Comparative Polymerization in the Gas Phase and in Clusters. 2. Electron Impact and Multiphoton-Induced Reactions in Isobutene and Benzene/Isobutene Clusters

M. Samy El-Shall,* George M. Daly, Zhongde Yu, and M. Meot-Ner (Mautner)

Contribution from the Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia 23284-2006

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Abstract: Electron Impact (EI) ionization of isobutene clusters leads to the production of predominantly the radical cation series $(C_4H_8)_n^{\bullet+}$ with a small fraction of the carbocation series $C_4H_9(C_4H_8)_n^+$. The dimer radical cation exhibits unusual abundance under a wide range of experimental conditions which is consistent with a covalent bond formation in agreement with the gas phase results. The observed trimer stability at low ionization energy suggests the formation of a cyclic structure. Several closed and open shell ions have been observed within the clusters and have been attributed to dissociation products from the dimer and trimer. Mixed benzene/isobutene clusters (B_mI_n) have been ionized by EI, resonant two-photon ionization in the vicinity of the benzene's $A_{1g} \rightarrow B_{2u}$, 6_0^1 transition (~259 nm), and two-photon ionization using 248- and 193-nm photons. In all cases, the resulting ion distributions are dominated by the series $I_2^+B_m$, thus reflecting the stability of the covalent bonded isobutene dimer cation. The study of clusters indicates that the formation of the dimer cation is more favorable than that of the carbocation under the cold beam conditions. This is consistent with the gas phase behavior where the condensation channel increases at low temperatures. Metastable peaks associated with the *tert*-butyl cation series $C_4H_9(C_4H_8)_n^+$, $n > 2$, have been observed in the time-of-flight (TOF) experiments indicating a significant change in the rate of the addition reactions past $n = 2$. This is consistent with the gas phase measurements which showed that the second polymerization step leading to the formation of $C_4H_9(C_4H_8)_2^+$ exhibits an unusually large entropy change. Correspondingly, the cluster results indicate that the third and higher polymerization steps are delayed after ionization. The relation between the gas phase and cluster studies and the implications for the bulk polymerization are discussed.

1. Introduction

Several recent papers have provided evidence for sequential polymerization reactions following the ionization of molecular clusters of olefinic,[1,3] diolefinic,[4] and acetylenic[5] monomers as well as other molecules such as CS_2.[6] Anionic polymerization has also been reported in acrylonitrile and chloroacrylonitrile clusters.[7,8] These studies are motivated by the possibility of converting van der Waals (vdw) clusters into size-specific covalent-bonded polymeric species which promises unique results not only for a fundamental understanding of ionic polymerization, including the elucidation of new initiation mechanisms, but also for the development of novel materials with unique properties.[9]

The cluster environment represents an unusual medium for polymerization in the intermediate regime between gas-phase and condensed-phase chemistry. In this environment, one can directly observe the simultaneous growth of a polymeric chain and the monomer evaporation from the cluster. This occurs because ion–molecule condensation reactions are exothermic and the energy released could evaporate the non-reacted monomers from the cluster. The energy transfer to the low-frequency cluster modes leading to evaporation is analogous to collisional stabilization of the ionic intermediates in the gas phase at high pressures.[10-12] The analogous condensed-phase process is the evaporative control of temperature by adding volatile solvents (internal coolant) to ionic polymerization mixtures, which is a well-established method in polymer chemistry.[13] The competition between sequential condensation and monomer evaporation controls the ultimate size that a polymer molecule can reach in the cluster. This kinetic competition depends on the relative rates of the chemical reactions and of energy transfer that leads to evaporation.

Kinetics and energetics information about gas-phase sequential polymerization steps can be obtained from ion–molecule reactions using High-Pressure Mass Spectrometry (HPMS).[14]

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1995.

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This approach has been used to study the cationic reactions of isobutene as presented in the preceding paper of this issue.[15] By studying the same reactions in clusters, where the role of collisional stabilization is replaced by cluster evaporation, a more comprehensive picture of the early stages of cationic polymerization in the condensed phase can be obtained. Of particular importance is the ability to integrate the new information from the gas phase and the cluster studies with the existing knowledge from the condensed phase on the same system to provide molecular level interpretations of some of the trends and phenomena observed in bulk cationic polymerization.

All the intracluster polymerizations reported so far involve reactions initiated by radical ions. Cationic polymerization may also be initiated by a proton or a carbocation instead of a radical cation. Isobutene is one of the few monomers which are known to be polymerized in the condensed phase exclusively by cationic mechanisms.[13] Depending on the method and conditions of polymerization, the polymers produced can range from liquids containing dimers, trimers, and low oligomers to viscous oily products with medium molecular weights up to tough, nonflowing elastomers with molecular weights in the millions.[16] The production of these different polymers is attributed to different types of propagating chains ranging from tight ion pairs, solvent-separated or "loose" ion pairs, to free ions. Although it is generally accepted that high molecular weight polyisobutene is formed through the propagation of the *tert*-butyl carbocation $C_4H_9^+$, the exact nature of the mechanism and the contributions from the reactions of the radical cation $C_4H_8^{\bullet+}$ are poorly understood. It is therefore valuable to compare the reactivity of the radical cations with their carbocations in order to achieve a better understanding of the mechanism of cationic polymerization.

In the present work, we investigate the ion−molecule reactions within isobutene clusters, I_n, in the size range $n = 2-10$. Our main emphasis is to compare the intracluster reactions of the radical cation $C_4H_8^{\bullet+}$ and the carbocation $C_4H_9^+$ under different clustering and ionization conditions and to relate the cluster's observations to the gas-phase kinetics and energetics information obtained on the isobutene system presented in the preceding paper.[15]

Another objective of this study is to investigate the charge transfer initiation mechanism in the mixed clusters of benzene and isobutene. For this purpose, mixed benzene−isobutene clusters (B_mI_n) are generated and ionized using the resonant two-photon ionization (R2PI) of the B_mI_n clusters in the vicinity of the benzene's $A_{1g} \rightarrow B_{2u}\ 6_0^1$ transition. This is one of the most intense vibronic transitions which occurs at 38 609 cm^{-1} in isolated benzene (C_6H_6), i.e. almost halfway to the ionization continuum (IP = 9.25 eV).[17] Therefore, after excitation of the benzene to the S_1 state via a resonant absorption step, the cluster, for example BI_n, is ionized by the nonresonant absorption of a second photon. Since the ionization potential of benzene is higher than that of isobutene (IP = 9.239 eV),[18] the initially formed cluster ion (B^+I_n) can undergo an electron transfer reaction from B^+ to I_n to generate the ($I^+{}_nB$) species. The $C_4H_8^{\bullet+}$ ion may then undergo the ion−molecule reactions with neutral isobutene within the cluster and the product distributions can be compared with the gas-phase reactions. Of specific interest here is the effect of the excess energy deposited within the cluster ion as a result of the ionization process. Since cluster ions may dissipate any internal energy into the heat bath of the cluster modes, the product distributions should reflect this process. Therefore, the effect of excess energy can be examined by varying the energy of the two photons used to ionize the mixed clusters B_mI_n and measuring the product distributions corresponding to different reaction channels. To investigate this effect, we compare the 6_0^1 R2PI of the B_mI_n clusters where the energy of the two photons is in the range of 9.50 eV with two photon ionizations using 248- and 193-nm photons where the two photon energies are 10.00 and 12.85 eV, respectively. The R2PI in the region of benzene's quasicontinuum absorption (6−7 eV) enables one to observe simultaneously the entire distribution of benzene-containing clusters by time-of-flight mass (TOF) spectrometry.

The outline of the paper is as follows: First, we consider the results from the EI ionization of isobutene clusters. This section is concerned with comparing the intracluster ion−molecule reactions with their gas-phase analogues and identifying any intensity anomaly in the distribution of cluster ions which could arise from the generation of some stable ions. Second, we examine the mixed clusters of benzene and isobutene following their EI ionization. The goal here is to see if the presence of benzene within the isobutene clusters will significantly change the distribution of clusters ions from that observed in the homogeneous (neat) clusters. Third, we investigate the 6_0^1 R2PI of the B_mI_n mixed clusters in order to characterize the intracluster charge-transfer process and examine the reactions following the generation of the $C_4H_8^{\bullet+}$ ion within the clusters. We also compare the product distributions in the benzene−isobutene clusters obtained via the 6_0^1 R2PI vs two-photon ionizations using higher energy 248- and 193-nm photons. Finally, we conclude this paper with a discussion of several issues, including a comparison of the cluster ion chemistry with the gas-phase reactions and the implication of the results for the condensed-phase polymerization of isobutene.

2. Experimental Section

Isobutene clusters were generated by pulsed adiabatic expansion in a supersonic cluster beam apparatus.[4,19] The essential elements of the apparatus are jet and beam chambers coupled to a quadrupole mass spectrometer. During operation, a vapor mixture of 1−10% isobutene (Aldrich, 99.9% purity) in He (ultrahigh purity, Spectra Gases 99.999%) at a pressure of 2−4 bar is expanded through a conical nozzle (500-μm diameter) in pulses of 200−300 μs duration at repetition rates of 6−10 Hz. The jet is skimmed and passed into a high-vacuum chamber which is maintained at 8×10^{-8} to 2×10^{-7} mbar. The cluster beam enters the ion source and quadrupole mass filter in an axial configuration. The mass spectrometer is an Extrel-500 equipped with a 324-9 mass filter (pole diameter 1.9 cm) which provides a high transmission efficiency. The amplified signal from the particle multiplier is processed using a boxcar integrator (EG&G model 166) set to sample at arrival times appropriate for the detected ions. The spectrometer is typically stepped in 0.1-amu increments averaging 1−5 nozzle shots per data point.

Mixed benzene−isobutene clusters are formed in a He-seeded jet expansion and probed as a skimmed cluster beam in collision-free high vacuum (operating pressure: 2×10^{-7} to 8×10^{-8} mbar) with a delay between synthesis and probe (i.e. the neutral beam flight time) on the order of 1 ms. In order to enhance the formation of the mixed clusters, we found that it is necessary to have a very low ratio of benzene to isobutene in the expansion. Of course, if this ratio is too low, then too few benzene-containing clusters would be present in the beam for good signal-to-noise. If the ratio is high, the beam becomes dominated by

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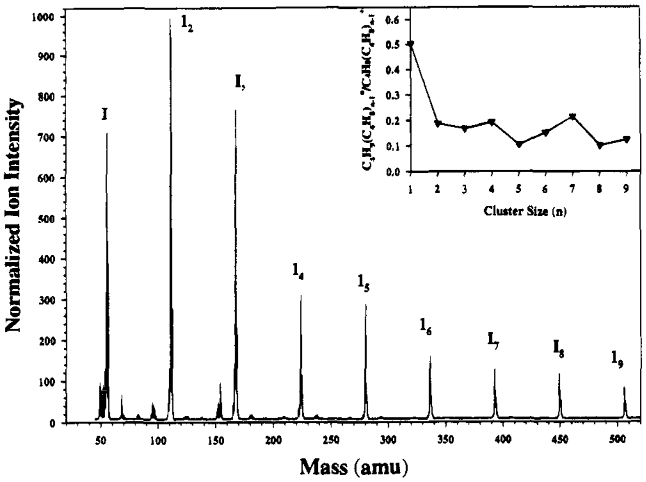

Figure 1. 70-eV, EI mass spectrum of isobutene clusters (I_n) produced from isobutene/He expansion (266 mbar in 2.66 × 10^3 mbar of He). Inset: The ion intensity ratio of the $C_4H_9(C_4H_8)_{n-1}{}^+/C_4H_8(C_4H_8)_{n-1}{}^+$ as a function of n (after correction for the ^{13}C contribution).

benzene clusters and ionization results in a distribution with benzene cluster ions as the most abundant species. The collimated cluster beam passes into the ionization region of a TOF mass spectrometer where it intersects a laser pulse from a frequency-doubled dye laser. The tunable radiation was provided by a dye laser (Lambda Physik FL3002) pumped by an excimer laser (Lambda Physik LPX-101). Coumarin 503 (Exciton) dye laser output passes through a β-BaB_2O_4 crystal (CSK Co.) cut at 52° to generate a continuously tunable frequency-doubled output of 10^{-8}-s pulses. The spatially filtered ultraviolet radiation (0.2–0.4 mJ per pulse) was shaped with a 60-cm lens to provide a 0.1-mm^2 beam in the ionizing region. The laser system has ≈0.40 cm^{-1} bandwidth at 40 000 cm^{-1} (250 nm). The two-photon ionization at a fixed frequency was achieved by either KrF (248 nm) or ArF (193 nm) radiation provided by an excimer laser (Lumonics Hyper Ex-400). Our TOF mass spectrometer is based on the Wiley-McLaren three-grid space focusing design.[20] The cluster ions formed by the R2PI process are electrostatically accelerated in a two-stage acceleration region (300–400 V/cm), travel a field-free region (≈110 cm in length), and are then accelerated to a two-stage microchannel-plate detector. Deflection plates are used to compensate for the cluster beam velocity. The deflection voltage is adjusted to optimize the signal for a particular mass range of interest. The TOF spectrum is recorded by digitizing the amplified current output of the detector by a 350-MHz digitizer (LeCroy 9450) and averaged over 500–1000 pulses.

3. Results and Discussion

3.1. Electron Impact Ionization of Isobutene Clusters. A. Ion Intensity Anomaly.

Figure 1 displays a typical mass spectrum resulting from the 70-eV ionization of isobutene clusters. In addition to the major sequence $C_4H_8{}^{\bullet+}(C_4H_8)_n$, the spectrum contains other series such as $C_4H_9{}^+(C_4H_8)_n$, $C_5H_9{}^+(C_4H_8)_n$, $C_6H_{11}{}^+(C_4H_8)_n$, and $C_7H_{13}{}^+(C_4H_8)_n$. The intensities of these sequences fall off rapidly in clusters with $n > 2$.

The relative ion intensities within the $(C_4H_8)_n{}^{\bullet+}$ sequence show an enhanced intensity for $n = 2$ and a drop or discontinuity past $n = 3$. Overall spectra of this type were found over a wide range of experimental parameters which can influence the size distribution of the neutral clusters such as the carrier gas used in the beam expansion, the isobutene/carrier gas seed ratio, and the stagnation pressure. The experimental parameter which has the greatest effect on the relative enhancement of the dimer and trimer ions is the energy of the EI ionization. Under low EI energies, the trimer ion $(C_4H_8)_3{}^{\bullet+}$ exhibits a similar enhancement as the dimer as shown in Figure 2, which displays the mass spectrum observed following the 15-eV EI ionization of the isobutene cluster beam. We also note that the pentamer peak $(C_4H_8)_5{}^{\bullet+}$ exhibits some intensity enhancement although less pronounced than the trimer. Figure 3 exhibits ion intensity plots which illustrate the dependences of the ion abundance profiles on different experimental parameters. Inspection of these data indicates that the enhanced intensities of the dimer and the trimer are invariable over a wide range of experimental parameters and this may reflect special stabilities of these ions among the $(C_4H_8)_n{}^{\bullet+}$ series.

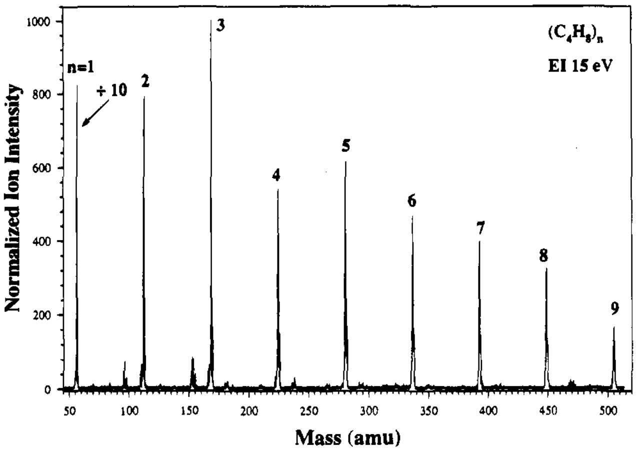

Figure 2. 15-eV, EI mass spectrum of isobutene clusters in expansion of 300 mbar of isobutene in 3100 mbar of He.

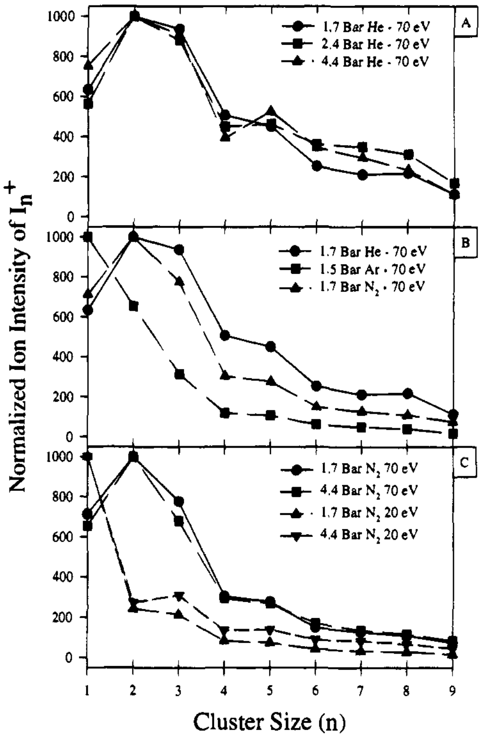

Figure 3. Dependences of the ion intensity of isobutene clusters (I_n) on (A) stagnation pressure (He) at 70 eV in a 10% isobutene/He pre-expansion mixture and (B) carrier gas at 70-eV EI for a 10% isobutene in He pre-expansion mixture and (C) electron energy (eV) for a 10% isobutene mixture in N_2 at the stagnation pressures indicated.

B. Generation of the *tert*-Butyl Cation ($C_4H_9{}^+$). The observation of the $C_4H_9(C_4H_8)_n{}^+$ series indicates the generation of the *tert*-butyl cation ($C_4H_9{}^+$) within the clusters in competition with condensation, similar to the well-known gas-phase proton transfer reaction:[21-25]

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$$[C_4H_8^+ + C_4H_8]\,(C_4H_8)_n \rightarrow C_4H_9^+(C_4H_8)_n + C_4H_7^{\bullet} \quad (1a)$$

$$\rightarrow C_8H_{16}^{\bullet+}(C_4H_8)_n \quad (1b)$$

We noted in the preceding paper[15] that condensation becomes dominant with decreasing energy. Several cluster observations are consistent with this trend. First, it is noted that the ion intensity of the $C_4H_9(C_4H_8)_n^+$ series represents only 20–25% of the intensity of the radical cation series $(C_4H_8)_n^{\bullet+}$. This behavior is illustrated in the inset of Figure 1 where a plot of the ion intensity ratio $C_4H_9(C_4H_8)_{n-1}^+/C_4H_8(C_4H_8)_{n-1}^{\bullet+}$ versus n is shown. The dependences of this ratio on the nature of the carrier gas used in the beam expansion and on the energy of the EI ionization have been investigated. A significant increase in the intensity ratio of $C_4H_9^+/C_4H_8^{\bullet+}$ is observed in the isobutene clusters generated by expansion in N_2 as compared to He or Ar. It is known that clusters produced in neat molecular expansions or N_2 coexpansions are characterized by higher internal temperatures than those produced in He or Ar coexpansions.[26] A similar result is observed when neutral clusters produced under identical expansion conditions are ionized with higher electron energies (70 eV as compared to 20 eV). These observations suggest that the $C_4H_9^+/C_4H_8^{\bullet+}$ ratio increases by increasing the internal energies of the neutral and/or the ionized clusters. Higher coexpansion temperatures, as well as higher EI energies, provide additional intracluster energy. This can lead to a higher $C_4H_9^+/C_8H_{16}^{\bullet+}$ product ratio similar to the effect of increasing temperature in the gas phase.[15] The higher energy can also induce extensive evaporation, essentially stripping the cluster.

We also note in the Figure 1 inset that the $C_4H_9^+/C_4H_8^{\bullet+}$ intensity ratio is larger in the smaller clusters. This may be due to more efficient quenching of the internal energy in the larger clusters, leading to smaller $C_4H_9^+/C_8H_{16}^{\bullet+}$ ratios as in the gas phase at lower temperatures and to evaporation from larger clusters following the exothermic polymerization of $C_4H_9^+$.

C. Other Intracluster Reactions. In addition to the observation of the $C_4H_9^+$ cation, the cluster mass spectrum indicates the generation of other cations such as $C_5H_9^+$, $C_6H_{11}^+$, $C_7H_{13}^+$ as well as their higher sequences which contain several isobutene units. Figure 4 displays the mass spectrum observed for these sequences. The generation of these ions has been observed in the gas phase following radiation and photoionization of isobutene under high-pressure conditions, and a sequential pattern of consecutive ion–molecule reactions involving monomer fragment ions such as $C_3H_3^+$, $C_3H_5^+$, and $C_4H_7^+$ have been proposed.[22,27] In clusters, the formation of these ions could be observed even under conditions where the monomer fragments are nearly absent. By decreasing the EI ionization energy, the intensities of the cluster fragment sequences such as $C_5H_9^+I_n$ and $C_7H_{13}^+I_n$ do not correlate with the sharp drop in intensities of the monomer fragments. This suggests that the observed cluster series arise not only as a result of sequential intracluster reactions between monomer fragments and neutral isobutene but mainly from the dissociation of excited products such as $C_8H_{16}^{\bullet+*}$ and $C_{12}H_{24}^{\bullet+*}$. The projected extra energy resulting from the formation of these condensation products would promote their dissociation along with neutral evaporation from the cluster thus leading to enhanced formation of the fragment sequences. For example, the species resulting from the dissociations of the dimer radical cation and carbocation can be written as:

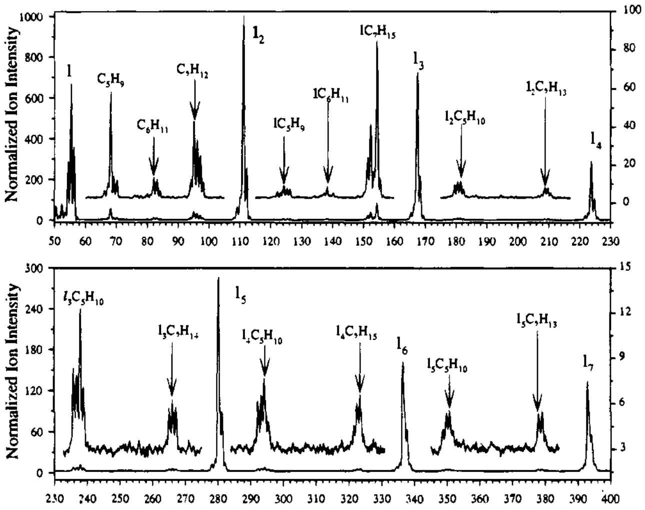

Figure 4. Sequences of ion–molecule reactions produced by 70-eV ionization of isobutene clusters (12% pre-expansion mixture of isobutene in N_2 at 3.1 bar stagnation pressure).

$$\begin{aligned}(C_4H_8^{\bullet+} + C_4H_8)I_n \rightarrow{}& (C_8H_{16}^{\bullet+*})I_n\\ &\rightarrow (C_5H_9^+)I_1 + C_3H_7^{\bullet}\\ &\rightarrow (C_6H_{11}^+)I_1 + C_2H_5^{\bullet}\\ &\rightarrow (C_7H_{13}^+)I_1 + CH_3^{\bullet}, \quad n > 1 \quad (2)\end{aligned}$$

$$\begin{aligned}(C_4H_9^+ + C_4H_8)I_n \rightarrow{}& (C_8H_{17}^{+*})I_n\\ &\rightarrow (C_5H_{10}^+)I_1 + C_3H_7\\ &\rightarrow (C_6H_{12}^+)I_1 + C_2H_5\\ &\rightarrow (C_7H_{14}^+)I_1 + CH_3, \quad n > 1 \quad (3)\end{aligned}$$

The use of the index 1 with $n > 1$ implies possible evaporation of monomer units along with the generation of the dissociation product ions. Figure 4 also indicates a manifold of peaks with the empirical formula $C_8H_{14}^{\bullet+}I_n$ beginning with a peak corresponding to $C_8H_{14}^{\bullet+}$. The production of this ion in the gas phase has been observed as a result of the reaction[15,21]

$$C_8H_{16}^{\bullet+} + C_4H_8 \rightarrow C_8H_{14}^{\bullet+} + C_4H_{10} \quad (4)$$

D. Discussion of the Electron Impact Results. The most important result from the EI study of isobutene clusters is the observation of the enhanced ion intensity of the dimer under a wide range of experimental conditions and of the trimer, and to a lesser extent, the pentamer at low ionization energy. The behavior of the dimer is consistent with a covalent bond formation in agreement with the gas-phase results presented in paper 1. These results indicated that the dissociation energy of the dimer radical cation must be greater than 132 kJ/mol, and based on the thermochemistry estimate of ΔH_f, a tail-to-tail (TT) addition is suggested for the dimer formation.[15] The observation of dissociation products from the dimer (reaction 2) is also consistent with the proposed TT structure. For example, the eliminations of $CH_3^{\bullet}$, $C_2H_5^{\bullet}$, and $C_3H_7^{\bullet}$ from the dimer to generate the even-electron ions $C_7H_{13}^+$, $C_6H_{11}^+$, and $C_5H_9^+$, respectively, can be illustrated as

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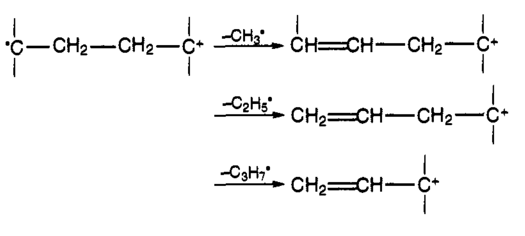
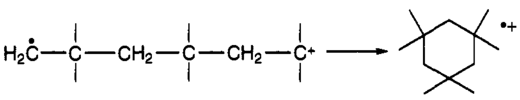


(5)

The behavior of the trimer at low ionziation energy may be explained by a further addition to the dimer followed by cyclization of the distonic ion $C_{12}H_{24}$ according to



(6)

We assume that both the TTH and the HTH isomers of the trimer are formed. At lower EI energy, the HTH trimer undergoes cyclization reaction 6 to form the 1,1,3,3,5,5-hexamethylcyclohexane ion which is expected to be energetically more favorable than the cyclization of the TTH trimer due to steric interaction among the methyl groups of the latter. The enhanced intensity of the pentamer could also be explained by cyclization of the radical cation chain $(C_4H_8)_5^{•+}$. It is well-known that the formation of stable ionic species (usually cyclic structures) can often interrupt the general pattern of successive addition or elimination reactions. For example, in the isoprene cluster ions.[3] the observation of a magic number corresponding to $C_{14}H_{21}^+$ has been attributed to a bicyclic structure similar to those observed in the bulk cationic polymerization of isoprene.[28] Similar observations were found in olefinic cluster ions where the formation of six-membered ring structures has been suggested to explain their anomalous ion intensity distributions.[2] A critical test of this interpretation can be provided by measuring the photodecomposition products of the $C_4H_8^{•+}(C_4H_8)_n$ clusters in order to obtain structural information. It should be noted that the discussion relating to the trimer and the pentamer is rather preliminary. Further studies to probe the reactivity and structure of these ions are needed, particularly at low temperatures and under controlled ionization conditions.

3.2. Benzene–Isobutene Mixed Clusters. A. EI Ionization of the Mixed Clusters. In this section we examine the cluster ion distributions $B_mI_n^{•+}$ following the EI ionization of the mixed neutral clusters under variable experimental conditions. In this experiment, a coaxial quadrupole mass spectrometer is used with an electron-impact source to characterize the overall composition of the benzene–isobutene cluster beam, including such species as I_n clusters which are transparent in the laser photoionization experiments. Figure 5 exhibits a mass spectrum resulting from the 70-eV ionization of the mixed cluster beam generated from the expansion of a 37-mbar benzene, 2.6-mbar isobutene vapor mixture in 3100 mbar of He. The most prominent species in the mass spectrum are those containing $I_2^{•+}$, i.e. $I_2^{•+}B_m$ series. The persistent dominance of the clusters containing $I_2^{•+}$ ions is observed under a very wide range of clustering conditions (vapor composition, carrier gas, seed ratio, etc.) as well as different ionization energies. It should be noted that in all cases the distribution of the mixed cluster ions is characterized by a large intensity ratio of B_mI_2/B_mI and a small ratio of B_mI_3/B_mI_2. This observation suggests that the dominant fragmentation pathways of the $B_mI_2^{•+}$ and $B_mI_3^{•+}$ species involve the loss of a benzene or an isobutene, respectively, thus generating the $B_{m-1}I_2^{•+}$ and $B_mI_2^{•+}$ sequences, respectively. This provides further evidence for the stability of the $I_2^{•+}$ which again is totally consistent with the covalent bond nature of this ion quantitatively established in the preceding paper[15] and observed in the EI of neat isobutene clusters.

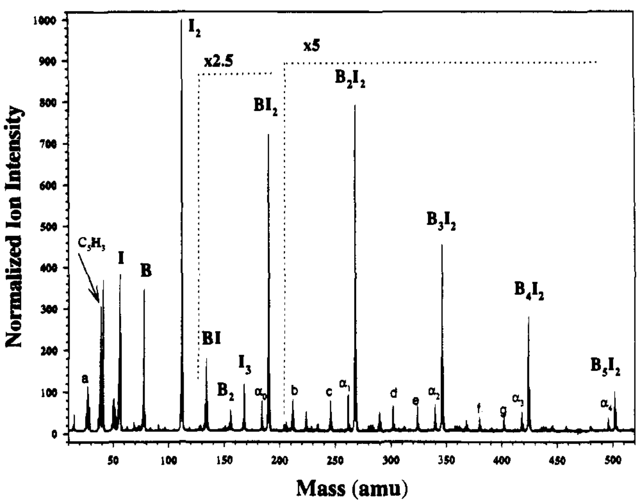


Figure 5. 70-eV, EI mass spectrum of isobutene (I)/benzene (B) mixed clusters (pre-expansion mixture: 2.6 mbar of isobutene and 37 mbar of benzene in 3100 mbar of He). Assignments for labeled peaks are (a) $C_2H_3^+$, (b) B_2I^+, (c) BI_3^+, (d) BI_4^+, (e) $B_2I_3^+$, (f) $B_2I_4^+$, (g) $B_3I_3^+$; the α_0 is tentatively assigned to $I_3H_2O^+$ (m/z 186) and α_n to $I_3H_2O^+B_n$.

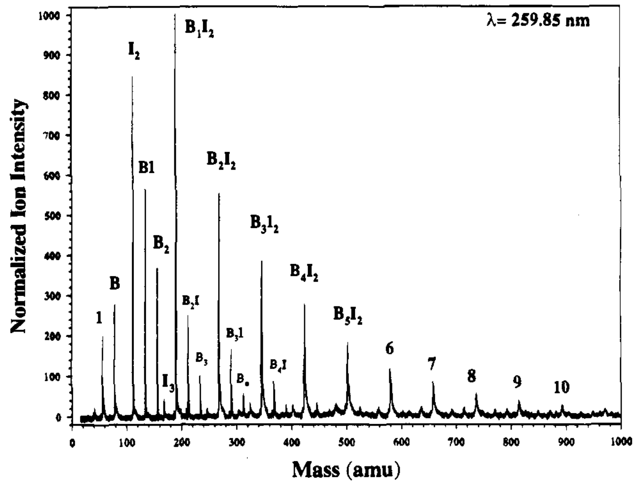


Figure 6. Mass spectrum of isobutene/benzene mixed clusters (I_nB_m) taken at $\lambda = 259.85$ nm, pre-expansion mixture: 155 mbar of isobutene, 100 mbar of benzene in 3100 mbar of He.

B. 6_0^1 R2PI of the Mixed Clusters. Selective ionization of the benzene–isobutene clusters could be achieved by using a frequency-doubled dye laser (4.5–5.0 eV) tuned to one of the sharp ultraviolet resonances of the benzene molecule. In this experiment, the mixed clusters were ionized by scanning the tunable radiation across the 6_0^1 resonance region of benzene and measuring the ions produced mass selectivity by TOF mass spectrometry. For neat isobutene clusters, i.e. in the absence of benzene, no ions could be detected in this frequency region by using the same laser power used in the photoionization of the mixed clusters. Therefore, all of the observed ions must be derived either from the mixed clusters I_nB_m or from the neat benzene clusters, B_m. Figure 6 displays a representative mass spectrum of these clusters taken at a wavelength longer than isolated benzene's resonance. Overall spectra of these types were obtained over a wide range of composition (i.e. relative concentration of benzene to isobutene in the expansion), stagnation pressures, seed ratios, and laser powers. On the basis

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[28] Agnihotri, R. K.; Falcon, D.; Fredericks, E. C. J. Polym. Sci., Part A 1972, 10, 1839. Stolka, M.; Vodehnal, J.; Kossler, I. J. Polym. Sci., Part A 1964, 2, 3987.

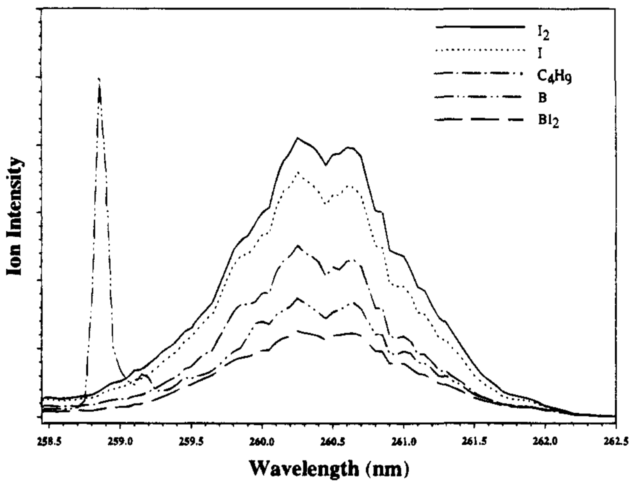

Figure 7. Integrated ion intensities as a function of wavelength recorded for the mass channels corresponding to benzene (B), isobutene (I), benzene–isobutene$_2$ (BI_2), isobutene dimer (I_2), and C_4H_9 cation. Expansion conditions are 273 mbar of isobutene and 99 mbar of benzene in 3100 mbar of He.

of the analysis of these spectra, the following major features were established:

1. All the mixed clusters exhibit absorption features shifted to the red with respect to the isolated benzene's 6_0^1 transition (Figure 7) and the clusters containing more benzene molecules are more red shifted. However, the photoabsorption spectra (or equivalently, ion intensity spectra) of all the mixed clusters show very similar features. Therefore, the spectral intensity observed at each mass channel cannot be associated with the corresponding neutral I_nB_m cluster. This is clearly seen in Figure 7 which displays the integrated ion intensities recorded in different cluster mass channels as a function of the laser wavelength. The appearance of unresolved broad features and the lack of detailed structures indicate that extensive fragmentation takes place following the ionization process which, in turn, suggests that significant geometrical changes and major structural reorganization accompany ionization. It should also be noted that the generation of larger mixed clusters I_nB_m and not just clusters containing a single chromophore (i.e. I_nB) leads to clusters that are usually too warm to observe sharp absorption features. The post-ionization processes, including the intracluster ion–molecule reactions, will be discussed in more detail in Section 3.D.

2. Among the observed cluster ions, the series containing the isobutene dimer and several benzene molecules, i.e. $I_2^{\bullet+}B_m$, again exhibits a remarkable intensity enhancement at all wavelengths (where the mixed clusters absorb) and over a wide range of expansion conditions including the relative concentration of isobutene–benzene vapor which controls the composition of the neutral clusters. The trend of the enhanced intensity of the species with $m > 2$ is observed at longer wavelengths but in all cases the intensity of the isobutene dimer ion ($I_2^{\bullet+}$) is a maximum. This trend suggests that, independent of wavelength, the series $I_2^{\bullet+}B_m$ undergoes extensive evaporation by sequential loss of benzene molecules which results in an unusual abundance of the $I_2^{\bullet+}$ ion. This result is similar to the patterns observed in the EI ionization of the mixed clusters which provides further support for the intracluster formation of a covalently bonded isobutene dimer ion.

3. Another interesting feature of the $I_2^{\bullet+}B_m$ clusters is the lack of any significant abundance of the $I_n^{\bullet+}$ ions with $n > 2$. The dependences of the ion intensities of the $I_n^{\bullet+}$ series on the laser wavelength and on the mixing ratio of isobutene:benzene in the pre-expansion vapor mixture have been investigated. The results indicate that while the generation of the $I_2^{\bullet+}$ ion is very efficient under all conditions, no such efficiency is found for the $n > 2$ ions such as $I_3^{\bullet+}$ or $I_4^{\bullet+}$. This observation appears to be a direct result of the covalently bonded nature of $I_2^{\bullet+}$ with the assumption that larger $I_n^{\bullet+}$ containing species consist of an $I_2^{\bullet+}$ core with several isobutene or benzene molecules weakly bound to it.

4. The enhanced intensity pattern of the $I_2^{\bullet+}$ ion observed under a wide variety of experimental conditions within the two-photon ionization process is not observed under high laser fluences where the absorption of more than two photons by the mixed cluster is expected. At higher laser intensities multiphoton absorption by the mixed clusters takes place as indicated by the appearance of chemical fragment ions from both benzene and isobutene in the mass spectra. We note that the ion intensity of $C_4H_8^{\bullet+}$ increases with increasing fragmentation in the mass spectra and this can be explained by dissociative charge transfer from excited benzene ions within the BI complexes followed by unimolecular fragmentation of the isobutene ion. We also note that the increase in the intensity of $C_4H_8^{\bullet+}$ is accompanied by a significant increase in the intensity of $C_4H_9^+$ and a decrease in the intensity of the $I_2^{\bullet+}$ ion. For example, the ion intensity ratio $I_2^{\bullet+}/C_4H_9^+/I^{\bullet+}$ is 1.0:0.25:0.62 and 0.74:0.56:1 at low and high laser fluences, respectively. This observation suggests that the dissocaiton of $I_2^{\bullet+}$ can take place under high laser intensity where the absorption of more than two photons is likely. This is also supported by the observation of characteristic fragments of $I_2^{\bullet+}$ such as $C_7H_{13}^+$ and $C_5H_9^+$ under high laser intensity. Since no isobutene ions could be produced in the absence of benzene-containing clusters even under the highest laser fluence used for the mixed clusters, we can eliminate the possibility of MPI of neat isobutene clusters. As an explanation of the dissociation of $I_2^{\bullet+}$ we may consider the possibility of $I_2^{\bullet+}$ or $BI_2^{\bullet+}$ absorbing a third photon within the length of the laser pulse (15 ns) and then fragmenting to generate $C_4H_8^{\bullet+}$ or $C_4H_9^+$. This would mean that the formation of $I_2^{\bullet+}$ is very fast which is consistent with the gas-phase measurements which indicate that the condensation reaction to form $I_2^{\bullet+}$ occurs near the collision rate.[15]

5. To observe the benzene/isobutene system under gas-phase-like conditions, we carried out a brief attempt to generate benzene ions inside the supersonic expansion during the early time of the production of clusters. In this experiment the dye laser, tuned to the 6_0^1 resonance of isolated benzene (λ = 258.85 nm), intersects the beam expansion within a distance X from the nozzle orifice such that $X/D = 10$, where D is the nozzle diameter (500 μm). Under the conditions of high density and multiple collisions, the benzene cations undergo direct charge transfer to isobutene molecules during the supersonic expansion. The isobutene cations, in turn, undergo a number of collision events with neutral isobutene molecules thus generating the covalent product $I_2^{\bullet+}$ as well as simple ionic clusters. A cluster ion continues to grow experiencing a number of collision events until it reaches the collision-free region. The length of the collision region (for a flat nozzle) is usually estimated to be about 20 times the nozzle diameter.[26] With the use of a conical nozzle taken into account, the length of the collision region in our setup could be much longer (estimated to be at least 5 cm). The ions are detected after about 1 ms using a coaxial quadrupole mass spectrometer as shown in the inset of Figure 8. The mass spectrum displayed in Figure 8 shows that the predominant species produced in this experiment is $I_2^{\bullet+}$. Another interesting feature is the observation of significant abundance of the $C_4H_9(C_4H_8)^+$ ($m/z = 113$) which

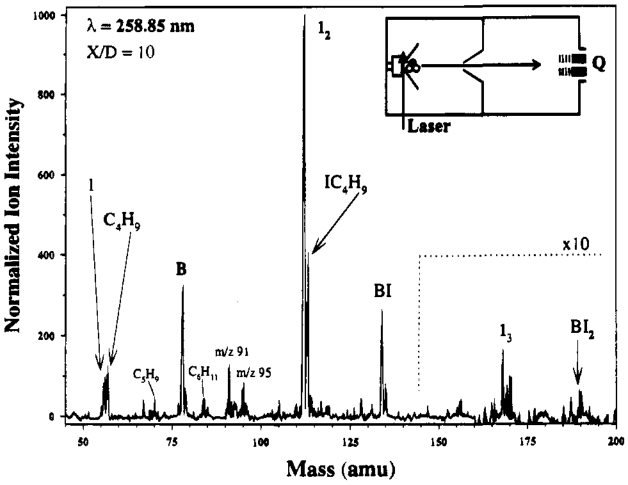

Figure 8. Mass spectrum obtained by R2PI of benzene monomer ($\lambda = 258.85$ nm) within the beam expansion.

represents the first step of the addition onto the carbocation $C_4H_9^+$. Indeed, the $C_4H_9^+$ cation is generated with a higher intensity than the $C_4H_8^{\bullet+}$ and the ion intensity of $C_4H_9(C_4H_8)^+$ represents more than 40% of the intensity of the dimer cation $C_8H_{16}^{\bullet+}$. Comparison with the cluster mass spectra also demonstrates the quenching effect of the cluster environment of the internal energy thus leading to more condensation product ($C_8H_{16}^{\bullet+}$) in the clusters. It is interesting to compare the R2PI in the supersonic expansion (Figure 8) with the R2PI of the preformed neutral clusters in the TOF mass spectrometer at the same wavelength ($\lambda = 258.85$ nm). In the latter experiment, the major species that can be ionized with this wavelength are single benzene molecules. Therefore the spectrum shown in Figure 8 provides evidence for charge transfer from the gas-phase benzene cations in the high-collision region of the beam expansion. It is interesting to note that the product ions produced by the intracluster charge transfer mechanism via the 259.85-nm ionization of the BI_n clusters (Figure 6) are very similar to those produced by the ionization of benzene at 258.85 nm in the gas phase under high-collision conditions. This observation demonstrates that the role of the cluster in stabilizing the reaction intermediate via evaporative cooling is very similar to the gas-phase collisional stabilization at high pressures.[11]

6. The final important feature of the R2PI-TOF experiment of the I_nB_m clusters is the observation of weak metastable peaks for all the species containing $C_4H_9(C_4H_8)_n^+$ ions with $n > 2$. This effect manifests itself in the broadening of the mass peaks as shown in Figure 9. Note that no such broadening is observed in ions containing less than three isobutene molecules, e.g. BI_2, B_2I_2, or B_3I_2. This effect is due to dissociation within the acceleration region of the TOF mass spectrometer. The outer part of the TOF mass peak (the longer time tail part) contains the fragmentation products and the hot ions. A typical time spent in the acceleration region of a 5000-V, 1-cm acceleration region is $0.05M^{1/2}$ μs, where M is the cluster mass in atomic mass units.[29] If the time scale for the fragmentation process from larger $C_4H_9(C_4H_8)_n^+$ ions is nearly the same or shorter than the time of acceleration in the mass spectrometer, metastable peaks will be observed. The significance of this observation and its relation to the kinetics of the addition reactions of the carbocation $C_4H_9^+$ will be addressed in section 4.

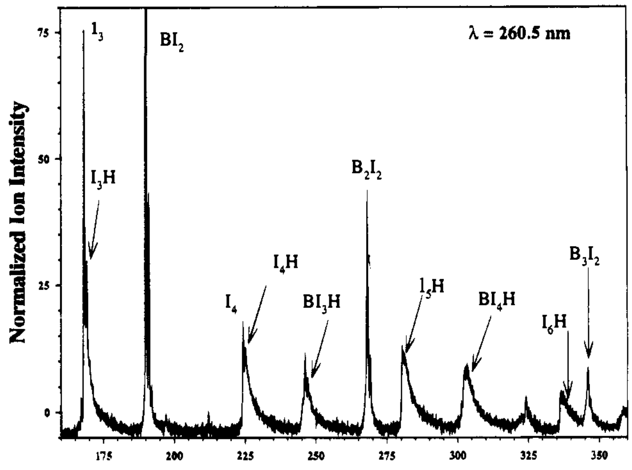

Figure 9. Metastable peaks observed for the series $C_4H_9(C_4H_8)_n^+$ with $n > 2$. Expansion conditions are 627 mbar of isobutene and 99 mbar of benzene in 3800 mbar of He.

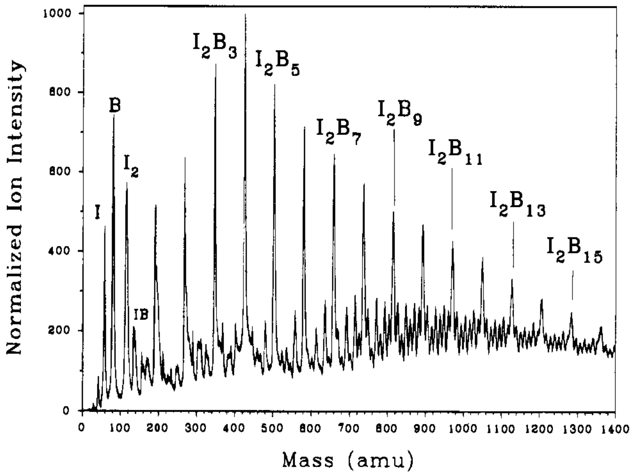

Figure 10. Mass spectrum of isobutene/benzene mixed clusters (360 mbar of isobutene and 38 mbar of benzene in 1700 mbar of He) taken at 248-nm and 60-mJ/pulse averge excimer laser output.

C. 248- and 193-nm Multiphoton Ionizations of the Mixed Clusters. To investigate the effect of the ionizing energy, multiphoton ionizations of the benzene–isobutene clusters using the 248- and 193-nm photons were investigated. In the absence of benzene in the beam expansion no isobutene ions could be generated at these wavelengths under power density conditions identical to those used to ionize the mixed clusters.

Figure 10 exhibits the mass spectrum obtained at 248 nm for the clusters generated from the expansion of a 38:360:1700 mixture of B:I:He at a total stagnation pressure of 2 bar. A similar mass spectrum was obtained at 193 nm. In both cases the cluster ion distribution is almost exclusively populated with the $I_2B_m^{\bullet+}$ series. Note that the concentration of isobutene is much higher than that of benzene in the pre-expansion mixture, yet the distribution is still dominated by the $I_2B_n^{\bullet+}$ series. This is very similar to the distributions obtained from the 6_0^1 resonance or the EI ionizations of the mixed clusters. These results clearly reflect the covalent bonded nature of the $I_2^{\bullet+}$-($C_8H_{16}^{\bullet+}$) ion.

D. Discussion of the Benzene–Isobutene Mixed Clusters. The mass spectrometric features observed for the benzene–isobutene clusters can be explained in terms of the post-ionization processes within the clusters. The energies of the two photons used in the 6_0^1 resonance (259–261 nm), 248- and 193-nm photoionization experiments are above the IP of benzene

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[29] Whetten, R. L.; Hahn, M. Y. In *Atomic and Molecular Clusters*; Bernstein, E. R., Ed.; Elsevier Science Publishing Company Inc.: New York, 1990; p 765.

[30] Long, S. R.; Meek, J. T.; Reilly, J. P. *J. Chem. Phys.* **1983**, *79*, 3206.

by about 0.3, 0.8, and 3.6 eV, respectively. Of course, the IP of the mixed cluster is lower than that of benzene and it further decreases with increasing cluster size, with more pronounced changes for smaller clusters.[11] Although a significant portion of the cluster's energy is carried away by the photoelectrons during the ionization process,[30] the quantity $2h\nu$ − IP (B_mI_n) can still be regarded as an upper estimate of the energy available to the ionized cluster B_mI_n. The redistribution of this energy within the intermolecular modes of the cluster will lead to van der Waals (vdw) fragmentation which involves monomer evaporation from the cluster ion. Besides vdw fragmentation, the cluster rearranges in the ionized state via direct or concerted charge transfer processes which also release more excess energy. A direct charge transfer from benzene$^+$ to isobutene will generate the $C_4H_8^{\bullet+}$ ion which then undergoes the competitive proton transfer and the dimerization reactions to generate the $C_4H_9^+$ and $C_8H_{16}^{\bullet+}$ ions, respectively. The formation of the covalent bonded dimer cation $C_8H_{16}^{\bullet+}$ or the sequential additions to $C_4H_9^+$ to form the polymeric ions $C_4H_9(C_4H_8)_n^+$ will result in significant intracluster energy which will promote extensive evaporation of the weakly bound isobutene and benzene molecules from the cluster. The observation of the unusual abundance of the $I_2B_m^{\bullet+}$ series under variable clustering and ionization conditions (EI, 6_0^1 resonance, 248 and 193 nm) provides strong evidence for the intracluster formation of a covalent bonded $C_8H_{16}^{\bullet+}$ ion. The exothermicity of this reaction causes the evaporation of nearly all the nonreacted isobutene molecules from the cluster. This suggests that very large clusters are needed in order to accommodate the energy released from the polymerization and still leave a reasonable distribution of the nonreacted monomers. This also suggests an interesting role for mixed clusters containing weakly bound solvent molecules to remove the extra energy through fast evaporation. In this context, the use of *n*-alkanes as solvent molecules in mixed clusters, e.g. isobutene/*n*-pentane, would be useful. It is interesting to note that in the bulk polymerization of isobutene, *n*-pentane is typically used as an internal coolant for the evaporative control of temperature.[13]

It is interesting to speculate about the mechanism of formation of the $C_8H_{16}^{\bullet+}$ ion following the ionization of the mixed clusters. In other experiments, we photoionized benzene in a benzene/isobutene mixture in an HPMS source and found that both the addition reaction of $C_4H_8^{\bullet+}$ and exchange reaction of $C_6H_6C_4H_8^{\bullet+}$ with neutral isobutene contribute to the formation of $I_2^{\bullet+}$ in the gas phase.[31] In clusters, the formation of $I_2^{\bullet+}$ could take place by two mechanisms. The first involves direct charge transfer from $B^{\bullet+}$ to I followed by the reaction of $I^{\bullet+}$ to form $I_2^{\bullet+}$ within the cluster. This mechanism is known to be very dominant when exothermic as in the case of BI_n. The second mechanism involves charge transfer from $B^{\bullet+}$ to I concerted with the formation of $I_2^{\bullet+}$ in a cooperative process. In fact, recent work in our laboratory indicates that this intracluster concerted mechanism is operating in the mixed clusters X_mI_n where X = toluene, phenyl acetylene, and *p*-xylene, where the IP's are lower than that of isobutene but higher than the IP of the dimer.[32] With 1,2,4-trimethylbenzene, where the IP is lower than the IP of I_2, the formation of I_2^+ was not observed. These observations strongly support a mechanism of charge transfer concerted with condensation. The details of this study will be the subject of a separate report.[32]

4. Comparison with the Gas Phase and Implications for the Condensed Phase The results reported here for clusters demonstrate a remarkable consistency with the gas-phase kinetics and thermochemistry data reported in paper 1.[15] For comparison, the following major features are established:

(i) The observation of magic number behavior corresponding to $I_2^{\bullet+}$ and $I_2B_m^{\bullet+}$ species in neat isobutene and mixed isobutene−benzene ionic clusters, respectively, is in complete accord with the covalent bonded nature of the isobutene dimer cation established from the measured lower limit of the dissociation energy (132 kJ/mol) in HPMS (paper 1).[15] Another indication for the formation of intracluster covalent bonded $I_2^{\bullet+}$ comes from the observation of characteristic fragment ions corresponding to dissociation products of the excited dimer cation. Also, the H_2 transfer reaction from $I_2^{\bullet+}$ to isobutene has been observed both in the gas phase and in clusters and the product ion $C_8H_{14}^{\bullet+}$ appears unreactive toward further additions. The study of clusters also suggests that the isobutene trimer radical cation could also be a covalent adduct (probably cyclic) particularly under cold beam conditions and low ionization energy.

(ii) The IP value of the isobutene dimer (8.55 ± 0.15 eV) determined from a bracketing experiment in the gas phase (paper 1)[15] is consistent with the observation of a magic number ($I_2B_m^{\bullet+}$) within the sequence $I_nB_m^{\bullet+}$ with $m = 1-5$. Furthermore, the observation of a gradual increase in the intensity of the $I_2B_m^{\bullet+}$ series with decreasing *m* coupled with the weak $IB_m^{\bullet+}$ series strongly suggests that the dominant evaporation process after the formation of an $I_2^{\bullet+}$ core ion is the loss of benzene, whereas I is not lost from $I_2^{\bullet+}$. This is consistent with the estimated IP of I_2 which is lower than the IP of small benzene clusters such as $(C_6H_6)_5$.[11] As mentioned above, recent work in our laboratory[32] indicates that photoionization of the mixed clusters X_mI_n, where the IP(X) < IP(isobutene), results in the formation of $I_2^{\bullet+}$ only when IP(X) > IP(I_2). That work[32] estimates the IP of I_2 as 8.45 ± 0.1 eV in good agreement with the bracketing value determined from the gas-phase study.

(iii) The results concerning clusters indicate that the formation of the dimer cation is more favorable than that of the carbocation under the cold beam conditions. This is consistent with the gas-phase behavior where the condensation channel increases at low temperatures.[15] Also, the decrease of the t-$C_4H_9^+$ condensation channel with increasing cluster size, where energy dissipated to the cluster modes becomes more efficient, is consistent with the gas-phase temperature dependence.[15]

(iv) The observation of metastable peaks associated with the *tert*-butyl cation series $C_4H_9(C_4H_8)_n^+$, $n > 2$, in the TOF experiment indicates a significant change in the rate of the addition reactions past $n = 2$. This is consistent with the gas-phase measurements which showed that the second polymerization step leading to the formation of $C_4H_9(C_4H_8)_2^+$ exhibits an unusually large entropy change ($\Delta S° = -204$ J/(mol K)).[15] Therefore, the observation of metastable peaks in the cluster experiment suggests the existence of the same steric barrier past $n = 2$ which manifests itself in a slower rate of the subsequent polymerization steps. These slow exothermic polymerization steps are delayed after the ionization and occur in the acceleration region where they trigger the cluster's dissociation and induce the broadening of the associated mass peaks. Alternatively, the $C_4H_9(C_4H_8)_n^+$ adducts form rapidly after ionization and then dissociate slowly due to the same steric barrier in the reverse direction or to stronger binding energies as compared to the radical cation adducts.

It is useful to discuss the cluster results in relation to the bulk polymerization of isobutene. The present data suggest that at low temperatures and under the conditions of low ionizing energy, it is possible to exclusively produce dimers and trimers through the condensation reactions of the radical cation $C_4H_8^{\bullet+}$.

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(31) Daly, G. M.; El-Shall, M. S. Unpublished results.

(32) Yu, Z.; El-Shall, M. S. *J. Phys. Chem.* To be submitted for publication.

Note that the cluster data suggest that at low ionization energy, cyclization of the trimer could take place. It is interesting to note that Viswanathan and Kevan carried out photoionization experiments of isobutene (10.0−10.6 eV) in the vapor phase followed by ion injection into liquid isobutene at −128 °C.[33] Analysis of the products by gas chromatography showed that C_8 and C_{12} compounds comprised all the detectable products. Although the authors concluded that both t-$C_4H_9^+$ and $C_4H_8^{\bullet +}$ ions were striking the liquid, no mass spectrometric measure of the ratio of t-$C_4H_9^+/C_4H_8^{\bullet +}$ was made in the vapor phase. From the results of the present work and considering the low temperature and low photon energy used in Viswanathan and Kevan's experiments, it is quite likely that under their conditions the detected C_8 and C_{12} products were mainly produced by the condensation reactions of the radical cation $C_4H_8^{\bullet +}$ and not the t-$C_4H_9^+$.

In relation to the carbocation channel, we note that the high-energy γ-ray induced cationic polymerization is rationalized to occur via the propagation of t-$C_4H_9^+$ produced from the ion−molecule reaction of $C_4H_8^{\bullet +}$ with C_4H_8.[34] It is interesting to note that a recombination reaction between t-$C_4H_9^+$ and $C_4H_7^{\bullet}$ was proposed to explain the formation of the dimer radical cation in this system.[35] This is consistent with our observation of an increase in the intensity of $C_4H_9^+$ accompanied by a decrease in $C_8H_{16}^{\bullet +}$ under high laser power where the absorption of three photons can take place.

5. Conclusions

The combination of gas-phase and cluster studies on the isobutene system leads to some important conclusions which can improve our understanding of the early stages of cationic polymerization. These conclusions are summarized as follows:

1. The formation of a covalently bonded isobutene dimer radical cation is well demonstrated in the gas phase and in clusters. The evidence also suggests the formation of a cyclic covalently bonded trimer in clusters. These adducts also undergo H_2 transfer yielding unsaturated ions that do not polymerize further. These stable condensation products are not likely to propagate to larger polymers in the condensed phase either, and this is consistent with the fact that bulk polymerization of isobutene to high molecular weight polymers can only proceed by carbocationic propagation.

2. The steric entropy barrier observed in the gas-phase study for the second step of the carbocation propagation, i.e. formation of $C_4H_9(C_4H_8)_2^+$, is also present in clusters. This effect leads to slower propagation steps past the dimer formation in the carbocation channel. This barrier explains the need for low temperatures for the bulk polymerization of isobutene via the carbocation propagation.

3. The results in the gas phase and in clusters indicate that a higher ratio of the carbocation to the radical cation, i.e. $C_4H_9^+/C_4H_8^{\bullet +}$, can be produced by higher ionizing energies. This suggests that the use of high-energy photons may be efficient to initiate the carbocation polymerization. This is also consistent with the high efficiency of radiation-induced polymerization in bulk isobutene.

4. The main features of the gas-phase chemistry—covalent $I_2^{\bullet +}$ formation, increase of t-$C_4H_9^+$ formation with increasing energy, and steric entropy barrier to the polymerization of t-$C_4H_9^+$—carry over from the gas phase to the cluster (and possibly condensed phase). However, the cluster phase also exhibits unique cooperative phenomena such as concerted charge transfer/condensation.

5. The cluster study suggests that covalently bonded products of well-defined molecular mass are formed in cluster species. It would be possible, in principle, to mass select these covalently bonded products from a cluster beam and probe their structures and reactivity. It is also suggested that deposition of these mass-selected products from the gas phase on clean surfaces may lead to the production of ultrathin polymeric films of well-defined composition and narrow size distribution which could have several technological applications.

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Supporting Information Available: Figures showing the dependences of the ion intensity ratio $C_4H_9(C_4H_8)_{n-1}/(C_4H_8)_n$ on carrier gas and electron energy, normalized ion intensity of benzene/isobutene clusters, wavelength and laser fluence dependences, and mass spectrum obtained by 193 nm photoionization (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA950856H

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