All these observations taken together suggest that there is a systematic error in the theoretical R–O_2 heats of formation, that all values, including that of CCl_3O_2, are about 3 kcal mol^{-1} too large.

Implications in Oxidation Chemistry. Major changes occur in the mechanisms of hydrocarbon combustion or controlled oxidation with increasing temperature, typically between 600 and 750 K.[32,34] The change is due to the instability of the alkylperoxy radicals formed in R + O_2 reactions above about 750 K (at typical O_2 pressures). Chlorine substitution in the hydrocarbon fuel, particularly where it will result in the formation of free radicals with chlorine at the radical site, will cause mechanism changes at significantly lower temperatures due to the weakening of the R–O_2 bond energy, perhaps as low as 400 K in the case of the combustion of the most highly chlorinated compounds.

Such a low-temperature change in mechanism has been observed by Olbregts, who investigated product formation in the chlorine atom sensitized oxidation of $CHCl_3$.[10] He observed product changes that indicated a mechanism change between 400 and 430 K. He was able to account for these changes with a mechanism that takes the thermal instability of CCl_3O_2 into account.

In oxidation processes above 450 K, CCl_3 will be consumed by recombination/polymerization processes as well as by reactions with atoms and other free radicals (such as H, OH, and O).[4] The former processes can account, in part, for the soot-promoting characteristics of flames containing chlorinated hydrocarbons.[35]

Heat of Formation of CCl_3O_2. The measured Third Law enthalpy change for reaction 2 and the theoretical value of the heat of formation of CCl_3 (16.6 ± 2 kcal mol^{-1})[13] were combined to obtain the heat of formation of CCl_3O_2:

$$\Delta H_f^{\circ}{}_{298}(CCl_3O_2) = -3.3 \ (\pm 2.2) \text{ kcal mol}^{-1}$$

The theoretical heat of formation of CCl_3 differs from a value which has been derived from experiment (19 kcal mol^{-1}).[36] We consider the theoretical values to be at least as accurate as this reported value for two reasons. First, there has been considerable prior success of the theoretical method used to obtain accurate heats of formation of alkyl and other substituted alkyl radicals. Second, the derivation of the heat of formation of CCl_3 from the reported experimental results was indirect, and the uncertainty likely to be greater than stated, ±1 kcal mol^{-1}.[36]

Summary

The significant weakening of the C–O bond in CCl_3–O_2 caused by the substitution of Cl for H in CH_3–O_2 has been quantitatively characterized. The decrease in bond strength effect has been found comparable to that observed for other CH_3–X bonds (X = H, Cl, and $CHCl_2$) upon replacement of H by Cl.

Thermochemical properties of CCl_3O_2 have been obtained: the entropy by calculation and the heat of formation from a combination of calculation and experiment. This information will be of value in determining the likely fate of this radical in the atmosphere and in combustion processes.

Further studies of the kinetics and thermochemistry of R + O_2 reactions involving chlorinated methyl radicals are in progress.

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Kinetic Parameters for the Unimolecular Dissociation of Styrene Ion

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Time-resolved photodissociation measurements of the laser-induced fragmentation of styrene molecular ion have been carried out at 355 nm. Taking thermal energy content into account, a unimolecular dissociation rate of 6.3 × 10^3 s^{-1} at an internal energy of 3.66 eV was derived. The new measurement has been combined with previous data from photodissociation and photoionization to give a dissociation rate–energy curve spanning 2 decades of rate values. By RRKM fitting to this curve, unimolecular kinetic parameters E_0 = 2.43 ± 0.05 eV and $\Delta S^{\ddagger}(1000 \text{ K})$ = −3.9 ± 1 cal mol^{-1} K^{-1} were derived. The conclusion that this dissociation proceeds through a rate-limiting tight activated complex at E_0 = 2.43 eV was affirmed.

Introduction

The dissociation of gas-phase ions provides a particularly convenient field for experimental observation of unimolecular dissociation kinetics, first because of the ease of observing the ionic reaction product from reactants of known internal energy and second because of the ease of trapping isolated ions for arbitrarily long periods. Impressive photoelectron–photoion coincidence (PEPICO) experiments have exploited the first of these advantages to produce high-quality data for a number of reactions in the 10^4–10^7-s^{-1} dissociation rate regime.[1,2] Recently, our group has

succeeded in exploiting the second advantage in carrying out trapped-ion photodissociation studies of reactions slower than 10^5 s^{-1} in the ion cyclotron resonance (ICR) ion trap.[3–6] Putting data from these different experiments together makes available the dissociation rate versus internal energy function (the rate–energy curve) over sufficiently wide ranges so that kinetic parameters can be calculated with previously unachievable quantitative confidence. Styrene ion was recently discussed as an example

(1) For recent references to the PEPICO experiment see, for instance: Baer, T. *Adv. Chem. Phys.* 1986, *64*, 111.
(2) Smith, D.; Baer, T.; Willett, G. D.; Ormerod, R. C. *Int. J. Mass Spectrom. Ion Processes* 1979, *30*, 155.

(3) Dunbar, R. C. *J. Phys. Chem.* 1987, *91*, 2801.
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where these possibilities can be realized.[5] The photodissociation of this ion has now been extended to significantly longer wavelengths, and we describe here the calculation and significance of the more reliable kinetic parameters made possible by the new data.

The dissociation of energy-selected isolated molecules is clearly differentiated from thermal unimolecular dissociation, and the quasiequilibrium theory (RRKM) equations used for modeling within the framework of transition-state theory take a different form for the energy-selected, as opposed to the thermal, case.[8] As a result, there has been little intercomparison of thermal unimolecular kinetic studies on neutral molecules with energy-selected dissociation studies on ionic molecules. Rosenstock emphasized the possibility of making this connection.[9,10] In the approach which he advocated, the RRKM parameters of the energy-selected dissociation reaction are first derived from energy-selected ion dissociation data. These are then used to calculate the thermal RRKM parameters E_∞ and A_∞ (or equivalently ΔS^*) which the ion dissociation reaction would have if it were run as a thermal dissociation at high pressure at the standard temperature of 1000 K. He pointed out the interesting comparisons made possible between the thermal RRKM parameters derived in this way for ionic systems and those measured in thermal unimolecular rate studies on comparable neutral molecules. The interest in this useful bridge between two separate fields of unimolecular kinetics has sharpened the need for more satisfactory energy-selected dissociation kinetic data on a wider variety of ions.

The contribution of ion-trap photodissociation to these questions began with the realization that the ion cyclotron resonance (ICR) technique is capable of time-resolved dissociation measurements with time resolution of a few microseconds.[3] Measurements on chlorobenzene ion,[3] cyanobenzene ion,[4] thiophenol ion,[7] and styrene ion[5,6] have been described at 308 nm. Attachment of a Nd:YAG laser system to the instrument has extended the wavelengths available and made possible the measurement described here at 355 nm.

Styrene ion dissociates according to

$$C_8H_8^{\bullet+} \rightarrow C_6H_6^{\bullet+} + C_2H_2$$

which has a 0 K endoergicity of 2.42 eV.[5] Some dissociation to $C_8H_7^+ + H^\bullet$ was also observed, but this was hard to quantitate because of interference of the strong adjacent parent-ion peak. The m/z 103 intensity was less than or comparable to the value observed at 308 nm, viz., ~25% of the total product ions,[5] and as in the analysis at 308 nm, the possible small effect of this product channel on the calculation of the kinetic parameters will be ignored.

Experimental Section

The time-resolved photodissociation experiment followed closely the instrumentation and procedures described for the styrene ion work at 308 nm[5] and will not be replaced in detail. Ions are formed by electron impact, thermalized by a number of collisions and radiative cooling, and photoexcited by a single laser pulse. Following a variable delay time, a short (20 μs) ICR excite pulse is applied at the frequency of the photodissociation daughter ions, so that all those daughter ions formed up to that moment are cyclotron excited and subsequently detected by standard ICR signal acquisition. The dissociation at 355 nm is so slow that the time-resolved ICR experiment is entirely straightforward, without the need for the corrections to the signal equation worked out for faster dissociation reactions.[6]

The need for thorough ion thermalization before the laser pulse is even more severe than at shorter wavelengths, because the steepness of the rate–energy curve at low energy makes the
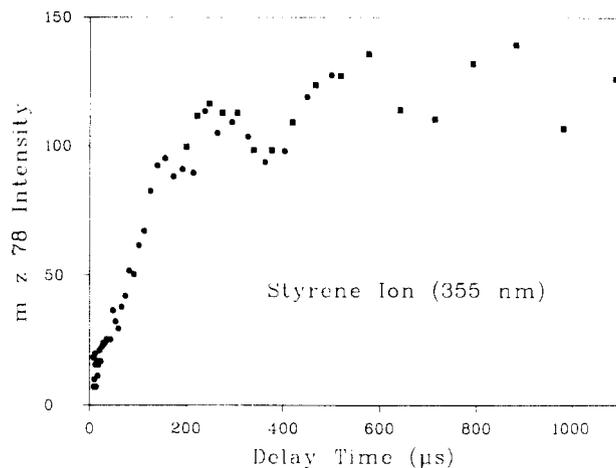

Figure 1. An illustrative raw data set for styrene ion dissociation to give m/z 78 at 355 nm. The delay time axis gives the time between the laser pulse and the beginning of the ICR excite pulse.

measurement more sensitive to small residual superthermal energy. Following electron impact at 10.6 eV (nominal), the ions are thermalized for 1.6 s at 1×10^{-6} Torr, which should provide about 50 collisions with parent neutral before the laser pulse. Some runs made at 3×10^{-7} Torr (2-s trapping, giving about 20 collisions) gave dissociation curves having the same risetime, further confirming that thermalization was complete long before the laser pulse. As before, the effective temperature of the cell was taken to be 375 K.[5]

The 355-nm pulse from the tripled Nd:YAG laser (Lumonics HY1200) was measured as 2 mJ outside the vacuum window, with a diameter of about 5 mm. Beam homogeneity was not perfect, and the effective intensity over the ion cloud may have been greater than this. The beam was unfocused, and the pulse width was 10 ns. The beam made a single pass across the cell.

Results

Raw data for photodissociation at 355 nm appear as in Figure 1, showing the intensity of the m/z 78 product ion as a function of the delay time between the laser pulse and the ICR excite pulse. An immediately obvious feature, superimposed on the expected exponential rise in product ion intensity, is the oscillation with a period of about 300 μs (~3 kHz). This is just double the frequency with which the ions circulate around the cell in their magnetron motion[11] and reflects a magnetron modulation of the ICR detection efficiency. The mechanism pictured is that the laser pulse strikes the ion cloud slightly off the cell axis (due to a small alignment error) and creates a packet of fragment ions which undergoes magnetron circulation at 1.5 kHz. If the ICR excite pulse fires when this ion packet is near either of the transmitter plates, ion excitation is more efficient than when the ion packet is near the receiver plates, the resulting cyclotron radius is larger, and the observed signal is more intense. Since the ion packet approaches a transmitter plate twice during each magnetron cycle, the ICR signal is thus modulated at 3 kHz. (For low ion density, the exact calculated magnetron frequency is 1.44 kHz, giving modulation at 2.88 kHz, slightly below the observed frequency of 3.1 kHz, but it has been shown that space charge effects can easily increase the frequency by 5–10%, so that the agreement is satisfactory.[11])

Since this magnetron modulation is a fully understood phenomenon, its effect on the signal may be modeled, either by imposing an amplitude modulation on the synthetic waveforms which are fitted to the experimental points or by demodulating the experimental waveform by dividing by a sinusoidal modulation

(8) These questions are thoroughly discussed in: Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Wiley-Interscience: New York, 1972.

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(10) Liftshitz, C. *Adv. Mass Spectrom.* **1989**, *11*, 713.

(11) Dunbar, R. C.; Chen, J. H.; Hays, J. D. *Int. J. Mass Spectrom. Ion Processes* **1984**, *57*, 39.

(12) This and other approaches to reduction of the frequency assignments to a one-parameter problem have recently been discussed by Lifshitz in ref 10.
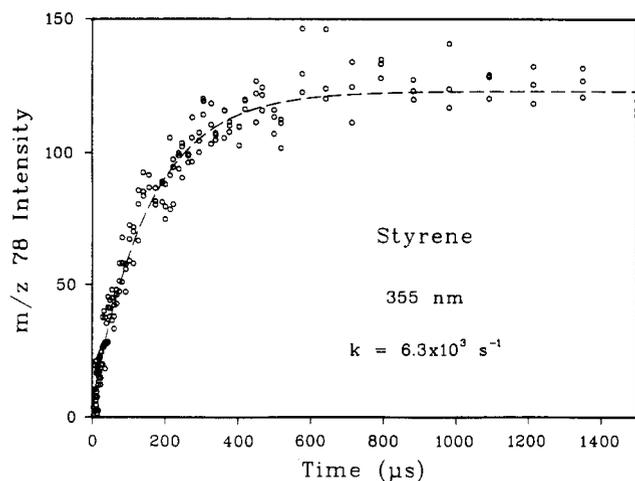
Figure 2. Data for 355-nm photodissociation, showing the fit of an exponential appearance function with a time constant of 160 μs. The magnetron modulation at 3.1 kHz has been removed as described in the text.

function at ~ 3 kHz. The latter procedure was chosen, and the demodulated signal $S'(t)$ was written as

$$S'(t) = S(t)\{1 - a \sin (2\pi ft + \phi)\}^{-1}$$

where $S(t)$ is the observed signal, t is the delay time following the laser pulse, and a, f, and ϕ are the (adjustable) amplitude, frequency, and phase of the modulation. It was found that a modulation amplitude of about 10% at a frequency of 3.1 kHz matched the observed modulation. All the data sets were demodulated by using the same frequency and amplitudes between 10% and 13%.

This magnetron modulation effect has been found, but not with such large amplitude, in other time-resolved photodissociation work and varies in amplitude depending on laser beam shape, intensity, and alignment. It presented no more than a minor nuisance in working up the data and is an interesting and graphic manifestation of the ion magnetron motion.

In Figure 2 three data sets similar to that of Figure 1 have been plotted, after removing the magnetron modulation. In these data there is no sign of a fast two-photon contribution to the observed product ion signal, which would be manifested by a nonzero intercept at zero delay time.[5] However, some runs made with a smaller laser beam (1–2-mm diameter, achieved by reducing the aperture and increasing the laser power) showed a substantial two-photon contribution, amounting to as much as 40% of the product ion signal. This was expected, because multiphoton processes increase with light intensity (at constant fluence), while one-photon photodissociation depends only on fluence and not on intensity. The data were fitted with the exponential rise curve shown, which has a time constant of 160 μs (6.3 $\times$ 10^3 s^{-1}). Properly speaking, the fitting curve should be a convolution of the rate–energy curve with the thermal distribution of ions, but as has been discussed,[5] we may with no significant loss of accuracy make the thermal approximation in which the thermalized ions are assumed to have a uniform internal energy equal to the average thermal energy (0.17 eV at 375 K). This then gives the new point on the rate–energy curve of 6.3 $\times$ 10^3 s^{-1} at 3.66-eV internal energy.

Discussion

The new rate measurement at 355 nm more than doubles the range of the experimental rate–energy curve, which is now known over 2 decades of rate values. This is valuable in the kinetic analysis: Just as with the kinetics of thermal reactions, the absolute value and the slope of the rate–energy curve must both be known in order to determine the frequency factor and the critical energy for the reaction. If the rate is known at a single energy value (or over a small range), a variety of frequency factor/critical energy pairs can be assigned; the wider the range of energies measured,
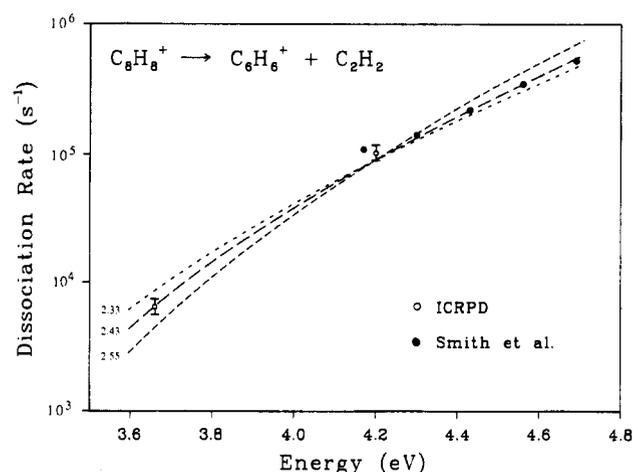

Figure 3. Rate–energy data points for styrene ion dissociation from the present photodissociation experiment (at 3.66 eV), the photodissociation experiment reported in ref 5 (at 4.20 eV), and the PEPICO results of Smith et al. from ref 2 (solid circles). The three RRKM fits shown as dashed lines were calculated as described in the text using E_0 values of 2.33, 2.43, and 2.55 eV.

the more precisely can the two parameters be separated.

The best way of determining the kinetic parameters for an energy-selected unimolecular reaction is fitting of calculated RRKM curves to the experimental rate–energy curve. There is great flexibility in the assignment of the vibrational frequencies of molecule and activated complex in the RRKM calculation; it is the entropy of activation corresponding to the assigned frequency sets which is important.[10] The calculations used here were similar to those described previously,[5] using the steepest descents approximation for state counting. Figure 3 shows the experimental rate–energy points known from Smith et al.'s coincidence experiment[2] and from photodissociation and displays the fit of three RRKM curves to them. In calculating these curves, the three critical energies shown were assigned, and then the activated complex frequencies were adjusted to give a rate of 9.0 $\times$ 10^4 s^{-1} at 4.2-eV internal energy in each case.

It is seen that the RRKM curve with $E_0 = 2.43$ eV gives an excellent fit to the experimental points. The curves with $E_0 = 2.33$ and 2.55 are quite clearly not acceptable. We assign the critical energy as 2.43 $\pm$ 0.05 eV. This is consistent with our previously assigned value[5] (2.32 $\pm$ 0.1) within the uncertainties but has moved slightly higher as a result of the new photodissociation measurement.

The value of $\Delta S^\ddagger_{1000}$ corresponding to this critical energy is -3.9 ± 1 cal K^{-1}, which corresponds to a frequency factor A_∞ of $(8 \pm 4) \times 10^{12}$ s^{-1}. (See ref 10 for discussion of the calculation and significance of $\Delta S^\ddagger_{1000}$.)

One commonly pictures two limiting types of transition state for an ion dissociation reaction. A loose transition state, becoming the orbiting transition state in the limit of extreme looseness, is characterized by a substantial positive entropy of activation, a high frequency factor, and a critical energy close to the endoergicity of the dissociation. A tight transition state (which would be typical of a rearrangement dissociation) is characterized by a near-zero or negative entropy of activation, a low frequency factor, and a critical energy which is not necessarily related to the reaction endoergicity. The (somewhat controversial) transition-state switching model postulates transition states of both types along the reaction coordinate, with the loose transition state being rate limiting at near-threshold internal energies and the tight one at high internal energies.[10,13]

The styrene ion dissociation, which clearly involves a structural rearrangement to reach the benzene ion product structure, behaves as one would expect for a rate-limiting tight transition state, with a negative entropy of activation and a low frequency factor. In

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(13) See, for instance: Bowers, M. T.; Jarrold, M. F.; Wagner-Redeker, W.; Kemper, P. R.; Bass, L. M. *Faraday Discuss. Chem. Soc.* **1983**, *75*, 57.

contrast, if the transition state were at the limit of extreme looseness, still with E_0 equal to 2.43 eV, the rate (at 308 nm) would be faster than that observed by a factor[14] of ~10⁵.

It is curious that the E_0 value measured for the reaction is equal, within experimental uncertainty, to the reaction endoergicity; this would be expected for a loose transition state but has no reason to be true for the tight transition state which seems indisputable for this reaction. We suggest that this is purely coincidental and that the tight transition state by chance has an energy equal to that of the dissociation products. Since the tight transition state has an energy not less than that of products, it is always rate limiting by virtue of its low frequency factor, and transition-state switching to the loose transition state would not be expected at any energy.

Conclusions

Among energy-selected unimolecular dissociations of polyatomic ions, the styrene ion dissociation is perhaps the one with the best-known kinetic parameters. The accuracy with which the rate-energy curve follows the RRKM predicted shape, with very reasonable parameters in the RRKM calculation, is a good indication of the validity of this theoretical framework for understanding the reaction. It does not appear that kinetic parameters for the corresponding neutral dissociation have been reported, but the fact that the reaction rate can be measured in a shock tube[15] gives reason to hope that they will be determined soon. It will also be of interest to try to map out the potential hypersurface along the reaction path by theory to identify the structure of the transition state at 2.43 eV.

Registry No. Styrene molecular, 34504-74-0.

(14) The rate in the limit of a loose orbiting complex is conveniently calculated from the equations derived by Klots from microscopic reversibility of Langevin orbiting collision rates: Klots, C. E. *Z. Naturforsch.* **1972,** *A27,* 553.

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Kinetic Energy and Temperature Dependences of the Rate Constants for Electron Detachment of NO⁻ by N₂O, CO₂, N₂, CH₄, C₂H₆, and C₃H₈

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Rate constants were measured as a function of average center-of-mass kinetic energy, $\langle KE_{cm}\rangle$, at several temperatures for the reactions of NO⁻ with N₂O, CO₂, C₂H₆, and C₃H₈. In addition, temperature dependences were measured for the rate constants of the reactions of NO⁻ with N₂ and CH₄. In the reactions of C₂H₆, C₃H₈, N₂, and CH₄, the only channel observed was electron detachment. N₂O and CO₂ reacted both by electron detachment and, at low temperature and low $\langle KE_{cm}\rangle$, by association. The rate constants for electron detachment were found to have positive temperature dependences and, in most cases, positive dependences on $\langle KE_{cm}\rangle$. An exception is that the rate constants for electron detachment for C₂H₆ and C₃H₈ at the higher temperatures showed negative dependences on $\langle KE_{cm}\rangle$. Rate constants for the association reaction channels were found to have negative temperature dependences. Rate constants for electron detachment from NO⁻ in collisions with CO₂ and N₂O in the $v = 0$ and $v = 1$ levels of the bending mode were derived from the data as a function of $\langle KE_{cm}\rangle$. Rate constants for the $v = 1$ level are approximately an order of magnitude larger than those for the $v = 0$ level.

Introduction

The reaction of O⁻ with N₂O produces NO⁻

$$O^- + N_2O \rightarrow NO^- + NO \qquad (1)$$
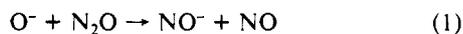
A recent value of the rate constant for reaction 1 is 2×10^{-10} cm³ s⁻¹ at 300 K.[1] The electron affinity of NO is extremely low. The most recent measured value is 0.026 ± 0.005 eV,[2] slightly higher than the best previous value of 0.024 eV.[3] The electron affinity is therefore lower than thermal energy (0.038 eV) at 300 K. The low electron affinity enables NO⁻ to lose its electron easily. In fact, almost no NO⁻ is seen as a product of reaction 1 in flow tube experiments using a helium buffer. In the early 1970s McFarland et al.[4] discovered that NO⁻ detaches only slowly in an argon buffer, enabling them to measure electron detachment rate constants of NO⁻ with several neutrals as a function of temperature. They found the thermal detachment rate constants to follow an Arrhenius expression with activation energies in the range 0.046–0.107 eV. They also found that polyatomic neutrals with low-frequency vibrational modes were the most efficient detachers.

In addition to undergoing electron detachment, NO⁻ has long been known to undergo chemical reaction with O₂ and HCl. Rinden et al.[5] have recently studied reactions of NO⁻ with a number of compounds. They found that the reactions proceeded by four pathways: electron detachment, charge transfer, dissociative charge transfer/nucleophilic displacement, and adduct formation. Maricq et al. have recently studied the vibrational autodetachment of NO⁻.[6]

In the present study we have measured rate constants for electron detachment of NO⁻ with several neutrals as a function of ion–neutral average center-of-mass kinetic energy ($\langle KE_{cm}\rangle$) at several temperatures. This technique also allows information to be derived on the dependence of the rate constants on the

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