Dependence of the Distributions of Kinetic Energies of Products on Photoionization Energy in the Photodissociation of Ethene at 157 nm

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The dependence of distributions of kinetic energies of H_2 and C_2H_2 products on energy of photoionization is investigated upon photodissociation of ethene at 157 nm. The average kinetic energy of each product decreases with decreasing energy of photoionization, but more markedly for H_2 than for C_2H_2. The dissociation of CH_2CD_2 into $C_2H_2 + D_2$ and $C_2HD + HD$ differentiates 1,1- from 1,2-elimination of molecular hydrogen. With increasing photon energy, the ratio of HD to D_2 decreases and of C_2HD to C_2H_2 increases in both kinetic energy and intensity of product signals.

Figures 1(*a*) and 1(*b*) show the distributions of kinetic energy derived from H_2 and the binary component of C_2H_2, respectively, after photolysis of CH_2CH_2. Figures 1(*c*) – (*f*) show the distributions of kinetic energy derived from HD, C_2HD, D_2 and C_2H_2, respectively, after photolysis of CH_2CD_2. All $P(E_t)$ distributions are normalized to unity, although they correspond to separate ensembles. The maximum probability of kinetic energy shifts to the large-energy part with increasing photon energy. The distribution of kinetic energy remains the same when the photon energy is greater than 17.1 eV for H_2/HD/D_2 and 12.8 eV for C_2H_2/C_2HD. That these two values are larger than the IE of H_2 and C_2H_2, respectively, we attribute to a difference in relative ionization efficiencies among quantum states of a product when the photon energy is not much larger than the IE.

The upper panel of figure 2 shows the relationship between average kinetic energy $\langle E_t \rangle$ and photoionization energy for dissociation into $C_2H_2 + H_2$, $C_2HD + HD$, and $C_2H_2 + D_2$. $\langle E_t \rangle$ is calculated with $P(E_t)$ dependent on photon energy as a weighting factor and has the same value for two momentum-matched products at large photon energies. Dissociations into $C_2H_2 + H_2$, $C_2HD + HD$ and $C_2H_2 + D_2$ have maximal $\langle E_t \rangle$ equal to 40.1, 40.4 and 34.1 kcal mol^{-1}, respectively. The value of $\langle E_t \rangle$ decreases with decreasing photon energy. C_2H_2 has a smaller slope than H_2 in the photolysis of CH_2CH_2; C_2HD and C_2H_2 have likewise smaller slopes than HD and D_2 in the photolysis of CH_2CD_2, reflecting that ethyne (or vinylidene) has more internal energy than its cofragment, molecular hydrogen. The dependence of $\langle E_t \rangle$ on photon energy pertains to a distribution of internal energy of a product, state-specific ionization cross sections of a product, and the distributions of kinetic energy of products at a specific internal energy. $\langle E_t \rangle$ for the $C_2HD + HD$ channel is nearer that of the $C_2H_2 + H_2$ dissociation than of the $C_2H_2 + D_2$ channel, because the HD-elimination channel has twice the branching ratio of the D_2-elimination channel. The lower panel of figure 2 indicates that in the photolysis of CH_2CD_2 the ratio of HD to D_2 in $\langle E_t \rangle$ decreases whereas the ratio of C_2HD to C_2H_2 increases with increasing photon energy; both ratios converge to the same value, 1.19, at large photon energies. These two opposite trends reflect that HD has more internal energy than D_2 whereas C_2HD has less internal energy than C_2H_2.

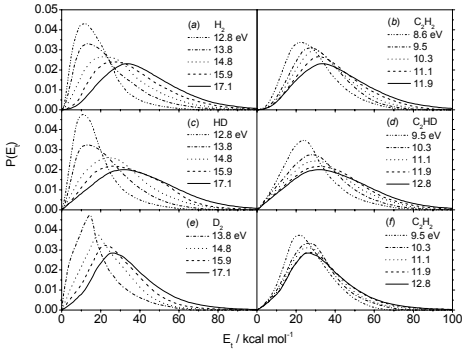

Figure 1. Distributions of kinetic energy derived from TOF spectra of products from photolysis of CH_2CH_2 (*a* – *b*) and CH_2CD_2 (*c* – *f*). Products and employed photo-ionization energies are shown in the panels.

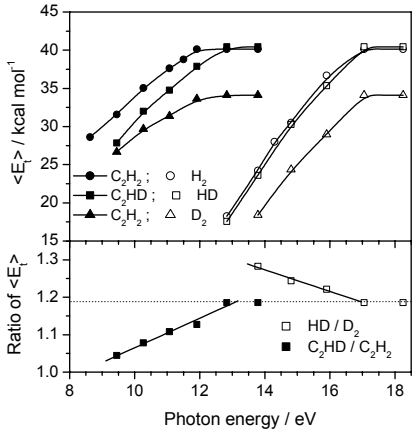

Figure 2. Relationships of product kinetic energy $\langle E_t \rangle$ vs. photon energy (upper panel) and kinetic-energy ratio vs. photon energy (lower panel).