Effect of HOMO Levels on Chemiionization of Substituted Ethylenes by Metastable Helium Atoms

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Chemiionization reactivity (Penning ionization cross section) of substituted ethylenes in collision with helium metastable atoms was studied by velocity-resolved Penning ionization electron spectroscopy. Collision energy dependences of ionization probabilities of π orbitals were found to correlate with the HOMO levels. The higher the HOMO levels, the more effectively the reactive site of the ethylenes is hit by metastable atoms because of increased attractive interactions.

Ethylene derivatives show peculiar attractive interactions in the π orbital region, as noted for forming alkene complexes with metal atoms.[1] On the other hand, metastable helium atoms $He^*(2^3S)$, which are usually used for the measurement of Penning ionization electron spectra,[2-4] resemble Li atoms in electronic structure and interaction potentials.[3,5,6] In these connections, it is interesting to investigate a kind of chemiionization reaction of He^* atoms with ethylene derivatives.

In a chemiionization process known as Penning ionization ($M + A^* \rightarrow M^+ + A + e^-$, where M is a molecule, A^* is an excited atom, such as metastable states of rare gas atoms, M^+ is an ion of M, A is a ground-state atom, and e^- is an ejected electron), ionization cross sections show an interesting behavior reflecting their interaction potentials.[3,7] In this process, an ionic state of a closed-shell molecule usually originates from the ionization of a molecular orbital, and the molecular orbitals are more or less localized on a special part of the molecule. Since Penning ionization occurs mainly at a high electron density area exposed outside the molecular surface, collision energy dependence of a partial ionization cross section $\sigma(E_c)$ (CEDPICS) reflects information on local interaction potential where the molecular orbital extends.[6,8-11]

Collision energy dependence of partial ionization cross sections can be explained as follows.[3] If the long-range attractive part of the interaction potential $V^*(R)$ plays a dominant role, $\sigma(E_c)$ decreases as the collision energy increases since the slower He^* atom is in more closer contact with reactive site of the target molecule because of attractive interactions. On the contrary, if the repulsive part of the interaction potential governs the energy dependence, the $\sigma(E_c)$ increases as the E_c increases. This is because the faster He^* atom can more deeply poke into the target molecular orbital. Thus the slope m of the log σ vs log E_c plots can be a good index for inter-molecular attractivity ($m < 0$) or repulsiveness ($m > 0$).

In this paper we investigated chemiionization reactivities of substituted ethylenes in collision with He^* by means of Penning ionization electron spectroscopy. The experimental apparatus used in this work has been reported in previous papers.[6,8-11]

Figure 1 shows the log σ vs log E_c plots for the highest occupied π orbitals of ethylene (C_2H_4),[12] vinyl chloride (C_2H_3Cl), propene ($C_2H_3CH_3$),[10] and methyl vinyl ether ($C_2H_3OCH_3$). The slope parameters m are -0.15, -0.18, -0.35, and -0.59 ± 0.03, respectively. Since the distributions of π electrons are comparable to lead to similar electron transition probabilities in these compounds, these inclinations reflect the order of strength of attractive interactions in the π orbital region during collisional ionization processes. The order of the attractive interaction is as follows:

ethylene < vinyl chloride < propene < methyl vinyl ether

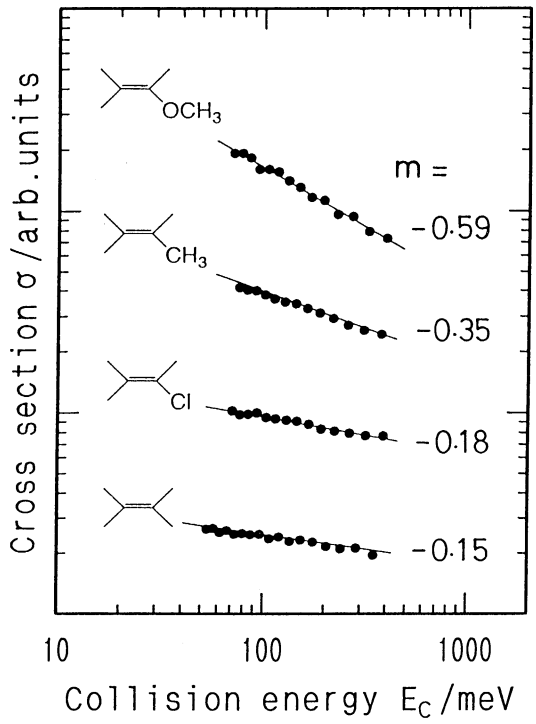

Figure 1. Collision-energy dependence of partial ionization cross sections for π orbitals of ethylene, vinyl chloride, propene, and methyl vinyl ether. The slope parameters m are -0.15, -0.18, -0.35, and -0.59 ± 0.03, respectively.

Figure 2 provides a plot of m against energy levels of the HOMOs, which were calculated in the scheme of the restricted Hartree-Fock (RHF) with a 4-31G basis set.[13] This plot shows a clear correlation; the deeper the energy level of the HOMO is, the smaller the absolute value of the inclination m becomes. The strength of the attractive interaction decreases as the HOMO level becomes lower.

This result indicates that the interaction between these ethylene derivatives and He^* atoms around the π orbital region mainly depends on the energy levels of the HOMOs. As the

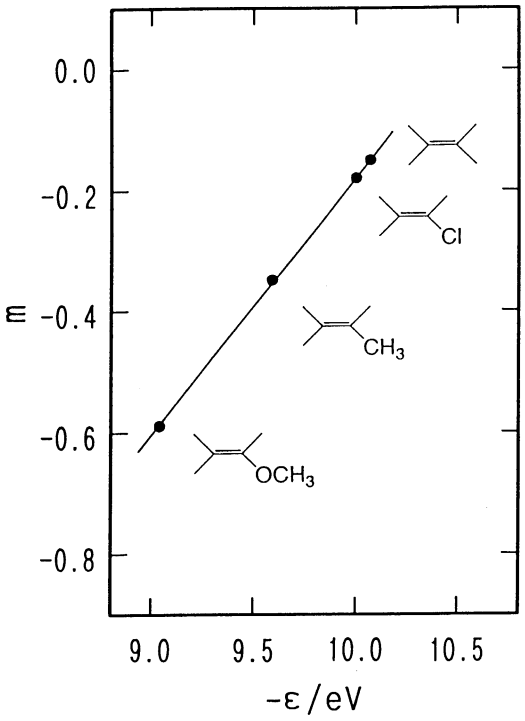

Figure 2. Slope parameters *m* plotted against orbital energies of the HOMOs for ethylene, vinyl chloride, propene, and methyl vinyl ether.

energy level of the HOMO becomes higher, its interaction with 2s-2p orbitals of He* becomes more effective to give attractive interactions. Since the energy levels of the HOMOs reflect degrees of the electron donation from the substituent, interaction around the π orbital region of the ethylene derivatives correlates with the capability of the electron donation of the substituent.

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