Gas-Phase Photodissociation of Alkylbenzene Cations

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Abstract: Ion cyclotron resonance photodissociation techniques have been used to determine photodissociation spectra and relative photodissociation rates in the visible wavelength region for a variety of mono- and dialkyl-substituted benzene cations. Several of the isomeric parent cations are readily distinguished by their spectra. The photodissociation products have been determined by double resonance techniques, and the most energetically favored products predominate in the cases for which data are available. It is argued that the threshold region of the photodissociation curves for all of the cations except cumene (and possibly toluene) are spectroscopically determined. The relative onset energies for the cations are reported and are taken to be a quantitative measure of the relative energies of excitation from the cation ground state to the first excited state of the cation. Photodissociation results show excellent agreement with photoelectron spectroscopic results for the five molecules for which data are available.

Several recent studies have investigated the photodissociation of cations,[1-5] and it appears that this approach may provide a useful new source of information about gaseous cations. Several questions about the photodissociation process remain of interest, among them (1) what determines the preferred dissociation products among various possibilities, (2) what factors determine the wavelength onset and curve shape for photodissociation, (3) how do the spectra of isomeric ions differ, and how may the differences be interpreted and exploited? We have found the alkylbenzenes to provide a particularly tractable set of parent cations for detailed investigation of these questions, and we describe here the photodissociation behavior for a number of different compounds, with particular reference to these three points.

Several studies of photodissociation of polyatomic ions have been reported. The photodissociation of methyl chloride cation was found to proceed to form methyl cations and chlorine;[1] the wavelength onset for this process was not sharp, but was definitely not much less than 0.5 eV above the thermochemical lower limit for the process. The photodissociation peak was consistent with excitation to either of the two lowest known excited states of the cation, while a polarized source study[4] indicated a probability that the higher of these states (^2E) was actually responsible. A study of several olefins[2] indicated that photodissociation occurs to a significant extent only when the photon wavelength makes the dissociation thermochemically possible for ground-state cations and at the same time permits initial excitation of the cation into its first (or higher) excited state. It was shown that isomeric butene cations could be distinguished in some cases. Photodissociation of isotopically labeled toluenes[3] showed complete hydrogen scrambling prior to dissociation, and a large deuterium isotope was observed. Extrapolation to infinite isotope effect gave support to a heat of formation of 212–213 kcal for the photoproduced $C_7H_7^+$ cation, and this is the value we will use below. Finally, a photodissociation study[5] of three isomeric $C_7H_8^+$ cations showed that they could very easily be distinguished by their photodissociation spectra.

Experimental Section

The experimental arrangement used in these experiments was the same as in previous studies.[2,3,5] The Varian ICR-9 spectrometer was fitted with a window to admit the light. A standard "square" icr cell was used, with a trapping voltage of 2–3 V and normally zero drift potentials. The marginal oscillator frequency was normally 153 kHz, but was varied as necessary to allow operation between about 9 and 13 kG. The radiofrequency amplitude was 20 mV peak-to-peak. Operating pressures were normally near 1×10^{-7} Torr.

Double resonance ejection could be accomplished with equal success using either source or analyzer irradiation. Substantial ion ejection begins to be apparent at amplitudes less than 0.03 V (peak-to-peak), but for quantitative ejection of an ionic species, amplitudes of 0.10 V or greater appeared to be necessary. Since severe interference between the marginal oscillator and the double resonance oscillator begins to be a problem above 0.10 V, it was not always possible to work under conditions of assured quantitative ion ejection. This leads to some ambiguity in the results for some molecules.

Light was generated with a 2.5-kW xenon arc and following passage through a water filter was wavelength selected using Baird-Atomic interference filters. The filters had bandwidths of 100 Å spaced 200 Å apart from 4200 to 7000 Å and had bandwidths of 150 Å at 7500 and 8100 Å. Relative light intensity with each interference filter in place was measured using an Eppley thermopile, and the measured photodissociation rate constants were corrected by dividing by the relative light intensity at each wavelength. The relative calibration data were assumed not to drift significantly over a few months and were probably good to ±5%.

We are indebted to Professor George A. Olah for supplying many of the hydrocarbons used in this study. The compounds were not purified other than by freezing and degassing at the spectrometer inlet.

Data Treatment

In the icr photodissociation technique, photodissociation is studied under steady-state conditions, in which the production of ions by electron impact and reactions, the loss of ions by reaction and by diffusion to the cell walls, and the dissociation of ions by the light all occur simultaneously to establish steady-state concentrations of all of the ionic species present. These steady-state concentrations are conveniently measured using well known icr single resonance techniques. Since in the present study substantial effort was made to obtain quantitative comparisons of photodissociation rate constants for different ions and different wave-

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(1) R. C. Dunbar, *J. Amer. Chem. Soc.*, **93**, 4354 (1971).
(2) J. M. Kramer and R. C. Dunbar, *J. Chem. Phys.*, in press.
(3) R. C. Dunbar, *J. Amer. Chem. Soc.*, **95**, 472 (1973).
(4) R. C. Dunbar and J. M. Kramer, *J. Chem. Phys.*, **58**, 1266 (1973).
(5) R. C. Dunbar and E. Fu, *J. Amer. Chem. Soc.*, **95**, 2716 (1973).

lengths, it is of some importance to examine critically the theoretical basis for analysis of the icr spectra.

We consider the case of a primary ion with concentration (P) which undergoes a single photodissociation reaction to give a secondary ion of concentration (S). We assume that the secondary ion is not reactively formed from the primary ion by means other than photodissociation and furthermore, as is normally the case, that these secondary ions are of sufficient stability to preclude their being photodissociated; it is then readily seen that the concentration (S_0) of secondary ions existing in the absence of light constitutes a set of ions which is neither increased nor decreased by turning on the light and may for the present purposes be ignored. Accordingly, we may define a concentration $(S') = (S) - (S_0)$ which is the concentration of photoproduced secondary ions. The steady-state kinetic equations governing this system may then be written

$$\frac{d(P)}{dt} = 0 = C(P) - (K^{P}_{loss})(P) - (K_{phot})(P) \quad (1)$$

$$\frac{d(S')}{dt} = 0 = (K_{phot})(P) - (K^{S}_{loss})(S') \quad (2)$$

where K^{P}_{loss} and K^{S}_{loss} are the rate constants for the disappearance of primary and secondary ions by all mechanisms other than photodissociation, $C(P)$ is the rate of formation of primary ions at the electron beam, and K_{phot} is the rate constant for photodissociation of primary ions into secondary ions. K^{P}_{loss} is readily determined by a simple experiment: with the light off and the spectrometer set to monitor continuously primary ion concentration, the electron beam is abruptly terminated, and the ensuing exponential decay of the primary ion signal is recorded as a function of time.[6]

A good check on the assumption that K^{P}_{loss} is indeed a quasi-first-order rate constant is obtained by checking to see whether the decay of the primary ion's signal is exponential. This was done for all of the ions for which quantitative data were sought. It was found that, depending on the precise instrumental conditions, there was sometimes a delay of up to 5 sec following electron-beam termination before decay of the signal set in, or in other cases the initial rate of decay over a few seconds was somewhat faster than the subsequent rate. Following these first few seconds of positive or negative deviations from exponential decay, the decay curves always showed a very good fit to an exponential decay curve. Values of K^{P}_{loss} ranged from about 6 to 25 sec^{-1}. The initial slightly nonexponential decay behavior did not appear severe enough to introduce important errors.

With an independent measure of K^{P}_{loss}, eq 1 is readily solved to yield the following relation

$$K_{phot} = K^{P}_{loss}\frac{(P_0) - (P)}{(P)} \quad (3)$$

where (P_0) is the steady-state primary ion concentration with the light off. Thus to obtain relative photodissociation rate constants, it is necessary only to measure the quantity $[(P_0) - (P)]/(P)$ and normalize for light intensity.

An alternative approach to determining the photodissociation rate constant is provided by eq 3 in ref 1, which may be written in the present notation as

$$K_{phot} = K^{S}_{loss}[(S')/(P)] \quad (4)$$

However, in many cases the photoproduced secondary ions undergo one or more subsequent ion–molecule reactions, and also it has been shown that under some conditions photoproduced secondary ions may be lost by recoil from the cell,[4] which would introduce errors into eq 4. In spite of these difficulties, the determination of K_{phot} from eq 4 is useful, because in practice it is possible to obtain accurate measurements for much slower photodissociation processes than can be treated using eq 3.

In the present study, eq 3 was normally used for the quantitative calculation of relative photodissociation rate constants, but where the rates were slow, as in the threshold region, eq 4 was used. Good quantitative agreement was found between rate constants calculated using eq 3 and 4 in the threshold region of the curves, but at shorter wavelengths, as expected, eq 4 underestimated the dissociation rate constants by progressively larger factors (up to a factor of 2). We believe that eq 3 provides a reliable calculation of the relative photodissociation rate constant for all wavelengths, without complications due to the subsequent ion–molecule chemistry of the photodissociation products. The only circumstances which would render this analysis invalid appear to be cases in which ions at the mass of the primary ion are regenerated with the light on, either by photodissociation of a higher mass ion, or by an ion–molecule reaction process occurring only with the light on. We have no reason to suspect such complications in any of the systems reported here.

A considerable effort was made to obtain for the molecules studied a consistent quantitative set of relative photodissociation rates whose values could be compared directly. This was accomplished by determining, at several wavelengths, the photodissociation rates for all of the compounds under identical instrumental conditions, with careful measurement of ion residence times in order to permit application of eq 3. (Ion residence times were found to vary from 6 to 25 sec, depending on the ion.) In making these comparisons, it seemed more important to keep the total ion concentration approximately constant than to keep the electron energy constant, and accordingly the electron energy was varied for the different ions to produce approximately the same parent ion single resonance signal in each case. With the exception of the three diethylbenzenes, such calibration spectra were taken for all of the compounds at two or more wavelengths, permitting the photodissociation spectra to be related to a uniform instrumental sensitivity. Experience suggests that this calibration procedure was reliable to within perhaps ±20%, and accordingly all of the spectra reported below (with the exception of the diethylbenzenes) may be directly compared within this uncertainty.

Results

The photochemistry and ion–molecule chemistry of these molecules at low electron energy was found to be

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[6] In ref 1 some pains were taken to obtain ion decay curves under conditions where the ions were not perturbed by the marginal oscillator. By contrast, in the present experiments the photodissociation process was normally followed by monitoring continuously the primary ion concentration, and it is therefore appropriate to measure K^{P}_{loss} under conditions where the ion motion is influenced by the marginal oscillator.

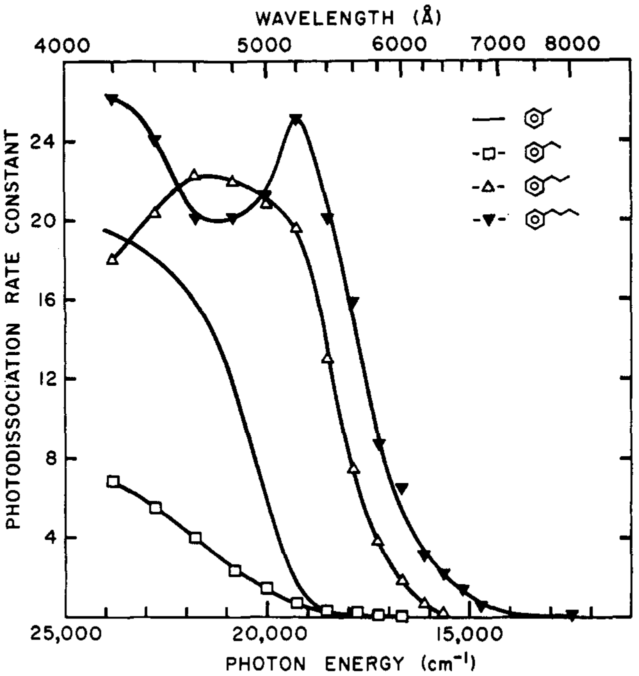

Figure 1. Relative photodissociation spectra for *n*-alkylbenzene parent cations. The vertical scale is directly comparable with Figures 2 and 3. The toluene spectrum is from ref 3.

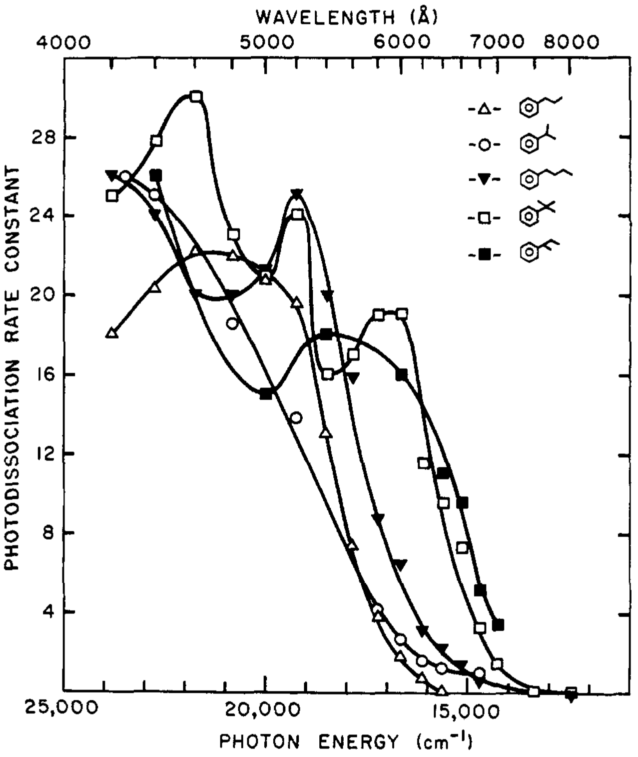

Figure 2. Relative photodissociation spectra for several alkylbenzene parent cations. The vertical scale is directly comparable with Figures 1 and 3.

quite simple, involving usually only two or three important peaks. Each system was examined both with and without illumination, and ion ejection double resonance was used to identify all of the ion–molecule reactions. Only one direct photodissociation pathway was normally found and was directly verified by parent ion ejection. Subsequent reactions of the product ion

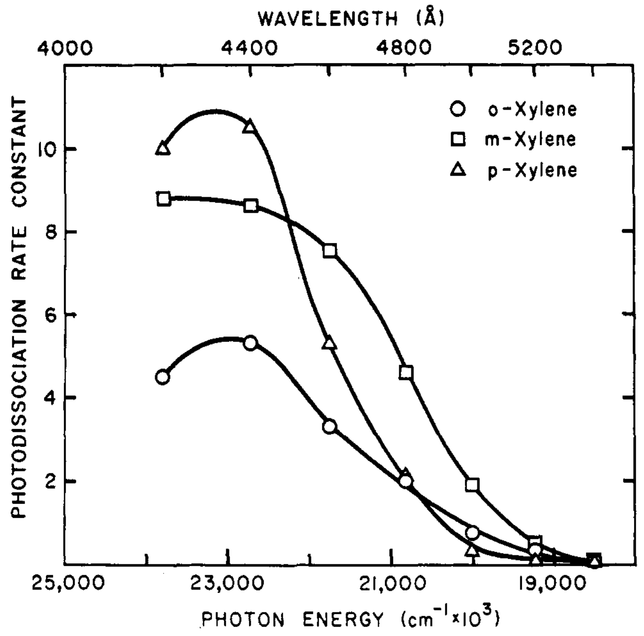

Figure 3. Relative photodissociation spectra for xylene parent cations. The vertical scale is directly comparable with Figures 1 and 2.

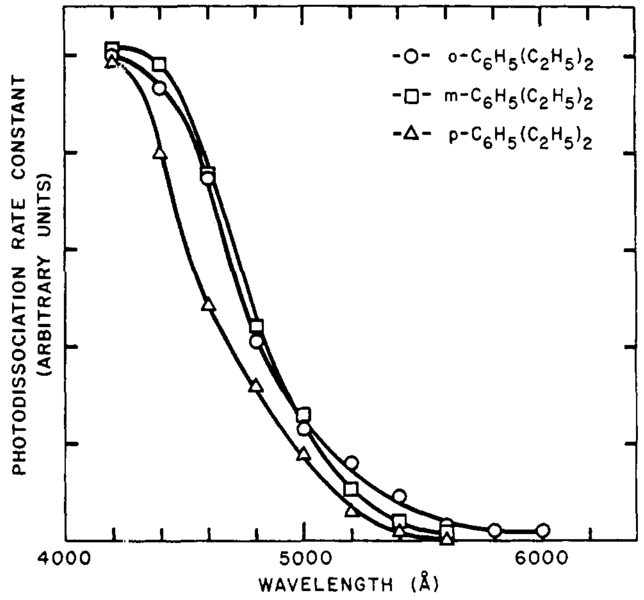

Figure 4. Relative photodissociation spectra of diethylbenzene parent cations. The vertical scale for each curve is arbitrary.

were easily identified by double resonance. Where competing photodissociation and reactive processes were possible, ion ejection double resonance was used for quantitative comparison.

For many of the systems, the spectrum was scanned to high mass, often above twice the parent ion mass. No larger mass ions were found in abundance comparable with the parent ion. We have no evidence, and no reason to suspect, that high mass ions undergo photodissociation reactions which would complicate or invalidate the results presented below. Photodissociation spectra are shown in Figures 1–4.

The photodissociation products observed were as follows. $C_7H_7^+$ was the only product observed for toluene, ethylbenzene, *n*-propylbenzene, *n*-butylbenzene, and the xylenes. $C_8H_9^+$ was the only product for isopropylbenzene and composed roughly two-thirds of the *sec*-butylbenzene products. $C_9H_{11}^+$ was the only product for *tert*-butylbenzene, was about a third of the *sec*-butylbenzene product, and, because of inconclusive double resonance data, cannot be ruled out as a product in isopropylbenzene. $C_{10}H_{13}^+$ was the only diethylbenzene product and also was not ruled out conclusively for *sec*-butylbenzene.

For many of the molecules the photodissociation product ion reacted with the parent, presumably by hydride extraction, to give parent minus one. This was observed and verified by double resonance for ethylbenzene, *n*-propylbenzene, isopropylbenzene, *n*-butylbenzene, *sec*-butylbenzene, *tert*-butylbenzene, and *p*-xylene (wavelength <5000 Å). In addition, in all three xylenes the $C_7H_7^+$ ion reacted with parent to give $C_9H_{11}^+$. For *tert*-butylbenzene near threshold the product ion is unreactive, but at shorter wavelengths peaks appear at 57 and 91, and the ion–molecule chemistry at 4000 Å is quite complex.

Discussion

Internal Excitation of Parent Ions. The question of whether the parent ions in experiments such as these are formed with, and retain, enough vibrational excitation to cause significant changes in their photodissociation spectra has been frequently raised.[2,3,5] Several control experiments in previous studies of various systems in which a nonreactive gas was introduced at a pressure allowing hundreds of collisions during the ion residence time have shown that, if such excess internal energy is present, it is not significantly dissipated by third-body collisions under these conditions.[2,3,5] It seems most reasonable to suppose that any excess internal energy is in general rapidly thermalized.

While it did not seem necessary to test all of the cations of the present study, it did seem desirable to make one check for internal excitation (in addition to toluene, for which a nonreactive gas study was reported in ref 3). The obvious choice was cumene, which, as Figure 2 shows, exhibits severe tailing of the curve in the threshold region, such as might result from substantial internal excitation. The photodissociation spectrum of i-$C_9H_{12}^+$ alone at 1.4×10^{-7} Torr was taken and compared with the spectrum in the presence of 7.5×10^{-7} Torr of ethane. The photodissociation rates at all wavelengths were reduced by about 30% by the ethane, due to reduction in ion residence time. However, the shape of the curve did not change at all, and the photodissociation rates in the long-wavelength tail of the curve were unquestionably as great (relative to the short-wavelength rates) with ethane present as with ethane absent. The number of collisions which a typical ion would undergo with ethane present was about 100 compared with 25 for cumene alone. This result again suggests that excess internal energy is not significant under the photodissociation conditions or that it is remarkably resistant to thermalization by nonreactive ion–molecule collisions.

Thermal Energy. The heat content function $(H° - H_0°)/T$ has been evaluated for a number of alkylbenzenes[7] and ranges from 14.5 cal/deg for toluene to 25.2 cal/deg for *n*-butylbenzene at 300°. Subtracting the translational and rotational parts, and multiplying by 300°, we obtain a measure of the internal thermal energy of a typical molecule (or, presumably, molecular ion) ranging from 2.5 kcal for toluene to 6.4 kcal for butylbenzene. This is an average of less than 0.1 kcal per internal degree of freedom.

If the photodissociation threshold curve is thermochemically determined, then the presence of this thermal energy could result in a displacement of the observed threshold by several kilocalories to longer wavelength. If, on the other hand, the threshold curve is spectroscopically determined, as we will argue is generally the case for alkylbenzenes, the effect should be much less. The effect on the threshold in this case will show up in the appearance of hot bands, in which the transition to the excited electronic state of the cation is accompanied by a decrease in one or more of the internal energy quantum numbers, governed by Franck–Condon factors. A significant effect on the threshold region would require several of the excited internal modes to be deexcited simultaneously, which is very improbable.

Thermochemistry. For those cases where the necessary data are available, it is of interest to compare the energetics of the various reasonable dissociation channels. Heats of formation of Franklin, *et al.*,[8] will be accepted. The $C_7H_7^+$ heat of formation will be taken as 212 kcal.[3]

Toluene, as previously discussed,[3] has only one reasonable low-energy fragmentation, whose energy corresponds well with the observed threshold.

The observed dissociation for ethylbenzene is endothermic by 36 kcal (7800 Å), which is much less than the observed threshold energy. Direct dissociation to $C_8H_9^+ + H\cdot$ is endothermic by 61 kcal (4600 Å, with substantial uncertainty because of the unreliable $C_8H_9^+$ heat of formation[9]).

For *n*-propylbenzene, dissociation is endothermic by 34 kcal (8300 Å), again substantially below the observed threshold. One alternative dissociation, to $C_8H_9^+ + CH_3$, is endothermic[10] by 48 kcal (5800 Å), while data are not available on the dissociation to $C_9H_{11}^+ + H$.

Dissociation for *n*-butylbenzene is endothermic by 37 kcal (7600 Å).

The observed reaction for cumene is endothermic by 50 kcal (5600 Å), subject to the uncertain $C_8H_9^+$ heat of formation.[10]

The difference in appearance potentials for $C_{10}H_{14}^+$ and $C_9H_{11}^+$ in *tert*-butylbenzene has been measured,[11] giving an endothermicity of 28 kcal (10,000 Å) for its dissociation.

Of the xylenes, *o*- and *m*-xylene have identical thermochemistry, with dissociation being endothermic by 43 kcal (6400 Å). For *p*-xylene, dissociation is endothermic by 46 kcal (6100 Å). The alternative dissocia-

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(7) W. J. Taylor, D. D. Wagman, M. G. Williams, K. S. Pitzer, and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, 37, 95 (1946).

(8) J. L. Franklin, *et al.*, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, Washington, D. C., June 1969.

(9) The $C_8H_9^+$ heat of formation for ethylbenzene in ref 8 is an appearance potential measurement which must be considered as neither precise nor reliable.

(10) Assuming the same heat of formation of $C_8H_9^+$ as ethylbenzene. See ref 9.

(11) I. Howe and D. H. Williams, *J. Amer. Chem. Soc.*, **91**, 7137 (1969); A. N. H. Yeo and D. H. Williams, *Org. Mass Spectrom.*, **5**, 135 (1971).

tion to give $C_8H_9^+ + H$ is endothermic by about 55 kcal (5000 Å) for all three xylenes.

From these figures, some conclusions may be drawn. All of the dissociations observed can be formulated as simple cleavage of a bond to the benzylic carbon, and for ethylbenzene, *n*-propylbenzene, and xylene, where the energetics are known, the lowest energy dissociation is the predominant, if not the only, dissociation pathway. In all cases this dissociation pathway also corresponds to the base peak in the mass spectral fragmentation pattern induced by energetic electron impact.

Of the cations whose energetics are known, only toluene and cumene have observed thresholds near the thermochemical threshold. For the other ions, dissociation drops to very low rates (1% or less of the maximum) at energies substantially above the thermochemical threshold. This provides evidence that the photodissociation curves are in general spectroscopically determined; this will be further supported below.

Curve Shapes. All of the photodissociation spectra have some common features. The curves rise rapidly from very low values over several thousand wave numbers and then level off or peak; the energy interval over which the rate constants increase from 1 to 90% of their maximum value is about 4000 cm^{-1}. At the 200-Å resolution available with interference filters, little structure is seen in most of the curves. However, the three butylbenzenes show marked structure with two or more peaks separated by thousands of wave numbers. Reexamination of these spectra of high resolution will be reported in a subsequent study, and speculation on the significance of this spectral structure would not be fruitful at present.

In most cases, the gross shapes of the photodissociation spectra are sufficient for immediate identification of isomeric ions. Thus the curves for the three butylbenzenes are instantly distinguishable from each other and from diethylbenzene; the two propylbenzenes show a difference of 3000 cm^{-1} or more in the position of the maximum, and *m*- and *p*-xylene show a difference of almost 1000 cm^{-1} in the threshold regions of their curves. On the other hand, it would require careful measurement to distinguish *o*- and *m*-xylene; distinguishing *m*-xylene and ethylbenzene would probably be impossible. Thus, this technique offers a very convenient and definitive means of distinguishing between many, but not all, isomeric parent cations.

In Figure 5, the threshold regions of all of the spectra are replotted in logarithmic form, with the vertical scale for each spectrum adjusted so that the first maximum of each curve falls at the same value. This plot provides a convenient means of displaying the spectral similarities and differences. It is immediately apparent that the curve shapes are similar, and for most of the ions the only substantial difference is displacement along the energy axis. For most of the ions, in fact, the curves in Figure 5 may be fitted with excellent agreement to the Gaussian line shape

$$K = Ae^{-(1/\alpha^2)(E-E_0)^2} \qquad (5)$$

where K is the photodissociation rate constant, A is adjustable, E is the photon energy in reciprocal centimeters, and E_0 is the photon energy at which the curve peaks. The width parameter α has a value near 2000 cm^{-1} for all the ions except ethylbenzene and *n*-butylbenzene, whose curves are a bit broader (larger α), and cumene, which is badly non-Gaussian.

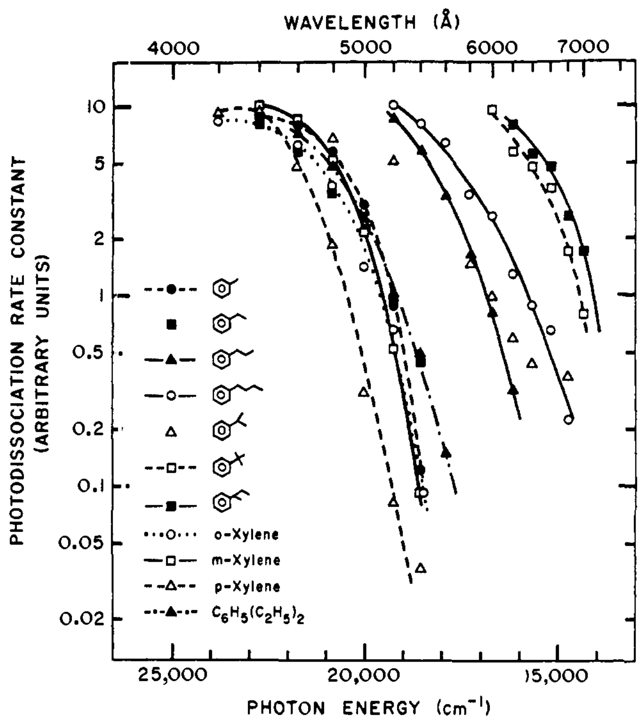

Figure 5. Logarithmic plots of the alkylbenzene cation photodissociation spectra, with the vertical scale for each curve adjusted to give the same maximum value. Of the diethylbenzenes, only meta is plotted.

The Gaussian shapes of the curves are consistent with, and suggestive of, excitation to a single electronic excited state with broadening due to populating several vibrational levels of the excited state according to a roughly Gaussian distribution of Franck–Condon factors. An entirely reasonable width for such a Franck–Condon envelope is 2000 cm^{-1}. Only for cumene does the long low-energy tail suggest a different origin for the curve shape.

Photodissociation Onsets. Since, as discussed above, the photodissociation curves show a Gaussian energy dependence in the threshold region, it is not possible to define an absolute onset energy for any of the ions. However, much more importance attaches to differences in onset energies for this series of closely related compounds, as a sensitive measure of the effect of the alkyl group on the energy levels of the aromatic system. Such differences in onset energies are readily and precisely available from the photodissociation spectra.

As a prerequisite to making use of the onset energies, we discuss the origin of the onset curves. Two extreme types of behavior may be distinguished. (1) For a thermochemically determined onset, the photon absorption rate is assumed to show insignificant wavelength variation over the onset region, and the onset curve is assumed to reflect the unimolecular decay of the excited cation in competition with reradiation or collisional deactivation processes. Prediction of the curve shape for an onset of this type would be very difficult. (2) For a spectroscopically determined onset, it is assumed that the curve shape is dominated by the absorption spectrum of the cation, and that once excited the probability of dissociation of the cation relative to the probability of deexcitation is relatively independent of energy. Except very close to the thermochemical limit for dissociation this last assumption is reasonable, since reradiation should not be strongly energy dependent, and unimolecular decay is very rapid compared with collision rates at these pressures. Examples of both types of behavior are thought to occur in photodissociation of the olefin parent ions.[2]

It appears likely that nearly all the alkylbenzene cations studied exhibit spectroscopically determined onsets. One test of this is a comparison of the observed curves with known thermochemistry. Such a comparison is presented in Table I for compounds where data are available. The photodissociation onsets are arbitrarily taken as being the energy at which the dissociation rate constant falls to 5% of its maximum value in Figure 5. While arbitrary, this 5% point can be accurately measured and appears to be a reasonable approximate measure of the energy at which photodissociation becomes important.

As the table shows, the observed thresholds lie at substantially higher energy (several thousand reciprocal centimeters) than the thermochemical onset in all cases for which data are available, except cumene and toluene. This strongly suggests that the onsets are spectroscopically determined. The fact that for toluene photodissociation is observed very close to the thermochemical onset, and for cumene in fact below the thermochemical onset, suggests that if photon absorption is spectroscopically allowed at the thermochemical onset energy, photodissociation will be observed. It seems significant that cumene, the only case for which the thermochemical onset can reasonably be assumed to lie above the spectroscopic onset, is also the only ion showing marked long-wavelength tailing of the curve and a seriously non-Gaussian line shape. We believe that in the cases for which energetic data are not available, the good fit of the curves to eq 21 with $\alpha \simeq 2000$ cm^{-1} constitutes good evidence that the onsets in these cases are also spectroscopically determined.

It is of interest also to compare the photodissociation onsets with the value obtained by photoelectron spectroscopy for the energy difference between the ion ground state and its first excited state.[12-14] Probably (in the absence of resolved vibrational structure) the most defensible way of estimating this energy gap from the photoelectron spectra is to measure from the base of the ground-state peak to the base of the excited-state peak,[15] as we have done for the five available spectra of the compounds studied, as shown in Table I. The very good agreement between the observed photodissociation onsets and the photoelectron spectroscopy data is of course partly an artificial result of the arbitrary 5% onset criterion, but indicates that these two techniques are in excellent agreement. It is perhaps even more significant that the two techniques agree very well in giving relative values of the excitation energy for different ions, so that, for instance, the difference of 1000 cm^{-1} between *m*- and *p*-xylenes shows up in both techniques. The photodissociation method measures such differences with very good precision and may be more accurate than the photoelectron spectroscopic approach in favorable cases. The simple semiempirical Hückel model proposed by Klessinger[14] to account for benzene substituent effects in photoelectron spectra breaks down for larger alkyl groups, and a more exact theoretical treatment is needed for comparison with the present results.

Table I. Observed Onsets, Thermochemical Data, and Photoelectron Spectroscopy Data (cm^{-1})

Alkyl substituents	Observed photodissociation onset[a]	Onset energy relative to *p*-xylene[b]	Thermochemical onset[c]	Excited state of cation[d]
Methyl	19,000	−1050 ± 50		18,000
Ethyl	18,600	−1400 ± 200	12,800	
n-Propyl	16,500	−3600 ± 100	12,000	
Isopropyl	(16,000)[e]		(17,900)[f]	
n-Butyl	15,200	−4800 ± 300	13,200	
sec-Butyl	13,900	−6250 ± 100		
tert-Butyl	14,200	−6000 ± 100	10,000	14,000
o-Dimethyl	19,100	−1000 ± 50	15,600	19,300
m-Dimethyl	19,100	−1000 ± 50	15,600	19,300
p-Dimethyl	20,050	0	16,400	20,200
o-Diethyl	18,000	−2100 ± 200		
m-Diethyl	18,500	−1600 ± 200		
p-Diethyl	18,800	−1300 ± 200		

[a] Energy at which the rate of photodissociation is 5% of its (first) maximum value. [b] The uncertainties reflect the fact that the value relative to *p*-xylene reflects the point on the vertical axis at which the comparison is made. The quoted spread is appropriate to making the comparison somewhere in the approximate range of 0.2 to 2.0 on the vertical scale of Figure 5. Direct comparison between some pairs of ions, such as *sec*-butylbenzene and *tert*-butylbenzene, can be made with much greater precision than implied by these uncertainties. [c] Reference 8. [d] References 12-14. [e] Probably not meaningful. See text. [f] Uncertain value. See text.

The series of monosubstituted benzenes shows a smooth trend toward lower excitation energies with larger substituents. The data suggest a qualitative correlation between excitation energy and polarizability of the substituent, the only anomaly being *sec*-butylbenzene which, having a less highly substituted α carbon, might be expected to lie higher than *tert*-butylbenzene.

The xylenes confirm and strengthen the photoelectron spectroscopy results. *o*- and *m*-xylene have identical excitation energies to within a hundreth of an electron volt, while *p*-xylene is 1000 cm^{-1} higher, in agreement with both the prediction and observation of Klessinger, but with greater experimental precision. This being the case, it would be expected that *p*-diethylbenzene would differ by at least as much from the other isomers, and it was surprising to find that the difference between the diethylbenzenes was somewhat less.

The significant quantities which were determined with precision and confidence in this study are the differences in excitation energy for well-behaved members of the alkylbenzene family. These are tabulated relative to *p*-xylene in Table I for convenience in comparison with future work on these systems.

Acknowledgment. Acknowledgment is made to the

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(12) D. W. Turner, *et al.*, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London, 1970.

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(15) For unresolved spectra, this should provide an approximation of the adiabatic ionization potential difference. Photodissociation probably occurs by a vertical excitation from a thermalized ground-state cation, and there is no obvious way to extract the precise energetics of this process from the photoelectron spectra. These vibrational-energy effects are small compared with the energy differences between different cations and do not appear to warrant deeper analysis at present.

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Photochemical 1,3 Addition of Benzene to Olefins. Orientational Specificity Induced by Methyl Substituents on Aromatic and Olefinic Rings

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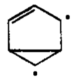
Abstract: Photochemical addition of toluene and *o*-, *m*-, and *p*-xylenes to cyclopentene gave principally 1,3 adducts (3,7-*endo*-tetracyclo[6.3.0.0^{2,11}.0^{3,7}]undecene-9) in which a methyl group was oriented specifically in C-1 position. Addition of mesitylene to cyclopentene was exceptional in that both the 1,9,11- and 2,8,10-trimethyl derivatives were formed although the former predominated. From quantum yields for these additions, it was concluded that a methyl substituent on a benzene ring exercised a significant activation in the excited state on the ortho positions and possibly a deactivating effect on the meta positions. With increasing substitution of the aromatic ring with methyls, steric effects also came into play, the quantum yield for 1,3 addition for mesitylene being only ~0.1 of the value for benzene. Addition of benzene to 1,2-dimethylcyclobutene was as efficient as to cyclobutene. Addition of toluene to 1,2-dimethylcyclobutene was sixfold slower than to cyclobutene or *cis*-3,4-dimethylcyclobutene. At the same time, the orientational specificity was retained in all these additions. A model of the complex between the singlet excited benzene and olefins is proposed which takes into account the features of the 1,3 additions.

Although numerous examples of the photochemical 1,3 addition of benzene to olefins are known,[1–7] the factors which control the peculiar features of this reaction are largely unknown. Three of the most striking peculiarities follow. (i) 1,2, 1,3, and 1,4 additions all occur from the same (singlet) excited state of benzene but their relative importance is olefin dependent.[1c,5] 1,3 addition is the predominant process in linear and cyclic monoolefinic hydrocarbons. (ii) 1,3 addition is not directly related to the formation of benzvalene[1b,8] even though a diradical intermediate (I) may appear to serve as a common precursor. (iii) Mono- and dimethyl substituted benzenes have been shown[9] to add (in the 1,3 mode) to cyclobutene with a high degree of orientational specificity.



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Following an original suggestion by Morrison and Ferree,[6] Wilzbach and Kaplan[1c] have proposed that the addition reactions to olefins may proceed from a complex between the excited singlet benzene and the olefin. A detailed kinetic study[10] of the benzene–cyclopentene system lends support to this suggestion and offers a basis for explaining the peculiarities mentioned above.

In this work, the orientational specificity of the addition has been studied in order to establish its generality and its limitations and to explain it within the exciplex mechanism.

Results

The 1,3 photoadditions that were investigated fall into two general series. In one, the additions of methyl-substituted benzenes to cyclopentenes were studied both qualitatively and quantitatively. The second consisted of quantitative measurements on the addition of benzene and toluene to cyclobutene, 1,2-dimethylcyclobutene, and *cis*-3,4-dimethylcyclobutene.

Methylbenzenes–Cyclopentene. The methylbenzenes that were investigated are listed in Table I. In every instance one or more 1,3-addition products were isolated. Their mass spectra and analyses indicated that they were 1:1 adducts. Since spectroscopic data showed that they contained only one olefinic group per molecule, they should be tetracyclic. In their infrared spectra, the adducts had a weak absorption at 1595–1603 cm^{-1} (or at 1648–1650 cm^{-1} when a methyl substituent was present at the double bond) which showed the presence of a cyclopentene ring. In their ultraviolet spectra, the adducts had an absorption maximum or shoulder at

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