SECURITY CLASSIFICATION OF THIS PAGE

2

AD-A234 233

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION: Unclassified

1b RESTRICTIVE MARKINGS

2a SECURITY CLASSIFICATION AUTHORITY

2b DECLASSIFICATION / DOWNGRADING SCHEDULE

3 DISTRIBUTION / AVAILABILITY OF REPORT
Approved for public release;
distribution unlimited

4 PERFORMING ORGANIZATION REPORT NUMBER(S)
Technical Report #20

5 MONITORING ORGANIZATION REPORT NUMBER(S)

6a NAME OF PERFORMING ORGANIZATION
SUNY/Buffalo

6b OFFICE SYMBOL *(If applicable)*

7a NAME OF MONITORING ORGANIZATION
Office of Naval Research

6c ADDRESS *(City, State, and ZIP Code)*
Dept. of Chemistry, Acheson Hall,
SUNY/Buffalo, Buffalo, NY 14214

7b ADDRESS *(City, State, and ZIP Code)*
Chemistry Program
800 N. Quincy St., Arlington, VA
22217

8a NAME OF FUNDING / SPONSORING ORGANIZATION
Office of Naval Research

8b OFFICE SYMBOL *(If applicable)*

9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
#N00014-88-K-0483

8c ADDRESS *(City, State, and ZIP Code)*
Chemistry Program, 800 N. Quincy St.,
Arlington, VA 22217

10 SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO

11 TITLE *(Include Security Classification)*
CATIONIC POLYMERIZATION WITHIN VAN DER WAALS CLUSTERS OF THE FORM $(CH_2=R)_n$ WHERE $R=CH_2$, CF_2 and $CHCH_3$

12 PERSONAL AUTHOR(S)
M. T. Coolbaugh, G. Vaidyanathan, W. R. Peifer and James F. Garvey

13a TYPE OF REPORT
Technical

13b TIME COVERED
FROM ________ TO ________

14 DATE OF REPORT *(Year, Month, Day)*

15 PAGE COUNT

16 SUPPLEMENTARY NOTATION

17 COSATI CODES

FIELD	GROUP	SUB-GROUP

18 SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*

19 ABSTRACT *(Continue on reverse if necessary and identify by block number)*

The cluster ion mass spectra resulting from electron ionization of van der Waals clusters composed of ethene, 1,1-difluoroethene or propene molecules were observed as a function of expansion and ionization conditions. Expansion conditions favoring the formation of large neutral clusters lead to the observation of anomalous ion intensity distributions characterized by strong peaking as a function of cluster size. Comparisons are made between the present results and previous observations in both the gas and condensed phases. We propose that the anomalous cluster ion distributions arise as a consequence of the production of molecular (i.e., covalently bonded) ions produced by a series of intracluster addition (polymerication) reactions. The anomalous intensity distributions may then be accounted for in terms of kinetic bottlenecks in the addition reaction sequences which most likely result from the production of ions of low reactivity, most likely cyclic ions.

20 DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21 ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a NAME OF RESPONSIBLE INDIVIDUAL
Dr. David L. Nelson

22b TELEPHONE *(Include Area Code)*
(202) 696-4410

22c OFFICE SYMBOL

83 APR edition may be used until exhausted
All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE

91 4 02 109

OFFICE OF NAVAL RESEARCH

GRANT N00014-88-K-0493

R & T Code 412m008

Technical Report No. 20

CATIONIC POLYMERIZATION WITHIN VAN DER WAALS CLUSTERS OF THE FORM $\{CH_2{=}R\}_n$ (WHERE R = CH_2, CF_2, $CHCH_3$)

by

M. Todd Coolbaugh, Gopal Vaidyanathan,
William R. Peifer and James F. Garvey*

Prepared for Publication
in
The Journal of Physical Chemistry

Dist
A-1

Acheson Hall
Department of Chemistry
University at Buffalo
The State University of New York at Buffalo
Buffalo, NY
14214

Cationic Polymerization within van der Waals Clusters of the form $(CH_2{=}R)_n^+$ (where R = CH_2, CF_2 and $CHCH_3$)

M. Todd Coolbaugh, Gopalakrishnan Vaidyanathan, William R. Peifer and James F. Garvey* Acheson Hall, Department of Chemistry, State University of New York at Buffalo, Buffalo, New York, 14214.

Submitted 2/1/91 J. Phys. Chem.

Revised 3/18/91

RBB Memorial issue

Abstract. The cluster ion mass spectra resulting from electron ionization of van der Waals clusters composed of ethene, 1,1-difluoroethene (1,1-DFE) or propene molecules were observed as a function of expansion and ionization conditions. Expansion conditions favoring the formation of large neutral clusters lead to the observation of anomalous ion intensity distributions characterized by strong peaking as a function of cluster size. Comparisons are made between the present results and previous observations in both the gas and condensed phases. We propose that the anomalous cluster ion distributions arise as a consequence of the production of molecular (i.e. covalently bonded) ions produced by a series of intracluster addition (polymerization) reactions. The anomalous intensity distributions may then be accounted for in terms of kinetic bottlenecks in the addition reaction sequences which most likely result from the production of ions of low reactivity, most likely cyclic ions.

Introduction. Clusters are the subjects of an ever increasing number of experimental and theoretical studies.[1-7] The current interest in clusters stems from their unique position as an aggregated state of matter intermediate between the gas and condensed phases of matter. Since clusters exist as isolated particles in the gas phase, they are susceptible to study by many of the powerful techniques used in the observation of gas phase reactions, which have led in many cases to fundamental understanding of chemical reactivity at a truly microscopic level.

For the physical chemist clusters represent a singular opportunity to directly observe the influence of solvation and solvent structure on chemical reactivity. At the same time, clusters represent a medium of greatly reduced simplicity in which to study processes of chemical interest including charge and energy transfer, bond formation and cleavage, etc.

Supersonic expansions are the most widely utilized methods for generating clusters.[8] Unfortunately, these molecular beam cluster sources do not allow one to selectively produce a given cluster size. Instead a distribution of cluster sizes is produced which generally cannot be directly characterized. However, judicious choice of expansion conditions allows one to shift the distribution of neutral clusters from 'small' to 'large' sizes thus affording the experimentalist a considerable degree of qualitative control of the cluster distribution.

At present, mass spectrometry represents the most convenient means of detecting size selected clusters. This of course requires that the initially neutral cluster be ionized, most commonly via either electron impact or photoionization. This process nearly always leads to extensive fragmentation and, in many cases, reactions within the cluster.[1-7] As a result, the relationship between the neutral cluster distribution and the observed cluster ion distribution is impossible to specify. It is still possible to come to qualitative conclusions regarding the relative sizes of the precursor clusters based on the initial expansion conditions.

The olefin molecules which are the subject of this paper (ethene, 1,1-difluoroethene (1,1-DFE) and propene) have several properties which make them ideal systems to study by the technique of cluster ion mass spectroscopy. 1) The reactions of olefin molecules, especially ethene, have been studied extensively both in the gas and bulk (solid and liquid) states. 2) The reactivity of the olefins is dramatically dependent on the state of 'solvation' (or more precisely density). Under bimolecular conditions, the products of a single ion-molecule reaction are observed.[9] At high pressures and in the condensed phases, however, the olefin monomers may be induced to polymerize by interaction with high energy particles.[10,11] Free cationic polymerization was suggested as one mode of reaction propagation in these systems.[10,11]

The ion chemistry of the olefins has been studied extensively[9], the results for ethene being illustrative. The ion chemistry of ethene has been the subject of intense study since it represents one of the first ion-molecule reactions which was conclusively demonstrated to involve a long-lived reaction intermediate.[12] The products from the bimolecular reaction are determined by the decay of this intermediate which, because of the exothermicity of the addition reaction, is created in a highly excited state.[13] The bimolecular reaction scheme is represented by reactions (1) - (3).

$$C_2H_4^+ + C_2H_4 \dashrightarrow C_4H_8^{+*} \dashrightarrow C_2H_4^+ + C_2H_4 \qquad (1)$$

$$\dashrightarrow C_3H_5^+ + CH_3 \qquad (2)$$

$$\dashrightarrow C_4H_7^+ + H \qquad (3)$$

At higher gas pressures two effects become obvious. 1) The excited state intermediate may be collisionally stabilized;[12-15] and 2) the dissociation products, $C_3H_5^+$ and $C_4H_7^+$, may participate in a succession of ion-molecule addition reactions.[13,15]

In a particularly interesting experiment, Kebarle and coworkers studied the ion chemistry of ethene using a near atmospheric pressure ion source mass spectrometer.[16-18] The experimental geometry made use of what may be considered a preionized expansion; that is, expansion of a partially ionized gas from a region of high pressure into a low pressure region through a small orifice. Under these conditions an ion is expected to undergo many thousands of collisions before detection. It was observed in these experiments that an increase in the concentration of ethene in an expansion of constant pressure led to the observation of polymer ions, $(C_2H_4)_n^+$. It was also noted that the disappearance of the smaller ions (i.e. $C_2H_4^+$, $C_4H_8^+$, $C_6H_{12}^+$) which occurred at high ethene concentrations was not accompanied by the appearance of increasingly larger polymer ions. Instead, the $C_{12}H_{24}^+$ ion remained of maximum intensity for the concentration and pressure ranges studied. Rough estimates for the relative rates of successive ion molecule reactions were obtained from plots of the relative ion intensities as a function of ethene concentration. Analysis of the data was based on a steady state approximation.[17] Assuming a rate for the first reaction, $k_{12} \approx 1 \times 10^{-9}$ cm^{3}molec.$^{-1}$sec^{-1}, successive rate constants $k_{23} \approx 2 \times 10^{-12}$, $k_{34} \approx 8 \times 10^{-13}$, $k_{45} \approx 2 \times 10^{-13}$ and $k_{56} \approx 8 \times 10^{-14}$ cm^{3}molec.$^{-1}$sec^{-1} were obtained. These decreases in the addition reaction rate constants were attributed to structural effects arising from the formation of branched tertiary and quaternary cations.

In addition to the $(C_2H_4)_n^+$ ions Kebarle et. al.[16-18] observed ions of the type $C_nH_{2n-1}^+$ with n = 5, 7 and 9. The formation of these ions could be suppressed by increasing the pressure of the inert Xe buffer gas. It was speculated that these ions arose from reaction sequences initiated by the $C_3H_5^+$ ion formed by the decomposition of $C_4H_8^{+*}$. The Xe serving here to suppress this reaction sequence by effectively stabilizing $C_4H_8^+$. This reaction sequence was confirmed by ICR[13] and triple quadrupole experiments.[15]

Kebarle et. al. also observed the effects of increasing the temperature of the ion source.[16,18] It was found that the ethene mass spectra were remarkably insensitive to the temperature of the source, the mass spectra remaining nearly unchanged even at temperatures which suppressed the formation of protonated water clusters in water containing vapors. This observation implies that the ethene cluster ions are much more stable than the water clusters. This observation is easily explained if it is assumed that the ethene cluster ions are covalently bound molecular ions.

The most surprising conclusion drawn from this study was that ionic polymerization of ethene is not an efficient process even though energetically favored. Essentially identical conclusions were drawn from the condensed phase radiolysis experiments.[10,11] Wagner concluded that cationic processes following radiolysis of solid ethene produced products only up to around $C_{12}H_{24}$.[10] In this case the inefficiency of the polymerization was attributed to competition between the propagation and neutralization reactions.

One of the chief advantages which cluster ion investigations may have to offer is the ability to study the reactions of ionic species without complications arising from the presence of free electrons or counterions since in the mass spectrometric experiments the electrons are permanently removed from the clusters. This situation may be particularly advantageous in terms of understanding free cation polymerization since it should, in principle, be possible to observe the growth of a single polymer chain.

B. Experimental. The experimental apparatus has been described in detail previously[19] and is shown schematically in Fig. 1. In brief it consists of a continuous cluster beam source of the Campargue design[20] coupled to a chamber housing a mass spectrometer. The cluster beams were generated by expansion of the neat gases through a 250 μm nozzle. The other expansion conditions (i.e. stagnation pressure, P_0, and stagnation temperature, T_0) are reported in the figure captions.

In general, the present report will be concerned with the results of experiments in which the cluster ion mass spectra were observed as a function of source conditions, in particular the expansion pressure, P_0. For the purposes of this discussion the principle effect of changing source conditions is to alter the distribution of neutral clusters present in the expansion. Qualitatively one expects an increase in P_0 or a decrease in T_0 to favor the production of larger clusters.

After being skimmed and collimated the neutral cluster beam enters the ionizer of the mass spectrometer where some the neutral species are ionized via electron impact, mass filtered and detected with a particle multiplier.

C. Results. 1) Cluster Ion Mass Spectra. Figs. 2 - 4 display portions of the cluster ion mass spectra of ethene, 1,1-DFE and propene, respectively, obtained with high source pressures (i.e. under conditions of maximal clustering). The electron impact energies used to obtain these spectra were determined to be the highest which could be used without leading to fragmentation of the monomer. As a result only reactions arising from the molecular ion need be considered. We would note that additional reaction channels are observed at higher electron impact energies which may be correlated to creation and reactions of monomer fragment ions.

The mass spectra of all three cluster systems are dominated by the stoichiometric ions (i.e. M_n^+). At low values of n a number of 'fragment' ions may be observed. These ions are not fragments of the monomer ion, but are either solvated products of a single intracluster ion-molecule reaction or, as is likely, products of sequential ion-molecule addition reactions originating from $C_3H_5^+$ and other $C_4H_8^{+*}$ decomposition products. In any case the intensities of these ions fall off very rapidly with increasing n. The relative intensities of these ions also falls as the expansion conditions increasingly favor the production of larger clusters.

The 'fragment' ions of 1,1-DFE display similar qualitative behavior. However, the specific ions observed in the fragment regions are different for each value of n. The ions in the dimer fragment region (i.e. between the monomer and dimer ions) agree with the reported ion-molecule chemistry of 1,1-DFE[21] and consist of ions generated by loss of CH_xF_y (where x + y = 3) radicals from $C_4H_4F_4^+$, with the loss of

CH_2F being by far the dominant fragmentation channel. A number of the ions observed in the trimer and tetramer regions of the mass spectrum may be identified as C_5 and C_6 ions containing various combinations of hydrogen and fluorine atoms which cannot be accounted for in terms of the CH_xF_y reaction channel.

2). Pressure Behavior. Figs. 5 - 7 display the development of the stoichiometric ion intensity distributions as a function of pressure. The ethene and 1,1-DFE cluster ion mass spectra display nearly identical qualitative behavior but 1,1-DFE is considerably easier to cluster because of its high dipole moment. The stoichiometric ions at n = 4 and 5 for both of these cluster systems increase in intensity very rapidly with increasing pressure while the intensity of the n = 2 and 3 ions fall off with increasing expansion pressure. The intensity distribution of ions with n > 5, increases slowly and becomes broader as a function of expansion pressure. This unequal development leads to a very sharp peaking in the ion intensities as expansion conditions increasingly favor formation of larger clusters. The drop in intensity between n = 5 and 6 'cluster' ions has also been noted by Shinohara et. al. in the photoionization of what were presumed to be argon/ethene heteroclusters.[22]

Several minor differences are observed between the intensity distributions of the ethene and 1,1-DFE cluster ions. The 1,1-DFE dimer ion is always more prominent than the trimer ion. The relative intensities of the n = 4 and n

= 5 ions for these two systems are also somewhat different, the n = 5 ion being observed with slightly higher intensities in the 1,1-DFE cluster ions mass spectrum.

The behavior of the propene cluster ion system is somewhat more complex. Initially, as the expansion pressure is increased the ion intensity is observed to peak at n = 3. As the expansion pressure is further increased, the intensity maximum shifts out to n = 6. The intensity of ions with n > 6 does not fall off as dramatically in this system as was observed for ethene and 1,1-DFE display for n > 5. This gives the propene ion distribution a considerably broader appearance.

3) Energy Dependence. We have also observed the energy dependence of the olefin cluster ion distributions. The results for ethene were reported previously[23] and only the results will be discussed here. We observed that as the nominal energy of the ionizing electrons was increased from 13 eV to 100 eV, the intensities of the ions at n = 2 and 3 increased relative to those at n = 4 and 5. The peaking at n = 4 and the drop in intensity beyond n = 5 was still observed. The behavior of the 1,1-DFE clusters is nearly identical. Once again the main difference in behavior between the 1,1-DFE clusters and ethene clusters lies in the fact that the n = 2 ion of 1,1-DFE shows a more pronounced increase with increasing electron energies than does the n = 2 ion of ethene.

The appearance of the propene cluster ion mass spectrum displays a stronger dependence on the electron energy as shown in Fig. 8. It can be seen that at a high expansion pressure (2.0 atm.) and low electron impact energies a rather broad ion distribution is observed which is peaked at n = 6. As the ionization energy is increased, the maximum in the ion intensity distribution shifts back towards smaller values of n. At high electron energies (e.g. 50 eV) the maximum is once again found at n = 3. The n = 6 ion still displays some enhanced intensity even at 50 eV.

D. Discussion. 1) Ethene and 1,1-DFE. The term 'magic number' has been applied to describe intensity anomalies observed in cluster ion mass spectra for some time and are usually attributed to the formation of ions possessing special stability. Magic numbers are often very marked in hydrogen bonded cluster ions, being associated with completion of a solvation shell about a central ion. The observed distribution of cluster ions may often be taken as a reflection of the relative stabilities of the cluster ions.

Some care must be taken in the analysis of cluster ion mass spectra, however, since the resulting cluster ion distributions arise as a direct result of the kinetics and energetics of all intracluster ion-molecule reactions and cluster fragmentation reactions following ionization and will also be dependent on the distribution of neutral clusters. The present experimental observations, for example, are not well accounted for simply in terms of cluster stabilities. Hydrogen bonding is not expected to be of great importance in olefin clusters since these molecules do not have large proton affinities. It is in fact rather difficult to conceptualize structures for the observed magic number ions which could lead to the exceptional stability which the can be inferred from the sharp drop in intensity in the direction of smaller ions.

An additional factor which must be considered in the case of olefin clusters is the possibility of extensive intracluster ion-molecule reactions. In view of the results discussed in the introduction section it is doubtful that the cluster ions observed can be thought of as consisting entirely of ethene units, i.e. $(C_2H_4)_n^+$, at all. The experimental results of Buck et. al.[24] provide convincing evidence that at least one reaction takes place in small ($n \leq 12$) ethene cluster ions. Therefore $(C_2H_4)_n^+$ ions must be considered to be composed of at least solvated $C_4H_8^+$ ions, i.e. $(C_2H_4)_{n-2}C_4H_8^+$.

We would suggest that the possibility of several ion-molecule reactions within a single cluster must also be considered as probable. As support for this position we would note the very close resemblance between the high pressure mass spectra obtained by Kebarle[16-18] and coworkers to the cluster ion mass spectra which we observe in Fig. 2. Both exhibit the same sharp drop in intensity beyond the $C_{10}H_{20}^+$ ion. Addition of Xe bath gas led to many of the same qualitative effects in Kebarle's MS as observed in the cluster MS at increased expansion pressures- namely, a decrease in the relative intensities of the 'fragment' ions and a peaking of the ion intensity at $C_8H_{16}^+$ and $C_{10}H_{20}^+$.

It is our speculation then that the ions (at least up to the $C_{10}H_{20}^+/C_{10}H_{10}F_{10}^+$ ions) are covalently bonded molecular ions produced by a series of intracluster ion-molecule addition (polymerization) reactions. The observed pressure dependence of the cluster ion MS is consistent with such an interpretation since it indicates that as the average cluster size increases the probability of formation of ions up to the C_{10} ions increases. Buck[24] noted that the probability of formation and stabilization of the $C_4H_8^+$ ion from small ethene clusters increased very rapidly as a function of cluster size in the range n = 5 - 12. We could expect to observe more extensive reactions since our experimental setup should favor the production of much larger clusters than were examined in the previous report because of our use of a larger, chilled nozzle in conjunction with the Campargue geometry.[20]

The increasingly dramatic drop in ion intensities observed beyond the C_{10} ions on the other hand, implies that the *extent* of reaction *does not* increase indefinitely with increasing cluster size. This result is consistent with both the high pressure mass spectrometric[16-18] and solid state radiolysis[19] results.

If the extent of reaction is not limited by the gross size of neutral clusters it seems reasonable to assume that the limitation is inherent in the chemistry. Since the same limitations are apparently encountered in the gas-, cluster- and condensed-phase reactions, the limitation does not appear to be medium related and so would seem to arise as a consequence of the kinetics of the ion-molecule association reactions.

It may then be postulated that the observed cluster ion distributions of ethene and 1,1-DFE arise as follows: Ionization of a large neutral cluster leads to a series of very rapid ion-molecule addition reactions. These reactions proceed until an ion is formed which is characterized by very low reactivity towards the monomer; i.e. the reaction proceeds until a *kinetic bottleneck* is reached. The vibrationally excited ion formed then dissipates its internal energy leading to extensive monomer evaporation.

The nearly identical behavior displayed by the ethene and 1,1-DFE systems is somewhat surprising since the kinetics and energetics of the ion-molecule reactions and cluster dissociations should be considerably different. The great similarity may then serve as an indication that the kinetic bottlenecks proposed to explain the cluster ion distributions may be associated with the structures of the carbon skeleton of the ions formed by the intracluster addition reactions.

Such structure-kinetic correlations are certainly nothing new to polymer chemistry.[23] One very important consideration that governs the kinetics of polymerization, and which can severely limit the extent of polymerization, is the competition between chain growth (propagation) and ring formation reactions. The formation of a cyclic ions with low ring strain energy may serve as an 'energy trap' in the reaction sequence, i.e. further reaction of the cyclic ion, although energetically favored, is kinetically unfavorable because of the high activation required to reopen the ring.

We would further speculate, on the basis of the preceding discussion, that the $C_8H_{16}^+/C_8H_8F_8^+$ and $C_{10}H_{20}^+/C_{10}H_{10}F_{10}^+$ ions observed in the ethenen/1,1-DFE cluster ion mass spectra are cyclic ions. Statistical and energetic considerations[25] would suggest that these ions are most likely five- or six-membered rings (i.e. cyclopentane or cyclohexane ions) as shown in Fig. 9, Scheme I. Further support for this speculation is provided by the propene system as discussed below.

2). Propene. The pressure and energy behavior of the propene cluster system is more complex. Initially, under low electron impact energies and intermediate expansion pressures, the ion at n = 3 (i.e. $C_9H_{18}^+$) is the predominant ionic product. This observation may be rationalized rather easily in terms of a kinetic bottleneck associated with the formation of a cyclic ion as discussed above.

It has been established that the preferred product of the propene ion-molecule reaction is formed by end-to-end addition.[15,26] The initial product of this reaction may be expected to be a 1,4-distonic radical cation.[27,28] One more addition reaction in a similar fashion would then be expected to result in a 1,6-distonic radical cation. Such an ion could then readily undergo a facile ring closure to form a trimethylcyclohexane radical cation as outlined in Fig. 9, Scheme II.

The shift in the ion intensity observed at higher expansion pressures, Figs. 4 and 7, is not so easily rationalized. At the maximum expansion pressures utilized in the present studies[29] (3.5 - 4.0 atm.), the maximum is found at n = 6 (i.e. $C_{18}H_{36}^{+}$). The fall-off in ion intensity beyond n = 6 observed for the propene system is not as drastic as that observed beyond n = 5 for the ethene and 1,1-DFE systems. It is not clear then, whether the maximum observed in the propene systems would continue to shift to larger values for conditions favoring larger clusters. It is pointless therefore to speculate as to the origins of these effects based on this data.

The propene cluster ion mass spectra displays considerably more dependence on the electron impact energy, Fig. 8, than does the ethene[23] or 1,1-DFE systems. The shift of the ion distribution maxima from n = 6 to n = 3 emphasizes the significance of the $C_9H_{18}^{+}$ ion. Unfortunately, without additional information concerning the nature of the n = 6 ion (e.g. identity, $C_{18}H_{36}^{+}$ vs. $(C_3H_6)_3C_9H_{18}^{+}$ etc.) further speculations are not useful.

E. Conclusion. Electron impact ionization of large clusters composed of the simple olefin molecules (ethene, 1,1-

difluoroethene and propene) lead to anomalous ion intensity distributions. The smaller 'cluster' ions are likely covalently bound molecular ions formed by intracluster ion-molecule association (polymerization) reactions, whose counterparts are the free cationic polymerization reactions observed in radiolysis of bulk samples of the olefins. The available body of evidence suggests that the very strong anomalies observed in the ion intensity distributions arise from kinetic bottlenecks in the ionic chain growth reactions associated with the formation of cyclic molecular ions.

Acknowledgement. We gratefully acknowledge the financial support of this work provided by the Office of Naval Research.

References.

1) Mark, T.D.; Castleman, A.W., Jr. *Adv. Atom. Mol. Phys.* **1986**, *20*, 65.

2) Castleman, A.W., Jr.; Keesee, R.G. *Annu. Rev. Phys. Chem.* **1986**, *37*, 525.

3) Mark, T.D.; *Int. J. Mass Spectrom. Ion Proc.* **1987**, *79*, 1.

4) Mark, T.D. In *Electronic and Atomic Collisions*, Gilbody, W.R.; Newell, W.R.; Read, F.H.; Smith, A.C.H., Eds.; Elsevier: Amsterdam, 1988, 705.

5) Jortner, J. *Ber. Bunsen. Phys. Chem.* **1984**, *88*, 188.

6) *Physics and Chemistry of Small Clusters, NATO ASI Series B, 158*, Jena, P.; Rao, B.K.; Khanna, S.N., Eds., Plenum: New York, 1987.

7) Castleman, A.W., Jr.; Mark, T.D. In *Gaseous Ion Chemistry and Mass Spectrometry*, Futrell, J.H., Ed.; Wiley Interscience: New York, 1987.

8) Kappes, M.; Leutwyler, S. In *Atomic and Molecular Beam Methods*, Scoles, G., Ed.; Oxford University Press: New York, 380, and refs. therein.

9) *Ion-Molecule Chemistry, Advances in Chemistry Series, 58*. Ausloos, P., Ed. Am. Chem. Soc.: Washington, D.C., 1966.

10) Wagner, C.D. *J. Am. Chem. Soc.* **1962,** *66*, 1158.

11) Wagner, C.D. *Tetrahedron* **1962,** *14*, 164.

12) Field, F.H. *J. Am. Chem. Soc.* **1961,** *83*, 1961.

13) LeBreton, P.R.; Williamson, A.D.; Beauchamp, J.L.; Huntress, W.T. *J. Chem. Phys.* **1975,** *62*, 1623.

14) Bowers, M.T.; Elleman, D.D.; Beauchamp, J.L. *J. Phys. Chem.* **1968,** *72*, 3599.

15) Mitchell, A.L.; Tedder, J.M. *J. Chem. Soc. Perkin Trans. II* **1986,** 1197.

16) Kebarle, P.; Hogg, A.M. *J. Chem. Phys.* **1965,** *42*, 668.

17) Kebarle, P.; Haynes, R.M. *J. Chem. Phys.* **1967,** *47*, 1676.

18) Kebarle, P.; Haynes, R.M. Searles, S. In *Ion-Molecule Reactions in the Gas Phase. Advances in Chemistry*

Figure Captions.

Figure 1) Schematic sideview of the differentially pumped cluster beam appartus and quadrupole mass spectrometer. The temperature of the stagnation region and nozzle is regulated by a circulating chiller.

Figure 2) Raw spectrum of neat ethene clusters for the mass range 35 - 534 amu at 13 eV. P_o = 3.5 atm.; T_o = 296 K.

Figure 3) Raw spectrum of neat 1,1-difluoroethene clusters for the mass range 60 - 959 amu at 14 eV. P_o = 2.2 atm.; T_o = 247 K.

Figure 4) Raw spectrum of neat propene clusters for the mass range 50 - 649 amu at 10 eV. P_o = 4.0 atm.; T_o = 297 K.

Figure 5) Plots of the stoichiometric ethene cluster ion intensities, $(C_2H_4)_n^+$, as a function of expansion pressure, P_o. T_o = 296 K; Electron energy, E_e = 13 eV.

Figure 6) Plots of the stoichiometric 1,1-difuoroethene cluster ion intensities, $(C_2H_2F_2)_n^+$, as a function of expansion pressure, P_o. T_o = 247 K; E_e = 14 eV.

Figure 7) Plots of the stoichiometric propene cluster ion intensities, $(C_3H_6)_n^+$, as a function of expansion pressure, P_o. T_o = 297 K; electron energy, E_e = 10 eV.

Figure 8) Plots of the stoichiometric propene cluster ion intensities, $(C_3H_6)_n^+$, as a function of Electron energy, E_e. T_o = 297 K; P_o = 2.0 atm.

Figure 9) Proposed reaction schemes for ionic reactions within ethene (Scheme I) and propene (Scheme II) cluster ions.

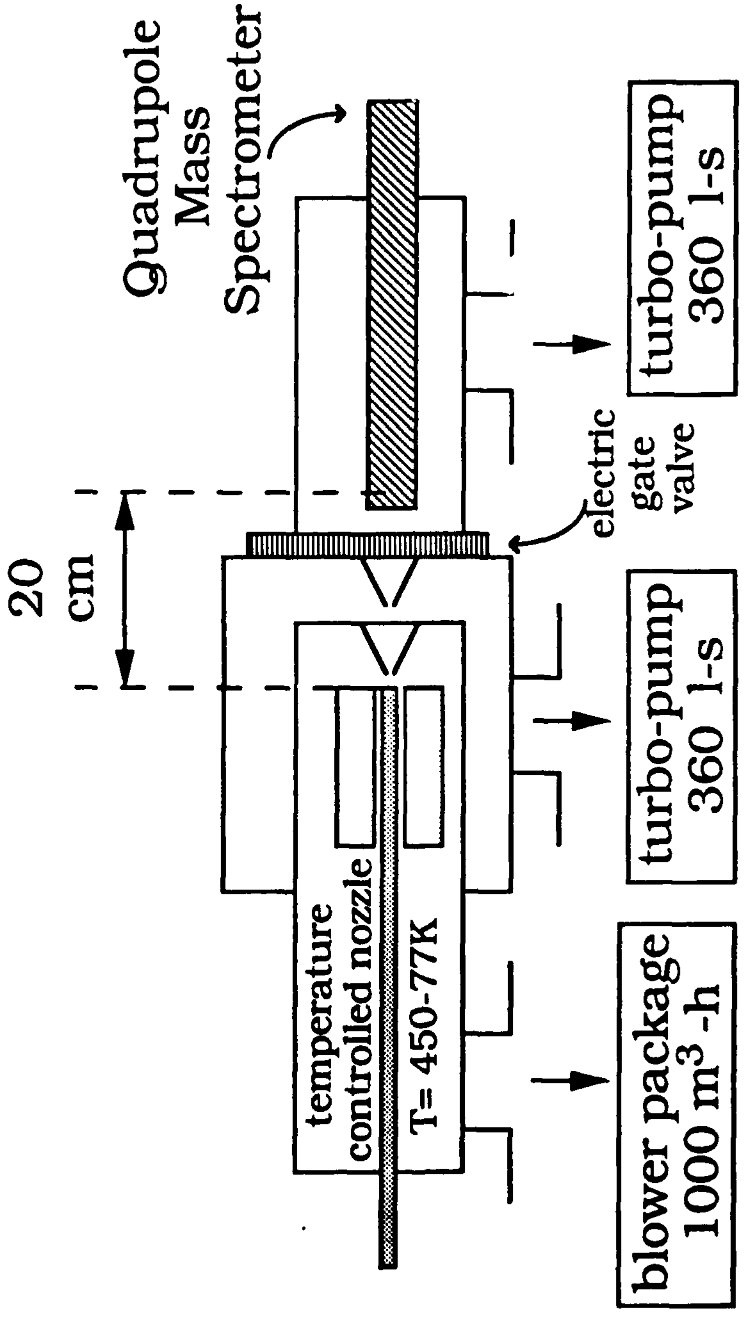
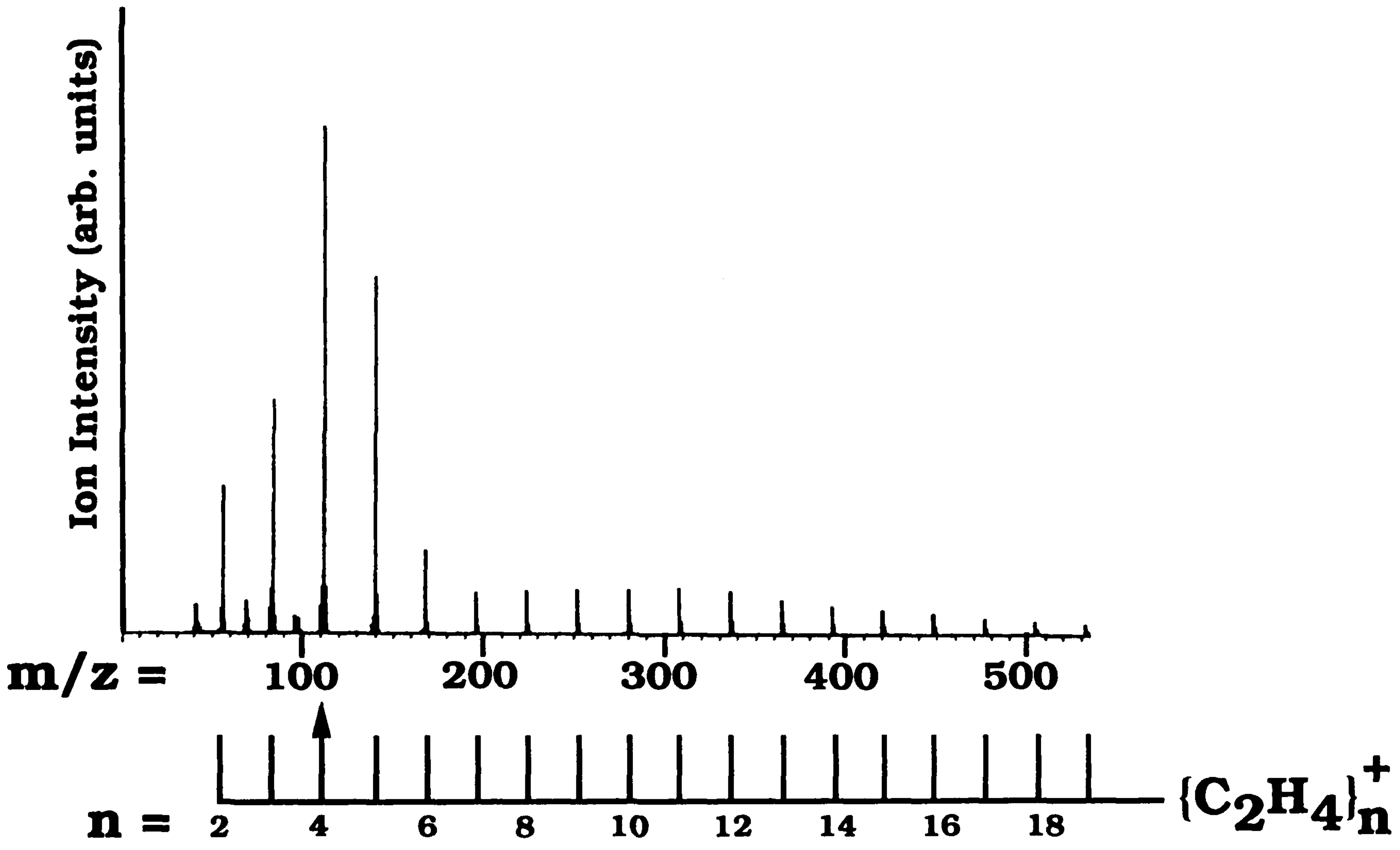


Fig. 1, Coolbaugh et al, "Observation of cationic polymerization."


Ion Intensity (arb. units)
m/z =
100
200
300
400
500
n =
2
4
6
8
10
12
14
16
18
$\{C_2H_4\}_n^+$

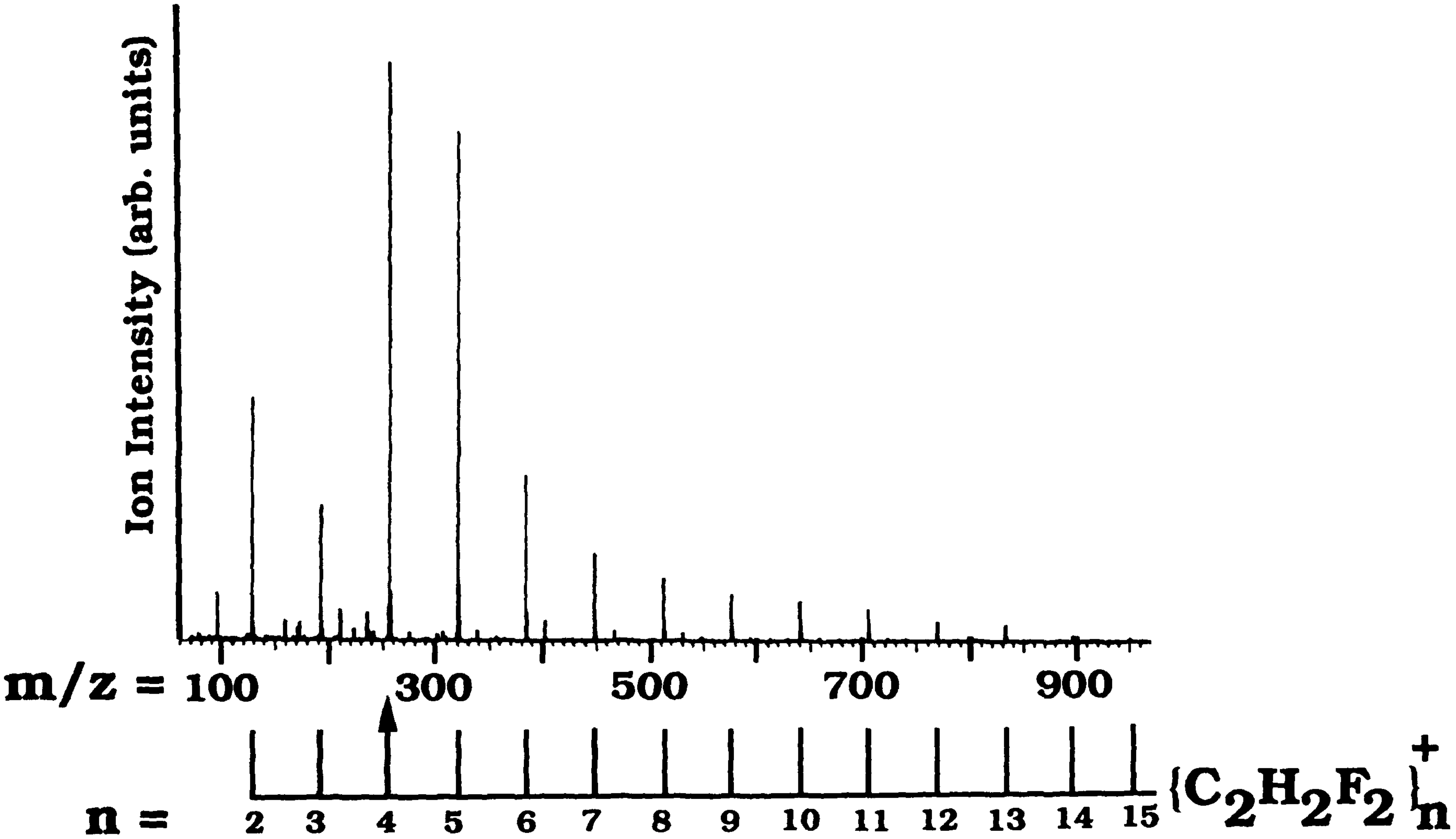
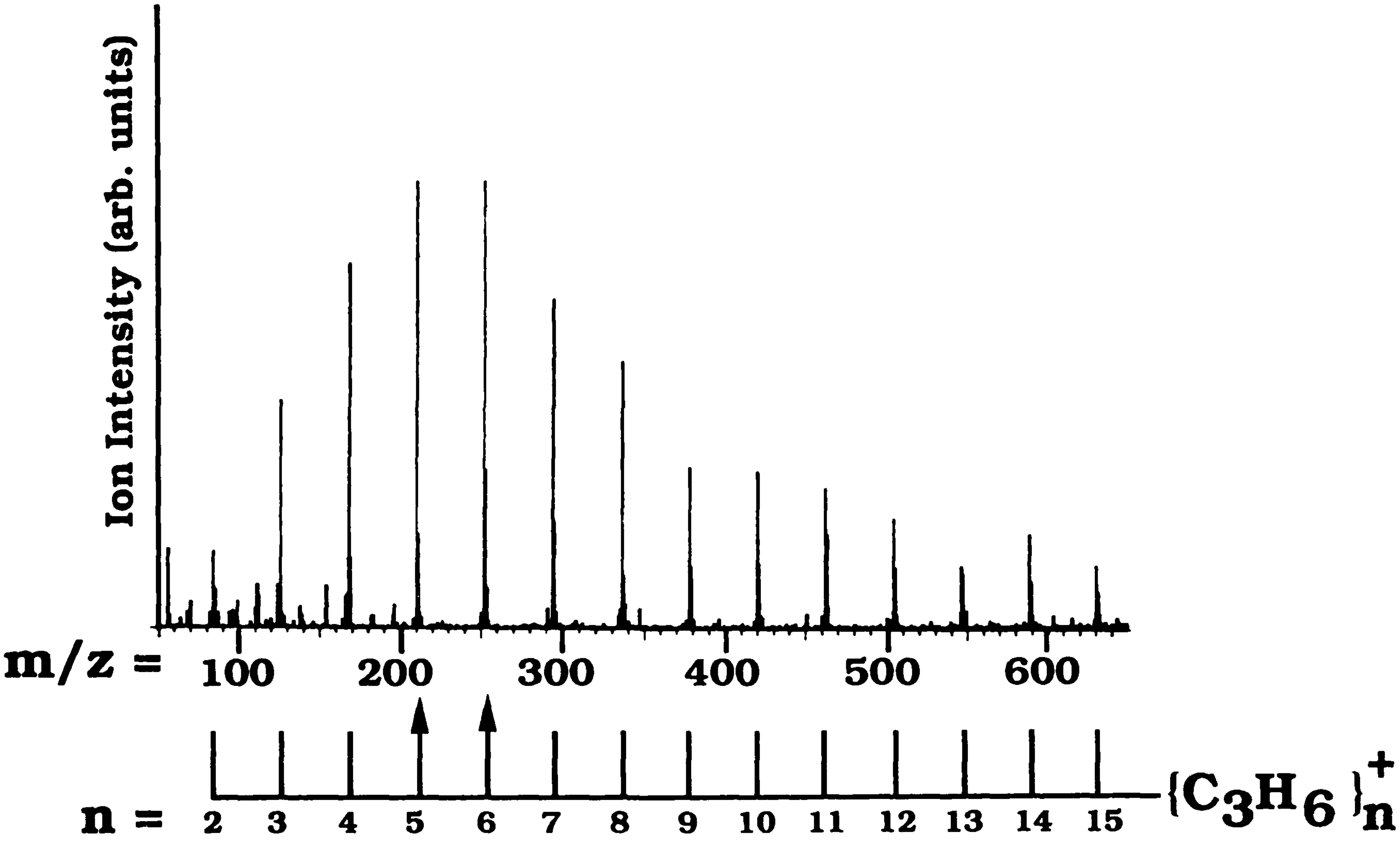
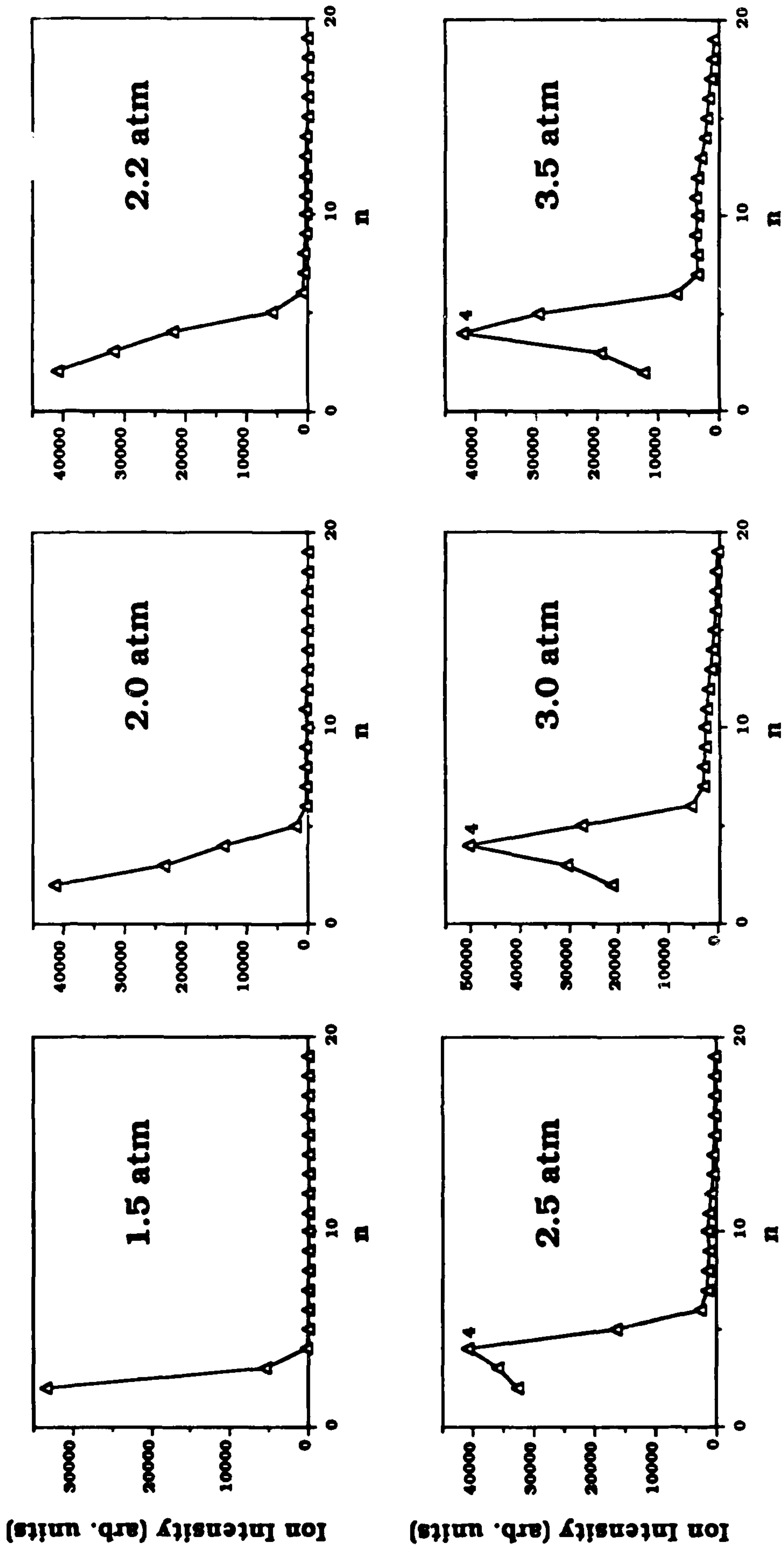
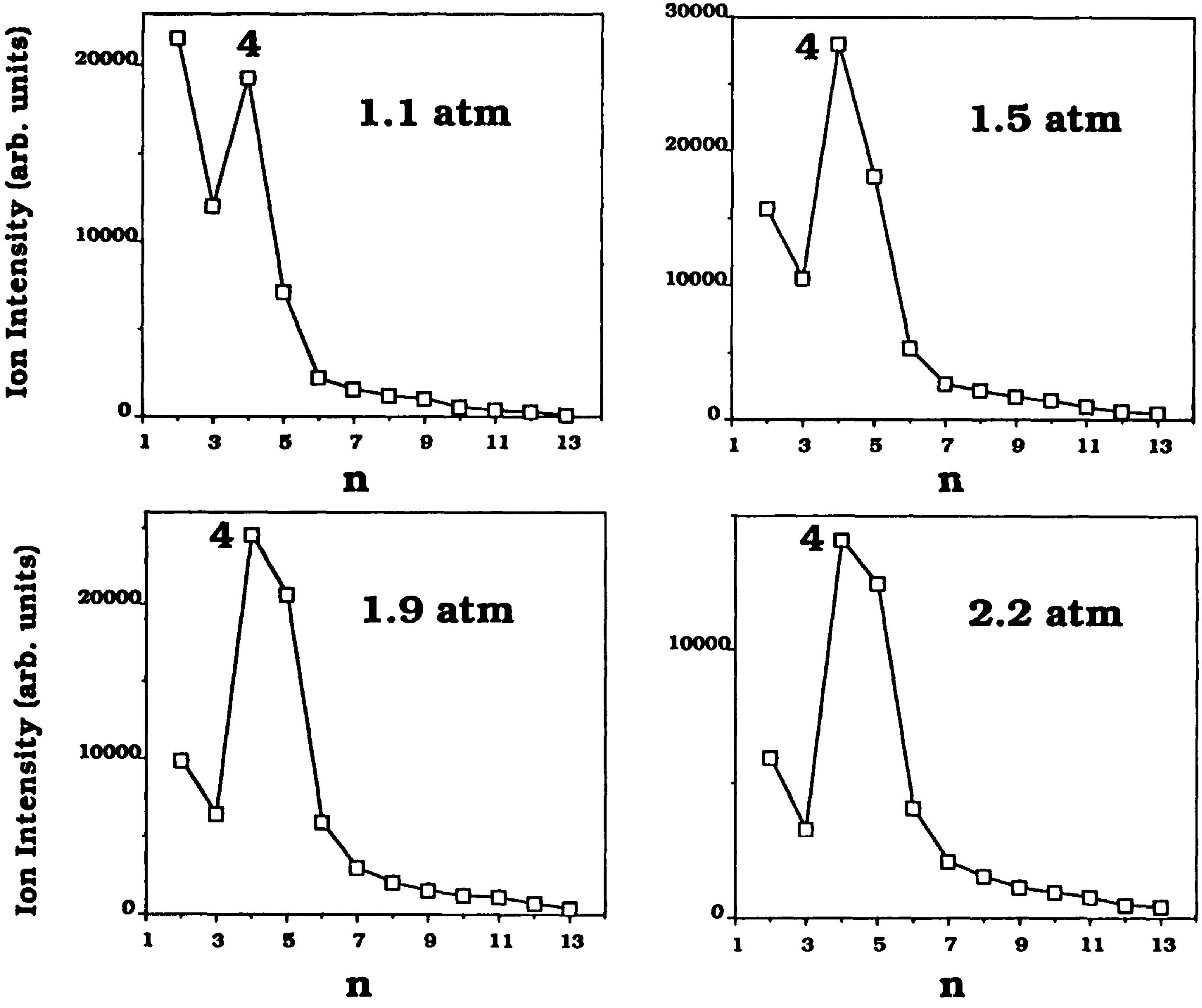
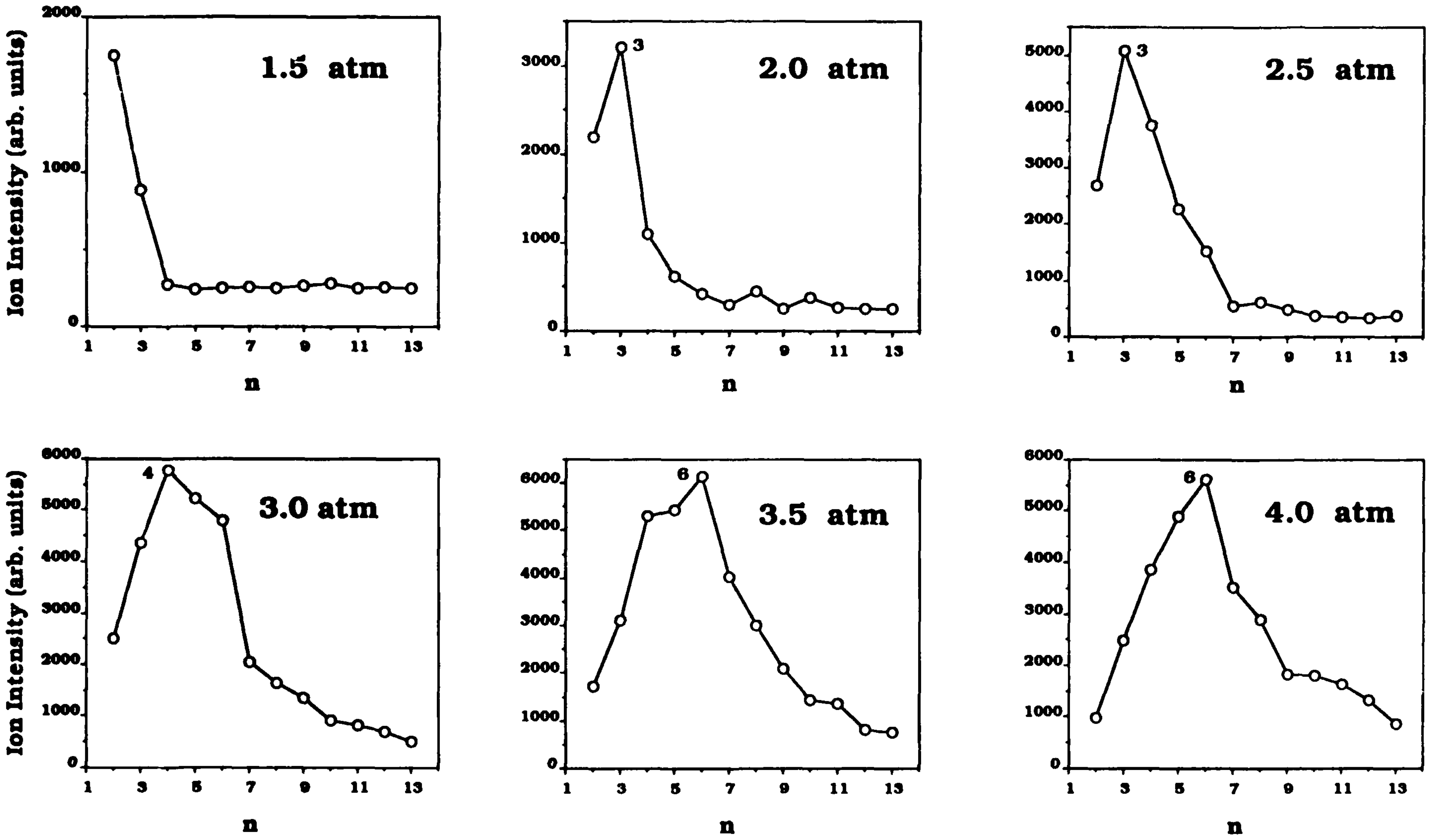


Fig. 3 Coolbaugh, et al., "Observation of Cationic Polymerization


Ion Intensity (arb. units)
m/z =
100
200
300
400
500
600
n =
2
3
4
5
6
7
8
9
10
11
12
13
14
15
$\{C_3H_6\}_n^+$


1.5 atm
2.0 atm
2.2 atm
2.5 atm
3.0 atm
3.5 atm
4
4
4
Ion Intensity (arb. units)
Ion Intensity (arb. units)
n
0
10
20
30000
20000
10000
40000
50000


Ion Intensity (arb. units)
20000
10000
0
4
1.1 atm
1
3
5
7
9
11
13
n
30000
20000
10000
0
4
1.5 atm
1
3
5
7
9
11
13
n
Ion Intensity (arb. units)
20000
10000
0
4
1.9 atm
1
3
5
7
9
11
13
n
10000
0
4
2.2 atm
1
3
5
7
9
11
13
n


Ion Intensity (arb. units)
2000
1000
0
1
3
5
7
9
11
13
n
1.5 atm
3000
2000
1000
0
3
2.0 atm
5000
4000
3000
2000
1000
0
3
2.5 atm
6000
5000
4000
3000
2000
1000
0
4
3.0 atm
6000
5000
4000
3000
2000
1000
0
6
3.5 atm
6000
5000
4000
3000
2000
1000
0
6
4.0 atm

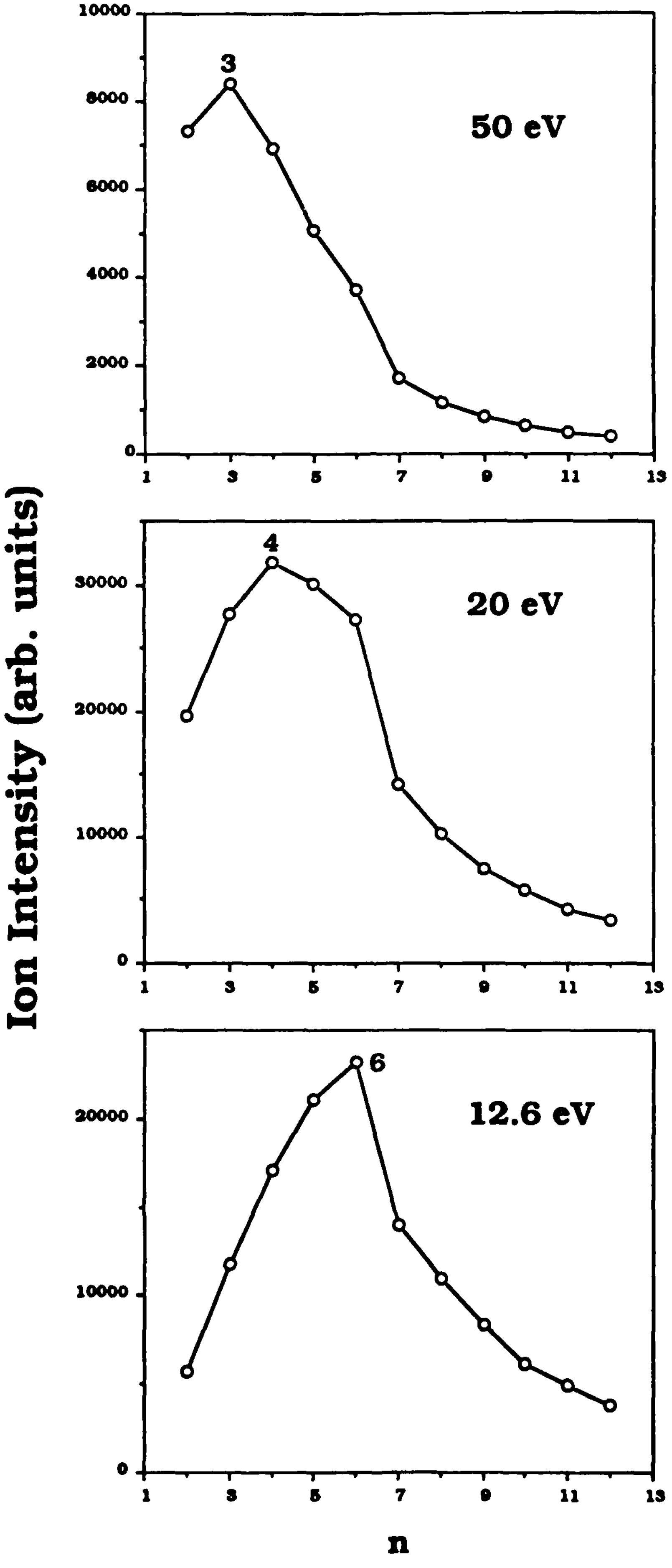
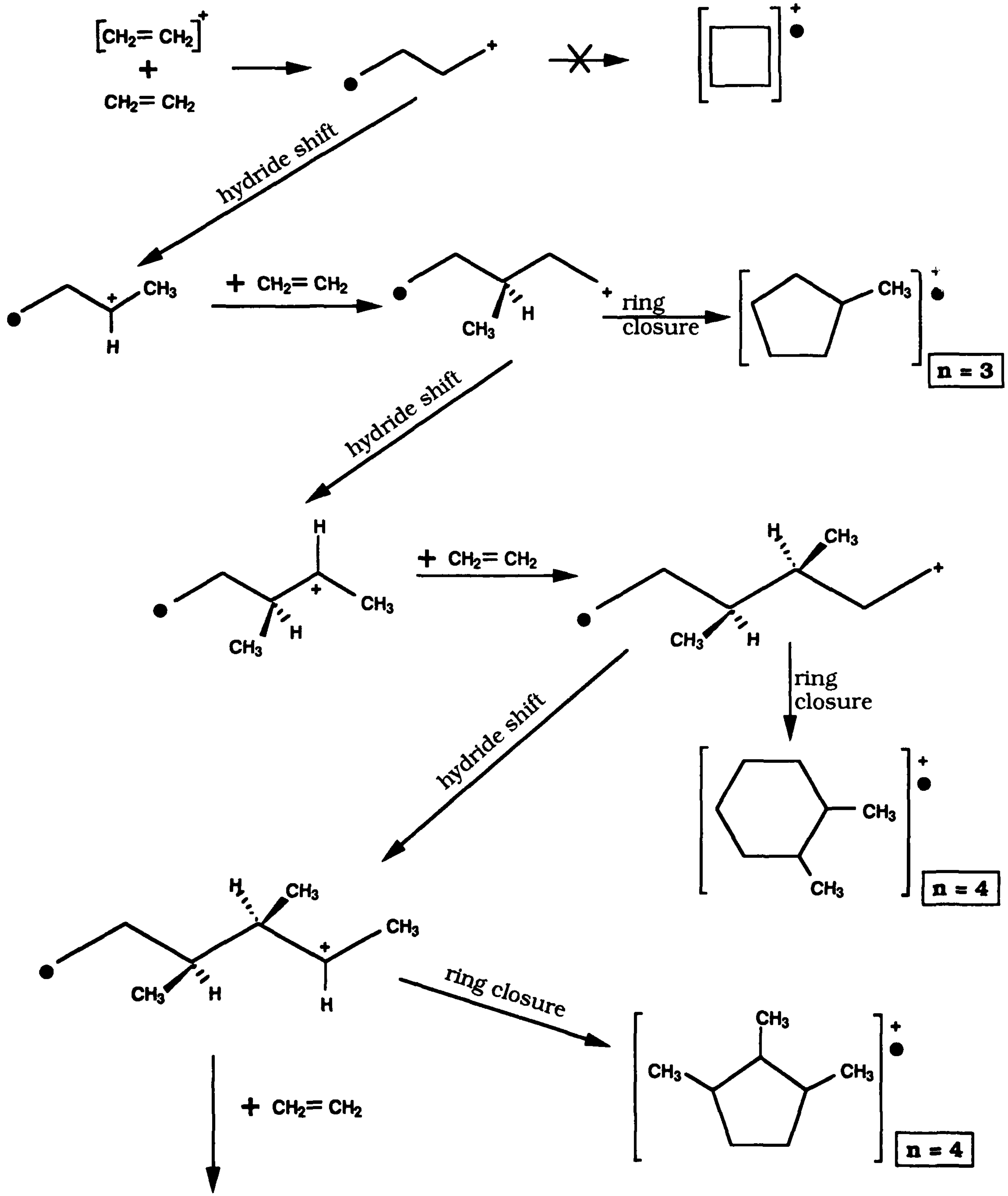

Ion Intensity (arb. units)
50 eV
3
10000
8000
6000
4000
2000
0
1
3
5
7
9
11
13
20 eV
4
30000
20000
10000
0
1
3
5
7
9
11
13
12.6 eV
6
20000
10000
0
1
3
5
7
9
11
13
n

Fig. 8. [illegible]

Scheme I: Ethylene Chemistry



Series, 58. Ausloos, P., Ed. Am. Chem. Soc.: Washington, D.C., 1968.

19) Peifer, W.R.; Coolbaugh, M.T.; Garvey, J.F. *J. Chem. Phys.* **1989,** *168*, 6684.

20) Campargue, R. *J. Phys. Chem.* **1984,** *88*, 4466.

21) O'Malley, R.M.; Jennings, K.R.; Bowers, M.T.; Anicich, V.G. *Int. J. Mass Spectrom. Ion Phys.* **1973,** *11*, 89.

22) Shinohara, H.; Sato, H.; Washida, N. *J. Phys. Chem.* **1990,** *94*, 6718.

23) Coolbaugh, M.T.; Peifer, W.R.; Garvey, J.F. *Chem. Phys. Lett.* **1990,** *168*, 337.

24) Buck, U.; Lauenstein, Ch.; Meyer, H.; Sroka, R. *J. Phys. Chem.* **1990,** *168*, 337.

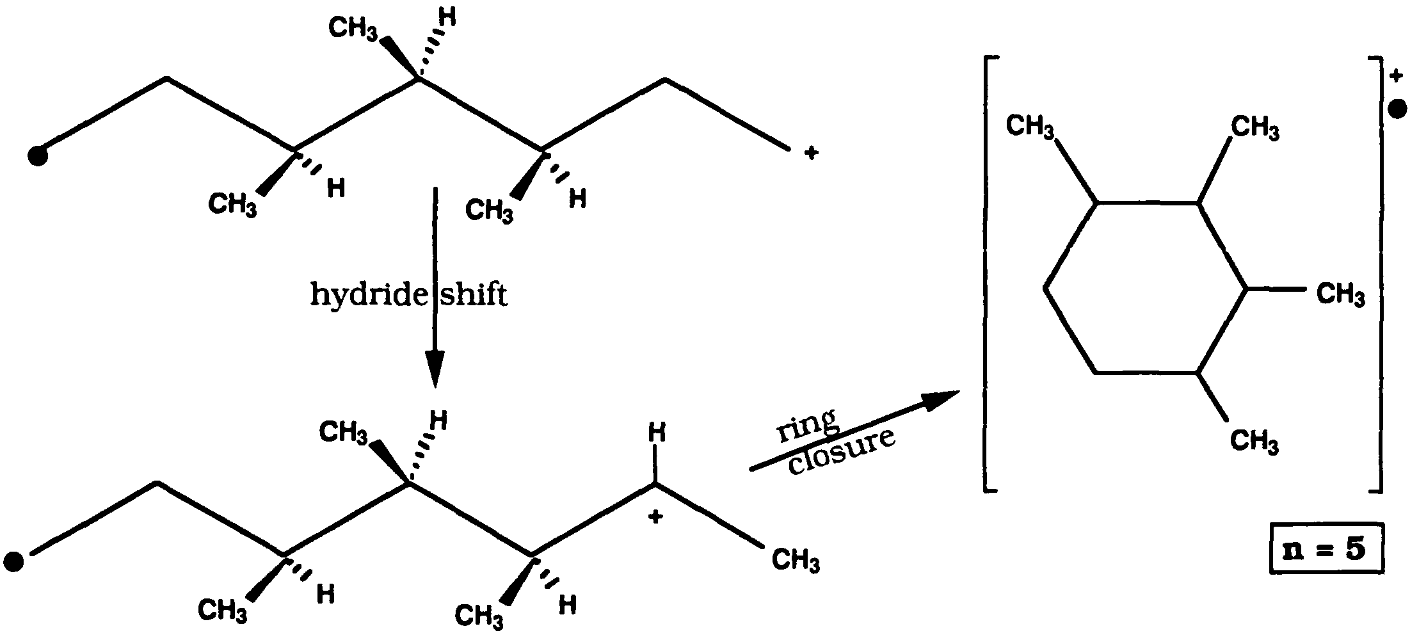
25) See for example, Allcock, H.R.; Lampe, F.W. *Contemporary Polymer Chemistry*; Prentice-Hall:Englewood Cliffs, N.J., 1981.

26) Abramson, F.P.; Futrell, J.H. *J. Phys. Chem.* **1968,** *72*, 1826.

27) Groenwald, G.S.; Chess, E.K.; Gross, M.L. *J. Am. Chem. Soc.* **1984,** *106*, 539.

28) Holman, R.W.; Rozenboom, M.D.; Gross, M.L.; Warner, C.D. *Tetrahedron* **1986,** *42*, 6235.

29) Difficulties were encountered with neat propene expansions when pressures greater than 3.5 - 4.0 atm. were utilized. Such expansions tended to form liquid jets. The same problem was encountered if T_0 was reduced.



Scheme II: Propene Chemistry