Thermal Dissociation of Acetophenone Molecular Ions Activated by Infrared Radiation

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The thermal dissociation of the molecular ions of acetophenone ($C_6H_5COCH_3^{\bullet+} \rightarrow C_6H_5CO^+ + {}^{\bullet}CH_3$) and acetophenone-*d*$_3$ ($C_6H_5COCD_3^{\bullet+} \rightarrow C_6H_5CO^+ + {}^{\bullet}CD_3$) induced by broad band infrared radiation has been studied in the cell of an FT-ICR spectrometer. Rate constants in the range of 0.5−10 s^{-1} have been obtained for the system of ions exposed to a radiation source equivalent to blackbody temperatures between 1100 and 1600 K. The unimolecular dissociation is almost pressure independent in the 4×10^{-8} to 5×10^{-7} Torr range indicating that the most important mechanism is of a noncollisional nature. Activation energies obtained from Arrhenius-type plots yield 46.6 ± 2.0 kJ mol^{-1} for acetophenone and 44.9 ± 2.2 kJ mol^{-1} for acetophenone-*d*$_3$. The dissociation process has been modeled by a Monte Carlo simulation and by numerical solution of the master equation of a process which takes into account interaction with the background radiation field through absorption and emission. These calculations reveal that meaningful activation energies can be obtained from these experiments even though the exact radiance viewed by the ions is not known. Solution of the master equation reveals that the experimental activation energies are consistent with a dissociation energy of 80.5 kJ mol^{-1} for the acetophenone molecular ion. This result is used to derive a heat of formation of 745 kJ mol^{-1} for the $C_6H_5CO^+$ ion.

Introduction

The ability to promote the dissociation of gas-phase ions with low-power cw CO_2 lasers by sequential absorption of photons is now well established.[1] Infrared multiphoton dissociation (IRMPD) becomes possible in these cases since ions trapped at low pressures are exposed to the laser radiation for long irradiation times (hundreds of milliseconds) and undergo stepwise multiphoton absorption processes without significant interference by collisions. While this kind of IRMPD of ions can be described within the theoretical framework formulated for infrared multiphoton excitation and dissociation processes,[2] a more specific analysis of the kinetics of low-intensity infrared laser induced photofragmentation of ions[3] reveals two interesting features: (i) dissociation energies can be extracted from photofragmentation rate constants obtained as a function of laser intensity, and (ii) under certain conditions, modeling of the process is equivalent to that of an ensemble of ions subject to irradiation by an incoherent blackbody source. The first aspect has yet to be largely explored although rate constants of infrared multiphoton induced photofragmentation have been used to determine the pumping rate of ions to their dissociation limit[4] and as a sensitive tool to differentiate between isomeric ions.[5] The second idea parallels an early prediction by Beauchamp and co-workers[6] who claimed the distinct possibility of inducing ion dissociation with incoherent infrared radiation.

The fact that near-ambient blackbody radiation could be instrumental in promoting collisionless dissociation of ions was first reported in 1994.[7] Loosely bound ion−neutral complexes were shown to suffer spontaneous dissociation in the cell of an FT-ICR spectrometer in a process mediated by absorption of thermal radiation from the surroundings. Furthermore, rate constants were shown to display isotopic selectivity.[8] A comprehensive interpretation of these experiments was developed by Dunbar[9] as an extension of his early work on low-power IR laser dissociation of ions. The general conclusion of this model is that medium sized ions with low dissociation energies (less than 1 eV) are likely to undergo collisionless induced dissociation by absorption of thermal radiation. A particularly important aspect of the approach proposed by Dunbar[9] resides in the fact that valuable thermochemical data can be derived from the kinetics of dissociation as a function of temperature. This was in fact verified experimentally for $Cl^-(H_2O)_2$ and $Cl^-(H_2O)_3$ ions.[10] At present, a growing number of molecular ions,[11,12] loosely bound cluster ions,[13−15] and ions derived from biomolecules[16,17] have been observed to undergo collisionless thermal dissociation within the cell of FT-ICR spectrometers. A comparison of techniques used in determining the thermochemistry associated with dissociation processes reveals that very reliable quantities can be obtained from experiments dealing with thermal dissociation of ions.[18]

A preliminary communication from this laboratory[11] reported the dissociation of the covalently bound acetophenone molecular ion, $C_6H_5COCH_3^{\bullet+}$, induced by thermal radiation

$$C_6H_5COCH_3^{\bullet+} \rightarrow C_6H_5CO^+ + {}^{\bullet}CH_3 \qquad (1)$$

This is an attractive case because reaction 1 represents a common low-energy fragmentation pathway which has been extensively characterized by mass spectrometry. For example, the metastable transition and the kinetic energy release associated with reaction 1 suggest a negligible reverse activation energy.[19] Thus, determination of the activation energy for reaction 1 provides a good estimate of the thermochemistry of the process. The dissociation energy for reaction 1 has been estimated to be anywhere from 37.6 to 84.9 kJ mol^{-1} from appearance energy measurements.[20] Yet, the reliability of the appearance potential data is still questionable, and the heat of formation of the benzoyl cation ($C_6H_5CO^+$) remains unsettled.

Our initial measurements regarding the thermal radiation induced dissociation of acetophenone molecular ions suffered from poorly defined temperature and infrared radiation conditions in the cell.[11] Thus, a more elaborate experimental study and theoretical modeling of the dissociation of acetophenone and acetophenone-*d*$_3$ ($C_6H_5COCD_3$) molecular ions activated by incoherent infrared radiation are presented in this paper in

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order to derive the thermochemistry of reaction 1. A simple technique has been developed to promote ion dissociation with a broad band infrared source which circumvents two important problems in dealing with spontaneous dissociation of reactive ions: (a) the need for a wide range variable temperature spectrometer to obtain activation energies and (b) slow dissociation rate constants at room temperatures which make the kinetic characterization of reactive molecular and fragment ions a complex procedure even at very low pressures. Modeling of the process through a Monte Carlo simulation and numerical solution of the master equation yield good agreement with the experimental results and allow the dissociation energy to be obtained for reaction 1. An extension of this work to the enol form of the acetophenone molecular ion reveals that thermal radiation activated dissociation can readily distinguish between isomeric ions.

Experimental Section

Experiments were carried out in a Fourier transform ion cyclotron resonance spectrometer interfaced to an IonSpec Omega Data System (IonSpec, Irvine, CA). The basic design of this instrument has been described previously.[21]

Ions are produced by electron impact from a heated rhenium filament mounted on a ceramic block attached to a 1 in. cubic cell and undergo cyclotron motion in a 1 T magnetic field of a 9 in. Varian electromagnet. The filament current of the ion source can be operated continuously or in a pulsed mode in the FT experiment. This latter mode allows the filament current to be turned on only during ion formation and eliminates possible postionization effects due to the light emitted by the filament (see Experimental Results). The majority of the experiments were carried out at electron energies in the vicinity of 10 eV to minimize ion−molecule reactions. Molecular ions of acetophenone were isolated at variable times after ion formation (200−700 ms) by ejection of the *m/z* 105 ($C_6H_5CO^+$) and 106 ($^{13}CC_5H_5CO^+$) ions from the cell. The amplitude of the ejection radio-frequency pulse was maintained at the lowest level compatible with ejection of the ions. The *m/z* 121 ions, a mixture of $(C_6H_5COCH_3)H^+$ and $^{13}CC_7H_8O^{\bullet+}$, were not ejected in order to avoid any undesirable excitation of the molecular ion (*m/z* 120). No difference was observed within experimental error for the dissociation rate constant of the molecular ion as a function of isolation delay time.

The temperature of the cell was measured with a calibrated Pt wire thermometer placed below the bottom receiver plate of the cell. The measured temperature in the pulsed filament current experiments was typically 323 ± 5 K, which is 20−30 K lower than that of experiments with the filament current operating continuously. The vacuum surrounding the cell is provided with heating tapes which allow the temperature of the cell to be raised to a maximum of 420 K.

A tungsten wire was installed inside the vacuum system but outside of the ICR cell and about 0.5 cm from one of the transmitter plates. These plates have a partial open structure to allow for optical experiments. More recently, a new support for the tungsten wire has been installed which allows the distance to the cell to be varied. This wire can be heated through an external circuit and act as an *in situ* lamp. Measurements of the resistivity, ρ ($\mu\Omega$ cm), of the tungsten wire (obtained from resistance measurements of the wire) can be transformed into temperature of the tungsten wire, T (K), by the expression[22]

$$T = 103.898 + 38.04\rho - 0.0938\rho^2 + 0.000024\rho^3 \quad (2)$$

In order to verify the significance of this temperature with respect to the photon emission properties of the wire, the resistivity was measured as a function of electrical power which was controlled by varying the current. A least-squares fit of the data (Figure 1) reveals that power dissipated on the filament and temperature (as obtained from eq 2) follow a relationship which closely resembles the blackbody Stefan−Boltzmann law

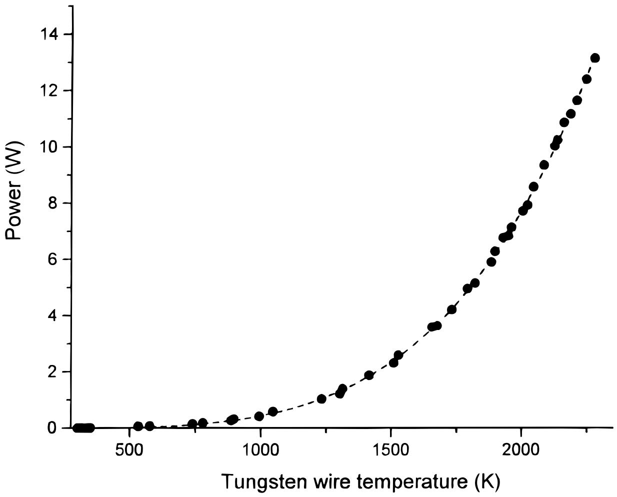

Figure 1. Temperature calculated (eq 2) for the filament of the *in situ* lamp as a function of electrical power dissipated on the tungsten wire.

$$P(W) = 1.8 \times 10^{-13}T^{4.13}$$

This equation strongly suggests that the emissivity of the filament in the temperature range essentially obeys one of the important laws of a blackbody source.

Pressure was measured with an ion gauge located on the side arm of a vacuum cross connecting the cell to the turbomolecular pump. The absolute pressure has been calibrated over the years using the $CH_4^{\bullet+}/CH_4$ reaction rate constant as a test case. This procedure yields methane pressures which are higher by at least a factor of 2 from those indicated by the ion gauge.[23]

Acetophenone (BDH Chemicals, Poole, England), 99.3% acetophenone-d_3, $C_6H_5COCD_3$, (Isotec), and butyrophenone (Aldrich) were subject to freeze, pump, and thaw cycles prior to use. Their conventional mass spectra revealed no detectable impurities. However, continuous baking of the vacuum system for at least 3 days was necessary to reduce traces of water from the spectrometer.

Impulse excitation[24] was used for detection purposes since this method has been observed in our laboratories to yield more reliable relative intensities in the mass range of interest.

The kinetics of the CO_2 laser infrared multiphoton fragmentation of the molecular ion was studied using a methodology similar to that previously described.[5] A tunable cw CO_2 laser (Synrad, Model 48-1) was used in these experiments, and irradiation times were electronically controlled with a variable Uniblitz shutter (Vincent Associates, Rochester, NY) triggered by the FT software of the experiment. An entrance and exit ZnSe window were installed in the vacuum system for these experiments.

Experimental Results

Preliminary Experiments. The mass spectrum of acetophenone at low electron energies (10 eV or lower) exhibits the molecular ion, $C_6H_5COCH_3]^{\bullet+}$ (*m/z* 120), the fragment ion C_6H_5-$CO]^{\bullet+}$ (*m/z* 105), and the corresponding ^{13}C species. Initial experiments[11] using electron impact ionization with a continuously heated filament revealed that the molecular ions of acetophenone undergo rapid spontaneous dissociation in the

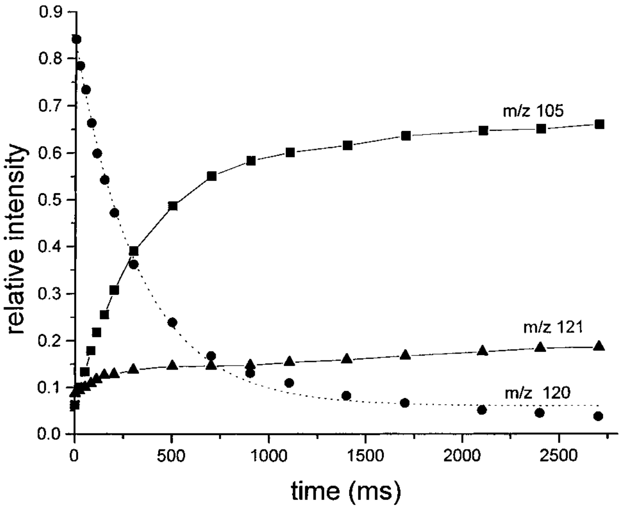

Figure 2. Typical experiment (with ionization filament operating continuously) showing spontaneous dissociation of the molecular ion of acetophenone (*m/z* 120) to yield the benzoyl cation (*m/z* 105) (reaction 1) at an acetophenone pressure of 4.9 × 10^{-8} Torr. Notice that ion−molecule reactions leading to protonated acetophenone (*m/z* 121) are slow under these conditions.

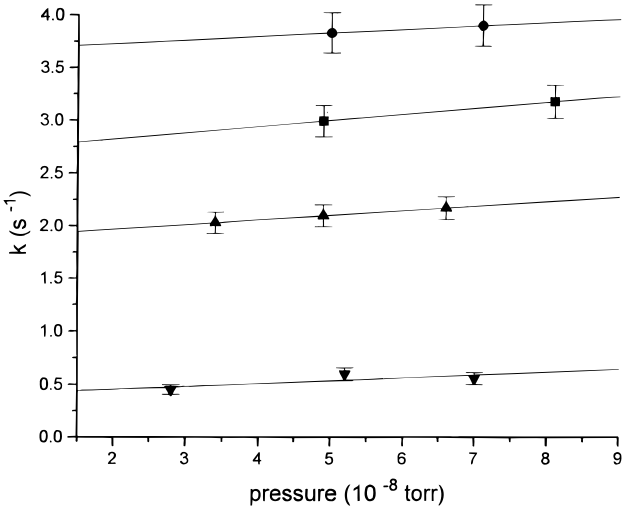

Figure 3. Dissociation rate constant determined as a function of acetophenone pressures in experiments with different emission currents of the ionizing filament under continuous heating (ions exposed to different radiation temperatures): ● emission current 4 μA; ■ emission current 1.5 μA; ▲ emission current 1.4 μA; ▼ emission current 0.3 μA.

ICR cell according to reaction 1 (Figure 2). At low ionization energies and at pressures of 4 × 10^{-8} Torr, dissociation was observed to be much faster than ion/molecule reactions leading to protonated acetophenone (*m/z* 121).[25]

Figure 3 shows typical plots of the dissociation rate constant determined at different acetophenone pressures and for different emission currents of the continuously heated ionizing filament. Extrapolation of these data to zero pressure clearly suggests that dissociation is essentially promoted by a noncollisional mechanism. This same behavior is observed for experiments carried out at fixed acetophenone pressures and variable pressures of buffer gases like Ar and SF_6.

Light emitted by the ionizing filament can be a critical factor in experiments of this nature when carried out in a single-cell arrangement. Unlike the results shown in Figures 2 and 3, spontaneous dissociation of the acetophenone molecular ion is much slower ($k_{\mathrm{diss}} \sim 0.08\ \mathrm{s}^{-1}$) than the rate of ion−molecule reactions leading to protonated acetophenone when the filament remains lit only during the ionization period of the FT-ICR experimental sequence. Thus, the dissociation illustrated in Figures 2 and 3 is promoted by radiation emitted by the ionizing filament. Further studies were then carried out exclusively in the pulsed current mode for the ionizing filament.

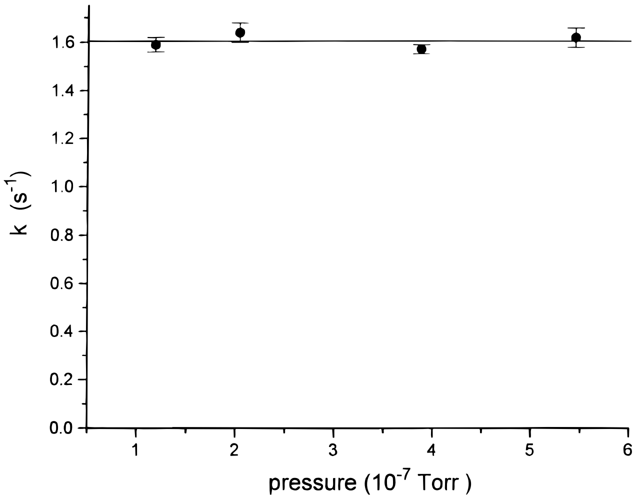

Figure 4. Dissociation rate constant of the acetophenone molecular ion promoted by broad band infrared radiation from the internal tungsten lamp as a function of nitrogen pressure used as a buffer gas.

The dissociation rate constant for reaction 1 is observed to increase when the temperature of the cell is raised to 400 K by heating the vacuum system. However, the rates of ion−molecule reactions leading to *m/z* 121 are also observed to increase significantly, a fact that may be due to considerable water desorption from the walls of the vacuum system.

The fact that the rhenium filament used for ionization was instrumental in promoting the dissociation of the acetophenone molecular ions (Figures 2 and 3) led us to investigate the effect of different radiation sources on the dissociation. For example, rapid dissociation of the acetophenone molecular ion can be achieved by continuous irradiation of the ions with an external commercial infrared lamp. The rate of dissociation was observed to decrease when a Ge filter was used to block the visible components of the lamp, but the decrease was comparable (within experimental error) to the infrared attenuation of the Ge filter as measured by using a cw CO_2 laser. This result is a strong indication that the dissociation process is promoted by absorption of infrared radiation. No dissociation was observed when acetophenone molecular ions were exposed to pulses of 532 nm light from the second harmonic of a Nd:YAG laser.

Experiments Using Broad Band Infrared Radiation. The tungsten wire installed outside the transmitter plate of the ICR cell can act as an *in situ* lamp and a versatile source of infrared radiation. Variation of the current applied to this tungsten wire allows the intensity and distribution of the radiation to be varied in almost near-blackbody fashion.

Experiments were then carried out with ions formed at low electron energies (~10 eV) while maintaining the tungsten wire at a fixed temperature as determined by its power rating (eq 3). Rate constants for the dissociation of the molecular ion were generally obtained at pressures of 4.8 × 10^{-8} Torr. While this pressure is considerably above the zero-pressure limit, the collisional contribution to the overall process is negligible as shown in Figure 4.

Figure 5 displays the dissociation rate constant for the acetophenone molecular ion obtained as a function of the power supplied to the tungsten lamp. At low power, an almost linear relationship is observed between rate constant and power. At

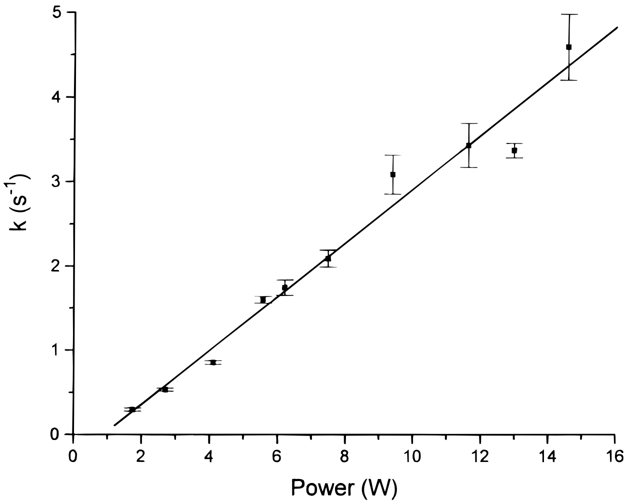

Figure 5. Dissociation rate constant for the acetophenone molecular ion as a function of power of the *in situ* tungsten lamp.

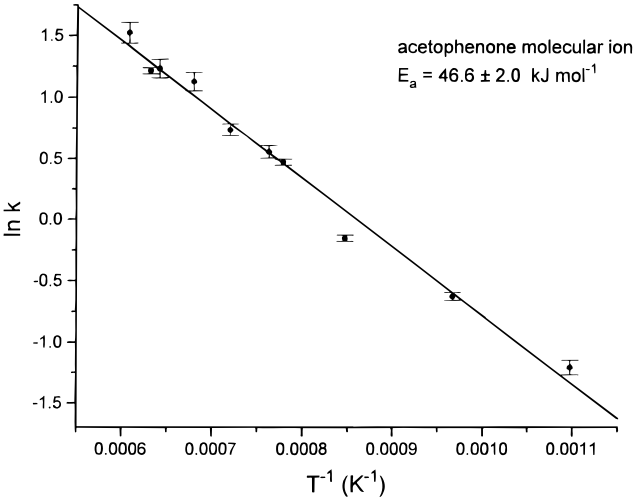

Figure 6. Arrhenius plot for the dissociation rate constants of the acetophenone molecular ion as a function of the equivalent blackbody temperature of the tungsten lamp.

higher powers (>6 W), and as rate constants become large, experimental uncertainty increases since a large fraction of the molecular ion population is depleted before ion isolation is achieved. A very similar graph is obtained for the dissociation rate constants of acetophenone-d_3.

A more interesting result can be obtained by using the temperature of the radiation source as the significant variable. While the temperature of the radiation source can be obtained from eq 2, the tungsten lamp can be treated as an approximate blackbody provided the radiance is corrected to that of an equivalent blackbody temperature. This correction entails a well-known conversion of the radiation emitted by tungsten at a certain temperature (T) to the equivalent integrated radiation emitted by a blackbody at a temperature T_b, which is considerably lower than that obtained from eq 2.[22] The use of these effective blackbody temperatures in Arrhenius-type plots is shown in Figures 6 and 7 for the dissociation rate constants of acetophenone and acetophenone-d_3 respectively. The corresponding activation energies obtained from these graphs yield 46.6 ± 2.0 kJ mol^{-1} for acetophenone and 44.9 ± 2.2 kJ mol^{-1} for acetophenone-d_3, and their significance is discussed below. The error quoted for these activation energies reflect exclusively the standard deviation of a linear regression analysis of the data. Excellent agreement is observed for the activation energies derived from these two independent graphs spanning a large range of radiation temperature.

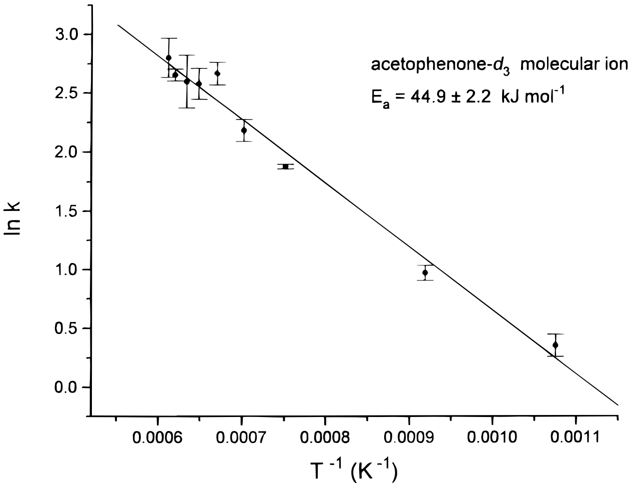

Figure 7. Arrhenius plot for the dissociation rate constants of the acetophenone-d_3 molecular ion as a function of the equivalent blackbody temperature of the tungsten lamp.

The effectiveness of the dissociation induced by the tungsten lamp can be compared with that promoted by an infrared laser. The photofragmentation kinetics of the molecular ion of acetophenone induced by a 1.5 W cw CO_2 laser tuned to the 10.57 μm line yields a rate constant comparable to that obtained with a 2.5 W tungsten lamp. Thus, the efficiency of incoherent infrared radiation to promote ion dissociation fully confirms the early predictions advanced in ref 6.

Model for Ion Dissociation Activated by Thermal Radiation. *Basic Model.* The formal approach for describing ion dissociation activated by continuous infrared light under collisionless conditions has been discussed for the case of low-power monochromatic radiation (CO_2 laser for example)[4] and for blackbody radiation.[9] The underlying theoretical model entails an analysis of the time evolution of the vibrational content of an ensemble of ions in the presence of a weak radiation field. In the present case, the acetophenone molecular ion can be represented by a collection of 45 harmonic oscillators exchanging energy (absorption and emission) with the radiation field as a function of time. While the vibrational frequencies for neutral acetophenone and acetophenone-d_3 are known,[26] the frequencies and the absorption and emission coefficients for the molecular ions must be estimated from theoretical calculations or by comparison with similar systems. Vibrational frequencies for the acetophenone molecular ion were first estimated using the semiempirical AM1 method contained in the Gaussian 92 suite of programs[27] and used without corrections since appropriate scaling factors for this level of calculation are not well defined. Vibrational frequencies were also computed from density functional and *ab initio* calculations at the Hartree–Fock level using a 6-31G** basis set for comparison purposes. While these frequencies are usually calculated within 10% of the experimental values, the Einstein absorption and emission coefficients which are obtained from calculated band intensities are expected to be subject to much larger uncertainties in the absence of correlation corrections.[28]

Two independent approaches were developed to study the time evolution of the acetophenone molecular ions: (1) a Monte Carlo simulation of a random walk process along the vibrational energy axis of the molecule and (2) solution of the appropriate master equation. The initial objective of these calculations was to estimate the dissociation rate constant expected for the molecular ion of acetophenone exposed to blackbody radiation at near-ambient temperature and to extract meaningful thermochemical parameters from the temperature dependence of the rate constants.

Monte Carlo Simulation. Our approach is based on a treatment originally proposed by Kramers[29] for chemical reactions activated through collisions. In this model, energy exchange between the radiation field and ions leads some of the reactant ions to acquire eventually sufficient energy to cross over the potential barrier for dissociation.[30] The reaction rate is then set equal to the rate of crossing, and a Monte Carlo algorithm is used to simulate the random walk of internal energy.[31]

For a given temperature, the initial internal energy and vibrational configuration of the ion is chosen at random using the probability distribution as a weight function. The probability distribution function is represented in this case by a Boltzmann distribution truncated at the dissociation threshold.[9] Each ion is then allowed to do a random walk in energy absorbing and emitting thermal radiation, and dissociation is assumed to occur instantaneously for ions with vibrational energies in excess of the dissociation level (sudden death approximation). The dissociation threshold was initially assumed to be 37 kJ mol^{-1} as suggested by the appearance potential measurements using photoionization techniques.[20d] The sudden death approximation can be corrected by incorporating explicitly the internal energy dependence of the RRKM rate constants for ions with energies just above the dissociation limit. However, this contribution is negligible for the case of acetophenone and for the time scale of the experiment.

The actual simulation considers that every oscillator can increase, decrease, or maintain unchanged its level of occupation (n) during a given time interval (δt). The probability (P) of these events for a level i can be represented by

$$P(n+1,t_0+\delta t|n,t_0) = 1 - \exp[-B_i\rho(\nu_i,T)\delta t] \tag{3}$$

$$P(n-1,t_0+\delta t|n,t_0) = 1 - \exp\{[-B_i\rho(\nu_i,T) - A_i]\delta t\} \quad (\text{for } n \neq 0) \tag{4}$$

A and B represent the Einstein coefficients obtained from the calculated intensities, and the radiation density at the appropriate frequency for a harmonic oscillator transition, $\rho(\nu_i,T)$, is assumed to be the Planck distribution for a blackbody source:

$$\rho(\nu_i,T) = \frac{8\pi h\nu^3}{c^3}\left(\exp\frac{h\nu}{kT} - 1\right)^{-1} \tag{5}$$

These transition probabilities allow the behavior of an ion undergoing random emission and absorption for every time step δt to be simulated.

This method was first tested with the dissociation channel turned off. The time average of the energy yields excellent agreement with that calculated from equilibrium statistical mechanics and remains constant provided that intramolecular vibrational redistribution (IVR) is explicitly included after every time step. Thus, IVR was included among the vibrational modes after every time step δt under the condition of constant total energy. For calculations with the dissociation channel open, 500 simulations were typically performed for each temperature and the rate constant was determined by a fitting process from the resulting list of dissociation times.

Assuming the dissociation energy of reaction 1 to be equal to 37 kJ mol^{-1}, a dissociation rate constant of 0.40 s^{-1} was calculated for the molecular ion of acetophenone at 346 K and 0.44 s^{-1} for the molecular ion of acetophenone-d_3 at the same temperature. No significant differences were obtained in calculated rate constant using AM1 or *ab initio* Hartree–Fock calculated vibrational frequencies and intensities. These calculated rate constants are about five times larger than the estimated experimental value (0.08 s^{-1}) obtained at this temperature under pulsed filament current and with the *in situ* lamp turned off. This result suggests that the assumed dissociation energy is incorrect.

Master Equation. The master equation approach for describing the process of ion dissociation is equivalent to the Monte Carlo simulation except for the fact that the random character of the process is hidden.[30,31] For the present case, a discrete form of the master equation[31] was used with an energy grain size of 50 cm^{-1}.

$$\frac{dx_i}{dt} = \sum_{j=0}^{\text{upper}} P_{ij}x_j - P_{ji}x_i \tag{6}$$

In eq 6, x_j represents the ion population of a level with an energy equal to j (an integer) × $\Delta\epsilon$ (the energy grain size). Transition probabilities are defined by

$$P_{ij} = P(x_i,\ t+\delta t|x_j,t) \tag{7a}$$

$$P_{\mathbf{ji}} = P(x_j,t+\delta t|x_i,t) \tag{7b}$$

and the probabilities P_{ij} and P_{ji} are assumed to be zero if the energy difference between states i and j does not correspond to the energy of a vibrational transition of the ion. If the energy difference coincides with a transition connecting the two states, these probabilities are identical to those used in the Monte Carlo simulation. The population of the upper limit in eq 6, x_{upper}, refers to a state with an energy just above the dissociation threshold and represents the fraction of population converted to products

Equation 6 is usually written in matrix notation

$$\frac{d\mathbf{x}}{dt} = \mathbf{Jx} \tag{8}$$

where $\mathbf{x}$ is a column vector with elements (x_0, x_1, ..., x_{upper}) and the operator matrix $\mathbf{J}$ is defined by elements

$$J_{ij} = (-\delta_{ij}\sum_{k=j} P_{kj}) - (\delta_{ij} - 1)P_{ij} \tag{9}$$

Equation 9 can be solved by a series expansion

$$\mathbf{x}(t) = \mathbf{x}(0) + \mathbf{Jx}(0)t + \frac{1}{2!}\mathbf{J}^2\mathbf{x}(0)t^2 + \frac{1}{3!}\mathbf{J}^3\mathbf{x}(0)t^3 + ... \tag{10}$$

For small values of t, and correspondingly small values of the $\mathbf{J}$ matrix elements, the linear term of eq 10 is a good approximation to the solution of the master equation. The approximate solution was then obtained with a corrector–predictor method yielding the time evolution of the distribution vector $\mathbf{x}$ including the number of dissociated ions. The internal energy of the ions was again represented by a Boltzmann distribution truncated at the dissociation energy for a given temperature, and initial conditions were obtained through the Beyer–Swinehart algorithm.[33]

Assuming again the dissociation energy of reaction 1 to be equal to 37 kJ mol^{-1}, the numerical solution of the master equation yields a dissociation rate constant of 0.38 s^{-1} for the acetophenone molecular ion and 0.43 s^{-1} for acetophenone-d_3 at 346 K. These values are in excellent agreement with those calculated by the Monte Carlo simulation.

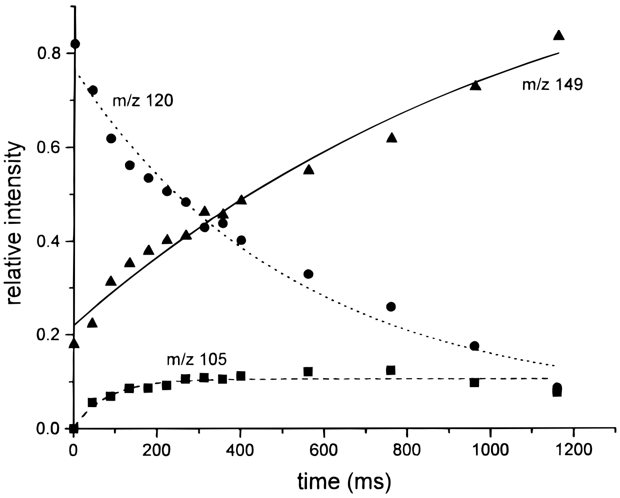

Figure 8. Kinetics of the *m/z* 120 enol ion obtained from butyrophenone and under irradiation with the tungsten lamp. Notice that protonation of butyrophenone (*m/z* 149) is much faster than dissociation.

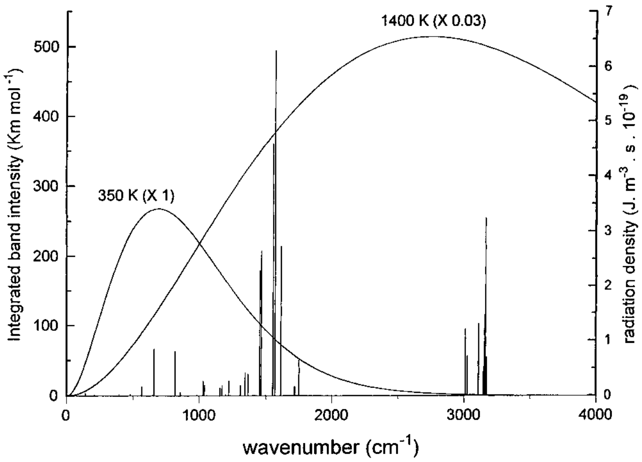

Figure 9. Calculated infrared spectrum of the molecular ion of acetophenone with integrated intensities shown on the left-hand scale (AM1 caclulation) and blackbody radiation distribution plotted at 350 and 1400 K with radiation densities shown on the right-hand scale.

Calculation of Dissociation Energies and Thermochemistry. The models described above can be used to extract thermochemical parameters from experiments carried out as a function of power, or temperature, of the light source provided proper adjustments are made for the actual radiation density viewed by the ions in experiments like those shown in Figures 5−7.

The heated tungsten wire can be considered as a gray body source with an emittance lower than that of a true blackbody source. At temperatures ranging from 1000 to 2000 K, the emission is almost entirely in the infrared region (only 1% is in the visible region), and the total radiance can be approximated as being equal to that of a blackbody at an effective temperature T_b (lower than the temperature of the filament).[34] This procedure was used in Figures 6 and 7 where the tabulated temperatures refer to T_b. The blackbody-like behavior of the light source is in fact confirmed by the measurements displayed in Figure 1 which show the heated tungsten wire to follow a near Stefan−Boltzmann-type law. While the light source can then be reasonably approximated as a blackbody source, with an effective blackbody temperature, the actual radiation density sampled by the ions is dependent on the geometry of the lamp, the geometry of the cell, and the distance between the ion cloud and the light source. In principle, the effective radiation density reaching the ion cloud could be estimated from geometric considerations, but this procedure is subject to considerable arbitrariness. Thus, calculated absolute rate constants for dissociation promoted by the tungsten lamp using the procedures outlined above are not expected to be very meaningful under these conditions. However, the effectiveness of the higher temperature radiation in promoting dissociation of the acetophenone molecular ion can be illustrated by comparing the calculated infrared spectrum of the acetophenone molecular ion and the radiation spectral distribution at a higher temperature. Figure 9 shows the superposition of the calculated infrared spectrum of the ion (AM1 calculation) with the blackbody radiation distribution at 350 and 1400 K. It is clear from this plot that the most intense vibrations of the molecular ion of acetophenone (1450−1620 cm^{-1} and 3000−3200 cm^{-1}) have a particularly good overlap with the high-temperature radiation spectral distribution.

The fact that the ion cloud samples only a fraction of the radiation density emitted by the source implies that ions would come to equilibrium at a much lower temperature than that of the radiation source in the absence of the dissociation channel. The consequences of this situation on the ion dissociation process can be analyzed by either of our theoretical methods. For example, calculations can be performed for a given radiation source temperature and variable degrees of attenuation for the blackbody radiation density effectively viewed by the ions. Using the master equation approach, absolute rate constants are found to be sensitive to the attenuation considered for the radiation density (an essentially linear relationship). This is obviously the expected type of behavior since it ultimately reflects different ion temperatures. However, for a fixed attenuation factor the variation of the absolute rate constants with radiation source temperature reveals some very interesting and useful results. For a hypothetical system similar to the acetophenone molecular ion, and assuming a critical energy of 50 kJ mol^{-1}, model calculations reveal that Arrhenius plots of rate constants estimated for radiation densities (corresponding to temperatures similar to those of Figures 6 and 7) attenuated by as much as 94% yield at most a variation of less than 10% in activation energy. Thus, while absolute rate constants are critically dependent on radiation density, activation energies obtained from Arrhenius plots are largely insensitive to the actual radiation viewed by the ions but sensitive to the spectral radiance distribution as a function of temperature. This conclusion begins to break down at attenuation factors higher than 95%, presumably because superposition of the blackbody radiation from the walls of the cell must be taken into consideration.

The results of this calculation are supported by experiments in which the tungsten wire is placed at different distances from the cell. While the absolute values of the dissociation rate constants are sensitive to the position of the tungsten wire, *activation energies obtained for different fixed positions of the heated tungsten wire from plots similar to those in Figures 6 and 7 are similar within the quoted error.*

The results of these model calculations suggest then that activation energies obtained from plots like those shown in Figures 6 and 7 can be can be used to recover the dissociation energy of the molecular ion of acetophenone from master equation calculations. This can be done by using the dissociation energy as a parameter to be adjusted in master equation calculations of dissociation rate constants as a function of temperature until the experimental activation energies are reproduced. Using a constant attenuation factor of 94% for the radiation density, master equation calculations for the acetophenone molecular ion reveal that a dissociation energy of 80.5 kJ mol^{-1} is capable of reproducing the experimental activation energy of 46.6 kJ mol^{-1}. For these calculations, the internal energy of the ions was initially assumed to be at room temperature. Under these condtions, an induction period of about 500 ms is observed before ions undergo a dissociation which can be represented by a simple exponential decay. Simulations carried out with higher initial internal energies (from 350 to 600 K) reveal a decrease in the induction time, but the steady state dissociation constant remains the same. An induction period has no direct consequences on the experimental rate constants since the experimental procedure involving the use of pulsed filament currents for ionization and ion selection requires at least 600 ms.

These calculations above allow us then to conclude that

$$C_6H_5COCH_3^{\bullet+} \rightarrow C_6H_5CO^+ + {}^{\bullet}CH_3$$

$$D_0 = 80.5 \pm 2.1 \text{ kJ mol}^{-1}$$

The error quoted for the dissociation energy was estimated from solutions of the master equation with activation energies allowed to vary between the error limits determined in Figures 6 and 7. A more serious source of error in the determination of the dissociation energy by the present procedure is the accuracy of our temperature measurements which are derived from the resistivity of the tungsten wire. The accuracy of these measurements and the eventual contribution to the error in the dissociation energy are difficult to assess at present without an independent check for the temperature measurements.

An alternative procedure to verify the consistency between the calculated dissociation energy and the activation energy obtained for acetophenone is to estimate the dissociation energy from the relationship previously proposed by Dunbar[9] within the context of Tolman's theorem.

$$E_0 \approx E_a + \langle E \rangle - 3.6 \text{ kJ mol}^{-1}$$

In this equation, $\langle E \rangle$ represents the average energy of the ions calculated over the reaction depleted internal energy distribution of the reagent ion. Calculation of $\langle E \rangle$ for the reaction depleted ensemble of acetophenone ions yields $\langle E \rangle = 40.3$ kJ mol^{-1} for a typical case of the tungsten wire at 1250 K and the radiation density attenuated by 94%. This value then leads to $E_t \approx 83.3$ kJ mol^{-1}, in excellent agreement with the value obtained from the master equation calculations and consistent with similar comparisons in other systems.[10,12]

The dissociation energy obtained from the master equation approach can be compared with a value of 67 kJ mol^{-1} obtained by *ab initio* calculations at the 6-31G** level. This theoretical value is probably no better than ± 20 kJ mol^{-1} in the absence of any corrections for electron correlation. Unfortunately, MP2 calculations for the acetophenone system proved infeasible with our present computational facilities.

The calculated dissociation energy can also be used to establish the appropriate thermochemistry for the benzoyl ion, $C_6H_5CO^{\bullet+}$ The heat of formation of the molecular ion of acetophenone is 809 kJ mol^{-1} assuming an adiabatic ionization potential of 9.28 eV for acetophenone as obtained by photoionization techniques.[20d,35,36] The thermal corrections necessary to calculate the heat of formation of $C_6H_5CO^+$ at 298 K from the dissociation energy, D_0, are estimated to be 3 kJ mol^{-1} from the *ab initio* calculations. On the basis of these assumptions, the heat of formation of $C_6H_5CO^+$ at 298 K is calculated to be 746 kJ mol^{-1}. The error limits for this heat of formation cannot be easily estimated because of two important limitations: (a) the unknown accuracy of our temperature measurements discussed above which affects the activation energies obtained from the Arrhenius plots and consequently the dissociation energies obtained from the master equation calculations and (b) the accuracy of the ionization energy of acetophenone.

The present value obtained for the dissociation energy and the heat of formation of the benzoyl cation can be compared with several measurements reported in the 1970s. For example, heats of formation of 753,[20b] 669,[19a] and 778 kJ mol^{-1} [37] have been proposed on the basis of the appearance potential of electron impact experiments and are of questionable validity. A more reliable result is probably the one obained from appearance potential measurements of a variety of benzoyl compounds by photoionization techniques[20d] which results in a mean value of 705 ± 6 kJ mol^{-1} for the heat of formation of the benzoyl cation. Yet, this last value must also be viewed with caution because the low-intensity tail of the ion yield curves is structure dependent, and participation of isolated electronic states of the molecular ion located below the appearance potential in the fragmentation process is still a distinct possibility. Furthermore, the threshold values derived in ref 20d were not corrected for the thermal energy content of acetophenone. We therefore believe that our result for the heat of formation of the benzoyl cation is reliable within the limitations imposed by the accuracy of our temperature measurements. It is important to point out that significant differences (20 kJ mol^{-1}) have already been reported between bond dissociation energies obtained from thermal radiation induced dissociation and CID[18] and those obtained by PEPICO techniques.[38]

Thermal Dissociation of $C_8H_8O^{\bullet+}$ Isomeric Ions. An interesting application of the type of dissociation discussed in this paper is its sensitivity toward ionic structure. The enol form of molecular ions of ketones, ($C_6H_5C(OH)CH_2]^{\bullet+}$ in acetophenone) is known to be more stable than the keto isomer[39] and can be independently generated from different precursors. For example, butyrophenone, $C_6H_5COCH_2CH_2CH_3$, provides an easy way to generate the enol ion of acetophenone as a result of a McLafferty rearrangement of the molecular ion.[40]

Experiments carried out with the *m/z* 120 enol isomer ion generated from butyrophenone, and under continuous irradiation by the *in situ* tungsten lamp, reveal that $C_6H_5C(OH)CH_2]^{\bullet+}$ promotes proton transfer readily to neutral butyrophenone while essentially no dissociation is observed in this case (Figure 8). Such an observation is consistent with the much higher dissociation energy for the enol form and the fact that it is prone to undergo proton transfer reactions to substrates of high proton affinity.

This particular feature in the acetophenone system can be used as a powerful technique to establish the relative amount of keto and enol ions generated in acetophenone.[41]

Discussion

The present experiments reveal that the molecular ion of acetophenone can undergo readily thermal dissociation induced by broad band incoherent infrared radiation. Modeling of the process reveals that dissociation energies can be obtained from our experiments using activation energies derived from Arrhenius-type plots of the rate constants as a function of the temperature of the radiation source. The modeling reveals that these experiments yield meaningful activation energies even though the radiation viewed by the ions represents only a fraction of the radiation field of the lamp source.

A number of possible applications of the present methodology can be envisioned by suitable experimental development. The determination of dissociation energies by this method looks particularly attractive for the case of reactive ions where larger unimolecular dissociation rate constants are needed even if the experiments are carried out at lower pressures than those used in this study. The ultimate accuracy in obtaining thermochemical parameters from these experiments depends on several variables which have been repeatedly emphasized. For example, the temperature of the lamp is assumed to be well represented by eq 2 but ideally should be checked by independent methods such as optical pyrometry. Furthermore, the tungsten lamp used in our experiments is treated as a pseudoblackbody source represented by an effective temperature. While the radiation distribution closely resembles that of a blackbody, the color temperature of tungsten is typically 30 K higher than the temperature measured by eq 2. Thus, different radiation sources could be used to ensure that the blackbody equivalency yields consistent results. A second alternative would be to use commercially available blackbody sources to eliminate any possible effects from an uneven radiation density distribution. Errors associated with the Einstein absorption and emission coefficients obtained from theoretically calculated band intensities are difficult to estimate, but their effect is more important in the calculation of absolute rate constants than in the variation of the rate constant with temperature which is used to obtain dissociation energies.

Finally, these experiments suggest the possibility of using near-blackbody sources with infrared filters to obtain infrared spectra of ions either by direct dissociation or in conjunction with a CO_2 laser in analogy with the two laser experiments advocated by Eyler and co-workers.[41] These experiments also extend the application of thermal dissociation by infrared dissociation and may be of particular interest in dealing with ions derived from biomolecules.

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