PICOSECOND MASS-SELECTIVE MEASUREMENTS OF MOLECULAR CLUSTER REACTIONS: $(CH_3I)_n$ $\tilde{A}$ STATE EXCITATION

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Received 18 October 1989; in final form 14 December 1989

The picosecond reaction dynamics of $(CH_3I)_n$ clusters, initiated by $\tilde{A}$ state excitation, were studied by molecular beam mass spectroscopy. Time-resolved measurements indicate that the prominent I_2 and $I_2(CH_3I)_{n-2}$ fragments are formed within the 10 ps limit of our resolution. The cluster dynamics and geometries allow for sequential loss of CH_3 radicals and substantial caging of fragment I atoms and recombined I_2 molecules. Loss of up to five CH_3 radicals for cluster sizes $n \geqslant 8$ occurs within the 25 ps excitation pulse duration as indicated by the presence of ion signals such as $I_5(CH_3I)_3^+$. The evidence suggests that the extensive demethylation in the larger clusters is driven in part by the energy of intracluster recombination of two CH_3 radicals and the elimination of ethane.

1. Introduction

The study of chemical reactions in molecular clusters provides an exceptional medium for investigating the role of solvation on a single molecule basis. Recent studies have demonstrated that just a few solvent molecules can exert a profound influence on the energetics of both unimolecular and bimolecular reactions [1–5]. In some instances, specific solvent sizes have been identified to represent the onset of bulk-type behavior and that this critical solvent size varies in a predictable manner for different solvents [1,4]. Small molecular clusters represent an uncommon state of matter that is neither gas phase nor condensed phase [6], hence one can expect novel reaction mechanisms to occur. The emerging field of size-selective cluster chemistry has thus far been limited to measurements of equilibrium properties or extent of reaction over the experimental lifetime (e.g. residence time in a mass spectrometer) [1–7]. Very recently, picosecond MPI was demonstrated as a way to ionize clusters that dissociate rapidly in neutral excited states [8,9]. However, we are unaware of any studies in which picosecond mass-selective detection has been used to measure the rates of rapid intermolecular cluster reactions. Previous picosecond work has focused on van der Waals (vdW) dissociation [10,11].

In this paper, we report on picosecond pump–probe measurements of reactions in $(CH_3I)_n$. The photoreactions were initiated by exciting into the directly dissociative $\tilde{A}$ state. The monomer reaction dissociates into CH_3+I in less than 1 ps [12], however for certain cluster sizes one can expect sufficient caging of the initially formed radicals to induce chemistry within the cluster. For example, Vaida et al. suggested that I_2 is produced in $(CH_3I)_n$ clusters on the basis of the detection of I_2^+ by nanosecond $\tilde{A}$ state MPI [13]. An important concern, however, is whether detected ion fragments are due to neutral or ionic cluster reaction. To establish the neutral reaction channels, we have first identified the purely ionic fragmentation processes by employing direct variable energy electron-impact (EI) ionization, and by recording size-specific cluster ion photodissociation mass spectra [9].

2. Experimental

The molecular beam time-of-flight (TOF) mass spectrometer is a pulsed differentially pumped two-

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0009-2614/90/$ 03.50

chamber apparatus that has been described before [14]. The picosecond measurements based on MPI product detection used the collimated molecular beam in the high vacuum (10^{-8}–10^{-7} Torr) chamber. The ion photodissociation experiments made use of a crossed electron–laser–molecular beam configuration [9,14]. The $(CH_3I)_n$ clusters were directly ionized by electron-impact (EI) excitation and the cluster ions resonantly photodissociated using nanosecond laser pulses. Mass-selective photoexcitation and product ion detection was performed using a new technique in which a time-of-flight (TOF) mass spectrometer was operated as a low mass rejection filter [9,14].

Tunable picosecond pulses were produced by a pulsed mode-locked Nd:YAG laser pumping a short cavity dye laser. A single Nd:YAG oscillator pulse is selected from the pulse train by a double pockels cell and passed twice through an amplifier rod (60 mJ, 25 ps 1.064 μm, 10 Hz). Excitation was provided by 266 nm pulses and the probe by either 532 nm pulses or the dye laser fundamental and/or frequency-doubled output. In the latter case, the doubled Nd:YAG output (20 mJ, 25 ps, 532 nm) was split into equal portions to pump the dye laser (580–600 nm, 10 ps, 0.5–1.0 mJ) and a doubling crystal (266 nm, ≈0.4 mJ). In all cases, the ω_1 pump pulse and the ω_2 probe pulse traveled along separate variable delay lines and were then combined using a dichroic beamsplitter and directed collinearly into the molecular beam apparatus. Polarizing attenuators and neutral density filters were used to reduce pulse energies. A 350 mm focal length lens was positioned so that the ω_2 pulse overlapped with the ω_1 pulse diameter of about 200–400 μm at the intersection with the molecular beam.

The ω_2 delay line was repetitively scanned using a stepper motor controlled digital data acquisition system. Three-gated channels of detection were recorded for each run. The CH_3I samples were prepared by flowing Ar (20–30 psi) through a bubbler that was cooled in a bath of dry ice/acetone or ice water, depending on the extent of clustering desired.

3. Results and analysis

3.1. Neutral versus ionic cluster reactions

The absorption maximum in the dissociative $\tilde{A}$ state of CH_3I lies near 260 nm, hence our excitation wavelength of choice was the quadrupled Nd:YAG output at 266 nm. Picosecond and nanosecond REMPI mass spectra of $(CH_3I)_n$ under 266 nm excitation are given in fig. 1a. Nanosecond excitation conducted in our laboratory and elsewhere [13] proved ineffective at ionizing unreacted clusters or photoproducts other than I_2. On the other hand, picosecond resonance-enhanced MPI (REMPI) produced a considerable amount of parent cluster signal $(CH_3I)_n^+$ and an extensive series of cluster fragments. Ionization from the dissociative $\tilde{A}$ state requires two 266 nm photons or three 532 nm photons, hence, cluster dissociation is expected to be strongly favored over ionization as has been demonstrated for picosecond monomer excitation [15,16].

An important issue in this work is to verify that the detected ion signals are due to neutral cluster reactions and not due to ion cluster reactions. The competition between dissociation, ionization, and dissociative ionization is well understood for monomer CH_3I from the nanosecond experiments of Bersohn and co-workers [17] and Bernstein and coworkers [18], and from the picosecond experiments of Szaflarski and El-Sayed [15] and Khundkar and Zewail [16]. For the cluster case, we begin by comparing the picosecond MPI mass spectra in fig. 1a to the EI mass spectra in fig. 1b. EI excitation is a direct ionization process; consequently, the observed ion fragments are formed exclusively by ion dissociation mechanisms [3]. Clearly large differences between REMPI and EI mass spectra are evident in fig. 1. The picosecond REMPI spectrum (fig. 1a) exhibits extensive fragmentation that is conspicuous for the appearance of I_2^+ and highly demethylated products. The EI mass spectrum (fig. 1b) on the other hand leads predominantly to cluster ion dissociation of a single CH_3 radical or simple vdW dissociation even to excitation energies up to 100 eV. Similar results were obtained by Garvey and Bernstein in EI excitation of $(CH_3I)_n$ clusters [3]. It is possible that photoionization from a repulsive surface accesses ion Franck–Condon regions that could cause cluster dissociation that does not occur by direct EI bound state ionization. This mechanism, however, would cause at most a single dissociation to a stable ion; no further chemistry would occur.

The possibility that cluster ions may absorb light

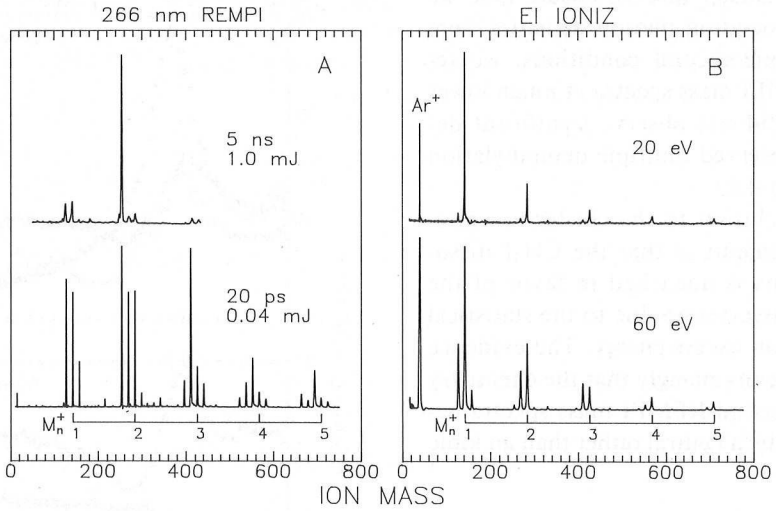

Fig. 1. $(CH_3I)_n$ cluster ionization mass spectra ($M=CH_3I$). (a) Picosecond versus nanosecond $\tilde{A}$ state REMPI at 266 nm. (b) Direct ionization by EI at 20 and 60 eV energy (the Ar^+ signal in the latter has been truncated). Expansion conditions for all figures were 5% CH_3I in 1200 Torr Ar.

and dissociate to products not produced by EI was explored by recording mass-selective cluster ion photodissociation spectra using a crossed electron–laser–molecular beam configuration and a low mass filter (LMF) technique [9,14]. The typical picosecond photon densities were about $5\times10^{16}\,cm^{-2}$ (266 nm) and $1\times10^{18}\,cm^{-2}$ (532 nm) based on pulse energies of 30 and 300 μJ, respectively, and a beam diameter of about 300 μm. In the nanosecond ion photodissociation experiments it was necessary to work with a 4 mm diameter laser beam in order to completely overlap the volume defined by the intersection of the electron beam and molecular beam. This required pulse energies of 6 mJ (266 nm) and 60 mJ (532 nm) to achieve photon densities comparable to the picosecond conditions employed. In fig. 2, the $(CH_3I)_n^+$ cluster ion photodissociation mass spectra for 532 nm excitation (following LMF rejection of the lighter ion masses) reveals primarily van der Waals dissociation (figs. 2a and 2b). Also, the EI ionization fragments $I(CH_3I)_{n-1}^+$ do not dissociate by 532 nm excitation. These results are in accord with a previous study using 595 nm photoexcitation [9]. Cluster ion dissociation at 266 nm led mostly to vdW dissociation with a minor contribution toward $I(CH_3I)_{n-1}^+$ presumably due to dissociation of a

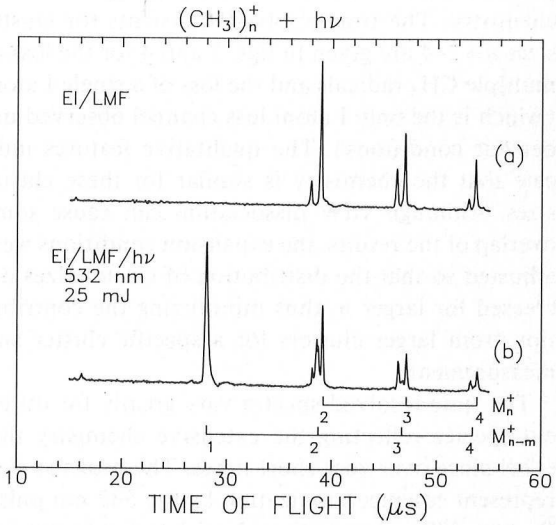

Fig. 2. Cluster ion photodissociation mass spectra. (a) EI ionization and low mass filter (LMF) to remove non-cluster-ion species from the excitation region: (b) same, but with 5 ns laser excitation revealing the pure vdW dissociation. Photofragment ions appear to slightly less time than parent ions of the same mass. Deflector plate voltages were adjusted to emphasize the M_I^+ photofragment. Conditions: 30 eV EI, 4 mm laser beam diameter.

neutral CH_3I in the cluster ion. To ensure that the nanosecond ion dissociation photon densities were comparable to the picosecond conditions, we recorded picosecond-MPI mass spectra at much lower pulse energies and did not observe significant departures from the observed multiple demethylation reactions (cf. section 4.2).

The principal conclusion to the cluster ion photodissociation experiments is that the CH_3I dissociation in cluster ions is quenched in favor of the lower energy vdW dissociation due to the statistical nature [19] of the ion excess energy. The evidence as a whole indicates convincingly that the chemistry evident in the picosecond-REMPI mass spectra occurs overwhelmingly by a neutral rather than an ionic mechanism.

3.2. Picosecond pump–probe measurements

The picosecond pump–probe responses for all major fragment signals (up to $n=5$) were measured using 266 nm pump (ω_1) and 532 nm probe (ω_2) pulses. The use of tunable UV and visible probe wavelengths from the picosecond dye laser did not prove as effective as 532 nm for probing the cluster chemistry. The time-resolved transients for cluster sizes $n=2$–4 are given in figs. 3 and 4 for the loss of multiple CH_3 radicals and the loss of a single I atom (which is the only I atom loss channel observed under our conditions). The qualitative features indicate that the chemistry is similar for these cluster sizes. Although vdW dissociation can cause some overlap of the results, the expansion conditions were adjusted so that the distribution of cluster sizes decreased for larger n, thus minimizing the contribution from larger clusters for a specific cluster size measurement.

The time-resolved spectra vary greatly for different species reflecting the extensive chemistry that takes place over very short times. The peaks at $t=0$ represent enhanced ionization by the 532 nm pulse. Because 532 nm excitation alone does not lead to ion signals, the negative delay region reflects ionization by 266 nm only. The parent cluster M_n ($M=CH_3I$) transient response is essentially symmetric and has a pulse-convolved response time (fwhm) that matches closely to the 35 ps cross-correlation time of the two pulses. The instrument limited estimate of

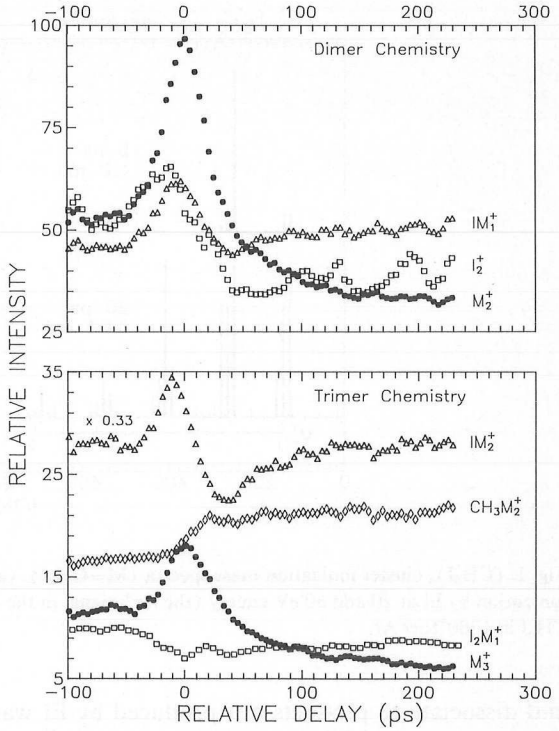

Fig. 3. Picosecond measurements using 266 nm pump and 532 nm probe: (top) M_2 ($M=CH_3I$) reaction (●) for loss of one and two CH_3 groups (IM_1 (△) and I_2 (□), respectively); (bottom) M_3 (●) reaction for loss of one (△) and two (□) CH_3 and loss of one I atom (CH_3M_2, ◇). The signal intensities represent closely the true relative intensities of each product in the mass spectrum. Note the offset in the ordinate.

the reaction time is therefore $\lesssim 10$ ps. Production of IM_{n-1} and I_2M_{n-2} also occurs within the instrument time constant. The IM_{n-1}^+ signal exhibits a complicated dependence during the ω_1–ω_2 overlap period possibly indicating that this signal derives from a reaction intermediate (cf. section 4.2). The $I_2M_{n-2}^+$ signal (for $n=2$–4, figs. 2 and 3) falls sharply at $t=0$ to a constant level with time. The latter behavior suggests that dissociation takes place in the long-lived ion, presumably due to the I_2 (or I_2^+) component. However the sharp threshold indicates that the ion, and therefore the neutral product, is formed within the instrument resolution of 10 ps.

Fig. 4 reveals a new and interesting reaction channel that opens up for cluster sizes of $n\geq 4$. The signal for I_3M_{n-3}, corresponding to loss of three CH_3 radicals, undergoes a rapid depletion at $t=0$ within the instrument response time and then recovers for $t>$

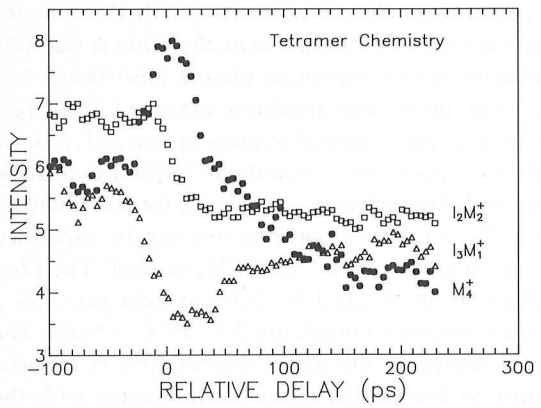

Fig. 4. Picosecond measurements of the M_4 (●) reactions for loss of two and three CH_3 groups (I_2M_2 (□) and I_3M_1 (△), respectively). The time dependence for loss of one CH_3 (IM_{n-1}, not shown for $n=4$) is similar to the responses for $n=2$, 3 in fig. 3. Note the offset in the ordinate. Excitation was by 266 nm (pump) and 532 nm (probe).

0. Because the signal recovers, it is unlikely that the dissociation occurs in the long-lived ion, but rather in the short-lived neutral. The $I_3M_{n-3}^+$ response is strong evidence for the neutral reaction mechanism.

The fast decay component for the parent $(CH_3I)_n$ ($n=2$–4) cluster (figs. 3 and 4) is followed by a slower 60–80 ps decay to a signal level below the 266 nm ionization baseline at negative delay time. A corresponding rise in the IM_{n-1}^+ signal level also seems to occur. A possible explanation is that these responses reflect a 532 nm ion photodissociation mechanism. The parent cluster ions M_n^+ are formed with substantial excess energy by three-photon ionization at 266 nm. It is possible that the cluster ions must await vibrational relaxation or nonradiative decay to an absorbing state (the latter process for $\tilde{X}\leftarrow\tilde{A}$ is estimated to be on the order of 100 ps [20] which is consistent with the observed time constant). The possibility that the slow components are a neutral reaction channel, however, cannot be ruled out. These features are under further study.

4. Reaction mechanism in the clusters

4.1. Production of I_2

The production of I_2 from $(CH_3I)_n$ clusters was first suggested by Vaida and co-workers [13] in work in which they detected I_2^+ by MPI through the valence $\tilde{A}$ state and the Rydberg $\tilde{C}$ state. Their results, however, did not distinguish whether I_2^+ originated from a reaction within a neutral cluster or an ionic cluster. In the present work, the absence of I_2^+ (and $I_2M_{n-2}^+$) by direct high energy EI ionization of $(CH_3I)_n$ and by 266 and 532 nm cluster ion photodissociation provides the most compelling evidence for production of $I_2M_{n-2}^+$ by neutral $\tilde{A}$ state cluster reactions. Also in support of a neutral reaction mechanism is the short reaction time ($\leqslant 10$ ps), which is consistent with the directly dissociating $\tilde{A}$ state, but not with the lower electronic bound states of the ion [19]. Finally, I_2 is known to form as an impurity in liquid CH_3I when exposed to light [21]. The production of I_2^+ by cluster reaction (and not impurity) is confirmed by an independent experiment in our laboratory involving 1+1 REMPI of CH_3I and $(CH_3I)_n$ through the Rydberg $\tilde{B}$ state [22]. Although, cluster ions are not observed by the nanosecond excitation (even by two-color threshold ionization), the excitation spectrum for I_2^+ detection exhibits a small red-shift relative to the monomer CH_3I spectrum [23] indicating that it derives from clusters (possibly as small as dimer).

4.2. Multiple demethylation by radical reactions

One of the most striking features of the $(CH_3I)_n$ cluster photochemistry is the extensive loss of CH_3 constituents. The 266 nm picosecond MPI mass spectra in fig. 5 show that the photoexcited clusters can lose a substantial fraction of the CH_3 groups allowable by cluster size. Also evident is an alternation of peak intensities separated by two CH_3 mass units. In fig. 5, the product distribution is observed to shift to greater demethylation at higher pulse energies suggesting that sequential photon absorption plays some role in demethylation. However, if we assume a single CH_3 dissociation per absorbed photon and assume that the product is ionized by three-photon ionization of a remaining CH_3I chromophore, then

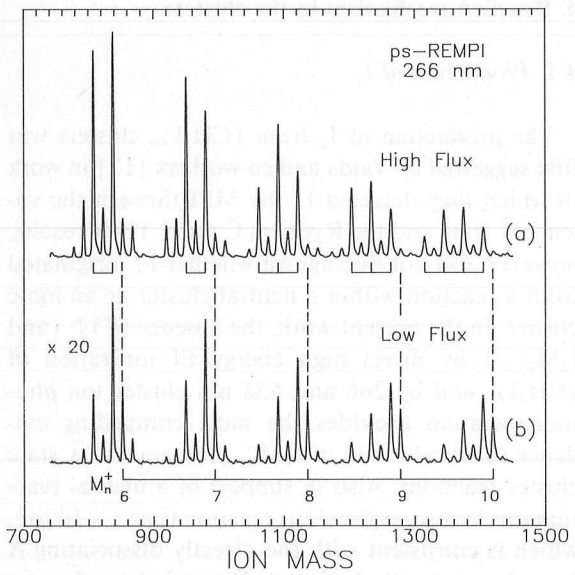

Fig. 5. Picosecond-REMPI mass spectra showing reactions in larger clusters. The 266 nm high and low photon flux conditions differ by about a factor of three (within the range of 10^{27}–10^{28} $cm^{-2}\,s^{-1}$). The scaling factor in (b) shows that the overall signal intensity is steeply dependent on photon flux, however, the relative intensities are much less sensitive.

the detection of products with the loss of m CH_3 groups requires the absorption of $m+3$ photons during the 25 ps pulse duration. Because demethylation is relatively extensive even at low pulse energies (fig. 5b), it seems unlikely that sequential photon absorption can account for all the products observed. This conclusion is supported by the photon flux and absorption cross-section data. The photon flux I under the most intense excitation conditions employed here (≈ 150 μJ, 200 μm diameter) was about 3×10^{28} $cm^{-2}\,s^{-1}$. The absorption cross section σ of CH_3I at 266 nm was estimated by direct absorption measurements in a vapor cell to be about 2×10^{-18} cm^2 (which would increase with cluster size). These values lead to an estimated absorption rate $\tau^{-1}=\sigma I$ of about $(20\ ps)^{-1}$ (again higher for clusters), although much lower rates better represent the results in this paper. Under these conditions, the sequential photodissociation mechanism cannot fully account for the extensive demethylation observed or the rapid rates measured (e.g., $k\geqslant(10\ ps)^{-1}$ for production of $I_3(CH_3I)+3CH_3$, fig. 4).

A simple, but plausible reaction mechanism can be constructed that is consistent with three major observations; (1) multiple demethylation is not fully accounted for by sequential photon absorption, (2) the most prominent products observed for larger cluster sizes are separated in mass by two CH_3 groups, and (3) I atom loss is essentially limited to a single atom and diminishes in importance for larger cluster sizes (fig. 5). These observations can be explained by the chemistry of a "hot" CH_3 radical. The photodissociation of CH_3I by 266 nm light provides a 4.66 eV photon to break the 2.30 eV C–I bond. The excess energy in the direct dissociation is released mainly as kinetic energy in the fragments with the CH_3 group acquiring either 1.91 or 1.14 eV [24] depending on whether the dissociation gives $I(^2P_{3/2})$ or $I(^2P_{1/2})$ (the latter being favored by a factor of 3.5) [24,25]. The dissociation of CH_3 directed towards the cluster can lead to the exothermic reaction

$$[CH_3+(CH_3I)_{n-1}]\rightarrow C_2H_6+I(CH_3I)_{n-2}\,,$$

$$\Delta H=-1.37\ eV\,,$$

where we assume that the photodissociated I atom is lost (recombination of I atoms would contribute an additional exothermicity of $\Delta H=-1.58$ eV). The activation energy for this reaction is not known, however it should be compared with the reported near zero activation for the H atom abstraction by CH_3 from CH_3I in the 257.3 nm photodissociation of liquid CH_3I [21]. It is not unreasonable then that the "hot" CH_3 reactive radical can induce the rapid exothermic reaction to produce ethane. Alternatively the absorption of two photons by $(CH_3I)_n$ would produce two CH_3 radicals that could recombine to release 3.81 eV of heat. In both cases the heat of reaction, which is augmented by the initial radical kinetic energy as well as further recombination including the dissociated I atoms, could drive additional chemistry based on the exothermicity of ethane formation. The hot cluster product above, for example, could undergo the thermal rearrangement

$$I(CH_3I)_{n-2}\rightarrow C_2H_6+I_3(CH_3I)_{n-4}\,,$$

$$\Delta H=-0.52\ eV\,,$$

with the additional heat sustaining further loss of ethane. The thermally hot cluster fragments will undoubtedly break vdW bonds, especially that involving the weakly bound ethane. However, these rates

may be much slower than radical reaction; also substantial heat should still remain to activate further radical reactions. Naturally subsequent photodissociation would enhance the rate of C–I bond breaking and exothermic production of C_2H_6.

Variations on the above reaction mechanism are certainly expected, especially with regard to the extent of caging of the radicals and the dependence on cluster size. The near absence of a multiple I atom loss product is consistent with efficient caging of this heavy mass, which acquires little kinetic energy (0.15–0.25 eV) by photodissociation and even less by the thermal route. This provides an efficient means for production of the major product I_2. The loss of I_2 from a fragment cluster, however, appears to be accompanied by loss of CH_3 radicals or ethane, otherwise products of the form $(CH_3)_mM_{n-m}$ for $m>1$ would be more apparent. The mechanism of CH_3 radical recombination to form ethane is particularly appealing because it is very exothermic and would explain the alternating product stabilities separated by two CH_3 units in fig. 5.

5. Summary and conclusions

Although the techniques are now well established for studying stepwise solvation, this report is believed to represent the first picosecond mass-selective measurements of rapid *intermolecular* photochemistry in clusters. The photodissociation of CH_3I cluster molecules leads to an extensive series of "hot" radical reactions. The chemistry is not yet fully understood, however, under the experimental conditions of this study, a series of distinct chemical processes have been observed that conform well to an energetically reasonable reaction mechanism.

The chemistry in the $(CH_3I)_n$ clusters was initiated by the picosecond dissociation of a CH_3I molecule in the cluster. The rate of formation of $I_2(CH_3I)_{n-2}$ and $I_3(CH_3I)_{n-3}$, representing loss of two and three CH_3 groups was measured to be less than the 10 ps limit of our resolution. Loss of up to five CH_3 radicals for cluster sizes $n \geqslant 8$ occurs within the 25 ps excitation pulse duration as indicated by the presence of ion signals such as $I_5(CH_3I)_3^+$. The extensive chemistry is described well by a mechanism in which a series of reactions are initiated by the sequence of photodissociation, CH_3 fragment kinetic energy, and heat of exothermicity. The principal driving force is the energy released by CH_3 radical recombination to form ethane. This process is accompanied by caged I atom recombination to form I_2.

This work highlights the capability for detecting and measuring rapid intermolecular cluster chemistry using mass-selective picosecond REMPI. Molecular beam mass spectrometry offers a powerful means for identifying a variety of product species and distinguishing precursor cluster size. However, such studies require a definitive means for differentiating neutral cluster reactions from ionic reactions. Our approach was to measure directly the ion dissociation mechanisms by high energy EI ionization and by mass-selective ion photodissociation. A distinctly different reaction mechanism operates for the ionic cluster versus the neutral $\tilde{A}$ state cluster which made it possible to obtain an unambiguous assignment of the neutral reaction pathways. The combination of picosecond REMPI and direct ion photodissociation studies holds great promise for studying complex reaction mechanisms in size-specific neutral clusters.

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