

Characterization of the anionic intracuster polymerization reaction product of 2-chloroacrylonitrile trimers by photoelectron spectroscopy

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Received 4 August 1996; in final form 25 January 1997

Abstract

Photoelectron spectra are presented for the $[(\text{CAN})_3-3\text{HCl}]^-$ product formed by electron attachment onto clusters of 2-chloroacrylonitrile (CAN; $\text{CH}_2=\text{CClCN}$), and for the molecular anion of 1,3,5-tricyanobenzene (TCB; $\text{C}_6\text{H}_3(\text{CN})_3$). The spectra show that the vertical detachment energy (VDE) of $[(\text{CAN})_3-3\text{HCl}]^-$ (1.83 ± 0.015 eV) is in good agreement with the VDE of TCB^- (1.84 ± 0.015 eV). This result suggests that electron attachment onto CAN clusters initiates an anionic polymerization reaction to form the cyclic trimer reaction product, TCB^- , as inferred previously by Kondow and co-workers from an analysis of mass-spectral data.

1. Introduction

Ionic polymerization within weakly bound molecular clusters is currently under investigation by several groups, since this phenomenon allows one to explore how chain reactions proceed in finite systems [1–10]. Typically, intracuster ionic polymerization has been studied by using mass spectroscopy to identify the ionic species produced by ionization or electron attachment onto neutral clusters. A major finding from these studies is that cluster cations and

anions of certain sizes exhibit extraordinarily high abundance in the mass spectra [1,2,4–7]. These features have been ascribed to cyclic molecular ions which represent chain termination by ring formation. In a series of papers, the Tokyo and Yale groups have presented mass-spectroscopic evidence for anionic polymerization within clusters of vinyl monomers [4–8]. For example, anionic polymerization is suggested to occur within the clusters of 2-chloroacrylonitrile (CAN; $\text{CH}_2=\text{CClCN}$) upon collisional electron transfer from highly excited Rydberg atoms of krypton. The negative ion mass spectrum produced from CAN vapor expanded in a free jet exhibits mass peaks assignable to sequential elimination of HCl molecules (denoted $[(\text{CAN})_n-m\text{HCl}]^-$, $n \geq m$) from the nascent $(\text{CAN})_n^-$ clusters.

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A sharp reduction in the intensity of the $[(\text{CAN})_n - m\text{HCl}]^-$ ion series in going from $n = 3$ to 4 has been attributed to preferential formation of cyclic molecular anions with six-membered carbon structures, namely the molecular anion of 1,3,5-tricyanobenzene (TCB; $\text{C}_6\text{H}_3(\text{CN})_3$) [5–7].

To test the cyclization hypothesis, we have characterized the cluster anions of the vinyl monomers using photodissociation, [8] photoelectron spectroscopy (PES) [9] and collision induced dissociation (CID) [10]. The CID study revealed the covalent nature of the intermolecular bonds in acrylonitrile (AN; $\text{CH}_2=\text{CHCN}$) cluster anions [10]. The structural transition from linear chain to ring at $n = 3$ has been implied for $(\text{AN})_n^-$ by PES [9]. A more direct method to identify the anionic products, however, would be to compare the chemical and/or physical properties of the putative ring compounds with the relevant chemical species when the latter can be prepared and isolated. In this Letter, we compare the negative ion photoelectron spectrum of the cluster-generated anionic polymerization product $[(\text{CAN})_3 - 3\text{HCl}]^-$ with that of the molecular anion, TCB^- (generated by vaporizing a solid sample of TCB prepared by conventional organic synthesis). This comparison indicates that both species have similarly shaped spectra with nearly identical vertical detachment energies (VDEs), leading us to conclude that stable anions with six-membered carbon rings are indeed formed in electron attachment onto CAN clusters.

2. Experimental

The photoelectron spectra of TCB^- and $[(\text{CAN})_3 - 3\text{HCl}]^-$ were recorded by the Johns Hopkins group (see Fig. 1a and 1b). Details of the experimental apparatus have been previously described. [11] Some measurements were also made by the Yale and Tokyo groups. The sample of TCB was synthesized by the Tokyo group using reported procedures and examined by NMR spectroscopy [12,13].

Mass-selected beams of TCB^- and $[(\text{CAN})_3 - 3\text{HCl}]^-$ were prepared using a temperature controlled, supersonic expansion ion source [14]. Typical mass spectra for these two experiments are shown

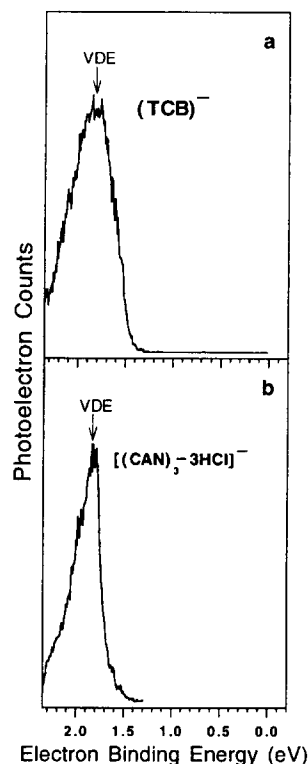


Fig. 1. Photoelectron spectra of (a) TCB^- and (b) $[(\text{CAN})_3 - 3\text{HCl}]^-$ both measured with the photon energy of 2.54 eV. The vertical detachment energies (VDEs) are indicated via arrows and were found to be 1.84 ± 0.015 eV and 1.83 ± 0.015 eV for TCB^- and $[(\text{CAN})_3 - 3\text{HCl}]^-$, respectively.

in Fig. 2a and 2b. To form TCB^- , a solid sample of TCB was heated to 134°C , and the resulting vapor was co-expanded with 3–4 atm of high purity argon into a vacuum through a $15 \mu\text{m}$ nozzle. The anion beam of $[(\text{CAN})_3 - 3\text{HCl}]^-$ was generated by expanding CAN vapor (over the liquid) with 2–3 atm of high purity argon into a vacuum through a $20 \mu\text{m}$ nozzle maintained at 25°C . In both cases, low energy electrons from a negatively biased (-40 to -60 V) filament were injected into the expanding jet in the presence of a magnetic field. The mass spectrum resulting from the evaporation of TCB (Fig. 2a) exhibited a substantial simplification over that resulting from the expansion of CAN vapor (Fig. 2b).

To record the photoelectron spectra, the ions of TCB^- or $[(\text{CAN})_3 - 3\text{HCl}]^-$ were mass-selected by a Wien filter and crossed with the intracavity photon

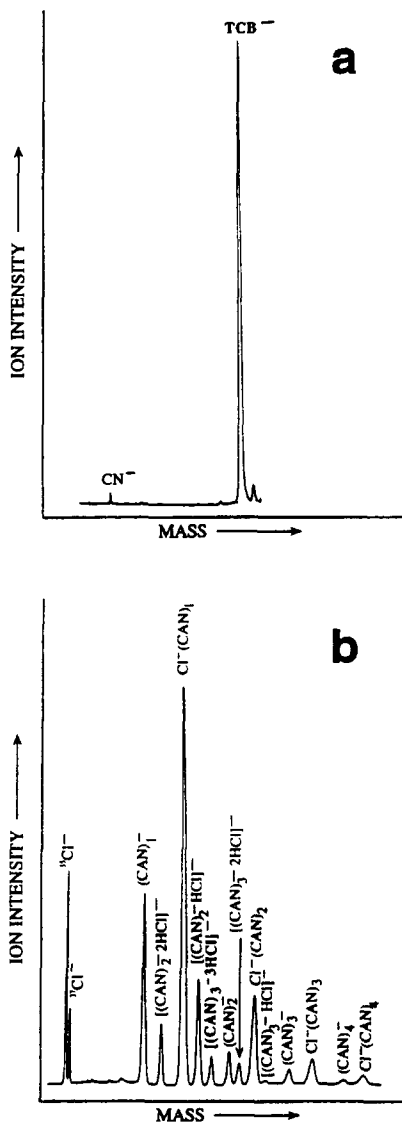


Fig. 2. Negative ion mass spectra of (a) the molecular anion TCB^- and (b) the $(\text{CAN})_n^-$ cluster anions and their fragments (including $[\text{CAN}_3-3\text{HCl}]^-$). Typical source operating conditions for ion production are described in the text.

beam of an argon ion laser operating at 488 nm and ≈ 200 circulating watts. A small solid angle of the resultant photodetached electrons were passed through a hemispherical electron energy analyzer, with a typical full-width-at-half-maximum (FWHM) resolution of 27 meV, and detected by an electron multiplier.

3. Results

The photoelectron spectrum of TCB^- is displayed in Fig. 1a. The VDE of TCB^- was determined to be 1.84 ± 0.015 eV by fitting the photoelectron spectrum to an asymmetric Gaussian and assigning VDE to the resulting fit at the peak maximum. The VDE of TCB^- is the energy difference between TCB^- in its ground state and the TCB neutral at the equilibrium geometry of the anion. The VDE is the upper limit to the value of the adiabatic electron affinity (AEA). Examination of the spectrum in Fig. 1a suggests that the AEA of TCB is around 1.5 eV. (An AEA of 1.17 eV had been previously reported for TCB [15]). The difference between the VDE and AEA values indicates that TCB experiences substantial structural change upon electron attachment, an observation that is consistent with the expectation that the symmetry of TCB^- is lowered to C_{2v} from D_{3h} due to the Jahn–Teller effect [16].

The photoelectron spectrum of $[(\text{CAN})_3-3\text{HCl}]^-$ is displayed in Fig. 1b. The PES consists of a single broad band peaking at 1.83 ± 0.015 eV. The similarity between the VDE values of $[(\text{CAN})_3-3\text{HCl}]^-$ and TCB^- (1.83 eV vs. 1.84 eV) strongly suggests that these two anions are the same chemical species. However, there is a noticeable difference between the FWHM of the photoelectron spectra (0.51 ± 0.025 eV for TCB^- and $0.32 \text{ eV} \pm 0.025$ for $[(\text{CAN})_3-3\text{HCl}]^-$). (The ± 0.025 eV error bar is from the uncertainty in the fit of an asymmetric Gaussian to the photoelectron spectra shown in Fig. 1a and 1b.) One explanation of the different FWHM values is that TCB^- possesses more internal energy than $[(\text{CAN})_3-3\text{HCl}]^-$, leading to the broadening of the red edge of the TCB^- spectrum by anion hot band transitions. This argument is consistent with the supersonic nozzle source conditions used in producing the ions. The nozzle temperature was 134°C for the production of TCB and was only 25°C for the production of $[(\text{CAN})_3-3\text{HCl}]^-$. Although nozzle temperature alone is not a measure of cluster temperature, other source conditions such as filament bias, emission current, stagnation pressure, and nozzle size were also consistent with higher ion temperature formation conditions for TCB^- anions relative to those used for the production of $[(\text{CAN})_3-3\text{HCl}]^-$ anions. The PES studied here are broad unstructured

peaks, making it difficult to unambiguously assign the spectra. Nevertheless, due to the similarity in the VDEs, we are led to conclude that the anionic polymerization product, $[(\text{CAN})_3-3\text{HCl}]^-$, can be identified as the molecular anion of TCB^- .

4. Discussion

A plausible reaction scheme for intracuster anionic trimerization is presented in Fig. 3. Upon electron attachment onto $(\text{CAN})_3$ (**1**) (or a larger neutral cluster, where the excess solvent molecules are lost during the reaction sequence due to the exothermicity of the reaction), one of the constituent molecules captures an electron and rearranges itself into the distonic anion–radical complex $[\text{Cl}^- \cdots \text{CH}_2=\text{C}\cdot\text{CN}]$ (**2**) [17]. This rearrangement is sufficiently exothermic (~ 1 eV) [17] such that the $\text{CH}_2=\text{C}\cdot\text{CN}$ free radical may overcome the anticipated activation barrier (≈ 0.3 eV) [18] and attack an adjacent CAN molecule. This addition reaction is again exothermic and may again liberate enough energy to initiate a second addition reaction, with the propagation step being terminated when the cyclic trimer (**3**) is formed. The exothermicity of the addition reactions is also sufficient to initiate a side reaction, namely sequential elimination of HCl molecules [19], which finally leads to production of $[(\text{CAN})_3-3\text{HCl}]^-$ (**4**). The sequential elimination of

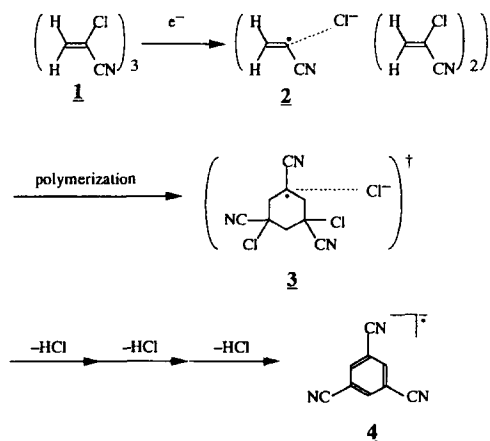


Fig. 3. A plausible reaction scheme for intracuster anionic trimerization.

HCl in the cluster regime is somewhat analogous to the thermal degradation of CAN polymers in the bulk phase [20]. Therefore, formation of the cyclic trimer (**3**) and the ensuing elimination of HCl molecules leads to production of the stable molecular anion, TCB^- , a reaction pathway that terminates free radical propagation and represents a local minimum on the complicated potential energy surface of this reaction. Aromatization of the ring is largely responsible for driving the reaction. Finally, it is worthwhile noting that cyclization is not the only reaction path open to a linear trimer radical, since if additional CAN molecules are present within the cluster, linear polymerization may proceed. Indeed, Squires has observed large quantities of $[(\text{CAN})_4-4\text{HCl}]^-$ in flow tube measurements [21].

Acknowledgements

The authors are indebted to Professor M. Ohashi and Dr. H. Hirano for their technical advice on the synthesis of TCB. Professor K. Kaya and Dr. A. Nakajima are greatly acknowledged for providing us with information on TCB^- . Additionally, the authors acknowledge Professor T. Nagata, for his encouragement of this study. This work was supported by the NSF INT-9016913 and JSPS MPCR-212 grants for international collaboration. MAJ and TK thank the NEDO foundation for facilitating the preparation of this manuscript through their travel support. MAJ thanks Professor R. Squires for access to unpublished results on the flow tube reactions of (CAN). The photoelectron and mass spectral studies of $[(\text{CAN})_3-3\text{HCl}]^-$ and TCB^- done at Johns Hopkins University were supported by NSF grant CHE# 9007445. KHB acknowledges helpful conversations with M.S. El-Shall and J.F. Garvey.

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