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International Journal of Mass Spectrometry 227 (2003) 135–145

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

Dissociation of *p*-cymene molecular ions induced by thermal radiation

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Received 29 October 2002; accepted 13 December 2002

Dedicated to Rob Dunbar on the occasion of his 60th birthday for his many inspiring contributions on photodissociation of ions.

Abstract

The dissociation of the molecular ions of *p*-cymene induced by a hot tungsten filament was investigated using FT-ICR techniques. The dissociation rate constants of ions generated either by electron ionization at 10.7 eV or by multiphoton ionization at 266 nm yield Arrhenius plots that result in identical activation energies, 87 and 88 kJ mol^{-1}, respectively, within experimental error. By comparison, similar experiments on the related cumene molecular ion yields an activation energy of 95 kJ mol^{-1}. A master equation treatment of the dissociation process under our experimental conditions results in a dissociation energy of 134 ± 8 kJ mol^{-1} for methyl cleavage (from the *iso*-propyl group) of the *p*-cymene molecular ion.

Keywords: Blackbody-induced dissociation; *p*-Cymene molecular ion; Master equation; Dissociation energy

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1. Introduction

The ability of blackbody radiation to induce the unimolecular dissociation of gas-phase ions trapped at very low pressures has been demonstrated in recent years for a variety of systems ranging from relatively simple ionic species [1] to large ionic clusters [2] and biomolecules [3]. One of the most useful applications of this slow heating technique of ions resides in the possibility of obtaining dissociation energies from rate constants determined at different temperatures. The calculations necessary for extracting dissociation energies from these experiments depend on the number of vibrational degrees of freedom and the magnitude of the activation energy [4–6], and a comparison of these different methods has been recently illustrated for the case of partially solvated ruthenium(II) complex ions [7].

Although the kinetics of the blackbody-induced dissociation process can be studied conveniently at low pressures by FT-ICR techniques, the temperature dependence studies suffer from experimental difficulties and limitations, such as: (i) achieving a uniform temperature distribution in the surroundings of the cell; (ii) the long time required for temperature equilibration; and (iii) the relatively small workable temperature range. Thus, it is interesting to consider alternative methods to promote the thermal dissociation of ions.

Some years ago we illustrated the fact that the radiation emitted by the ionizing filament can lead, in

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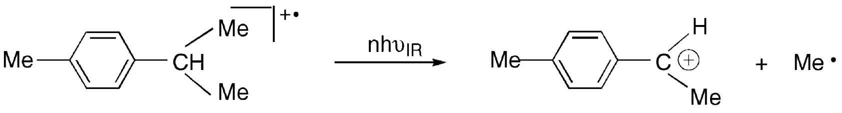
doi:10.1016/S1387-3806(03)00052-6

favorable cases, to complete dissociation of simple ions in a few seconds [8]. This led us to explore the use of a heated wire acting as a high-temperature near-blackbody source for activating ions and obtaining dissociation energies and structural information involving isomerization of molecular ions [9–11]. A distinct advantage of our approach is the much higher dissociation rates compared to those observed in near-room temperature blackbody radiation experiments. This feature can be particularly useful in the presence of competing bimolecular ion/molecule reactions. Our approach also offers the possibility of varying the internal temperature of the ions significantly by changing the spectral distribution and radiation density emitted by the heated wire.

In the present report, we have applied this technique to the study of the molecular ion of *p*-cymene (**1**) that undergoes blackbody radiation-induced dissociation by cleavage of a methyl group, as shown in Eq. (1). This methyl cleavage, β to the aromatic ring, is a common fragmentation in the mass spectra of alkylbenzenes.



1 (*m/z* 134) **2** (*m/z* 119) (1)

Although *p*-cymene is a common natural product found in essential oils, the gas-phase ion energetics are not well established. The vertical ionization energy of *p*-cymene has been reported to be 8.29 ± 0.02 eV based on photoelectron spectroscopy [12] but the appearance energy of **2** has not been previously reported. Thus, this is a case where some new thermochemical data could be generated for an important member of the alkylbenzenes. An additional point of interest in this case is the possibility of generating the molecular ion by electron ionization, or by multiphoton ionization resulting in ions with a well-defined internal energy. The results of these experiments coupled with a master equation analysis of process (1) has allowed us to derive the dissociation energy for the methyl cleavage as discussed before.

2. Experimental

Experiments were carried out in our FT-ICR spectrometer that is interfaced to an IonSpec Omega Data System (IonsSpec, Irvine, CA). The most important characteristics of this spectrometer have been described in recent publications relevant to the present work [8–11]. The spectrometer is typically operated at a magnetic field of 1 T, although some experiments were carried out at higher magnetic fields, namely 1.2 T.

A new cubic cell (with an approximate volume of 15.6 cm^3) has been used in this work that is specially designed for multipurpose experiments including laser and heated wire irradiation. Both transmitter plates are provided with a 0.5 cm diameter hole that allows for a laser beam to go through the cell, for laser alignment, and for laser energy measurements before and after the cell. In the present case, sapphire windows were used on the vacuum can containing the cell. The bottom receiver plate is also provided with an oblong opening (0.6 cm × 1 cm) to allow for exposure of the ions to light emitted by a heated tungsten wire. The tungsten wire (part number W340, Scientific Instrument Services, Inc., Ringoes, NJ) was spot welded on a mass spectrometer type filament block and was powered by a Hewlett-Packard 6621A power supply through a vacuum connection. The radiation temperature of this heated tungsten wire was determined as previously reported [9] from measurements of the resistance of the wire using a four wire arrangement. Some attempts were also made to measure the radiation temperature of the wire using a digital pyrometer (Model Ql2500C-2B, Quantum Logic, Westport, CT). However, this type of in situ pyrometry is awkward under the present experimental arrangement and independent measurements are necessary for a more accurate comparison between the two methods.

Electron ionization was typically performed at a nominal energy of 10.7 eV by using a pulsed filament current method. In this method the current on the rhenium filament used for ionization purposes is initially switched on by a relay activated by a TTL pulse from the data system while maintaining the filament at a positive voltage. Ionization is then initiated by pulsing the voltage on the filament to the desired negative value only 250 ms after the current pulse. This method allows for the study of the dissociation kinetics induced by the light emitted by the heated wire without interference from the high-temperature radiation emitted by the ionizing filament.

p-Cymene ions were also generated by resonance enhanced multiphoton ionization (REMPI) taking advantage of the low ionization potential of the substrate and the broad absorption band in the 260 nm region. Unfocused radiation from a Nd:YAG laser (GCR3, Spectra Physics, Mountain View, CA) operating at 266 nm was initially used and proved to be an extremely efficient procedure for producing ions. One or two laser shots of a few millijoules (mJ) were sufficient for very intense signals and data acquisition. In these experiments, the time scale for the FT-ICR sequence was externally triggered by the laser lamps [13]. Multiphoton ionization was also achieved at 280 nm by doubling the output of a pulsed Spectra Physics PDL-3 Dye Laser operating at 590 nm with an INRAD dye doubler provided with an autotracker and a UV harmonic separator [14]. At this wavelength, the 1 + 1 REMPI process is considerably less efficient and a much larger number of spectra acquisitions were required. A full temperature dependence was not pursued at this wavelength because of the low MPI efficiency and the slow dissociation observed for process (1).

p-Cymene and cumene were obtained from Aldrich and used without further purification. Samples were subjected to several freeze–pump–thaw cycles before introduction in the high vacuum part of the spectrometer. Experiments were carried either at constant pressure by maintaining a constant flow of the neutral gaseous substrate, or by introducing the sample through a pulsed valve and collecting data essentially at the background pressure of the instrument. This latter procedure considerably reduces ion/molecule reactions of the dissociation fragments with the parent alkylbenzene.

3. Experimental results

The mass spectrum of *p*-cymene (see below) obtained at low electron energies gives rise almost exclusively to the molecular ion, $M^{\bullet+}$ (*m/z* 134), and the $(M\text{-}15)^+$ fragment ion (*m/z* 119) originating from cleavage of a carbon–methyl bond in the *iso*-propyl group along with their respective ^{13}C satellite peaks.Isolation of the molecular ion, $M^{\bullet+}$, by ejection of all the other ions reveals a slow dissociation process induced by radiation from the additional filament in our cell. Fig. 1 shows a typical plot of the dissociation kinetics of the $M^{\bullet+}$ ion of *p*-cymene (Eq. (1)) under the influence of our heated tungsten wire operating at 12 W of power. The results displayed in this figure refer to molecular ions generated by multiphoton ionization at 266 nm with *p*-cymene introduced through a pulsed valve with the residual pressure typically around 6×10^{-9} Torr. The observed dissociation is considerably slower than that previously reported for the acetophenones [9–11] and a careful analysis of the dissociation kinetics reveals that no induction time is observed for the dissociation.

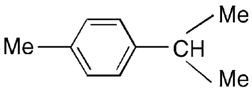


Fig. 1 also reveals the slow appearance of an *m/z* 133 ion that is presumably due to an ion/molecule reaction. This was confirmed by independent experiments carried out at much higher pressures. Isolation of the *m/z* 119 fragment ion obtained directly by electron ionization was found to lead to the formation of the *m/z* 133 ion and its ^{13}C isotopomer at *m/z* 134 as shown in Fig. 2. This reaction corresponds to a typical hydride abstraction reaction that is assumed to occur

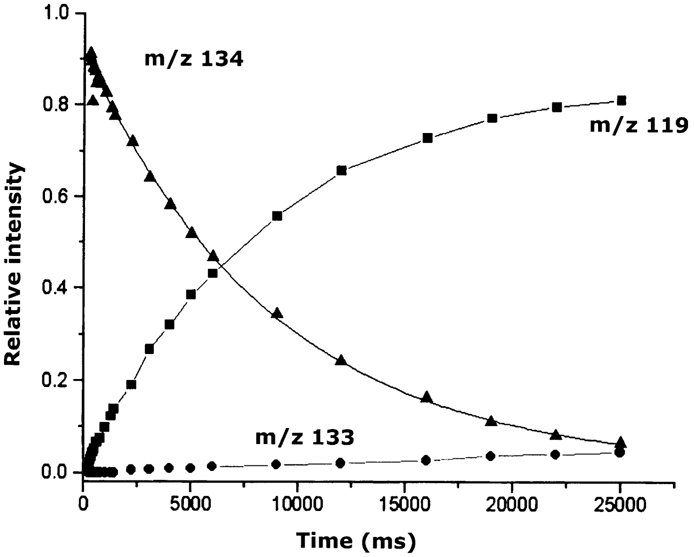


Fig. 1. Dissociation kinetics of the molecular ion of *p*-cymene, generated by multiphoton ionization at 266 nm, in the presence of a heated tungsten wire operated at 12 W of power. The observed rate constant amounts to $k = 0.11\,\mathrm{s}^{-1}$.

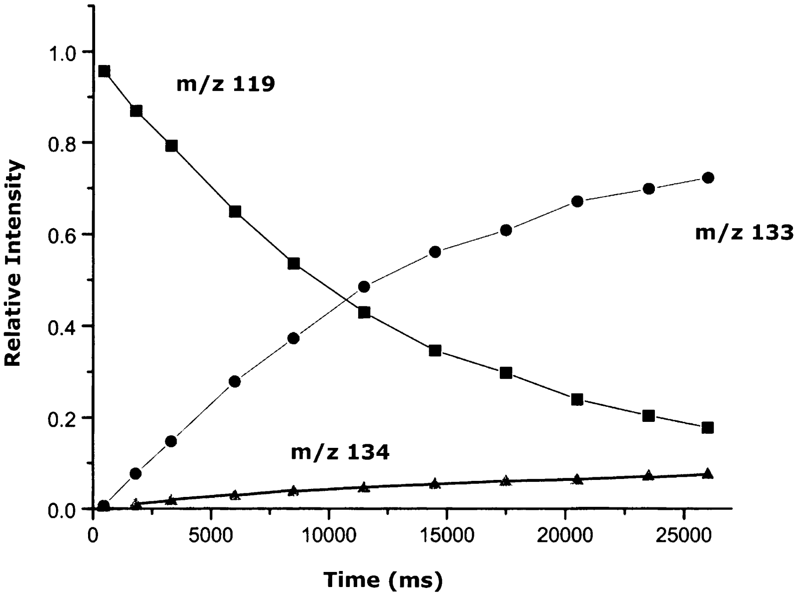
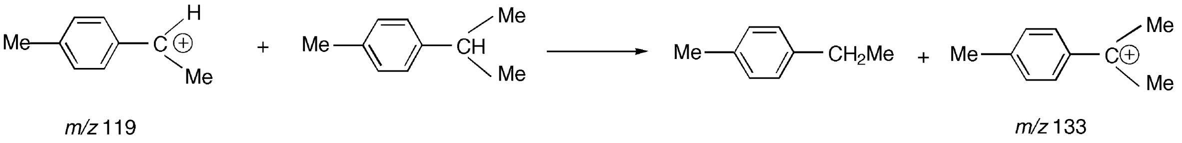


Fig. 2. Reaction kinetics of $C_9H_{11}^+$ (*m/z* 119) fragment ions, obtained from *p*-cymene by electron ionization at 14.5 eV at a pressure of 9.5×10^{-8} Torr, with the neutral precursor. The product ions, *m/z* 133 and its isotopomer *m/z* 134, are formed by hydride abstraction as shown in Eq. (2).

at the secondary C and to yield a stable tertiary carbenium ion as represented in Eq. (2).

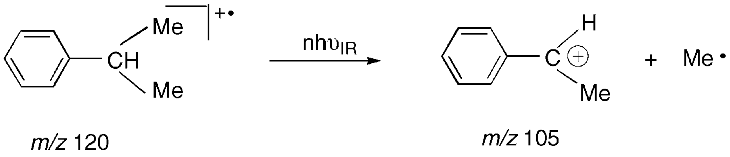


(2)

Reaction (2) is similar to a variety of hydride abstraction processes, some of them regioselective, that have been observed in alkylbenzenes in recent years by different mass spectrometric techniques [15,16].

Dissociation experiments were also carried out as a function of the radiation temperature of the heated wire as described in our previous papers [9,11] by varying the power dissipated across the tungsten wire. These previous experiments have shown that the tungsten filament obeys a Stefan–Boltzmann type law and that Arrhenius type plots can be constructed using the dissociation rate constants and the effective blackbody temperature (T_b) of the heated wire (see next section). These graphs are shown in Figs. 3 and 4 for ions generated by multiphoton ionization and by electron ionization, respectively, and for experiments carried out in the 5–10 × 10^{-9} Torr pressure range where the ion/molecule reaction (2) is very slow. The activation energies obtained from these two plots are identical indicating that the induced dissociation process is independent of the ionization process.

Similar type of experiments, but using only electron ionization, were carried out for comparison with the molecular ion of cumene as shown in (3),



(3)

The corresponding Arrhenius type plot for the dissociation rate constants of the cumene molecular ion, $[C_9H_{12}]^{\bullet+}$, as a function of the radiation temperature of the tungsten filament is shown in Fig. 5. The calculated activation energy is similar to that obtained for *p*-cymene and is indicative that in both case the methyl loss occurs from the *iso*-propyl group and not from the aromatic ring.

3.1. *Model for the dissociation process induced by a high-temperature blackbody source*

The dissociation promoted by the hot tungsten filament, ranging typically from 1000 to 1800 K in these experiments, differs from the conventional blackbody radiation experiments in the fact that ions view an attenuated fraction of the near-blackbody radiation source and thus do not achieve the temperature of the blackbody source. The actual radiation density sampled by the ions is dependent on several geometric parameters such as the size of the cell, the size and shape of the opening to view the radiation, and the size, shape and distance of the radiation source. Thus, the actual radiation density to be considered in these experiments can be written as a Planck distribution attenuated by some geometric factor, $0 \leq \Phi \leq 1$.

$$\rho(\nu_i, T) = (1-\Phi)\frac{8\pi h\nu_i^3}{c^3}\left(\exp\left(\frac{h\nu_i}{kT}\right)-1\right)^{-1} \tag{4}$$

The average internal energy of the ions under these conditions can then be calculated for different radiation temperatures by modeling the vibrational absorption and emission of radiation for several values of Φ, in the absence of any dissociation process. This type of calculation was implemented in our laboratories using both a Monte Carlo simulation and a master equation solution as previously described [9,17] for an ensemble of ions with an initial Boltzmann

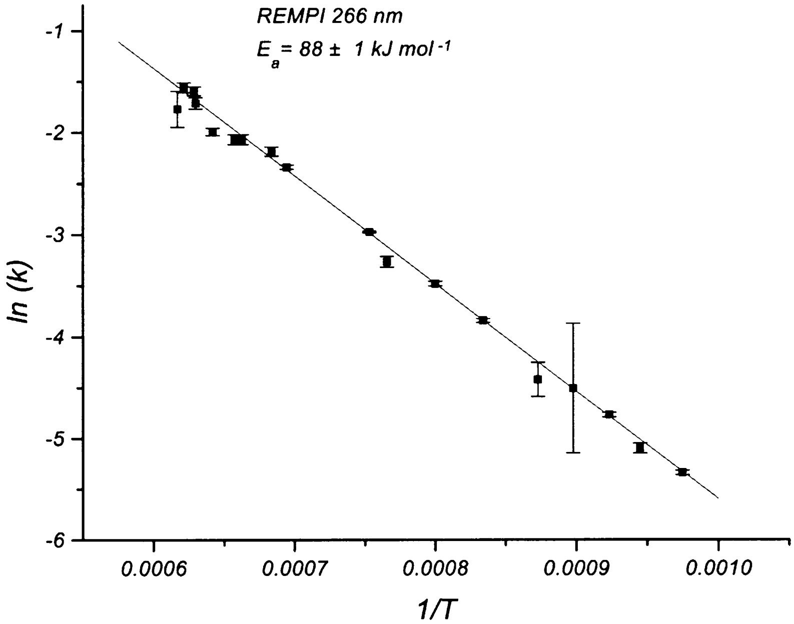


Fig. 3. Arrhenius type plot for the dissociation rate constant of the molecular ion of *p*-cymene, generated by multiphoton ionization at 266 nm, as a function of the radiation temperature of the tungsten filament. The neutral precursor was introduced through a pulsed valve. The error bars associated with the rate constants refer to the standard deviation of several experimental measurements.

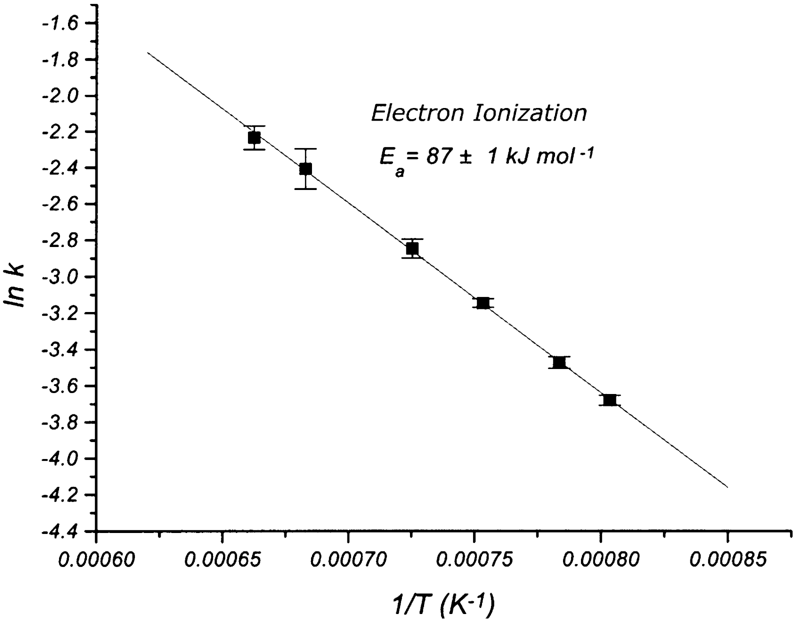


Fig. 4. Arrhenius type plot for the dissociation rate constant of the molecular ion of *p*-cymene, generated by electron ionization at 10.7 eV, as a function of the radiation temperature of the tungsten filament. The neutral precursor was introduced through a pulsed valve. The error bars associated with the rate constants refer to the standard deviation of several experimental measurements.

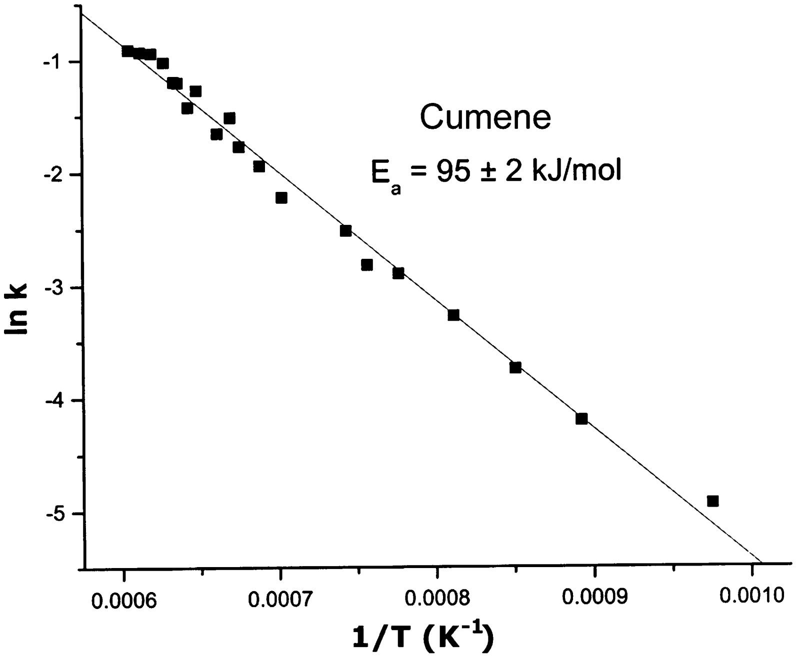


Fig. 5. Arrhenius type plot for the dissociation rate constant of the molecular ion of cumene, generated by electron ionization at 11 eV, as a function of the radiation temperature of the tungsten filament. The neutral precursor was introduced through a pulsed valve. The error bars associated with the rate constants refer to the standard deviation of several experimental measurements.

distribution at 300 K. These simulations reveal that the ensemble of ions reaches a Boltzmann distribution at an internal temperature (T_{ion}) that is dependent both on Φ and T. At very high values of Φ, the radiation density from the walls of the cell would need to be considered in the calculations and would lead to considerably more complex situation that have not been explored in detail.

The simulations were then extended to include dissociation within the "sudden death" approximation for the sake of simplicity. In this approximation, ions with internal energies above the dissociation threshold are assumed to undergo dissociation faster than any additional photon pumping. The results for this type of simulation are of course dependent on the magnitude of the dissociation energy as well as on the value of Φ and T, and the results do not yield a true Boltzmann distribution [4]. A different line of approach was used in our case and several situations were explored for typical cases of aromatic molecular ions. For example, the calculated vibrational frequencies for the molecular ion of acetophenone [9], $PhCOCH_3^{\bullet+}$, were used in a series of simulations in conjunction with an arbitrary dissociation energy of $D_0 = 50\,\text{kJ mol}^{-1}$ for cleavage of the methyl group. Results from solution of the master equation for this case for different values of Φ are shown in Fig. 6 as Arrhenius type plots of the calculated dissociation rate constant as a function of the effective blackbody radiation temperature of the hot tungsten wire.

Some very interesting conclusions can be drawn from the results displayed in Fig. 6. (1) The absolute value of the dissociation rate constants at a given temperature (of the filament) is of course strongly dependent on the value of Φ. (2) Activation energies calculated from these different plots, with widely different values of Φ, do not differ from each other significantly. This result is indeed surprising because it is far from obvious that a linear scaling of the power density and distribution over temperature of the

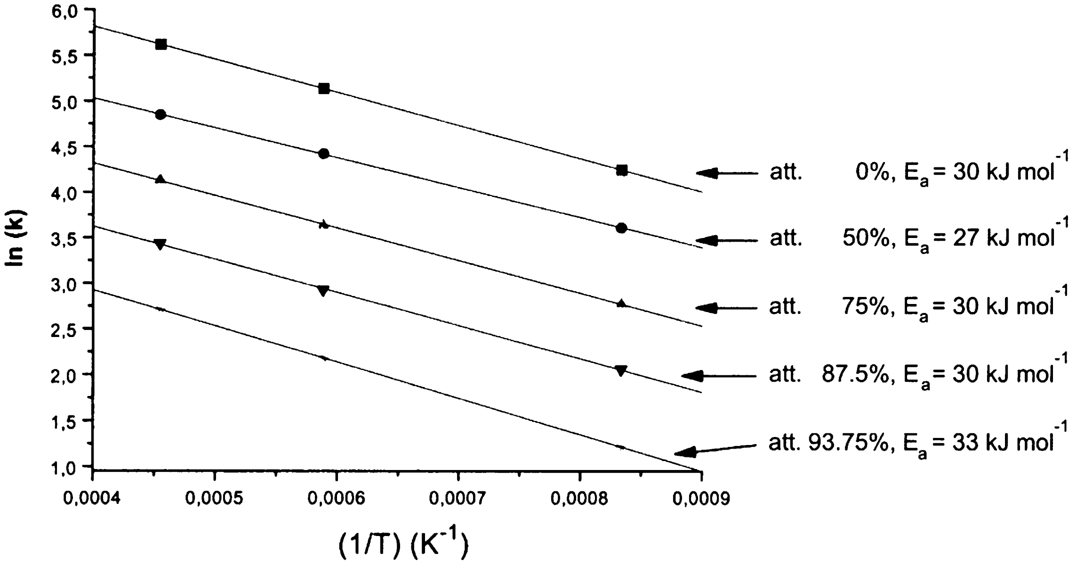


Fig. 6. Arrhenius plots of dissociation rate constants calculated by master equation simulations of a molecular ion such as acetophenone for which an arbitrary dissociation energy of $50\,\mathrm{kJ\,mol^{-1}}$ was used for the purpose of the calculation. The different graphs correspond to different values of the attenuation factor, Φ, of the radiation density emitted by the hot tungsten wire. The temperatures correspond to the effective blackbody temperatures of the wire.

radiation source should yield identical Arrhenius plots. (3) Thus, while absolute rate constants are critically dependent on the radiation density, activation energies obtained from these Arrhenius plots are largely insensitive to the actual radiation viewed by the ions. These results suggest that the activation energies obtained from our experimental data, as shown in Figs. 3–5, can be used to obtain dissociation energies through solution of the master equation by assuming a value of Φ (see below). Thus, it is not necessary to calculate the internal temperature of the ions in these Arrhenius plots which would demand knowing the dissociation energy of the ions.

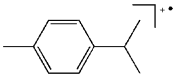
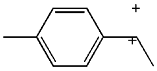
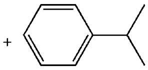
We have previously stressed the fact that the dissociation rate constants in our experiments scale linearly with the power dissipated on the tungsten wire and that this observation results in a linear Arrhenius plot [9]. It is interesting to point out that recent simulations regarding the dissociation rate constants for slow infrared laser dissociation of ions yield similar results [18].

3.2. Dissociation energy of the p-cymene molecular ion

The harmonic vibrational frequencies and the integrated vibrational intensities are necessary in order to obtain dissociation energies from experimental activation energies in these blackbody experiments. Thus, density functional calculations at the B3LYP/6-31G(d,p) level were carried out to optimize the structure of the molecular ion of *p*-cymene, and to estimate the vibrational frequencies, using the Gaussian 94 suite of programs [19]. This method was chosen because it usually yields very good estimates for vibrational frequencies even though band intensities are subject to considerable uncertainty. For the sake of comparison, electronic energies were then calculated for the optimized structure of the molecular ion and the fragments involved in the dissociation at the B3LYP/6-31+G(d,p) level. These results are given in Table 1 and are discussed further below.

Master equation calculations were then performed as described in our earlier paper [9] using the *A*

Table 1
Calculated electronic energies (B3LYP/6-31+G(d,p)//B3LYP/6-31G(d,p)) and zero-point energies (B3LYP/6-31G(d,p)) for some of the relevant species involved in the dissociation of the molecular ion of *p*-cymene

Structure	E (kJ mol^{-1})	ZPE (kJ mol^{-1})[a]	Relative energy (kJ mol^{-1})
1 	−1021964.91	542.584938	0
fragment **A** 	−917206.38	443.654232	–
fragment **B** 	−916921.23	435.41	–
Methyl radical, C	−104619.16	76.56	–
A + C	–	–	117
B + C	–	–	394

[a] Vibrational frequencies scaled by a factor of 0.98

and *B* Einstein coefficients obtained from the calculated band intensities, and the radiation density at the appropriate frequency for harmonic oscillator transitions with an attenuation coefficient Φ of 0.9. Furthermore, the "sudden death" approximation has been maintained for this molecular ion because for an ion with 66 oscillators, many of them of low vibrational frequencies, and a very loose transition state for dissociation, this is a very reasonable assumption[1]. The procedure adopted in our master equation approach starts by assuming a dissociation energy and calculating the dissociation rate constants for three different blackbody radiation temperatures. An activation energy is then obtained from an Arrhenius plot of the calculated rate constants at these three temperatures. Several rounds of calculations were carried out for different assumed dissociation energies as shown in Fig. 7. The results obtained for values close to the experimentally observed activation energies are well described by a simple equation, as shown below.

$$E_a = -70.01 + 1.18E_{\text{diss}} \tag{5}$$

We can now use the activation energies derived from the multiphoton ionization and electron ionization experiments, $E_a = 88 \pm 2\,\text{kJ mol}^{-1}$, to calculate a dissociation energy of the *p*-cymene molecular ion as $134 \pm 2\,\text{kJ mol}^{-1}$ from Eq. (5). However, our final estimate of the uncertainty in the dissociation energy needs to be more conservative. The temperature measurements are based on the power dissipated on the hot filament assuming negligible loss on the filament support and a uniform emission (i.e., no hot spots). Although this is a reasonable first order approximation, it is unclear what is the actual uncertainty in temperature and how this uncertainty changes with temperature. We believe this to be the most likely source of error. The calculated vibrational band intensities are also subject to considerable uncertainty but some leveling effect probably occurs because some intensity of some bands is probably overestimated at the expense of others. In a recent study of simple molecules the vibrational intensity sums at the B3LYP/6-31G(d,p) are consistently higher than the experimental vibrational intensity sums [20]. Our previous experience [9] indicates that dissociation energies obtained from master equation simulations with vibrational intensities obtained from different level of ab initio calculations differ by less than 5% of each other. In summary, we

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[1] Some trial calculations including an RRKM treatment for the transition state reveal negligible effect on the estimate of the dissociation energy.

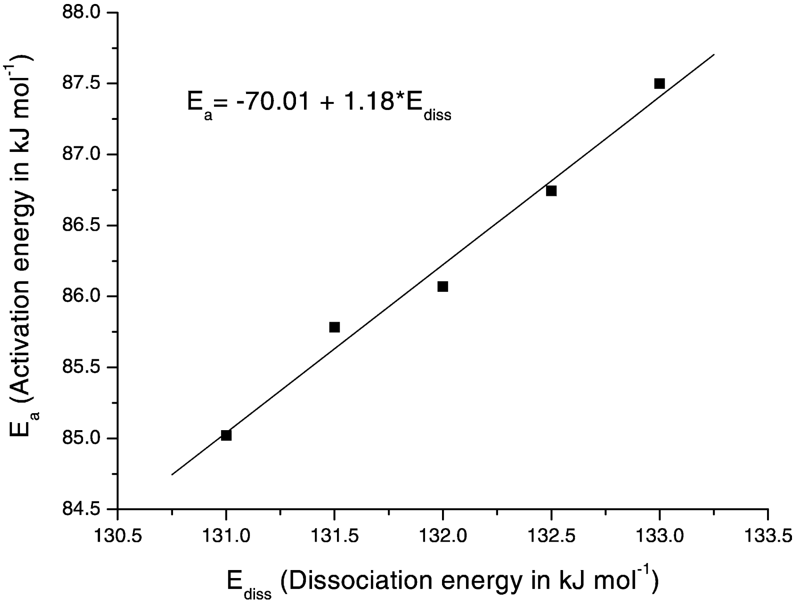

Fig. 7. This graph is a correlation of the calculated activation energies obtained from calculated dissociation rate constants at three different temperatures by solving the master equation for the molecular ion of *p*-cymene assuming different dissociation energies as inputs in the calculations.

propose a more conservative estimate,

$$D_0\ (p\text{-cymene molecular ion}) = 134 \pm 8\,\text{kJ}\,\text{mol}^{-1}$$

The value obtained in this fashion can be compared with the value of 117 kJ mol^{-1} predicted by the DFT calculations shown in Table 1. These same calculations predict a much higher value (394 kJ mol^{-1}) for cleavage of the methyl group attached to the aromatic ring. Unfortunately, it is difficult to estimate the expected accuracy of the DFT calculations at this level for a problem of this nature.

4. Conclusions

The results presented in this paper show that very useful thermochemical parameters can be obtained for relatively simple molecular ions from these hot wire-induced dissociations. For these aromatic hydrocarbon type ions, it is possible to suggest that ions exhibiting dissociation energies as high as 200 kJ mol^{-1} may be studied by using our method provided that competing bimolecular ion/molecule reactions do not play an effect, and that at the higher radiation temperatures required for these experiments significant dissociation does not occur by pumping the ion to an excited dissociative electronic state.

It is particularly important to emphasize the fact that the same results are obtained for the induced dissociation of the molecular ion of *p*-cymene from the electron ionization process and by the multiphoton dissociation process. This suggests that the thermally induced dissociation process is independent of whether the ionization process results in molecular ions with a well know energy deposition (multiphoton ionization) or a broad distribution of internal energy. It is also worthwhile to point out that master equation simulations that start with an ensemble of ions at equilibrium at 298 K display a typical induction time of about 500 ms before the system achieves the steady state for dissociation. This fact suggests that in both ionization processes ions are formed with enough internal energy such that no induction time is observed as verified by careful analysis of the initial points of Fig. 1.

The value of $134 \pm 8\,\mathrm{kJ\,mol^{-1}}$ obtained for the dissociation energy of *p*-cymene molecular ion is useful because previous estimates from appearance energies of similar compounds give a range between 124 and $186\,\mathrm{kJ\,mol^{-1}}$ for this dissociation energy [21,22].

Although the dissociation of the molecular ion of cumene is still under investigation, it is interesting to point out that the observed higher activation energy is probably indicative of a higher dissociation energy as predicted by preliminary DFT calculations.

Finally, the relatively slow ion/molecule reaction of the fragment ion of *p*-cymene and the absence of other competing bimolecular reactions make some of these alkylbenzenes interesting cases for studying blackbody-induced dissociations.

Acknowledgements

This work was supported by the São Paulo Science Foundation (FAPESP) and the Brazilian Research Council (CNPq) through its Millennium Institute of Complex Materials. The authors also thank Jair Menegon for his help with many of the experiments.

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