

# Ionized *o*-, *m*-, and *p*-Difluorobenzene Dissociate Through Ring-Opened Intermediates: A TPEPICO Investigation

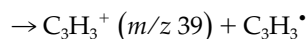
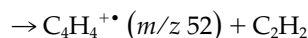
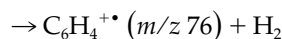
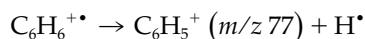
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Threshold photoelectron photoion coincidence (TPEPICO) experiments have shown that *o*-, *m*-, and *p*-difluorobenzene ions dissociate via a common, ring-opened intermediate and not via ionized *p*-difluorobenzene. Rice-Ramsperger-Kassel-Marcus (RRKM) modeling of the experimental breakdown curves yields activation energies for the initial isomerization of  $4.48 \pm 0.05$ ,  $4.55 \pm 0.05$ , and  $4.68 \pm 0.05$  eV for *o*-, *m*-, and *p*-difluorobenzene, respectively. These values place each ion at a similar absolute energy and thus similar transition states. A large positive  $\Delta S^\ddagger$  for each ion (ca  $100 \text{ J K}^{-1} \text{ mol}^{-1}$ ) suggests a ring-opened structure for these transition states. (J Am Soc Mass Spectrom 2009, 20, 20–24) © 2009 Published by Elsevier Inc. on behalf of American Society for Mass Spectrometry

The unimolecular dissociation of the benzene cation in the gas phase has been the subject of many experimental and theoretical investigations [1–13]. Four primary fragmentation processes lead to the formation of the following fragment ions:



Halo-substituted benzene ions have also been widely studied [14–26]. In particular, dihalobenzene ions tend to dissociate after rearranging to a common precursor ion, which has been assumed to be the *p*-dihalobenzene ion [18, 20]. Few studies have been performed on fluorinated benzene ions, probably because molecular ions containing a fluorine atom were frequently reported to dissociate nonstatistically [19]. While the para isomer of these ions is invariably the most thermodynamically stable, it is questionable that an entropically demanding process like halogen and hydrogen migration around a ring would be the kinetically favored pathway. Tandem mass spectra of metastable ions do not provide quantitative information on the overall kinetics of precursor ion dissociation; only the relative kinetics for the formation of the individual fragment

ions can be deduced. To answer the question of the nature of the common ion formed in the dissociation, we have employed threshold photoelectron-photoion coincidence spectroscopy (TPEPICO) to explore the isomerization in difluorobenzene ions near their dissociation threshold.

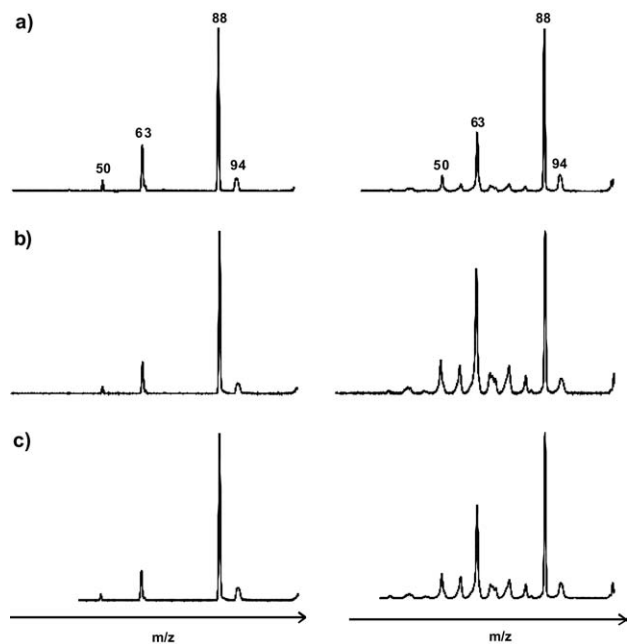
## Experimental and Computational Procedures

1,2-Difluorobenzene (Sigma-Aldrich Canada Ltd, Oakville, Ontario, 98%), 1,3-difluorobenzene (Sigma-Aldrich, 99%) and 1,4-difluorobenzene (Sigma-Aldrich, 99%) were used without further purification. The samples in the TPEPICO experiments were subjected to three freeze-pump-thaw cycles to remove air.

The mass-analyzed ion kinetic energy (MIKE) and collision-induced dissociation (CID) experiments were performed on a modified VG ZAB mass spectrometer [27] incorporating a magnetic sector followed by two electrostatic sectors (BEE geometry). Ions were generated in the ion source by electron ionization. The pressure inside the ion source was kept at  $\sim 1.0 \times 10^{-5}$  Torr as measured with an ionization gauge located above the ion source diffusion pump. Collision-induced dissociation experiments were performed using helium as the target gas. The helium pressure in the collision cell was  $\sim 1.0 \times 10^{-7}$  Torr corresponding to a beam reduction of 10%.

The TPEPICO experiments have been carried out at the Daresbury Laboratory synchrotron radiation source. The TPEPICO spectrometer [28], the 5 m normal incidence monochromator [29], and the experimental procedures [30, 31] have been described in detail previously. A

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**Figure 1.** MIKE (column 1) and CID (column 2) mass spectra of (a) ionized *o*-, (b) *m*-, and (c) *p*-difluorobenzene.

pulsed extraction technique allows the breakdown curve to be recorded as a function of parent ion residence time in the interaction region by changing the time between the detection of the threshold electron and the application of the ion drawout field [28, 31]. The minimum residence time in the current apparatus has been measured as  $1.116 \pm 0.050 \mu\text{s}$  using the experimental procedure described in Holland et al. [28]. The breakdown curves of the three isomers of difluorobenzene in the first cross-over region (between  $h\nu \approx 14.4$  and 15.8 eV) have been measured for three ion residence times:  $t_{\text{res}} = 1.116, 4.116, \text{ and } 7.116 \mu\text{s}$ . The electron transmission function used in the convolution of the calculated breakdown curves was derived from a threshold electron spectrum obtained from the photoionization of krypton in the region of the  $^2P_{1/2}$  ionization limit under the conditions used in the TPEPICO measurements [28].

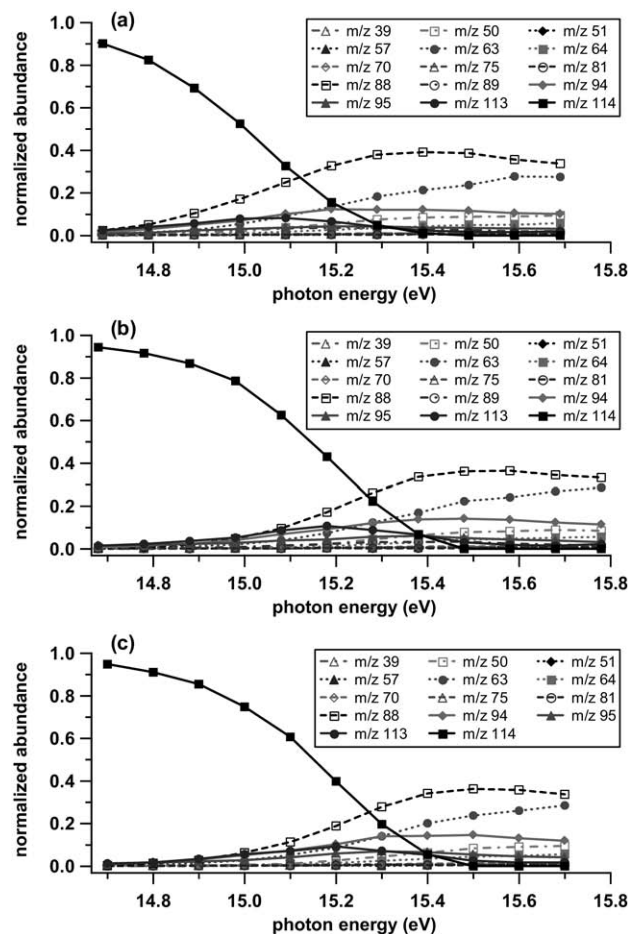
Ab initio molecular orbital calculations were performed using the Gaussian 98 [32] suite of programs. The geometries of the three difluorobenzene isomers and their respective molecular ions were optimized at the B3-LYP/6-31+G(d) level of theory. A modified G3 [33–36] (mG3) protocol based on the optimized B3-LYP/6-31+G(d) geometries and scaled B3-LYP ZPE (scaling factor = 0.9806) was used to calculate the  $\Delta_f H_0$  values of the difluorobenzene isomers.

A rovibrational Rice-Ramsperger-Kassel-Marcus (RRKM) approach [35–37] was used to calculate the rate constants  $[k(E_{\text{int}})]$  for the dissociation of the difluorobenzene ions. The properties of the transition states were estimated using the parent ion vibrational frequencies and rotational constants. One vibrational mode ( $\nu \approx 1000 \text{ cm}^{-1}$ ) was removed in the transition-

state corresponding to the reaction coordinate. The 0 K energy barrier ( $E_0$ ) and the five lowest vibrational frequencies in the transition state were scaled until a good agreement with the experimental breakdown curves was obtained for each difluorobenzene ion. To fit the experimental breakdown curves, the RRKM  $k(E_{\text{int}})$  was convoluted with the electron transmission function, the monochromator bandpass, and the thermal population distribution of the neutral difluorobenzene isomer [35, 36].  $\Delta S_{\text{rovib}}^\ddagger$  for the dissociation was calculated in the usual manner [38], employing the scaled transition-state vibrational frequencies obtained from the fitting procedure.

## Results and Discussion

The MIKE and CID mass spectra of the three difluorobenzene isomers (i.e., *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{F}_2^+$ ) are shown to be identical in Figure 1. The isomers share in common their major fragment ions:  $m/z$  88,  $\text{C}_4\text{H}_2\text{F}_2^+$ ,  $m/z$  63,  $\text{C}_5\text{H}_3^+$ , and  $m/z$  94,  $\text{C}_6\text{H}_3\text{F}^+$ . This confirms previous results [26] and illustrates that the three isomeric ions must dissociate via a common species, even upon collisional activation, which is typically connectivity specific [39].



**Figure 2.** Complete TPEPICO breakdown curves for (a) *o*-, (b) *m*-, and (c) *p*-difluorobenzene ions (residence time  $1.116 \mu\text{s}$ ).

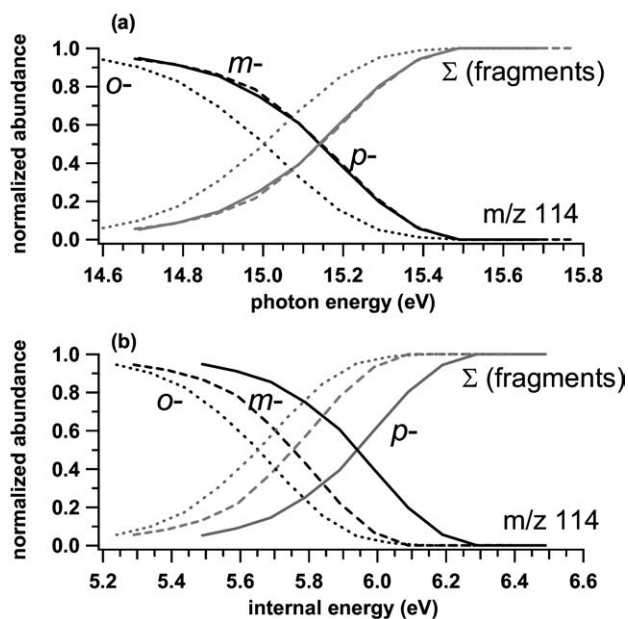


Figure 3. TPEPICO breakdown curves plotted with total fragment ion relative abundance as a function of (a) photon energy and (b) ion internal energy (residence time 1.116  $\mu\text{s}$ ).

The TPEPICO breakdown curves have been measured in the threshold region ( $h\nu \approx 14.4\text{--}15.8$  eV) in which more than ten fragment ions were observed (Figure 2). The three most intense fragment ions in the threshold region are fragment ions  $m/z$  63, 88, and 94, consistent with the MIKE mass spectra. When the breakdown curves (in which the total fragment ion relative abundance is used) are plotted as a function of photon energy, the curves for  $m$ - and  $p$ - $\text{C}_6\text{H}_4\text{F}_2^+$  overlap (Figure 3a). However, when plotted as a function of internal energy ( $E_{\text{int}}$ ), the experimental breakdown curves are shifted with respect to one another (Figure 3b)

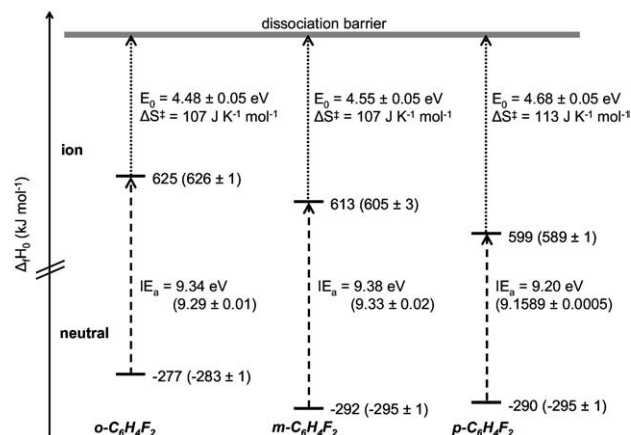


Figure 4. G3 calculated thermochemistry of the difluorobenzene molecules and ions at 0 K (ion and neutral  $\Delta_f H_0$  and IE), along with the results of the RRKM modeling of the TPEPICO breakdown curves ( $E_0$  and  $\Delta S^\ddagger$ ). Literature values for neutral  $\Delta_f H_0$  (derived from the quoted  $\Delta_f H_{298}$  value with the calculated thermal correction) and IE [40], and the subsequently derived ionic  $\Delta_f H_0$ , are shown in parentheses.

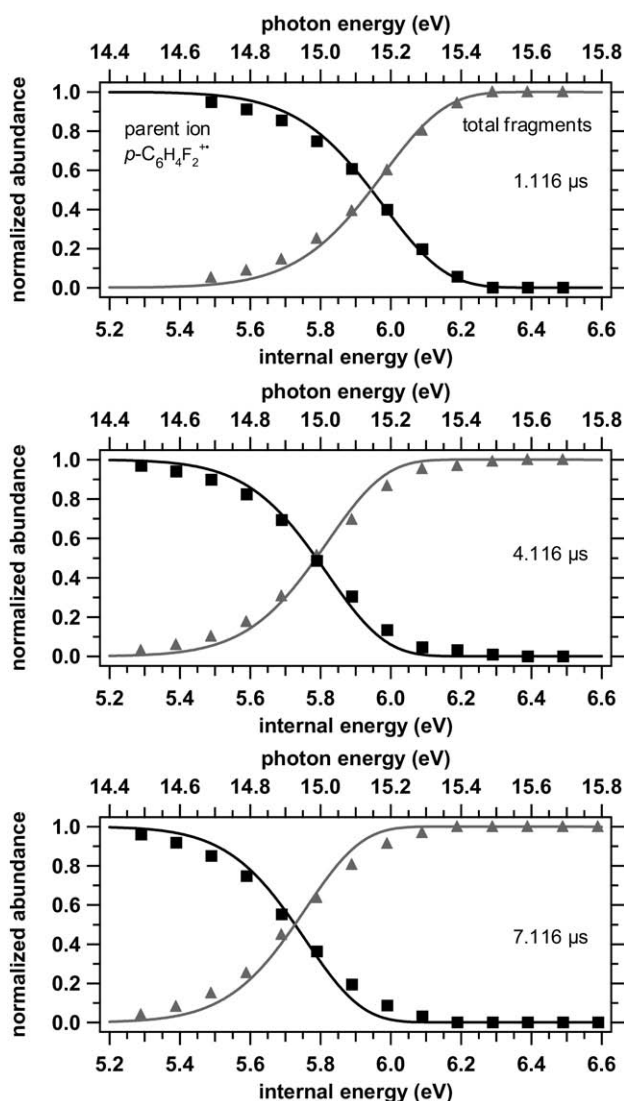


Figure 5.  $p$ -Difluorobenzene ion breakdown curves at ion source residence times of 1.116, 4.116, and 7.116  $\mu\text{s}$ . Symbols represent the experimental data and solid lines the RRKM fits ( $E_0 = 4.68 \pm 0.05$  eV and  $\Delta S_{\text{rovib}}^\ddagger = 113$  J K $^{-1}$  mol $^{-1}$ ).

according to their relative ionization energies (Figure 4). We have used the G3 calculated adiabatic IE values (Figure 4) to convert photon energy to internal energy. They all lie with 5 kJ mol $^{-1}$  of the literature values (Figure 4) and are a self-consistent set of data. This will place an upper limit to the uncertainty on the final  $E_0$  values obtained from the RRKM fitting of the experimental data of  $\sim 5$  kJ mol $^{-1}$ . The agreement with the literature for the neutral  $\Delta_f H_0$  values is also excellent once corrections are made to 0 K (Figure 4).

Given that the formation of all 10 fragment ions occurs after isomerization to an intermediate structure, the TPEPICO breakdown curves will reflect the  $E_0$  and  $\Delta S_{\text{rovib}}^\ddagger$  of the transition-state for this isomerization. Therefore, the plots in Figure 3b were modeled. Figure 5 shows the fitted breakdown curves of  $p$ -difluorobenzene ions acquired at the three ion source residence times.

The results for all three isomers are summarized in Figure 4. The energy barriers obtained from the fits are consistent with previously reported energy barriers for the dissociation of benzene and substituted benzene ions [10, 14, 21] and differ by amounts roughly equal to their relative energies, indicating that the three isomers access transition states of similar energies. The  $\Delta_f H_0$  values for the transition states structures (derived from the G3 ion  $\Delta_f H_0$  values and RRKM  $E_0$  values) are 1057, 1052, and  $1050 \pm 5$  kJ mol<sup>-1</sup> for the *o*-, *m*-, and *p*-ions, respectively. To simultaneously fit the three breakdown curves for each isomer, a large  $\Delta S_{\text{rovib}}^\ddagger$  was needed, 107 J K<sup>-1</sup> mol<sup>-1</sup> for *o*- and *m*-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub><sup>+</sup> and 113 J K<sup>-1</sup> mol<sup>-1</sup> for *p*-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub><sup>+</sup>. This large  $\Delta S_{\text{rovib}}^\ddagger$  suggests that the initial isomerization of the difluorobenzene ions involves a ring-opening reaction, and thus the common intermediate(s) shared by the three isomers before dissociation is likely not ionized *p*-difluorobenzene, but rather a linear isomer or collection of linear isomers. To test this, various linear structures of C<sub>6</sub>H<sub>4</sub>F<sub>2</sub><sup>+</sup> were optimized and the absolute entropy difference with the aromatic structures were calculated. The entropy difference between the two types of structures (i.e., linear and *o*-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub><sup>+</sup>) is  $\sim 72$  J K<sup>-1</sup> mol<sup>-1</sup>, consistent with the experimentally derived  $\Delta S_{\text{rovib}}^\ddagger$ .

## Conclusions

Tandem mass spectrometry shows that the three ionized difluorobenzene ion isomers dissociate via a common intermediate. RRKM modeling of TPEPICO breakdown curves for this initial isomerization resulted in (1) activation energies indicating the formation of transition-state species of similar energies and (2) large positive  $\Delta S_{\text{rovib}}^\ddagger$  values, indicating that these intermediates are likely ring-opened structures and not *p*-difluorobenzene.

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