

Photochemistry of haloethylenes

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【Introduction】 The photochemistry of haloethylenes (HEs) in gas phase was extensively studied. C_2H_2 , HC_2X , 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_2H_2 from photolysis of dichloroethylenes (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 haloethylenes 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 ($730\text{--}770\text{ cm}^{-1}$) after the photolysis of HEs.

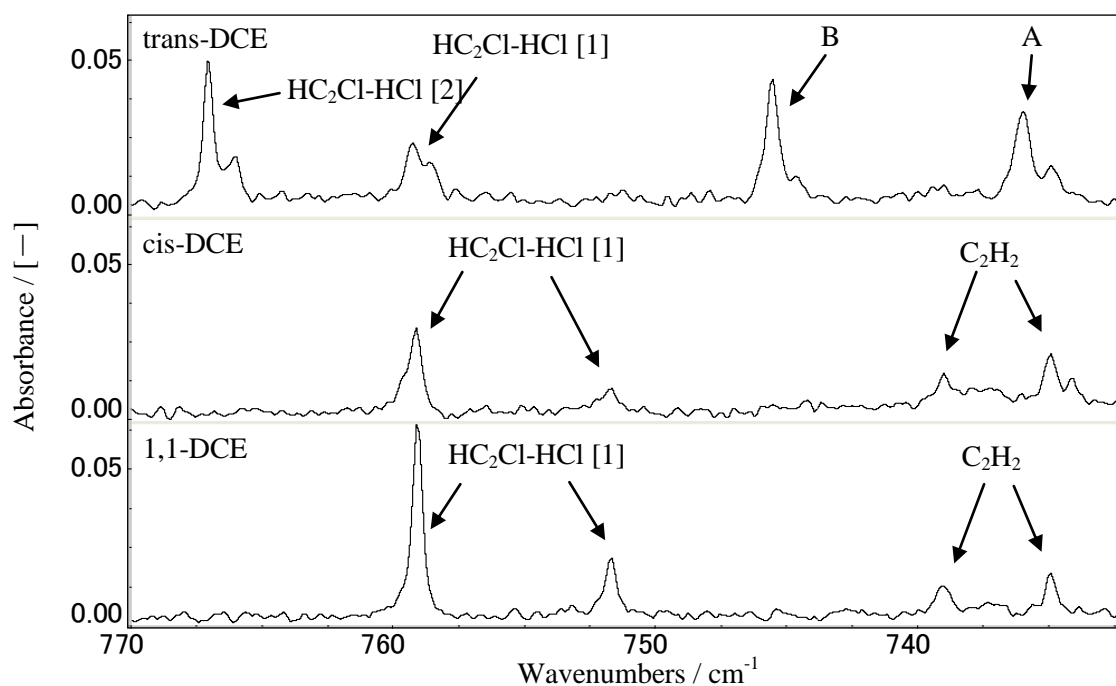


Figure 1. IR absorption spectra ($730\text{--}770\text{ cm}^{-1}$) after the photolysis of DCEs/Ar (1/2000) at 18K.

C_2H_2 and HC_2Cl were observed as photoproducts from cis- and 1,1-DCE. Photoproducts from trans-DCE included intermediates or unknown species. C_2H_2 and HC_2Cl were assigned by comparison with IR spectra of those in Ar matrix.

But there was a slight difference between IR spectrum of HC_2Cl as the photoproducts and of HC_2Cl in Ar matrix. We calculated the energies, equilibrium structures, vibrational wavenumbers and IR intensities of $HC_2Cl-HCl$ complexes using Gaussian03. The calculations show that the IR spectra of HC_2Cl were

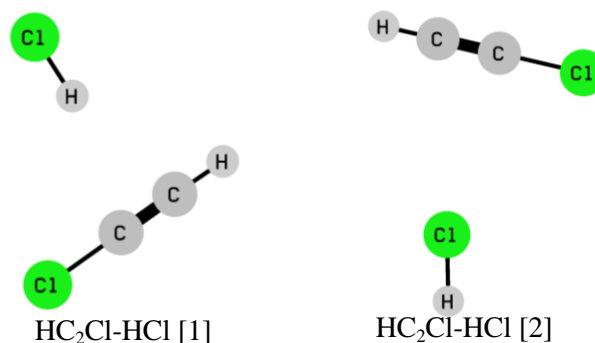


Figure 2. Geometry of $HC_2Cl-HCl$ [1] and $HC_2Cl-HCl$ [2]

sifted by forming complexes (Fig.2). $HC_2Cl-HCl$ [1] from photolysis of all of the DCEs formed hydrogen-bonded π complexes, and $HC_2Cl-HCl$ [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 HC_2Cl peaks. The calculations show that the carbene intermediates have the IR peaks in regions $700-800\text{ cm}^{-1}$. 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 C_2H_2 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 C_2H_2 and chlorine atom which is produced from the photolysis of DCEs.

【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.

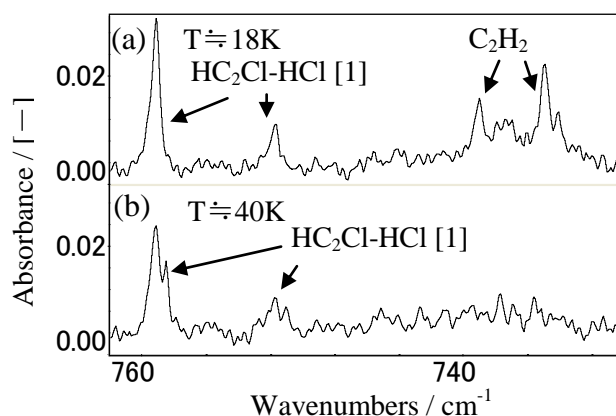


Figure 3. (a) IR spectrum of cis-DCE/Ar (1/2000) at 18K after the photolysis, and (b) the spectrum after raising the temperature of the substrate up to 40K following photolysis at 18K