Photochemistry of haroethylenes
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【Introduction】The photochemistry of haroethylenes (HEs) in gas phase was extensively studied. C$_2$H$_2$, HC$_2$X, HX, X (X; halogen atoms) are principally observed as products. Behavior of photoproducts was substantially studied in terms of kinetics, but the photodissociation pathways were not explicitly understood. It requires observation of intermediates to clarify the pathways.

A study of the photochemistry in solid phase is also useful for elucidation of the photodissociation in gas phase. Previously we reported that no C$_2$H$_2$ from photolysis of dichroloethylenes (DCEs) in solid phase was observed. Although the report provided some information of a Cl dissociation channel, we analyzed the photoproducts using indirect methods. A further research of in-situ spectroscopic data is necessary to reveal the mechanism for the dissociation channel.

In this work we try to explain the photodissociation pathways and the photochemistry of haroethylenes in solid phase using FTIR in-situ observation.

【Experimental】Gaseous mixtures of HEs/Ar (1/2000) were deposited onto a CsI substrate held at 18K before photolysis. For irradiation, a 193nm ArF excimer laser was employed. After irradiation of matrix samples, the substrate was raised the temperature annealing samples. IR absorption spectra were recorded at various stages of experiments with FT-IR spectrometer. Spectra were collected between 4000 and 400 cm$^{-1}$ with a resolution of 0.25 cm$^{-1}$.

【Results and Discussion】Fig.1 shows typical IR absorption spectra (730-770 cm$^{-1}$) after the photolysis of HEs.

Figure 1. IR absorption spectra (730-770 cm$^{-1}$) after the photolysis of DCEs/Ar (1/2000) at 18K.
C₂H₂ and HC₂Cl were observed as photoproducts from cis- and 1,1-DCE. Photoproducts from trans-DCE included intermediates or unknown species. C₂H₂ and HC₂Cl were assigned by comparison with IR spectra of those in Ar matrix.

But there was a slight difference between IR spectrum of HC₂Cl as the photoproducts and of HC₂Cl in Ar matrix. We calculated the energies, equilibrium structures, vibrational wavenumbers and IR intensities of HC₂Cl-HCl complexes using Gaussian03. The calculations show that the IR spectra of HC₂Cl were sifted by forming complexes (Fig.2). HC₂Cl-HCl [1] from photolysis of all of the DCEs formed hydrogen-bonded π complexes, and HC₂Cl-HCl [2] from only photolysis of trans-DCE formed chlorine-bonded π complexes. Therefore we proposed that HCl elimination process in the trans-DCE may be different from the process in the cis- and 1,1-DCE.

IR peaks A and B in Fig.1 observed as unassigned ones. In order to identify these peaks we calculated vibrational wavenumbers of carbene as is the case in the assignments of HC₂Cl peaks. The calculations show that the carbene intermediates have the IR peaks in regions 700-800 cm⁻¹. A further research is necessary for assignments of peaks A and B. The detection of carbene from only photolysis of the trans-DCE unreliably correlates with a different path to the carbene between trans-DCE and other DCEs reported in a previous work.

IR intensity of C₂H₂ decreased after raising the temperature of the CsI substrate up to 40K following the photolysis (Fig. 3). The decreasing of IR intensity may be due to reaction between C₂H₂ and chlorine atom which is produced from the photolysis of DCEs.

Figure 2. Geometry of HC₂Cl-HCl [1] and HC₂Cl-HCl [2]

Figure 3. (a) IR spectrum of cis-DCE/Ar (1/2000) at 18K after the photolysis, and (b) the spectrum after raising the temperature of the substrate up to 40K following photolysis at 18K

**Conclusion**

FTIR in-situ observation for Ar matrix photoproducts shows that the photodissociation paths of DCEs in Ar matrix is different between trans-DCE and other DCEs.