Cationic polymerization within clusters composed of unsaturated molecules

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Cationic polymerization within clusters composed of unsaturated molecules

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Electron impact ionization of large neutral clusters composed of simple olefinic molecules (ethene, 1,1-difluoroethene and propene) display highly anomalous ion intensity distributions. These cluster ion distributions typically exhibit a magic number at $n = 4$, for cluster ions of the type $\{M\}_n^+$, where M is an olefinic molecule. The explanation which best explains this observation is that these small 'cluster' ions are in actuality covalently bound molecular ions formed by sequential ion–molecule association (polymerization) reactions which have occurred within the cluster ion. This size dependent cluster chemistry is accounted for by kinetic bottlenecks which occur in the ionic chain growth reactions and which terminate with the formation of cyclic molecular ions (i.e. cyclopentanes and cyclohexanes ions). The condensed phase counterparts of these intracluster reactions are the free cationic polymerization reactions initiated by radiolysis of bulk samples of the olefins. In addition to reviewing our own efforts in this field, we will discuss previous work on cationic polymerization which is relevant to the new chemistry we have observed within clusters of olefinic molecules. We also will present work concerning acetylene and methylacetylene cluster ions where we also observe similar intracluster ion–molecule reactions giving rise to what are most likely benzene and trimethylbenzene ions. Lastly, we will show how mixed cluster of acetylene–acetone also are capable of producing covalently bonded cyclic molecular ions again via intracluster ion–molecule polymerization reactions. We therefore feel that these new cluster condensation reactions constitutes a more general family of chemical reactions for *all* cluster ions containing unsaturated molecules.

1. Introduction

The study of chemical reactions within van der Waals clusters is especially intriguing since clusters can conceptionally bridge the disparate fields of bimolecular gas-phase reaction dynamics and solution chemistry. In particular clusters composed of olefins have proven to be a very intriguing class of molecules to study via the technique of cluster ion mass spectrometry [1–3] since the ion chemistry of the olefins (particularly ethene) has been extensively studied both in the gas and condensed phases. Indeed, the reactivity of the olefins is dramatically dependent on the state of 'solvation' (or more precisely density). Thus, one might expect a marked variation in reactivity as a function of cluster size similar to that observed in the production of protonated cluster ions [4–17]. For olefins under bimolecular conditions, the products of single ion-molecule reactions are observed [18] yet at higher pressures and in the condensed phase, the olefin monomers may be induced to oligomerize and/or polymerize [19, 20]. Free cationic polymerization has been suggested as one of the modes of reaction propagation in these systems.

We have for the past 2 years studied the cluster ion chemistry of several olefin molecules, namely ethene [1], 1,1-difluoroethene (DFE) and propene [2, 3]. The cluster mass spectrum (CMS) of all of these molecules were characterized by the appearance of extremely anomalous ion intensity distributions (i.e., magic numbers) only under molecular beam expansion conditions which would be expected to favour generation of large neutral clusters. The raw mass spectra for these three systems are shown in figure 1. The initial observation of such strong magic numbers in the olefin CMS came as something of a surprise to our group. These magic numbers cannot be satisfactorily explained in terms of solvation shell structures since the strong hydrogen-bonding interactions encountered in the systems discussed in previous papers [21, 22] are not expected to play a significant role in olefin clusters. As will be discussed below, magic numbers in olefinic clusters seem to be best explained in terms of the kinetics of
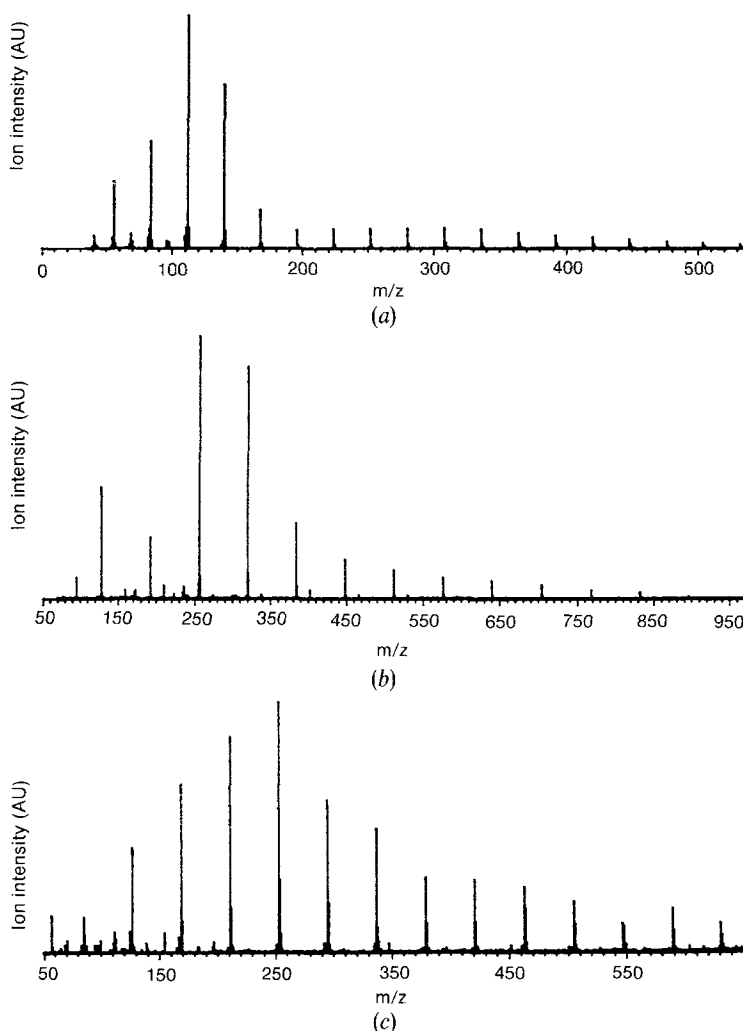

Figure 1.   Raw cluster mass spectra of van der Waals clusters, formed via electron impact ionization: (*a*) ethene clusters; $E_e = 13\,\text{eV}$, $T_0 = 296\,\text{K}$, $P_0 = 3\cdot5\,\text{atm}$. (*b*) 1,1-difluoroethene clusters; $E_e = 14\,\text{eV}$, $T_0 = 247$, $P_0 = 2\cdot2\,\text{atm}$. (*c*) propene clusters; $E_e = 10\,\text{eV}$, $T_0 = 297$, $P_0 = 4\cdot0\,\text{atm}$.
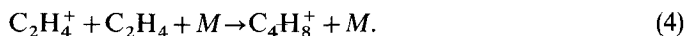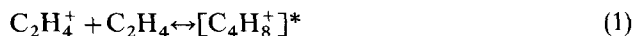
intracluster polymerization reactions, i.e. initiation and termination of a series of consecutive bond formation reactions, leading to the observation of molecular ions.

Since van der Waals clusters exist as finite aggregates in the gas phase they offer the experimentalist the unique opportunity to observe the products of reactions involving a *single ion in a solvated environment*. At the same time, additional complications associated with the need to maintain electroneutrality in the bulk (e.g. counterions, ion neutralization reactions, etc.) are, of course, avoided. These quantitative observations suggest that clusters may be useful media in which to observe such ionic polymerization processes.

1.1. *Ethene cluster ion chemistry*

1.1.1. *Low and medium pressure chemistry*

A discussion of the olefin ion chemistry is essential to an understanding of the CMS of van der Waals clusters containing unsaturated molecules. The ion–molecule chemistry of ethene has been studied extensively [23–33]. The majority of the observed bimolecular ion–molecule reactions of ethene proceed through a long lived intermediate, $C_4H_8^+$ (lifetime $\approx 2 \cdot 9 \times 10^{-7}$ s) [23]:

$$C_2H_4^+ + C_2H_4 \leftrightarrow [C_4H_8^+]^* \tag{1}$$

$$\rightarrow C_3H_5^+ + CH_3 \tag{2}$$

$$\rightarrow C_4H_7^+ + H, \tag{3}$$

$$C_2H_4^+ + C_2H_4 + M \rightarrow C_4H_8^+ + M. \tag{4}$$

Because of the high exothermicity of the C–C bond formation, the $\{C_4H_8^+\}^*$ intermediate is created in a highly excited state [32] and normally either back dissociates to reactants (reaction 1) or rearranges and decomposes (reactions 2 and 3). $C_3H_5^+$ is the favoured dissociation product, presumably because the heavier CH_3 fragment is more effective at removing excess energy from the products as translational energy.

Reactions (1–4) have been confirmed by high-pressure mass spectrometry, [23–26] ion cyclotron resonance studies [32] and tandem quadrupole (MS/MS) experiments [33]. These experiments have shown that the $C_4H_8^+$ intermediate can be efficiently generated through collisional stabilization of an excited intermediate, such that reactions (3) and (4) effectively are quenched. [24, 25]

At moderate ion source pressures, or in an ion cyclotron resonance mass spectrometer, a series of consecutive ion molecule addition reactions could also be detected [23, 27, 32, 33]. Gas phase chemists use the term 'condensation reaction' to describe this type of bond forming reaction. However, a large portion of the chemical community would describe such a reaction as an 'addition reaction', while the term 'condensation reaction' would describe a bond formation reaction accompanied by the expulsion of a small neutral molecule. In this manuscript we shall therefore adopt the more common usage of the term addition reactions.

The most important series of addition reactions result in the production of the $C_5H_9^+$ ion. The actual mechanism for formation of this ion was unclear with two likely possibilities considered. Field [23] proposed the $C_5H_9^+$ ion arose from alkyl loss from a higher-order addition reaction:

$$\{C_4H_8^+\}^* + C_2H_4 \rightarrow \{C_6H_{12}^+\}^*$$

$$\rightarrow C_5H_9^+ + CH_3. \tag{5}$$
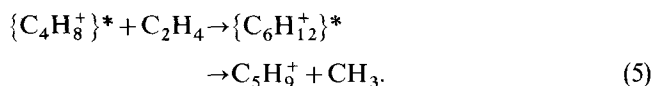
Tiernan and Futrell [28] proposed that it arose as a result of an addition reaction involving the product of reaction (2):

$$C_3H_5^+ + C_2H_4 \rightarrow C_5H_9^+. \tag{6}$$

Subsequent experiments conducted by Kebarle and Haynes, [25] Tiernan and Futrell [28] and Mitchell and Tedder [33] have shown that both reactions (5) and (6) contribute to the production of the $C_5H_9^+$ ion but that the rate constant for reaction (6) is much larger.

1.1.2. Kebarle's high pressure work

The results obtained by Kebarle and coworkers [24–26] have proven particularly valuable in understanding the CMS of ethene and will thus be considered in some detail. The experimental set-up employed by these workers consisted of a mass spectrometer equipped with a near-atmospheric pressure ion source. This ion source might be loosely described as a preionized expansion source, since a partially ionized gas is allowed to expand through a small orifice. Under these conditions the ions may be expected to undergo many thousands of collisions prior to detection.

Kebarle and coworkers observed [24–26] that an increase in the concentration of ethene in the ion source (at constant total pressure) led to the observation of 'polymer' ions, $(C_2H_4)_n^+$. These ions could be observed even at ion source temperatures that were sufficient to quench the formation of water cluster ions in water containing 'expansions' of the same pressures. Since the interactions present in weakly bound ethene *cluster ions* would not likely be stronger than the hydrogen bonding interactions of water cluster ions, it was concluded that the ions observed in the ethene experiments were covalently bound molecular ions.

The surprising finding of these studies was that the disappearance of smaller ions $(C_2H_4^+, C_4H_8^+$ and $C_6H_{12}^+)$ was not accompanied by the production of increasingly larger polymer ions. Instead, large increases in the intensities of the $n = 4$ $(C_8H_{16}^+)$ and $n = 5$ $(C_{10}H_{20}^+)$ ions were observed with sharp drops in all ion intensities beyond $n = 5$. This unexpected result indicated that the gas phase free cationic polymerization of ethene is a very inefficient process which produces only low molecular weight products, i.e. oligomers. The origin of this inefficiency was found to lie in the kinetics of the ion–molecule addition reactions. By applying a steady state assumption, and assuming a rate constant for the first addition reaction of $k_{12} = 1 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, the rate constants of the successive higher order reactions were estimated to be $k_{23} = 2 \times 10^{-12}$, $k_{34} = 8 \times 10^{-13}$, $k_{45} = 2 \times 10^{-13}$ and $k_{56} = 8 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. The dramatic drops in the sequential addition reaction rate constants were attributed to steric effects inhibiting any further reactions, possibly due to the formation of branched carbocations.

1.1.3. Condensed phase studies

The reactions initiated by irradiating solid ethene with high energy electrons has been examined by Wagner [34, 35]. These studies are particularly interesting since the experimental methods employed are conceptually quite similar to our own gas phase clusters studies. The results of the condensed phase studies were interpreted in terms of two sets of polymerization reactions, one involving free radicals and the other involving ionic species. The ionic reactions were found to be very inefficient, apparently producing products only up to around $C_{12}H_{24}^+$. It was suggested that the inefficient nature of the ionic reactions arose from rapid quenching of the polymerization

reactions by recombination of the growing ion by geminate electrons. The conclusions drawn from both the condensed phase and high pressure ion source experiments are then essentially identical: free cationic polymerization of ethene is not an efficient process and yields only low molecular weight oligomers.

1.1.4. *Previous cluster ionization studies*

We will conclude this introductory Section with a discussion of other studies of ethene clusters which have appeared in the literature. Ceyer *et al.* [36] have investigated the photoionization of ethene clusters and concluded that the ions with empirical formulae $C_{2m}H_{4m}^+$ and $C_{2m+1}H_{4m+1}^+$ represented $C_4H_8^+$ and $C_3H_5^+$ ions solvated by ethene molecules, i.e. the solvated products of a *single* ion molecule reaction. Buck *et al.* [37] studied the fragmentation of size selected neutral clusters following 50 eV electron impact ionization, using a crossed He beam to achieve size selection. This work showed that ionization resulted in extensive fragmentation of the clusters such that the probability of observing the $C_4H_8^+$ ion was found to increase rapidly for $(C_2H_4)_{n>5}^+$ cluster ions. These results were taken as an indication that the fragmentation behaviour is dominated by the ion–molecule chemistry of a *single* $C_2H_4^+$ ion within the cluster. A different conclusion was drawn from a reinvestigation of ethene cluster photoionization undertaken by Ono *et al.* [38] and Tzeng *et al.* [39]. Based on the photoionization efficiency curves and pressure behaviour of the product ions it was concluded that the ethene trimer ion isomerizes into a $C_6H_{12}^+$ intermediate ion prior to decomposing. This conclusion, of course, implies the occurrence of at least a two sequential addition reaction within the cluster ion.

1.2. *1,1-difluoroethene*

The ion molecule chemistry of 1,2-difluoroethene (DFE) has been studied by ion cyclotron resonance mass spectrometry as part of a thorough study of fluoroethene ion–molecule chemistry [40]. The ion–molecule chemistry of DFE was found to differ in several respects to that of ethene and the other fluoroethene's. At low pressures (e.g. 10^{-5} Torr) all of the other fluoroethene molecular ions reacted with the neutral molecules to form a complex which ejected a methyl or substituted methyl radical, analogous to ethene. DFE, by contrast, showed only one product at low pressures, that being the dimer ion. This product was produced, presumably, by a third-order reaction:

$$C_2H_2F_2^+ + C_2H_2F_2 \rightarrow [C_4H_4F_4^+]^* \xrightarrow{M} C_4H_4F_4^+, \tag{7}$$
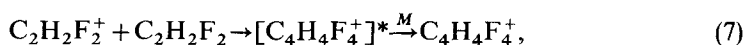
where $M = C_2H_2F_2$.

The overall third-order rate constant for reaction (7) was calculated to be $1.1 \pm 0.2 \times 10^{-24}$ cm^6 molecule^{-2} s^{-1}. It was noted that this value is very high in comparison to typical third-order reactions which range from 10^{-29}–10^{-26} cm^6 molecule^{-2} s^{-1}. It was suggested that this high rate constant might originate from an unusually stable structure of the dimer ion.

At higher pressures it was found that the $C_4H_4F_4^+$ ion reacted further to give a large variety of product ions including the collisionally activated losses of, respectively, CH_3, CH_2F and CHF_2 radicals from the dimer. No mention is made of formation of higher order products (such as the trimer, $C_6H_6F_6^+$).

1.3. The ion chemistry of propene

The ion–molecule chemistry of propene has been studied less extensively then ethene. The studies most relevant to our present work were those of Abramson and Futrell [41] and Mitchell and Tedder [33]. The majority of the bimolecular reaction products in the propene system are thought to arise, as in the case of ethene, from decomposition of a long-lived reaction intermediate.

$$C_3H_6^+ + C_3H_6 \leftrightarrows [C_6H_{12}^+]^* \rightarrow C_4H_7^+ + C_2H_5 \tag{8}$$

$$\rightarrow C_4H_8^+ + C_2H_4 \tag{9}$$

$$\rightarrow C_5H_9^+ + CH_3. \tag{10}$$
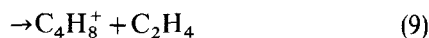
The tandem MS/MS experiments [33] revealed that these secondary ions were capable of also undergoing several addition reactions with the propene molecule.

2. Ion clusters composed of molecules containing C=C bonds

2.1. $\{CH_2=CH_2\}_n^+$ cluster ions

Figure 1 (a) displays a portion of the ethene CMS under conditions which may be expected to favour the growth of large neutral clusters. The CMS is dominated by a series of ions whose empirical formulae correspond to stoichiometric ethene clusters, $(CH_2=CH_2)_n^+$. Under these experimental conditions it is possible to observe ethene clusters with $n > 20$ and are the largest such ions to have been observed. The most striking feature of the ethene CMS is the strong maximum (magic number) at $n = 4$ and a strong drop in ion intensity at $n > 5$. These features have proven to be the keys to understanding the chemical behaviour of ethene cluster cations.

Figure 2 displays plots of the intensities of the stoichiometric ethene cluster ions under a variety of expansion conditions. The data displayed demonstrate that conditions favouring generation of larger neutral clusters lead to a sharp peaking of the cluster ion intensity distributions occurs at $n = 4$. The intensity of the $n = 5$ ion is also seen to rapidly increase throughout the range of molecular beam expansion conditions which could be studied (backing pressure behind nozzle = P_0, nozzle temperature = T_0). It is interesting to note that the intensities of the $n = 2$ and 3 ions are dramatically decreased under efficient clustering conditions. The intensities of the ions with $n > 5$ becomes slightly more intense as larger clusters are ionized. The intensity distribution for these larger cluster ions only become broader with either increasing P_0 or decreasing T_0 with an absence of any additional magic numbers.

2.2. $\{CF_2=CH_2\}_n^+$ cluster ions

Figure 1 (b) displays a portion of the 1,1-difluoroethene (DFE) CMS under conditions favouring efficient clustering. The similarity between the DFE and ethene CMS (figure 1 (a)) is immediately apparent. Both spectra are dominated by stoichiometric cluster ions whose intensity is strongly peaked at $n = 4$. Both the DFE and ethene CMS also show a strong drop in ion intensity for $n > 5$. The DFE CMS also displays a number of fairly weak peaks corresponding to non-stoichiometric cluster ions for $n < 6$. The precise identity and relative intensities of these 'fragment' ions vary considerably with n.

The effect of expansion pressures on the stoichiometric ion intensity distributions is shown in figure 3. The qualitative behaviour of DFE cluster ions and ethene cluster ion as a function of expansion conditions are found to be nearly quantitatively identical.

We have also examined the effect of the electron impact energy (E_e); and the results for DFE clusters are shown in figure 4. An overall increase in ion intensity is observed
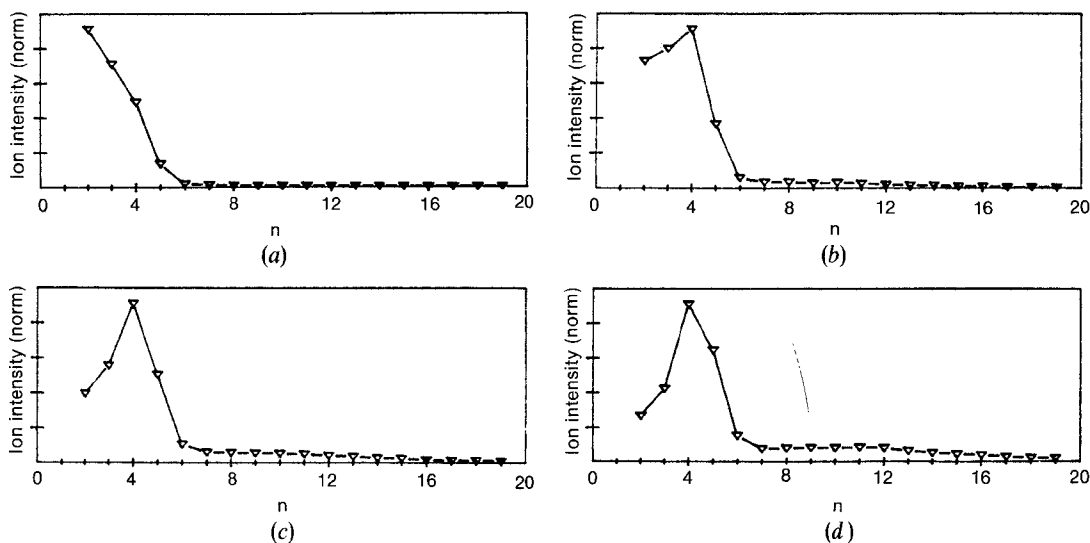
Figure 2. Expansion pressure dependence of ethene cluster ion distribution; ion intensity of $\{C_2H_4\}_n^+$ as a function of n. $T_0 = 296$ K, $E_e = 13$ eV. (a) $P_0 = 2\cdot2$ atm., (b) $P_0 = 2\cdot5$ atm., (c) $P_0 = 3\cdot0$ atm., (d) $P_0 = 3\cdot5$ atm.
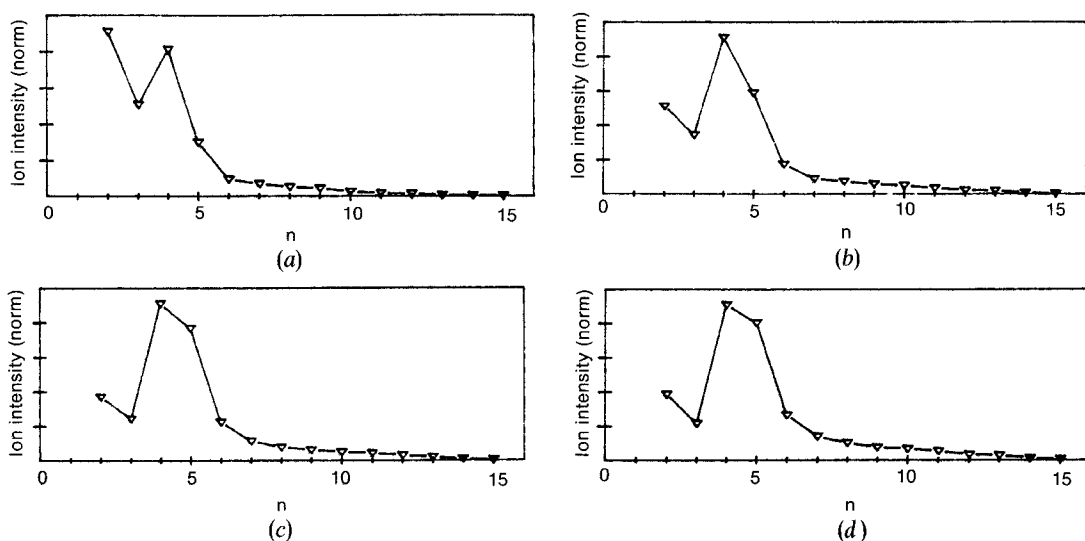
Figure 3. Expansion pressure dependence of 1,1-difluoroethene cluster ion distribution; ion intensity of $\{C_2F_2H_2\}_n^+$ as a function of n. $T_0 = 247$ K, $E_e = 14$ eV. (a) $P_0 = 1\cdot1$ atm., (b) $P_0 = 1\cdot5$ atm., (c) $P_0 = 1\cdot8$ atm., (d) $= 2\cdot2$ atm.

between 13 eV and 100 eV which is expected on the basis of the larger ionization cross-sections associated with higher energy electrons [42]. It can also be seen that an increase in the electron impact ionization energy appears to favour the production of ions with $n < 6$ such that the relative intensities of the $n = 2$ and 3 ions are enhanced at higher electron impact energies. The only primary difference between the effect electron impact energy has on the DFE and ethene CMS is that the DFE dimer ion signal is always observed with somewhat higher relative yields than the ethene dimer ion signal.
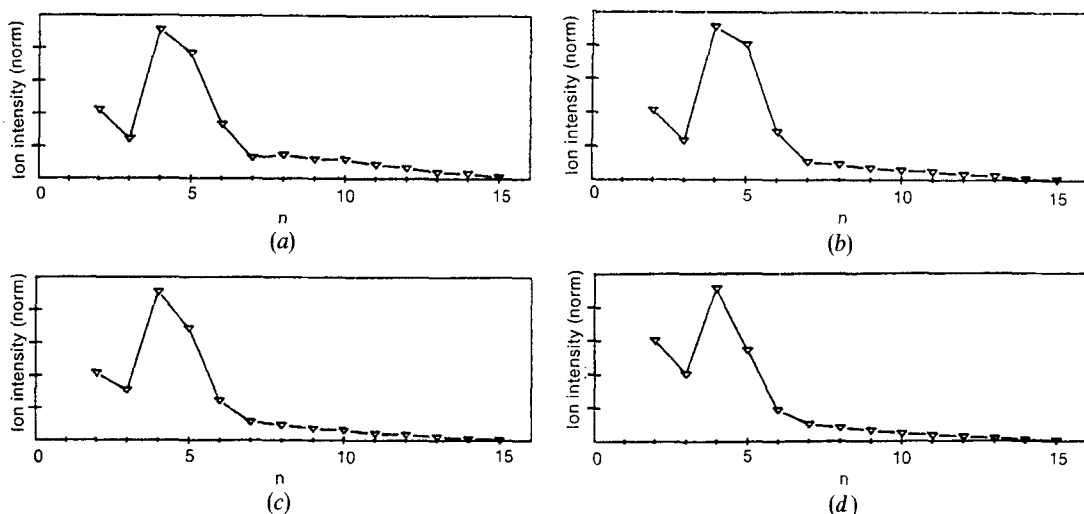
Figure 4.   Electron impact energy dependence of 1,1-difluoroethene cluster ion distribution; ion intensity of $\{C_2F_2H_2\}_n^+$ as a function of n. $T_0 = 247$ K, $P_0 = 2\cdot2$ atm. (a) $E_e = 13$ eV, (b) $E_e = 15$ eV, (c) $E_e = 30$ eV, (d) $E_e = 50$ eV.
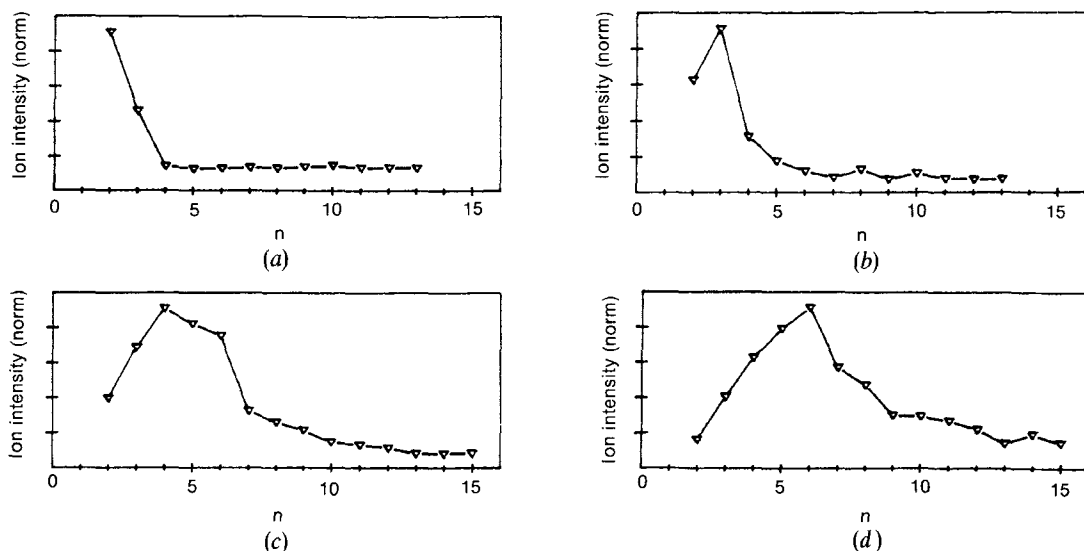
Figure 5.   Expansion pressure dependence of propene cluster ion distribution; ion intensity of $\{C_3H_6\}_n^+$ as a function of n. $T_0 = 297$ K, $E_e = 10$ eV. (a) $P_0 = 1\cdot5$ atm., (b) $P_0 = 2\cdot0$ atm., (c) $P_0 = 3\cdot0$ atm., (d) $P_0 = 4\cdot0$ atm.

2.3. $(CH_3CH{=}CH_2)_n^+$ cluster ions

A portion of the propene CMS under conditions favouring efficient clustering is shown in figure 1(c). Once again the CMS is dominated by stoichiometric ions, $(CH_3CH{=}CH_2)_n^+$, with non-stoichiometric ions observed only at small n values.

Figure 5 displays the pressure dependence of the stoichiometric propene cluster ions obtained with low energy (10 eV) electron ionization. The pressure behaviour of the propene clusters is somewhat more complex than that encountered in the ethene and DFE systems. Initially, as the expansion pressure is increased, the ion intensity is

observed to peak at $n=3$. As the expansion pressure (P_0) is further increased, the intensity maximum shifts out to $n=6$. The drop in ion intensities beyond the $n=6$ 'magic number' is not as drastic as observed in the ethene and DFE CMS. Unfortunately, the range of expansion temperatures and pressures which could be utilized for the propene studies were limited by the fact that propene was found to readily form liquid jets at high expansion pressures. As a result, it is not clear whether the propene magic number would continue to shift to higher n at higher P_0.

The electron impact energy dependence of the $(CH_3CH{=}CH_2)_n^+$ ion intensity distributions is shown in figure 6. Once again the propene system displays a more complex behaviour than either the ethene and DFE systems. Under conditions of high backing pressures and low electron energies the propene cluster distribution appears fairly broad and peaks at $n=6$. However, increasing the electron impact energy results in a shift of the ion distribution peak to lower values of n where the maximum is once again found to occur at $n=3$. The $n=6$ ion appears to display slightly enhanced intensity in all of these CMS distributions.

3. Olefinic intracluster polymerization reactions
3.1. $CH_2{=}CH_2$ and $CH_2{=}CF_2$

3.1.1. *Pressure effects*

One may now inquire as to the relationship between the observation of magic numbers and the production of particularly stable cluster ions, i.e. ions which are particularly stable with respect to decomposition into smaller ions. In most of the cases discussed in the general literature, the observation of a magic number indicates an enhanced stability of that particular cluster ion. This is usually associated with the formation of an central cation possessing a completely filled solvation shell structure
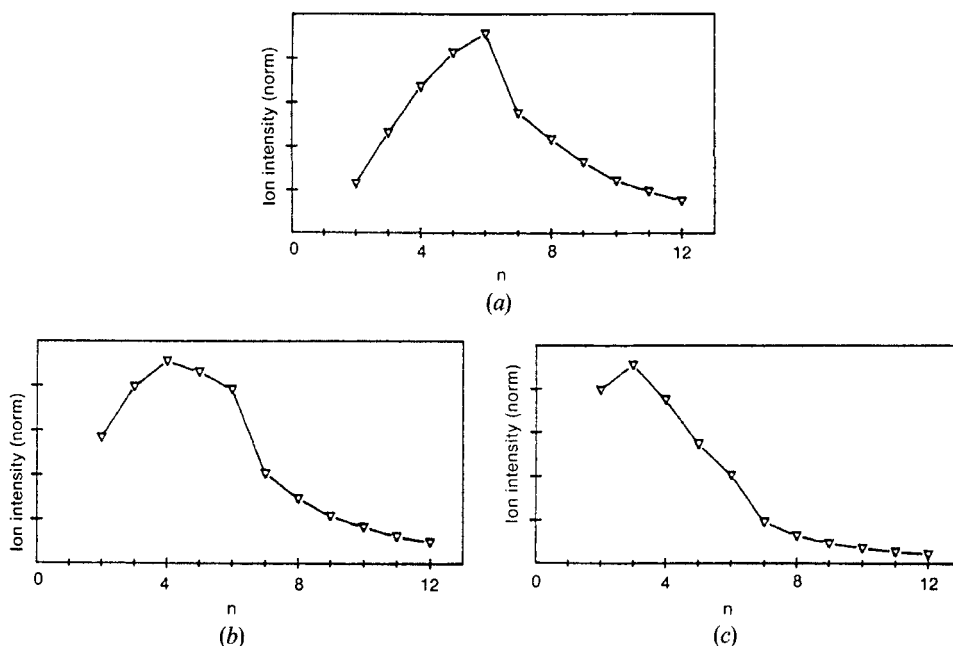

Figure 6. Electron impact energy dependence of propene cluster ion distribution; ion intensity of $\{C_2F_2H_2\}_n^+$ as a function of n. $T_0 = 247\,\mathrm{K}$, $P_0 = 4\cdot0\,\mathrm{atm.}$, (a) $E_e = 13\,\mathrm{eV}$, (b) $E_e = 16\,\mathrm{eV}$, (c) $E_e = 50\,\mathrm{eV}$.

[21, 22]. The present results, however, cannot be explained in terms of solvation shell effects and point out the problem of interpreting a CMS without careful consideration of the chemical nature of the cluster components.

It is clear that the stoichiometric ions observed in the ethene CMS cannot be $\{C_2H_4\}_{n-1}C_2H_4^+$ ions, i.e. solvated ethene ions. All of the studies cited in the introduction Section may be taken as near certain proof that *at least one ion–molecule reaction takes place in an ionized ethene cluster*. Thus the observed magic numbers at $n=4$ and 5 might be due to solvation of a $C_4H_8^+$ ion, i.e. $\{C_2H_4\}_2C_4H_8^+$ and $\{C_2H_4\}_3C_4H_8^+$, respectively. It should be noted that the strongly peaked ion intensity distributions shown in figures 2 and 3 imply a much stronger 'magic' in the ethene and DFE cluster ions than encountered in any of the other molecular systems thus far studied. Likewise, no other cluster system has exhibited such a pronounced drop of dimer ion intensity in comparison to the magic number ion. The trends observed for the ethene and DFE clusters suggest that very few of the larger cluster ions give rise to ions smaller than the tetramer, implying that the $n=4$ and $n=5$ cluster ions are extremely stable with respect to decomposition to smaller ions. However, it is not clear what factors could be responsible for the extraordinary stability displayed by these ions if they are fact weakly bound cluster ions of the form $(C_2H_4)_{n-2}C_4H_8^+$ since hydrogen bonding interactions are not expected to play an important role.

A much more cogent rationalization of the CMS results can be presented in terms of intracluster polymerization reactions. There is a great deal of evidence derived from both the gas phase and condensed phase studies cited previously in this paper (particularly Kebarle and coworkers' HPMS results [24–26] and the photoionization studies of Ng and coworkers [38, 39]) which supports the contention that ionization of an ethene cluster would likely result in a *series* of intracluster ion–molecule addition (polymerization) reactions. Technically it might be better to describe these reactions as oligomerization reactions since the predominant products are of low molecular weights. However, polymerization seems to be a general enough term to describe the actual bond forming reactions.

Most of the behaviour observed for the olefin cluster ions can be understood in terms of intracluster polymerization reactions where the products are covalently bound molecular ions. We can now begin to understand the pressure behaviour of the ethene and DFE clusters by assuming that at least the stoichiometric ions with $n < 6$ are covalently bonded molecular ions, i.e. $(C_2H_4)_n^+ \equiv C_{2n}H_{4n}^+$. This interpretation is strongly suggested by the obvious similarities between the CMS results and Kebarle's HPMS results [24–26]. The extreme stability for the $n=4$ and 5 ions then is a direct consequence of the much greater energy needed to dissociate covalently bonded ions.

The observed trends in the cluster ion intensity distributions can be explained as follows. Ionization of an ethene cluster results in formation of a $C_2H_4^+$ ion. This nascent ion reacts very rapidly with a neighbouring neutral to produce an excited $C_4H_8^{+*}$ intermediate ion. In a cluster of sufficient size (e.g. $n \gg 5$) [37] this excited intermediate ion may be stabilized by transfer of energy into the cluster modes. The stabilized $C_4H_8^+$ ion may then react with another ethene molecule to produce a $C_6H_{12}^{+*}$ ion which again may then be stabilized. This model would predict that the probability of multiple ion–molecule addition reactions should grow with cluster size since the ease with which the molecular ions may be stabilized should also increase, as the initial neutral cluster size increases.

A particularly intriguing question arises concerning the extent of polymerization within the clusters. Based purely on thermodynamic grounds it might well be suggested

that the polymerization reactions should only be limited by the size of the cluster since it is always energetically favourable to convert a non-conjugated π-bond to a σ-bond yet our ethene and DFE CMS data *do not* support this belief.

The strong 'piling up' of ion intensity at $n=4$ and 5 as expansion conditions favouring production of larger neutral clusters must be taken as an indication that the extent of polymerization does not increase indefinitely as a function of cluster size. Figures 2, 3 and 5 indicate that beyond some critical cluster size, the intracluster reactions favour predominately the production of $C_8H_{16}^+/C_8H_8F_8^+$ and $C_{10}H_{20}^+/C_{10}H_{10}F_{10}^+$ ions regardless of the starting neutral cluster size. This finding is also entirely consistent with both Kebarle's gas phase [24–26] and Wagner's condensed phase [34, 35] studies which clearly indicate that the free cationic polymerization of ethene occurs to a limited extent. This also suggests that the same factors must limit the polymerization reactions in both the gas, condensed and clustered phases of ethene.

Thus, it appears that the intracluster polymerization reactions do not proceed indefinitely. Instead, they proceed until an ion is formed which is unreactive with the surrounding monomers. The highly excited molecular ion will dissipate its excess energy into the cluster modes leading to extensive monomer evaporation and a high probability of observing the bare molecular ions. The magic numbers observed in the ethene and DFE cluster ion distributions may therefore be taken as evidence of *kinetic bottlenecks* in the addition reaction sequences. Kebarle and coworkers have noted that the rates of the cationic ethene polymerization reactions do in fact fall off very rapidly after the third and fourth addition reactions [24–26].

3.1.2. *Energy effects*

The most critical role of the 'solvent' molecules in the olefin clusters is the stabilization of the intermediate ion formed by the first addition reaction, $C_4H_8^{+*}$, as well as the molecular ions produced by the following intracluster polymerization reactions. It is clear from figures 4 and 6 that the principle effect of increasing the energy of the ionizing electron is to increase the relative amounts of $n=2$ and $n=3$ ions. This effect can be qualitatively understood in terms of the increased energy deposition into the cluster under higher ionizing electron energies. The majority of this excess energy is likely to be deposited into the internal modes of the ethene molecule which is ionized. Since the efficiency of energy dissipation is likely proportional to the cluster size, the molecular ions produced at higher electron energies will be more excited and more prone to decay/fragment to smaller ions.

3.2. $CH_3CH=CH_2$

We have noted that both the pressure and energy dependence of the propene CMS is far more complex than that of either ethene or DFE. Unlike ethene or DFE, the propene CMS was not characterized by an ion intensity distribution which remained relatively unchanged over a significant range of expansion conditions or ionizing electron energies. The distributions of the stoichiometric propene cluster ions peak at $n=3$ under moderate expansion conditions. At higher expansion pressures and low electron energies this maxima shifts to $n=6$. However, increased electron energies lead to a shift of the intensity maximum back to $n=3$. The differences between propene and the other olefin cluster ion systems, and the apparent special significance of the $C_9H_{18}^+$ cation allow us to make some reasonable speculations about the structures of the $n=3$ magic number ion and the mechanisms of the reaction giving rise to it.

3.2.1. *Structures and reaction mechanisms*

The nearly identical behaviour displayed by the ethene and 1,1-DFE cluster ion systems is quite surprising when one considers the properties of the two molecules. We have suggested that it is the kinetics of the intracluster ion–molecule reactions which govern the distribution of ions observed in the CMS. However, greatly differing ion–molecule reactions kinetics in the ethene and DFE systems might have been expected, just on the basis of the dipole moment difference between these two molecules (0 against 1·38 D, for ethene and DFE, respectively). In fact, it has been noted that the ion–molecule chemistry of DFE differs quite substantially from that the other fluoroethenes [40]. Significantly different energetics and kinetics for the monomer evaporations from ethene and DFE clusters would therefore also be expected. The remarkable similarities between the ethene and DFE CMS contrasts with the very different behaviour of the propene CMS. This evidence suggests that it is the carbon skeleton of the olefins which primarily determines the products observed from these intracluster polymerization reactions. That is, ethene and DFE react very similarly because they are both primarily C=C species while the reactivity of the propene system differs from the other two it is a C–C=C system.

Structure-reactivity correlations are certainly nothing new to polymer chemistry [43]. One of the most important processes that governs the kinetics of polymerization, and which can severely limit the extent of polymerization, is the competition between polymer growth (chain propagation) and ring formation. The formation of cyclic ions with low ring strain energy serves as an 'energy trap' in the reaction sequence; i.e. further reaction of the cyclic ion, although energetically favoured, is kinetically unfavourable because of the high activation energy required to reopen the ring. Such energy traps would be particularly effective in clusters since energy transferred into the
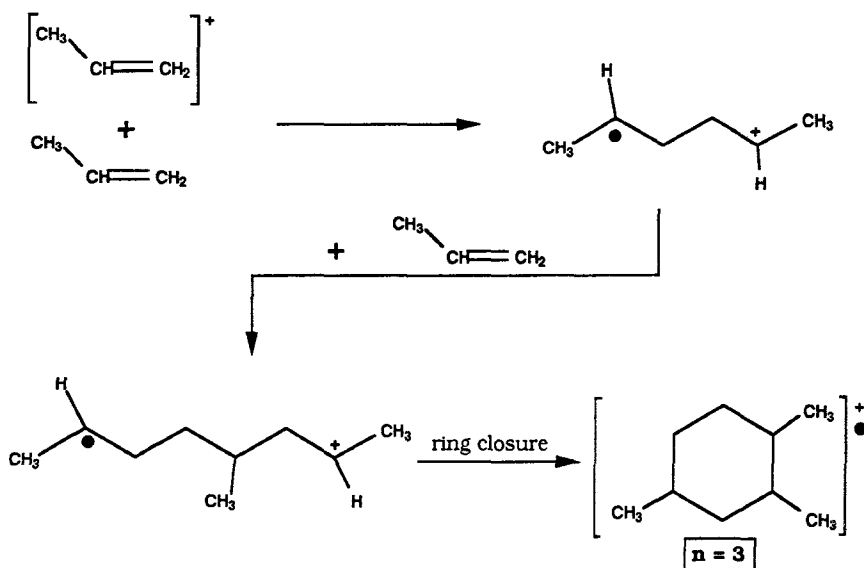

Figure 7. Proposed reaction scheme for ionic reaction within propene cluster ions. Reprinted with permission [2]. Copyright 1991 American Chemical Society.
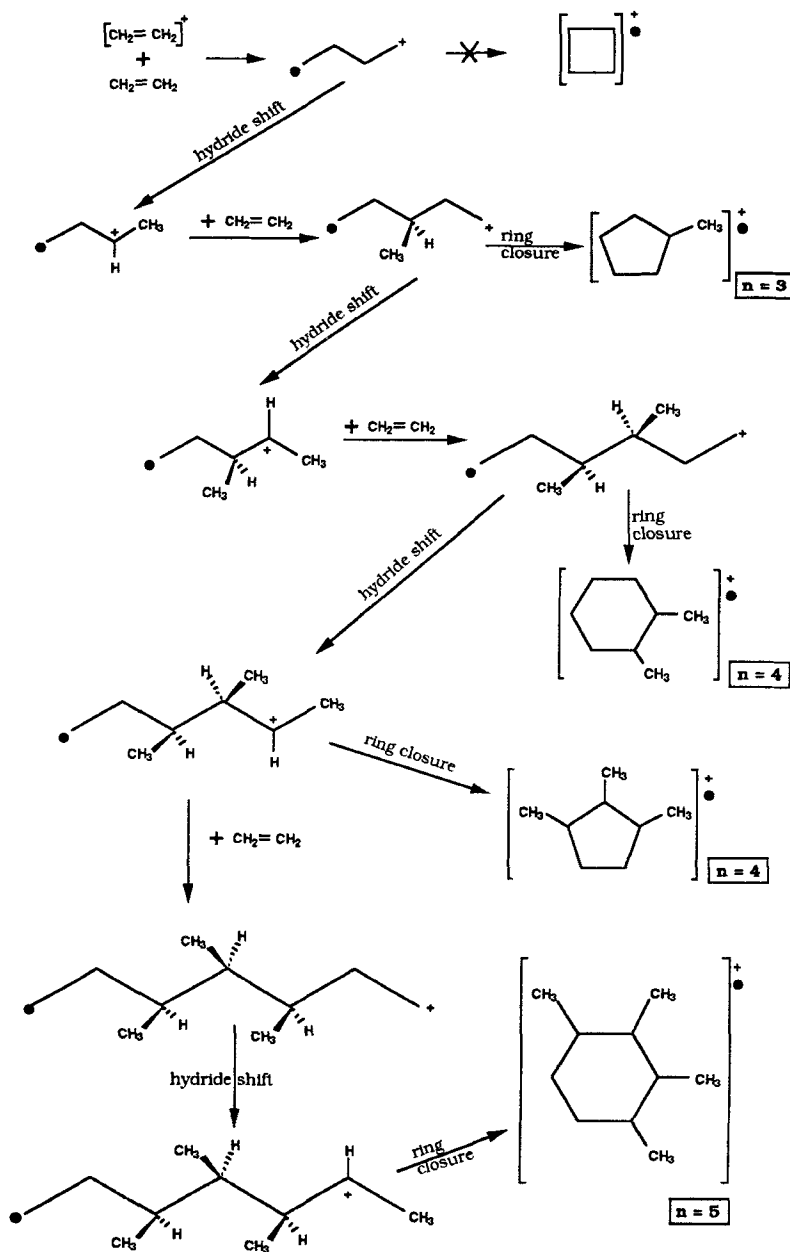
Figure 8. Proposed reaction scheme for ionic reaction within ethene cluster ions. Reprinted with permission [2]. Copyright 1991 American Chemical Society.

cluster modes can be permanently lost from the reaction system through evaporative monomer losses.

We therefore speculate that the $C_8H_{16}^+/C_8H_8F_8^+$ and $C_{10}H_{20}^+/C_{10}H_{10}F_{10}^+$ magic numbers ions observed in the ethene and DFE CMS, respectively, are cyclic ions. Statistical and energetic considerations [43] suggest that these ions most likely possess five- or six-membered rings, i.e. that they are substituted cyclopentane or cyclohexane ions.

The $n = 3$ magic number observed in the propene CMS, $C_9H_{18}^+$, adds supporting evidence for this proposal and may also suggest a possible mechanism for the ring closure reactions. It has been established [33,41] that the preferred product of the propene ion–molecule reaction is formed by end-to-end addition, as shown in figure 7. The initial product of this reaction is a 1,4-distonic radical cation [44,45]. One more addition reaction occurring in a similar fashion would then be expected to produce a 1,6-distonic ion. Facile ring closure to give a trimethylcyclohexane ion ($C_9H_{18}^+$) with delocalized radical/ion character can then occur as outlined in figure 7.

A similar reaction scheme may be envisaged for the ethene and DFE clusters, and is illustrated for ethene in figure 8. It must be stressed that the reaction schemes of figures 7, and 8 in particular, are greatly idealized representations but do explain the occurrence of the observed magic numbers. In the case of ethene clusters, for example, the model assumes a competition between three possible reactions: (a) chain propagation, (b) hydride shifts and (c) ring formation. (Assumptions concerning reactions (a) and (b) are discussed in the next paragraph.) The scheme outlined in figure 8 thus indicates at least two possible pathways to generate stable $n = 4$ ions ($C_8H_{16}^+$) and would explain the maximum found for the $n = 4$ ions in the ethene and DFE CMS.

Three major assumptions have been made during the construction of the reaction scheme of figure 8:

(1) Radical-molecule addition reactions have been ignored;
(2) primary ions are assumed to rearrange before they can react;
(3) ring closure is competitive with hydride shift reactions.

Assumption (1) is based on experimental studies which have shown that ionic polymerization reactions in bulk samples occur at rates as much as 10^6 times faster than radical processes [46]. Assumption (2) is based on the well known fact that primary carbocations are never observed as reaction intermediates in solution and for similar reasons are probably also unstable within clusters [47]. Such primary carbocations are expected to rapidly rearrange via hydride shifts into the more stable tertiary or secondary cations. The third assumption made in figure 8 is that the ring closure reactions are competitive with the hydride shift reactions when low strain five- and six-membered rings may be formed and is clearly more suspect than either of the first two assumptions since there have been no previous investigations of such reactions.

4.   Clusters composed of molecules with C≡C bonds
4.1. $\{CH{\equiv}CH\}_n^+$ and $\{CH_3C{\equiv}CH\}_n^+$

Figures 9 and 10 display plots of the intensities of the the acetylene (ACE) and methylacetylene (MACE) cluster ions against cluster size for several different sets of expansion conditions. It is clear that expansion conditions favouring the production of larger neutral clusters lead to the emergence of a very prominent magic number in the
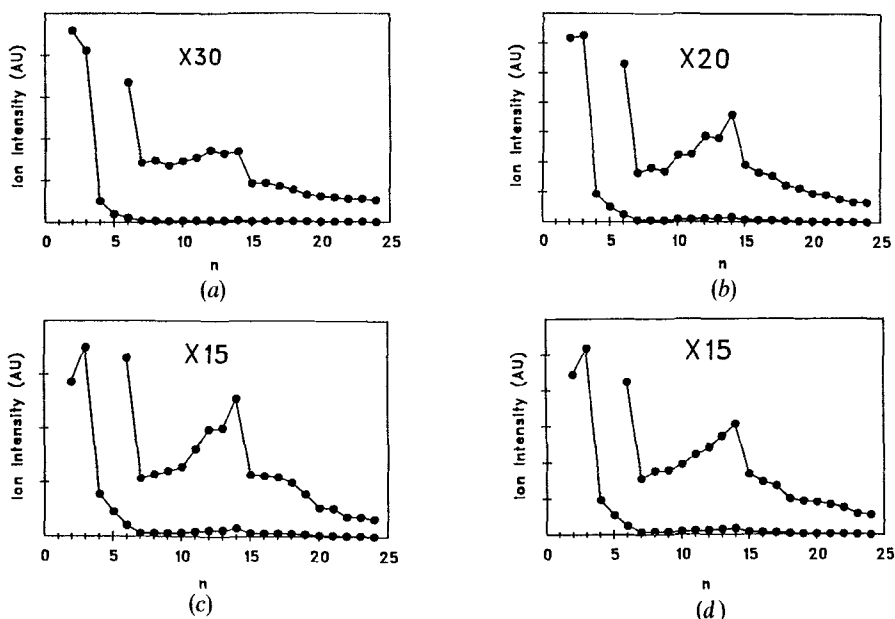
Figure 9. Plots of $\{C_2H_2\}_n^+$ ion intensities against n for several sets of expansion conditions. Data has been corrected for background noise and contributions to ion signals due to ^{13}C isotope. All data was obtained with 70 eV electron energy. Expansion conditions are: (a) P_0 = 1·5 atm., T_0 = 275·8 K; (b)1·3 atm., 268 K; (c) P_0 = 1·5 atm., T_0 = 268 K; (d) P_0 = 1·8 atm., T_0 = 268 K. Reprinted with permission [54]. Copyright 1992 American Chemical Society.
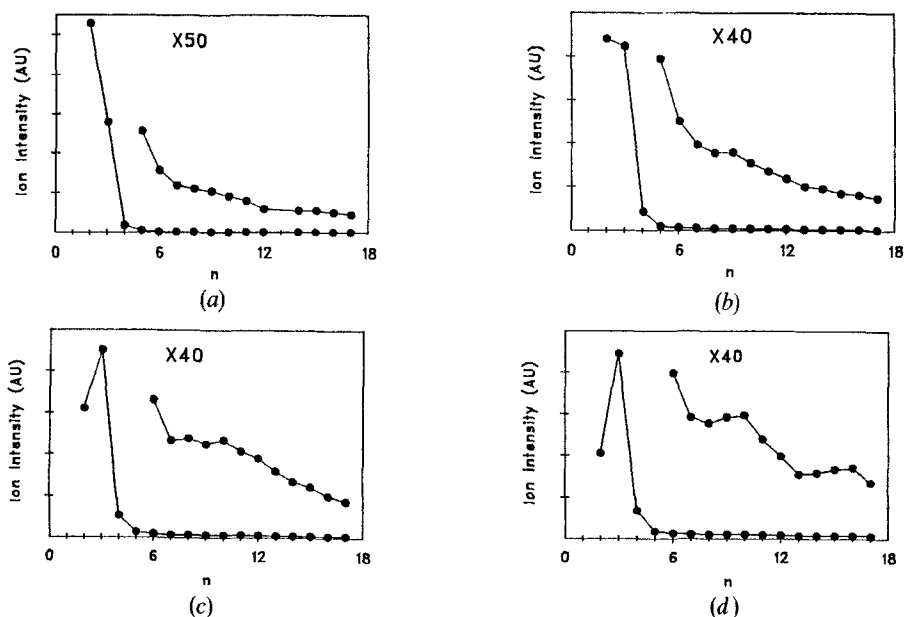
Figure 10. Plots of $\{C_3H_4\}_n^+$ ion intensities against n for several sets of expansion conditions. Data has been corrected for background noise and contributions to ion signals due to ^{13}C isotope. All data was obtained with 50 eV electron energy. Expansion conditions are: (a) P_0 = 1·5 atm., T_0 = 259·6 K; (b) 1·8 atm., 259·6 K; (c) P_0 = 2·1 atm., T_0 = 259·6 K; (d) P_0 = 2·7 atm., T_0 = 259·6 K. Reprinted with permission [54]. Copyright 1992 American Chemical Society.

$\{ACE\}_n^+$ and $\{MACE\}_n^+$ ion intensity distributions at $n=3$. Acetylene and methylacetylene clusters are thermodynamically unstable with respect to polymerization reactions. However, such reactions are unlikely because of large activation barriers. Yet these same reactions may be expected to be quite facile within $\{ACE\}_{n-1}ACE^+$ and $\{MACE\}_{n-1}MACE^+$ clusters since the activation barriers are much smaller for ion–molecule reactions, i.e. an acetylene or methylacetylene ion 'solvated' within such a cluster. The resulting ion product may also then be capable of reacting with other surrounding molecules. One of the more interesting questions which arises in connection with these clusters then concerns the extent of these 'polymerization' reactions within the clusters.

A similar line of reasoning which we have used to account for reactions within olefinic cluster, may be appropriate in connection to the alkyne clusters. In the case of acetylene, formation of benzene is a well known 'energy trap' in the polymerization sequence [48]. It is not surprising then to observe a strong magic number to emerge at $n=3$ in the CMS, as larger neutral clusters are produced. A similar interpretation was also offered by Shinohara et al. [49]. The gas phase analog of this termolecular reaction is shown in reaction (11).

$$C_2H_2^+ + 2C_2H_2 \rightarrow c - C_6H_6^+, \qquad \Delta H^\circ = -8\cdot23\,eV\,[50]. \qquad (11)$$

Further support for this hypothesis may be derived from the work to Ng et al. who studied the single photon ionization of $\{ACE\}_3$ [51]. The conclusion drawn from these studies was that the acetylene trimer ions isomerized to the same structure(s) as benzene ions produced with the same amount of internal energy. The observation of undissociated $C_6H_6^+$ ions in our experiments is a direct consequence of the production of large acetylene cluster ions since the large exothermicity of the ionic addition reactions must be dissipated by the evaporative loss of monomers from the cluster. This conclusion is consistent with the recent findings of Booze and Baer [52] who have shown that the $C_6H_6^+$ ion signal observed following ionization of neutral acetylene clusters arises entirely from dissociative ionization of higher-order clusters.

Applying these same criteria to the methylacetylene system leads one to the conclusion that one should observe a magic number at $n=3$ in this system corresponding to the production of trimethylbenzene ions. Reaction (12) depicts the analogous gas phase reaction.

$$C_3H_4^+ + C_3H_4 \rightarrow c - C_9H_{12}^+, \qquad \Delta H^\circ = -(7\cdot87 - 8\cdot09)\,eV\,[50, 53]. \qquad (12)$$
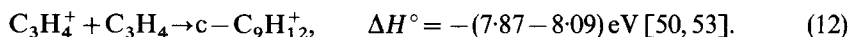
More direct support for this conclusion may be drawn from the trimer and tetramer ion 'fragment' regions of the methylacetylene CMS. Analysis of this fragmentation pattern [54] is consistent with the initial production of trimethylbenzene ions.

As shown in figure 9, for $\{ACE\}_n^+$ clusters, surprisingly a second magic number is observed for $n=14$. Based on the work already discussed in this paper, speculate that the $\{C_2H_2\}_{14}^+$ is a covalently bonded species, i.e. $C_{28}H_{28}^+$. We were unable to observe a magic number at $n=14$ in the methylacetylene CMS. We can only conjecture as to the structure(s) of the $n=14$ magic number ion and the origin of its enhanced stability. All our previous experiences with intracluster polymerization reactions suggests that this magic number may be associated with formation of an ion which is particularly stable towards any further reaction with other monomers within the cluster. In the case of the olefin clusters and the $n=3$ magic number ions in acetylene and methylacetylene, the stability is apparently associated with formation of cyclic ions. Thus there are some grounds to postulate that the same is true of the $C_{28}H_{28}^+$ ion. These ions, which might

then be thought of as hydrogenated carbon clusters of the form $C_{2n}H_{2n}^+$, and may therefore possess very interesting structures, perhaps similar to the caged structures of the fulleranes.

4.2. $\{CH{\equiv}CH\}_n-\{CH_3COCH_3\}_m^+$

In studying mixed clusters of acetylene/acetone [55] we have observed two prominent magic numbers for the heterocluster ions $(C_2H_2)_2C_3H_6O^+$ and $(C_2H_2)_2C_2H_3O^+$. The dependence of these cluster ions on expansion conditions (i.e., the CMS becoming progressively anomalous with increasing expansion pressures) again indicates that they may also be produced via intracluster polymerization reactions. We tentatively identify these molecular ions as the 2,2-dimethyl-2H-pyran radical $(\{C_2H_2\}_2C_3H_6O^+{\equiv}C_7H_{10}O^+)$ ion and the 2-methylpyrylium ion $(\{C_2H_2\}_2C_2H_3O^+{\equiv}C_6H_7O^+)$, respectively, and are depicted in figure 11.

The fact that the magic number occurs for $n=2$ is suggestive of the formation of a molecular ion and corresponds to replacement of one of the acetylene's by an acetone (or acetyl) ion during the ionic reaction (i.e., $\{2C_2H_2+CH_3COCH_3^+\}$ or $\{2C_2H_2+CH_3CO^+\}$). If the reaction proceeds by initial production of an acetone ion within the cluster, the observed product ion may be formed via reaction (13), where A = acetylene and T = acetone:

$$A_nT_m+e^-{\rightarrow}A_nT_{m-1}CH_3COCH_3^++2e^-{\rightarrow}C_7H_{10}O^++(n-2)A+(m-2)T. \qquad (13)$$
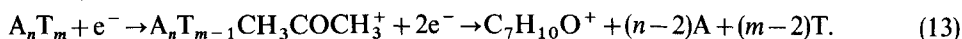
If this reaction is halted by production of a six-membered ring, as appears to be the case for neat acetylene clusters, the 2,2-dimethyl-2H-pyran radical cation would to be the expected product.

If the reaction should proceed by initial production of an acetyl cation, $(CH_3C{\equiv}O)^+$, within the cluster the reaction may proceed as shown in reaction (14)

$$A_nT_m+e^-{\rightarrow}A_nT_{m-1}(CH_3C{\equiv}O)^++CH_3+2e^-{\rightarrow}C_6H_7O^++(n-2)A+(m-2)T. \qquad (14)$$

If reaction (14) is halted by production of a six-membered ring, the 2-methylpyrylium ion would be the expected cation product. We also note that the magic numbers reported above are insensitive to the energy of the ionizing electrons in that ion intensity distributions measured at 12 eV were essentially the same as those measured at 50 eV.
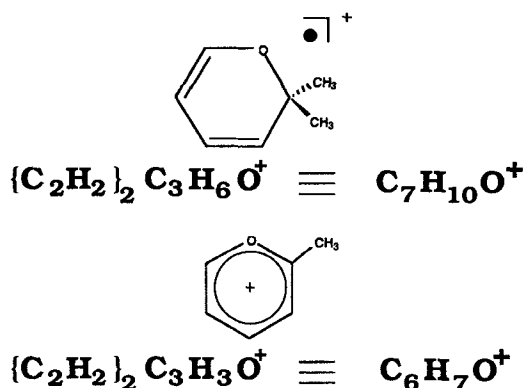
$$\{C_2H_2\}_2\,C_3H_6O^+ \quad {\equiv} \quad C_7H_{10}O^+$$

$$\{C_2H_2\}_2\,C_3H_3O^+ \quad {\equiv} \quad C_6H_7O^+$$

Figure 11. Postulated structures for the observed magic numbers corresponding to $\{C_2H_2\}_2C_3H_6O^+{\equiv}C_7H_{10}O^+$ and $\{C_2H_2\}_2C_2H_3O^+{\equiv}C_6H_7O^+$.

M. T. Coolbaugh et al.

5. Closing comments

The studies presented here only scratch the surface of this general family of ionic polymerization reactions which can occur within van der Waals clusters containing unsaturated molecules. We feel that the novel ion–molecule reactions discussed in this paper constitute a general family of chemical reaction for *all* cluster ions containing unsaturated molecules. Recently, other groups have now become involved in further investigations of intracluster polymerization reactions, both cationic [56,57] and anionic [58]. Our initial results suggest that it is possible to synthesize relatively complex molecules starting from simple molecular 'building blocks' within van der Waals clusters, through sequential ion–molecule reactions. Because of the differing stabilities and reactivities of ionic and neutral molecules, this method may be useful in production of ions of unusual structure, as well as providing insight into the basic mechanisms of ionic polymerizations and is a source of continuing study within our group.

Acknowledgments

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