*J. Phys. Chem. A* **1997,** *101,* 3699−3701

# Laser Multiphoton Dissociation Ionization of Acrolein Clusters

**Hiroshi Morita,[†] John E. Freitas, and Mostafa A. El-Sayed***

*Department of Chemistry and Biochemistry, University of California, Los Angeles,*
*Los Angeles, California 90024*

*Received: February 19, 1996; In Final Form: February 3, 1997*[⊗]

Clusters of acrolein, $C_3H_4O$, are formed by supersonic expansion techniques. The acrolein clusters are ionized and decomposed by 193 nm light from an excimer laser and detected by time-of-flight mass spectrometry. The dominant channel of decomposition involves the loss of a carbon atom from all the clusters. The loss of $C_2$, $C_3$, and even up to $C_6$ is also observed from larger clusters. The presence of clusters with more hydrogen atoms than expected for multiples of acrolein molecules suggests that reactions within the cluster and evaporation are important processes. The mechanisms of the dissociation routes are discussed in terms of ladder and ladder-switching processes within individual molecules within the cluster.

## Introduction

Acrolein (2-propenal) is well-known to be polymerized by radical, cationic, and anionic polymerization.[1] To study the characteristics of the excited state of acrolein, the photofragmentation dynamics of acrolein were investigated in the vapor phase[2−4] and in a supersonic molecular beam.[5] In the vapor phase, acrolein in $SF_6$ or in helium gas was reported to dissociate into ethylidene diradical ($CH_3CH$) and CO from irradiation with 193 nm ArF excimer laser light[3,4] which excites the acrolein molecule to the $S_2$ ($\pi-\pi^*$) state.[6−8] From the similarity of the CO vibrational energy distribution produced from acrolein with that produced from methylketene, Lin et al.[3,4] concluded that acrolein excited to the $S_2$ state rapidly isomerizes to a methylketene-type intermediate before dissociation. On the other hand, in a supersonic molecular beam, acrolein was found to dissociate into $C_2H_3$ and CHO radicals by one-photon excitation with the 193 nm ArF excimer laser light and into CH, $C_2$, and $C_2H_2$ radicals by multiphoton absorption.[5]

In a previous paper,[9] we have studied multiphoton ionization (MPI) dissociation processes of some acrylate molecular clusters via time-of-flight (TOF) mass spectrometry. We found that the dominant channel of decomposition is the loss of the methoxy group in methyl acrylate and the loss of the ethoxy group in ethyl acrylate. In the $S_2$ ($\pi-\pi^*$) state, acrolein has intramolecular charge-transfer (CT) character between C=C and C=O double bonds[10] and is expected to show chemical behavior different from that of the acrylates. In the present study, in order to investigate the MPI processes involved in the decomposition of the acrolein clusters in a supersonic molecular beam, ArF excimer laser light (193 nm) was used as the ionization source, and the resulting TOF mass spectra were measured. From the assignment of the observed mass peaks, we have been able to deduce the dissociation channels of the acrolein cluster ions.

## Experimental Section

Acrolein (AC) (Aldrich Chemical Co., 97%, inhibited with ≈3% water and 200 ppm hydroquinone and stored in a refrigerator) was distilled under vacuum and degassed three times in the dark by freeze−pump−thaw cycles immediately before use. The vapor of acrolein was mixed with pure (99.999%) helium gas at a pressure of 2.0 atm and was guided to a pulsed nozzle in a cluster beam apparatus constructed in this laboratory. The details of the cluster beam appratus and TOF mass spectrometer are described elsewhere.[11] A flat nozzle (1 mm diameter) attached to a conical aluminum block was driven by a pulsed valve and was used to produce cluster beam pulses of 150 $\mu$s. A molecular beam well collimated through a 2 mm skimmer was photoionized by use of a Lambda Physik EMG101 ArF excimer laser of wavelength 193 nm (6.4 eV), and photoions formed were analyzed by a 1.7 m TOF mass spectrometer. The ionizing laser fluences ranging from 1.3 to 6.4 mJ/cm$^2$ were varied by inserting several quartz plates in the optical path.

## Results and Discussion

Figure 1 shows a typical product distribution of acrolein clusters detected by the laser photoionization photofragmentation processes involved. The mass spectrum shows four main progressions. The first one is assigned to acrolein clusters [$(AC)_x^+$, $x = 1-13$] which are formed with up to 13 molecules. As is easily seen in the spectra of $(AC)_1^+$ to $(AC)_4^+$, each acrolein cluster band has fine structures which arise from the loss or gain of one or two hydrogen atoms. The appearance of the fine structures with more hydrogens shows that the smaller clusters are formed appreciably through the decomposition of the larger clusters. In this respect, it is noteworthy that the intensity of the $C_3H_2O^+$ (i.e., $[(AC)_1-H_2]^+$) band is stronger than that of the $(AC)_1^+$ band.

The second progression in the mass spectrum which has the strongest band intensity among the four progressions is assigned to the clusters that lose one carbon atom from one acrolein molecule in the clusters. These clusters are assigned to the molecular formula $[(AC)_{x-1}(CH_3CHO)]^+$ with $x = 2-13$. This progression extends to the monomer region, i.e., with $x = 1$ which gives very weak peaks at $m/e$ values corresponding to $[(AC)_1-C]^+$ (i.e., $[CH_3CHO]^+$) and to $[(AC)_1-CH_2]^+$ (i.e., $[CH_2{=}C{=}O]^+$) bands. The third progression is assigned to the clusters that lose two carbon atoms (most likely $C_2$) from one acrolein molecule in the clusters to give $[(AC)_{x-1}(CH_3OH)]^+$ with $x = 3-13$ or from two acrolein molecules to give $[(AC)_{x-2}(CH_3CHO)_2]^+$ for $x = 4-13$. Another progression can result from the loss of two carbon and two hydrogen atoms (most likely $H_2$) to give $[(AC)_{x-1}(HCHO)]^+$ with $x = 2-5$. The fourth mass progression in the spectrum corresponds to the clusters that lose three carbon atoms $[(AC)_x-C_3]^+$ for $x = 6-13$

---

[†] Permanent address: Graduate School of Science and Technology, Chiba University, Yayoi-cho, Inage-ku, Chiba, Chiba 263, Japan.

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1997.

S1089-5639(96)00501-4 CCC: $14.00

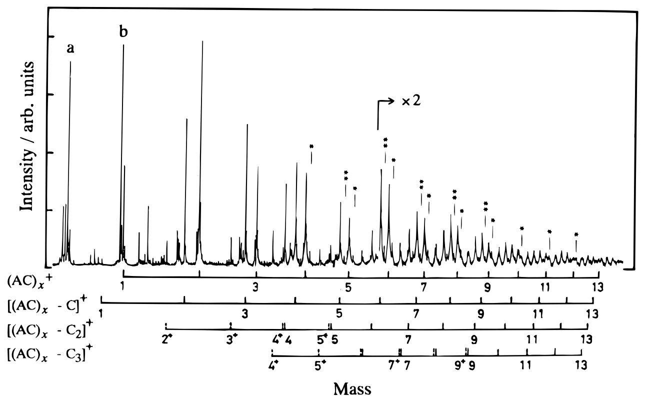

**Figure 1.** Mass spectrum of acrolein clusters ionized by 193 nm laser light. Weak bands assigned to $[(AC)_x{-}C_4H_2]^+$ are denoted by * and those assigned to $[(AC)_x{-}C_5H_2]^+$ by **. Strong bands assigned to $C_2H_3{}^+$ (loss of CHO) and $C_3H_2O^+$ (i.e., loss of $H_2$) are denoted by a and b, respectively. The number $x$ for $[(AC)_x{-}C_2H_2]^+$ and $[(AC)_x{-}C_3H_2]^+$ bands is denoted by $x^+$ on the abscissas for $[(AC)_x{-}C_2]^+$ and $[(AC)_x{-}C_3]^+$ bands, respectively.

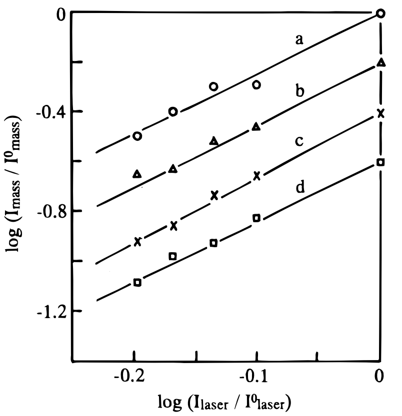

**Figure 2.** Ionizing laser intensity dependence of (a) $(AC)_4{}^+$, (b) $[(AC)_4{-}C]^+$, (c) $[(AC)_4{-}C_2]^+$, and (d) $[(AC)_4{-}C_3H_2]^+$. The ordinates are shifted consecutively by −0.2 from (a) to (b), (c), and (d).

**TABLE 1: *n*-Values of Some Acrolein Cluster Bands Determined from the Ionizing Laser Intensity Dependence**

| $x$ | $(AC)_x{}^+$ | $[(AC)_x{-}C]^+$ | $[(AC)_x{-}C_2]^+$ | $[(AC)_x{-}C_3H_2]^+$ |
|---|---|---|---|---|
| 1 | 2.5 | | | |
| 2 | 2.1 | 2.7 | | |
| 3 | 2.5 | 2.6 | | |
| 4 | 2.4 | 2.5 | 2.6 | 2.4 |
| 5 | 2.4 | | | |
| 6 | 2.4 | | | |

and/or three carbon and two hydrogen atoms (most likely $H_2$) $[(AC)_x{-}C_3H_2]^+$ for $x = 4{-}9$. Almost all of the main peaks in the spectrum can be assigned to a member of these four progressions. In addition to the four progressions, there are weak peaks which correspond to the loss of four carbon and two hydrogen atoms for $x = 5{-}13$, to the loss of five carbon and two hydrogen atoms for $x = 6{-}10$, and to the loss of six carbon and two hydrogen atoms for $x = 6{-}10$. All these observed mass peaks clearly show that the C=C double bond is dissociated by the MPI process with193 nm laser light. This markedly differs from the case of one-photon excitation of the acrolein monomer in which acrolein decomposes predominantly into $C_2H_4$ and CO in the vapor phase[4] and into $C_2H_3$ and CHO in a supersonic molecular beam.[5] In the present experiment, we can observe the strong $C_2H_3{}^+$ band together with a weak band ($m/e = 28$) which may be $C_2H_4{}^+$ or $CO^+$. In the multiphoton excitation with 193 nm laser light, $C_2H_2$, $C_2$, and CH fragments were reported for acrolein in a supersonic molecular beam.[5]

Undoubtedly, cluster dissociation occurs immediately upon interaction with the 193 nm laser light, since the monomer units within the clusters are bound by relatively weak van der Waals forces:

$$(AC)_x + nh\nu \rightarrow (AC)_{x-y} + [(AC)_{y-1}(C_3H_2O)]^+ + H_2 \tag{1}$$

Elimination of hydrogen is believed to occur upon cluster fragmentation. The most stable isomer of $C_3H_2O$ is undoubtedly propadienone,[12,13] $CH_2{=}C{=}C{=}O$. For the cationic species of $C_3H_2O^{\bullet+}$, a recent theoretical calculation by ab-initio methods[14] predicted that $[CH{=}CH{-}C{=}O]^{\bullet+}$ has a similar thermodynamic stability to that of the most stable cationic isomer, $[CH_2{=}C{=}C{=}O]^{\bullet+}$. Although the intensities are weak, other types of cluster peaks are observed in Figure 1 which show a loss of one oxygen atom $[(AC)_x{-}O]^+$ for $x = 1{-}4$, one oxygen and one hydrogen atoms $[(AC)_x{-}OH]^+$ for $x = 2{-}4$, and one oxygen and two hydrogen atoms $[(AC)_x{-}OH_2]^+$ for $x = 1{-}4$ from the acrolein clusters. One cannot know whether the $OH_2$ loss results from one or more than one acrolein molecules.

In order to investigate the dissociation process of acrolein clusters during multiphoton dissociation and ionization, the ionizing laser intensity ($I_{laser}$) dependence of the mass peak intensity ($I_{mass}$) was measured. As is shown in Figure 2, log($I_{mass}/I^0_{mass}$) was plotted vs log($I_{laser}/I^0_{laser}$), and the value $n$ was determined from the slope. The results are tabulated in Table 1. The $n$ value for the mass peaks of the acrolein clusters $(AC)_x{}^+$ is rather constant ($n = 2.4{-}2.5$) for $x = 1{-}6$ (except for $x = 2$), which means that the ionization process of the acrolein clusters we observe needs at least two, most likely three, photons of 193 nm. This corresponds to 19.3 eV. This is 9 eV higher than the ionization potential for acrolein (10.11 eV).[15,16] A good fraction of the ionized molecules must then dissociate or evaporate to result in the fragmentation into ions and radicals. Their formation from larger clusters is also a possibility.

The $n$ values for $[(AC)_4{-}C]^+$, $[(AC)_4{-}C_2]^+$, and $[(AC)_4{-}C_3H_2]^+$ have also been determined and compared. They do not change significantly from the value of $(AC)_4{}^+$, showing that to eliminate carbon atoms, absorption of additional photons is not needed. These results suggest that carbon atoms are eliminated during the relaxation process of the ionic excited state. It appears likely that ionization occurs prior to elimination of carbon atoms from the cluster. Two photons of 193 nm light provide 12.84 eV, which exceeds the ionization potential of acrolein by 2.73 eV. Thus, ionization is highly likely to be the initial step. This is supported by the fact that the mass peak intensities of the parent clusters are among the most intense. This usually suggests a ladder mechanism[17] in which ionization occurs first and is then followed by decomposition or by further photon absorption and then decomposition. An ion−molecule reaction between the parent ion and one or more of the neutral monomer units within the cluster is thus possible.

A strong mass peak corresponding to $C_2H_3{}^+$ (peak a) in Figure 1 was observed, accompanied with weaker mass peaks corresponding to $C_2H_2{}^+$ and $C_2H^+$. The $n$ value for the intensities of the $C_2H_3{}^+$ and $C_3H_2O^+$ (i.e., $[(AC)_1{-}H_2]^+$) bands (bands a and b in Figure 1) have both been determined to be 1.4. This value suggests that these ions are produced from the absorption of at least two photons. If they are produced from the absorption of only two photons, then they are produced from the parent ion by a ladder mechanism. If more than two photons are absorbed, then they could be produced from a ladder-switching mechanism involving dissociation first followed by

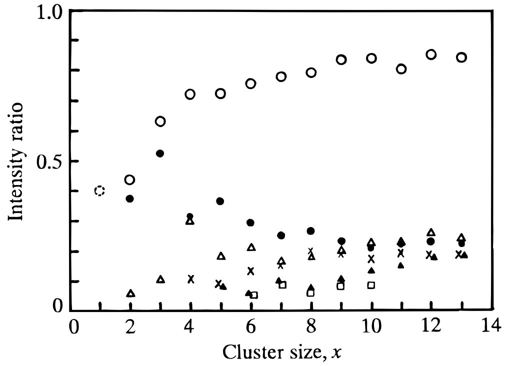

**Figure 3.** Dependence of the mass peak intensity ratio of individual fragment cluster daughter ions produced from cluster $x$ to the sum of mass peak intensities produced from cluster $x$, including the mass peak intensity of the parent ion cluster on the cluster size: (●) $[(AC)_x{-}C]^+$; (△) $[(AC)_x{-}C_2]^+$ and/or $[(AC)_x{-}C_2H_2]^+$; (×) $[(AC)_x{-}C_3]^+$ and/or $[(AC)_x{-}C_3H_2]^+$; (▲) $[(AC)_x{-}C_4H_2]^+$; (□) $[(AC)_x{-}C_5H_2]^+$. (○) is for the ratio of the total fragment peak intensity produced from cluster $x$ to the total mass peak intensity including that for the parent ion mass peak of size $x$. The figure gives a qualitative picture of the dependence of the probability of losing small fragmnents from the parent ion $x$ as well as the total fragmentation probability (○) on the cluster size ($x$).

the ionization of the radicals. It is thus possible that the laser intensity in our experiments is sufficiently high that two-photon absorption processes compete with the one-photon dissociation of the monomer which gave $C_2H_3$ and CHO radicals. Furthermore, the elimination of either the CHO radical or the $C_2H_3$ radical is not observed for the clusters with $x > 1$. This strongly suggests that the intense mass peak labeled (a) results from the dissociation of the monomer ion itself to give $C_2H_3^+$.

The loss of carbon atoms from the acrolein ions must be a high-energy channel and should have a very high barrier as well:

$$(H_2C{=}CH{-}CHO)^+ + nh\nu \rightarrow C + CH_3{-}CHO^+ \qquad (2)$$

This suggests that the absorbed energy must be sufficiently high and involves a number of photons in order to reduce the time of dissociation below the microsecond limit of the experimental time constant. Excess energy of over 9 eV of three photons above ionization could make it possible to observe this channel.

Acrolein is highly reactive to form polyacrolein in the vapor phase.[18,19] If the polymerization happened to occur in the acrolein cluster following the ionization, the C=C double bond converts into a C−C single bond, and elimination of C and/or $CH_2$ become easier. One may wonder about whether or not the energy randomizes over the whole cluster before dissociation occurs. This is unlikely since the evaporation of the acrolein monomers would be the lowest energy channel. It is thus likely that the multiphoton absorption occurs by one of the acrolein molecules within the cluster, which then leads to its ionization and dissociation. This also argues against the energy pooling mechanism[20] resulting from intermolecular energy transfer and exciton annihilation, as this would lead to more energy randomization and increase the probability of evaporation. Rapid ion−molecule reactions could be occurring within the clusters. The loss of carbon atoms might be a result of such reactions. Furthermore, it is very likely that the loss of more than one carbon atom occurs via the loss of molecular species (e.g. $C_2$, $C_3$) or from different excited molecules within the cluster.

Figure 3 shows a plot of the relative intensity of each fragment peak produced from a certain cluster $x$ to the total mass peak intensity of all the mass peaks produced from this particular cluster $x$ (including the parent cluster ion mass peak). In addition, it gives the ratio of the sum of intensities of all the mass peaks of the fragments produced to the same total peak intensity including that of the parent cluster ion.

It is seen that the probability of losing one carbon atom (the solid circles) decreases and then levels off at $x \approx 9$ as the cluster size increases. At the same time, the probability of the loss of two (△), three (×), and four (▲) carbon atoms as well as the total fragmentation probability (given by the open circles) increases with cluster size. The total probability reaches to a constant value at around $x = 9$. These results can be rationalized as follows. As the cluster size increases, the number of channels available for the photolysis increases beyond the channel of losing only one carbon atom as more molecules can absorb the radiation and lose carbon and hydrogen atoms.

**Acknowledgment.** The authors thank the Office of Naval Research for financial support. H.M. thanks the Yamada Science Foundation for a research scholarship.

## References and Notes

(1) Odian, G. *Principles of Polymerization*; Wiley-Interscience: New York, 1981; p 409.
(2) Coomber, J. W.; Pitts, J. N., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 547.
(3) Umstead, M. E.; Shortridge, R. G.; Lin, M. C. *J. Phys. Chem.* **1978**, *82*, 1455.
(4) Fujimoto, G. T.; Umstead, M. E.; Lin, M. C. *J. Chem. Phys.* **1985**, *82*, 3042.
(5) Shinohara, H.; Nishi, N. *J. Chem. Phys.* **1982**, *77*, 234.
(6) Walsh, A. D. *Trans. Faraday Soc.* **1945**, *41*, 498.
(7) Dykstra, C. E. *J. Am. Chem. Soc.* **1976**, *98*, 7182.
(8) Davidson, E. R.; Nitzsche, L. E. *J. Am. Chem. Soc.* **1979**, *101*, 6524.
(9) Morita, H.; Freitas, J. E.; El-Sayed, M. A. *J. Phys. Chem.* **1991**, *95*, 1664.
(10) Nagakura, S. *Mol. Phys.* **1960**, *3*, 105.
(11) St. Pierre, R. J.; El-Sayed, M. A. *J. Phys. Chem.* **1987**, *91*, 763.
(12) Komornicki, A.; Dykstra, C. E.; Vincent, M. A.; Radom, L. *J. Am. Chem. Soc.* **1981**, *103*, 1652.
(13) Brown, R. D.; Champion, R.; Elmes, P. S.; Godfrey, P. D. *J. Am. Chem. Soc.* **1985**, *107*, 4109.
(14) Bouchoux, G.; Hoppilliard, Y.; Flament, J. P.; Terlouw, J. K.; van der Valk, F. *J. Phys. Chem.* **1986**, *90*, 1582.
(15) Watanabe, K. *J. Chem. Phys.* **1957**, *26*, 542.
(16) Turner, D. W. *Adv. Phys. Org. Chem.* **1966**, *4*, 31.
(17) Gobeli, D. A.; Yang, J. J.; El-Sayed, M. A. *Chem. Rev.* **1985**, *85*, 529.
(18) Lewis, F. D.; Nepras, M. J.; Hampsch, H. L. *Tetrahedron* **1987**, *43*, 1635.
(19) Morita, H.; Shimizu, M. *J. Phys. Chem.***1995**, *99*, 7621.
(20) (a) Schriver, K. E.; Hahn, M. Y.; Whetten, R. L. *Phys. Rev. Lett.* **1987**, *59*, 1906. (b) Hahn, M. Y.; Schriver, K. E.; Whetten, R. L. *J. Chem. Phys.* **1988**, *88*, 4242.