retention of significant vibrational excitation through this number of collisions would be surprising, but not inconceivable.[15]

(6) As expected, no variation in isotope effect was observed, either for a considerable variation in the output of the arc light source (over a range from 80 to 40 A of operating current), or over a range of toluene pressure from 3×10^{-8} to 3×10^{-7} Torr.

(7) For photodissociation at a given wavelength, a statistical variation in apparent isotope effect of 10% or more on either side of the mean value was not unusual. Accordingly, the values reported here represent the average of a considerable number of different sweeps, and the error limits quoted are believed to represent a realistic assessment of the true values, based on the variation from one sweep to the next, and the variation between values obtained on different days using different experimental parameters. The uncertainties for $C_6H_5CD_3$ are considerably larger than for $C_6D_5CH_3$ because of a smaller total number of runs made, and because the statistical discrimination in this case against loss of D from the parent ion made this peak in many cases too small for good precision of the measurements.

(8) A small and variable, but not completely negligible, difference was observed in the isotope effects obtained on sweeping the spectrum to higher mass *vs.* that obtained on sweeping toward lower mass (even at very low sweep rates). As the origin of these differences is not understood, the values chosen represent the average of equal numbers of spectra taken sweeping toward higher and lower mass.

Figure 4 shows the isotope effects at wavelengths from 520 to 400 nm determined from the spectra with appropriate allowances for all of the above factors.

Discussion

Energetics. The calculation of the energetics of reaction 3 depends crucially on the value chosen for the heat of formation of the $C_7H_7^+$ product. Three choices seem reasonable. (1) If the product is tropylium ion, for which a reasonable heat of formation is 212 kcal,[11] then reaction 3 is endothermic by 48 kcal,[16] corresponding to a wavelength of 580 nm. (2) If the product is benzyl cation and we accept Lossing's electron-impact value[11] of 213 kcal for its heat of formation, then the energetics are similar to the tropylium ion case, with an endothermicity of 49 kcal and a wavelength of 570 nm. Both choices (1) and (2) are reasonable in light of our observed wavelength onset at about 540 nm. (3) If the product is benzyl cation and we accept Elder and Parr's photoionization value[12] of 221 kcal for its heat of formation, the endothermicity is 57 kcal, corresponding to a wavelength of 490 nm. Only by postulating that the $C_7H_8^+$ parent cation has in excess of 5 kcal of vibrational excitation, which it retains even in the presence of the ethane buffer, can our data be reconciled with this, and we regard our data as providing strong evidence that the product of reaction 3 is not benzyl cation with heat of formation 221 kcal. No further conclusion seems warranted given the existing confusion about $C_7H_7^+$ energetics.

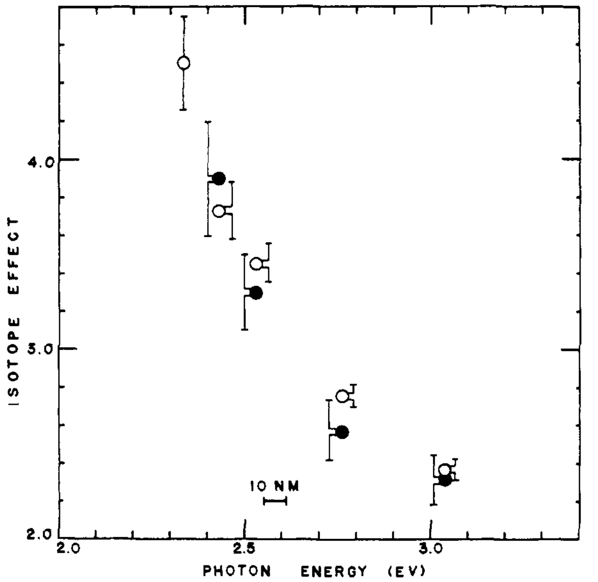

Figure 4. Isotope effects determined from the icr spectra, corrected for the systematic errors discussed in the text: open circles, $C_6D_5CH_3$; closed circles, $C_6H_5CD_3$.

It has been suggested that the onset of photodissociation is determined not only by the thermochemical threshold for the process, but also by the energy of the first excited state of the irradiated cation.[1] In the case of toluene, photoelectron spectroscopic results[17] show an excited state of the cation lying about 2.2–2.3 eV above the ground state, corresponding to a wavelength of 530–550 nm. This corresponds precisely to the observed onset in our experiments. Since both the $C_7H_8^+$ ground state and the first excited state correspond to removal of a ring π electron, it might be reasonable to expect relatively small changes in the $C_7H_8^+$ geometry upon excitation to the first excited state, and hence favorable Franck–Condon factors for photons near threshold. This gives a convenient justification for the threshold behavior in this reaction being so sharp as compared with previously studied photodissociation reactions. Thus, one may account for both the position of the onset and the sharp rise from the baseline for reaction 3 in terms of excitation to the first excited state of the cation. However, since the onset is so close to the expected thermochemical onset at 570–580 nm, it would be realistic to suppose that this onset curve is affected by both the energetics of the reaction and the optical properties of the cation.

Reaction 2 is probably close to thermoneutral. Assuming a heat of formation of 213 kcal for the $C_7H_7^+$ reactant, the reaction is calculated to be endothermic by 1 kcal for a *m*-methylbenzyl cation product,[16] and exothermic by 3 kcal for a *p*-methylbenzyl cation product. The possibility that the reaction might be slightly endothermic suggests one way of accounting

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(15) For a discussion of this question, see, for example, L. Friedman and B. G. Reuben, *Advan. Chem. Phys.*, **19**, 80 (1971).

(16) Thermochemical data not otherwise referenced are taken from J. L. Franklin, *et al.*, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, June 1969.

(17) D. W. Turner, *et al.*, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, New York, N. Y., 1970, Chapter 11.

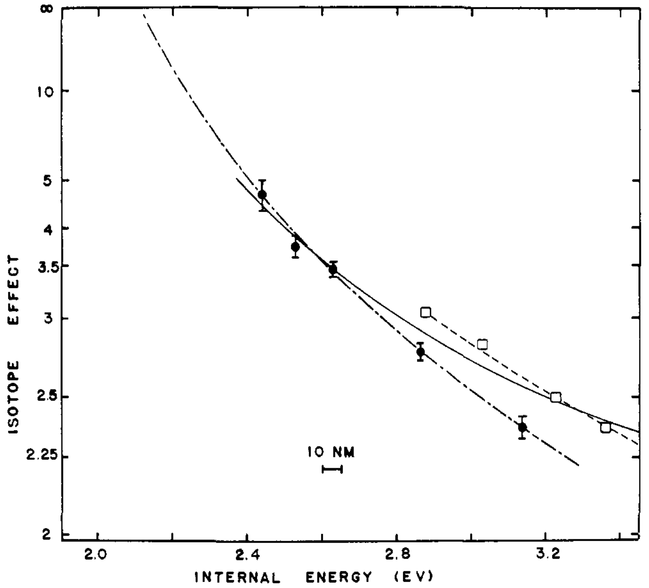

Figure 5. Isotope effect for $C_6D_5CH_3$ *vs.* cation internal energy from the present experiments (—●— — —) compared with mass spectrometric results (– – □ – –) and quasi-equilibrium theory calculations (solid line).

for the indication of Figure 2 that the reaction may have some activation energy.

Isotope Effect. Our results show that reaction 3 proceeds with complete loss of identity of ring and methyl hydrogens at all wavelengths used. The principal goal of these experiments was to determine the statistically corrected isotope effect for this reaction, which was shown *vs.* wavelength in Figure 4.

Before comparing the data with the theoretical results of Vestal and Lerner[10] and the mass spectrometric results of Howe and McLafferty,[9] a correction is necessary for the thermal vibrational energy of the $C_7H_8^+$ cation. If we assume that the vibrational frequencies of $C_7H_8^+$ are the same as those of C_7H_8 (surely an adequate approximation for the present purpose) and the normal modes are harmonic oscillators, the heat capacity of the $C_7H_8^+$ ion is readily calculated. Using vibrational frequencies for $C_6D_5CH_3$ estimated from values for benzene-d_6 and substituted benzenes,[18] $C_7D_5H_3^+$ may be estimated to have an average of about 2.5 kcal of thermal vibrational energy at 300°K. This energy may be added to the energy deposited by the photon to obtain a lower limit to the total internal energy of the excited cation.

Figure 5 shows the comparison of the present results with Vestal and Lerner's calculations[10] (as plotted by Howe and McLafferty)[19] and the experimental results of Howe and McLafferty.[9] It is evident that agreement between our results and the mass spectrometric results is quite close. Our curve lies slightly below that of Howe and McLafferty, suggesting that either the $C_7H_8^+$ ions in the present experiments were not completely thermalized at 300°, or that the energy scale of Howe and McLafferty (which, in the nature of their technique, is subject to substantial uncertainty) is in error by 0.1–0.2 eV. These two curves show very similar energy dependence.

The present results are of interest in that they extend to a cation energy of about 0.3 eV above the calculated thermodynamic threshold, as compared with a lowest energy of about 0.7 eV above threshold for previous work. This may be exploited to give a much more reliable extrapolation to infinite isotope effect.

It is expected that the isotope effect should become infinite at the bond dissociation energy of the C–D bond in the cation. Thus, determination of the energy of infinite isotope effect provides a promising approach to measuring the thermodynamic threshold for dissociation, without the complicating effects of the unknown optical absorption properties of the cation and the unknown shape of the photodissociation efficiency curve. The case of the toluene ion provides a valuable test of this approach, since the energetics in this case are already fairly well established.

The extrapolation to infinite isotope effect would be greatly facilitated by a reliable analytical expression for the energy dependence of the isotope effect near threshold, but this does not appear to be available. In Figure 5 we have plotted the function ln $(1 - 1/i)$, where i is the isotope effect, which is an arbitrarily chosen function having the virtue of reducing the curvatures of the lines to manageable proportions. By extrapolating our results along a line consistent with the curvatures of the previous mass spectrometric and theoretical lines, we find an extrapolated energy of infinite isotope effect of about 2.1 eV, and it seems reasonable to assign this number a value of 2.1 ± 0.1 eV. This is an energy of 47 ± 2 kcal, in very good agreement with the thermodynamic threshold of 48 or 49 eV calculated above.

The agreement of the isotope effect in these experiments with Vestal's calculations is also reasonably good. However, both our results and the mass spectrometric results appear to have a steeper slope than the calculated curve and suggest that further refinement of the theory could be fruitful. The good quantitative agreement of theory and experiment gives support to the quasi-equilibrium theory approach to this problem as a valid approach, and suggests that the quasi-equilibrium hypothesis may be valid for reaction 3.

Hydrogen scrambling and isotope effects show no distinction between the direct production of $C_7H_7^+$ from toluene by electron impact (reaction 1) and its formation from near-thermal $C_7H_8^+$ ions by photodissociation (reaction 3). It appears that loss of identity of ring and methyl hydrogens commonly occurs in low-energy $C_7H_8^+$ cations having enough energy to dissociate. A plausible hypothesis, which should be useful in directing further work on this system, is that the ground state of the toluene parent cation retains the toluene structure and the identity of methyl and ring hydrogens, while dissociation to $C_7H_7^+$ involves excitation to the first (or higher) excited state of the cation, in which hydrogen scrambling is rapid, followed by degradation of this electronic energy into vibrational energy with subsequent decomposition in a quasi-equilibrium process. Other models are of course also consistent with the existing experimental data, and further work on this system is needed.

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(18) D. H. Whiffen, *J. Chem. Soc.*, 1350 (1956); D. H. Braun, A. Mohammed and D. W. A. Sharp, *Spectrochim. Acta*, 21, 659 (1965); T. Shimanouchi, "Tables of Molecular Vibrational Frequencies," NSRDS-NBS 6, March 1967.

(19) Vestal and Lerner did not reduce their calculated decomposition rates for H-loss and D-loss to the form of an isotope effect. This was, however, done by Howe and McLafferty,[6] and we have used the curve taken from their Figure 1.