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Formation and Decomposition of Distonic *o*-, *m*-, and *p*-Benzyne Radical Cations from Photolysis of $\text{Mg}^+(\textit{o}, \textit{m}, \textit{p}\text{-C}_6\text{H}_4\text{F}_2)$

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Abstract: Distonic *o*-, *m*-, and *p*-benzyne radical cations (**1–3**) have been generated by a novel photolysis reaction of mass-selected Mg^+ -difluorobenzene complexes. The energy required for the formation of these radical cations is within 2.2 eV. The formation of *o*-benzyne cation is most facile. The benzyne radical cations dissociate further to yield ethyne and 1,3-butadiyne radical cation as major products given a sufficient amount of energy. The whole process involves only a single photon, and is very efficient. The calculated threshold for the formation of 1,3-butadiyne radical cation from $\text{Mg}^+(\textit{o}\text{-C}_6\text{H}_4\text{F}_2)$ is about 4.6 eV, quite comparable with the experimental estimate.

Introduction

Interest in the electronic structures and chemical reactivity of isomeric *o*-, *m*-, and *p*-benzynes has been prevalent for over half a century.^{1–15} This has been fueled by the recent discovery that *p*-benzyne derivatives from Bergman cyclization reac-

tions¹⁶ are involved in the DNA-cleaving activity of calicheamicin and related antitumor antibiotics.^{17,18} Recently, *o*-, *m*-, and *p*-benzynes were isolated by the matrix method and spectroscopically characterized.^{1d–f}

Recent success in the synthesis of *o*-, *m*-, and *p*-distonic benzyne anions prompted a series of experiments from collision-activated dissociation (CAD) to ultraviolet photoelectron spectroscopy (UPS).^{19a–d} Concomitantly, high-level quantum mechanics calculations were performed, which predicted high-symmetry and delocalized ground electronic states for the *o*-, *m*-, and *p*-benzyne anions.^{18e} Freiser et al.^{20a} produced an organometallic distonic ion $^+\text{FeC}_6\text{H}_4^*$ through the reaction of laser-desorbed Fe^+ with 1,4-diiodobenzene. The chemistry of

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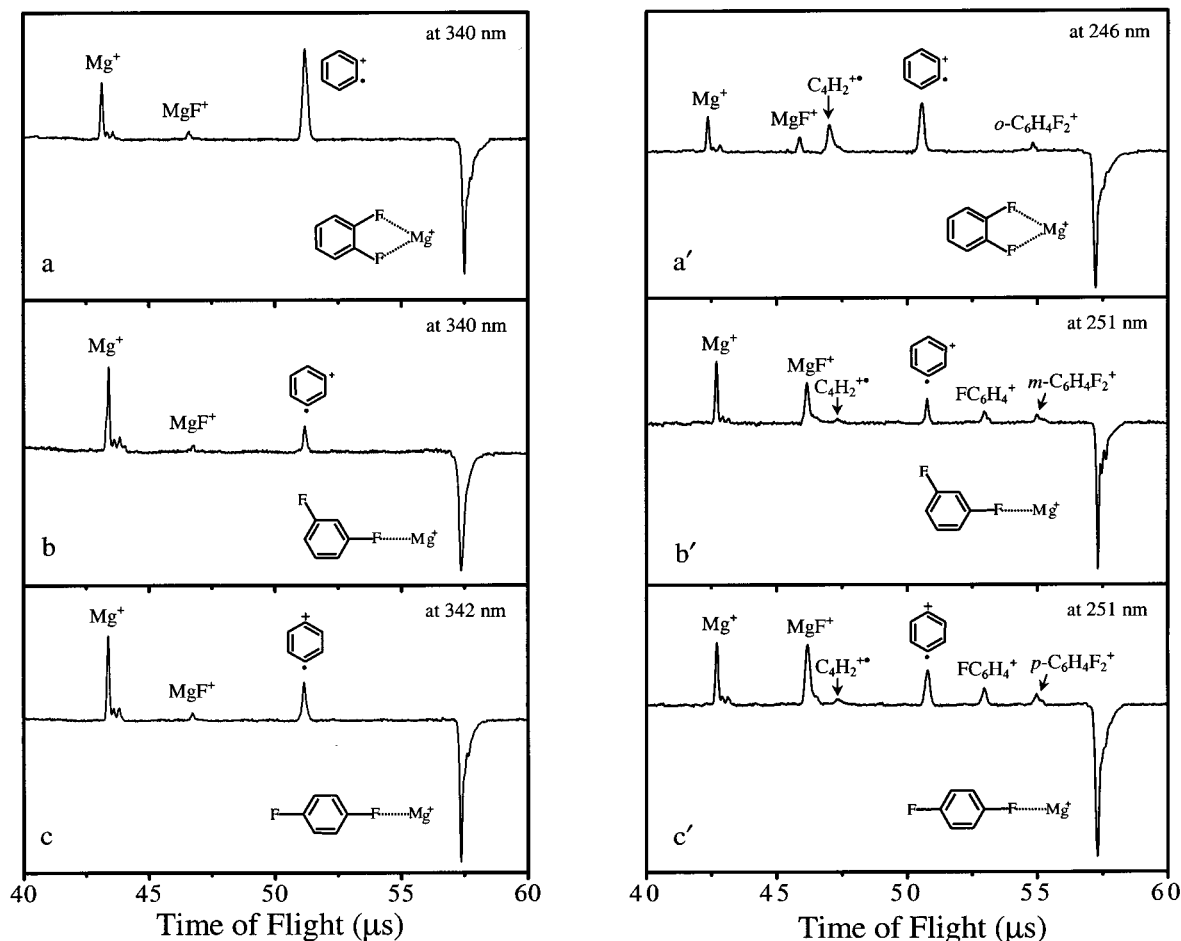


Figure 1. Photodissociation difference mass spectra at long (~ 340 nm, left panel) and short (~ 250 nm, right panel) wavelengths.

this species was found to be unique in comparison to its even-electron counterparts $\text{Fe}(\textit{o}\text{-benzyne})^{+\bullet}$.^{20b–c}

As opposed to the flood of research activities on benzyne and benzyne radical anions, little has been reported on benzyne radical cations.^{14,21} This is partly due to the difficulty of efficient synthesis of this type of distonic radical cations. Our recent experiments have shown that photodissociation of Mg^+XCH_3 gives the dominant product of CH_3^+ .²¹ We reasoned that this technique could be used to produce distonic benzyne radical cations through photodissociation of magnesium cation–dihalobenzene complexes. In this paper, we report this novel and versatile method for the gas-phase synthesis of *o*-, *m*-, *p*- $\text{C}_6\text{H}_4^{+\bullet}$ (**1**, **2**, and **3**) from photodissociation of mass-selected cationic complexes $\text{Mg}^+(\textit{o}, \textit{m}, \textit{p}\text{-C}_6\text{H}_4\text{F}_2)$ as well as the decomposition of these radical cations as shown in Scheme 1. In principle, dichloro- or dibromobenzenes can also be used for this study. For our first demonstration, we chose difluorobenzenes because they complex readily with Mg^+ without thermal reactions.

Experimental Section

The cluster apparatus for the photodissociation experiments was described elsewhere.^{22,23} Vapors of *o*-, *m*-, or *p*-difluorobenzene were seeded in He at a backing pressure of ~ 10 psi expanded through a 0.5 mm diameter orifice of a pulsed valve. The second harmonic

(532 nm) of a Nd:YAG laser (~ 40 mJ/pulse) was weakly focused on a ~ 1 mm diameter spot of a rotating magnesium disk. The laser-generated species traversed the supersonic jet stream, forming a series of metal cations solvated by the difluorobenzene clusters. The clusters then traveled to the extraction region of a reflectron time-of-flight spectrometer (RTOFMS). Afterward, the cluster cations were reflected and detected by a dual-plate microchannel plate detector (MCP). For photodissociation experiments, a two-plate mass gate equipped with a high-voltage pulser was used for mass selection. The mass-selected cluster cations, upon arrival at the turn-around region of the reflectron, were irradiated with a collimated beam of a photolysis dye laser. The parent and nascent daughter cations were re-accelerated by the reflectron electric field, and detected by the MCP detector.

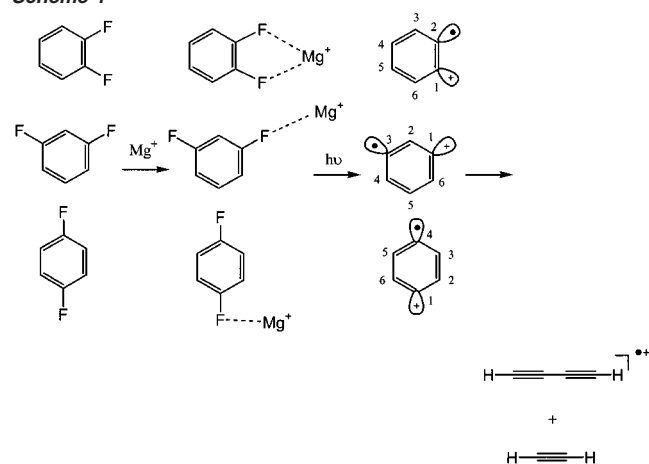
Results and Discussion

A. Photolysis of $\text{Mg}^+(\textit{o}, \textit{m}, \textit{p}\text{-C}_6\text{H}_4\text{F}_2)$. Figure 1 compares the photodissociation difference mass spectra at long (~ 340 nm, left panel) and short (~ 250 nm, right panel) wavelengths for the complexes $\text{Mg}^+(\textit{o}, \textit{m}, \textit{p}\text{-C}_6\text{H}_4\text{F}_2)$. The downward peaks indicate the disappearance of parent complexes, and the upward peaks correspond to the appearance of daughter ions. At long wavelengths (~ 340 nm), only three photofragments Mg^+ , MgF^+ , and the benzyne radical cation $\text{C}_6\text{H}_4^{+\bullet}$ were observed in all mass spectra. Among the fragments, FMg^+ is negligibly small. The major difference in the mass spectra is that, while

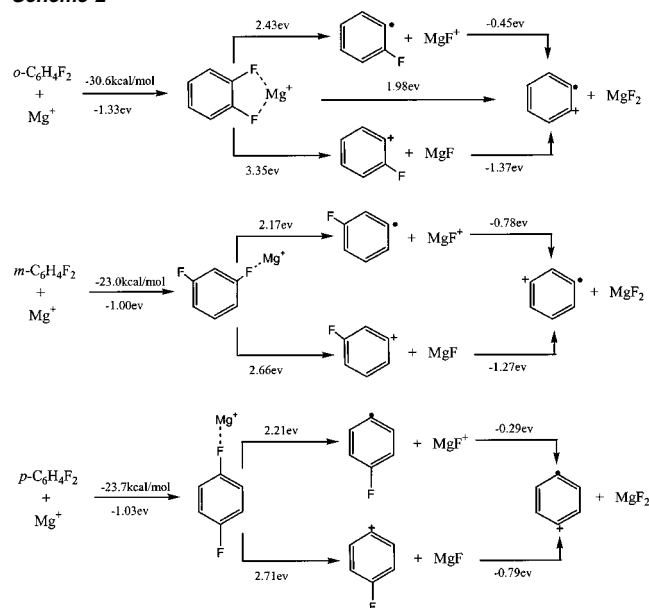
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Scheme 1



Scheme 2



Mg^+ is the dominant fragment from photolysis of $\text{Mg}^+(m\text{-}, p\text{-C}_6\text{H}_4\text{F}_2)$, it yields to $\text{C}_6\text{H}_4^{+\bullet}$ from photolysis of $\text{Mg}^+(o\text{-C}_6\text{H}_4\text{F}_2)$. The efficient production of $\text{C}_6\text{H}_4^{+\bullet}$ from photolysis of $\text{Mg}^+(o\text{-C}_6\text{H}_4\text{F}_2)$ is likely to originate from the coordination of Mg^+ to the two neighboring F atoms of $o\text{-C}_6\text{H}_4\text{F}_2$ as revealed in our ab initio calculations (Scheme 2). Although the production of $\text{C}_6\text{H}_4^{+\bullet}$ from photolysis of $\text{Mg}^+(m\text{-}, p\text{-C}_6\text{H}_4\text{F}_2)$ is not as efficient, the fact that the benzyne radical cations can be formed at all is remarkable because in this case, the Mg^+ cation has to abstract the two relatively distant F atoms.

The complexes of $o\text{-}, m\text{-},$ and $p\text{-C}_6\text{H}_4\text{F}_2$ with Mg^+ and the generation of benzyne radical cations from the complexes have been studied theoretical by using the density functional method. All calculations were carried out with the GAUSSIAN 98 program.²⁴ The geometries were first optimized with the density

functional method (DFT) of B3LYP/6-31G*.²⁵ Vibration frequencies were calculated to confirm each structure to be a minimum.²⁶ Energies were evaluated by using a much larger basis set of aug-cc-pVTZ²⁷ and with zero-point energy corrections. As shown in Scheme 2, the complexation energy between $o\text{-C}_6\text{H}_4\text{F}_2$ and Mg^+ is about 30.6 kcal/mol. As expected, the complexation energy is reduced for that of $m\text{-C}_6\text{H}_4\text{F}_2$ (23.0 kcal/mol) and $p\text{-C}_6\text{H}_4\text{F}_2$ (23.7 kcal/mol), since only one F–Mg bond is formed. In the cases of $\text{Mg}^+(m\text{-}, p\text{-C}_6\text{H}_4\text{F}_2)$, π -complexes were also found and they are only about 2 kcal/mol less stable than the σ -complexes. For the formation of **1** from the $\text{Mg}^+(o\text{-C}_6\text{H}_4\text{F}_2)$ complex, a concerted mechanism is indicated by experiments. Calculations support this because the loss of MgF_2 costs less energy than the loss of MgF^+ or MgF . The calculations gave reaction energy of about 45.8 kcal/mol (1.984 eV). In the cases of $m\text{-}$ and $p\text{-C}_6\text{H}_4\text{F}_2$, the formation of the radical cations has to be stepwise. The formation of the fluorobenzyl radical intermediate is somewhat less costly in terms of energy than the formation of the fluorobenzyl cation. For both $m\text{-}$ and $p\text{-C}_6\text{H}_4\text{F}_2$, the loss of the second fluorine to MgF^+ or MgF is exothermic. This explains the moderate efficiency for the formation of the $m\text{-}$ and $p\text{-}$ benzyne radical cations. The fact that the loss of the first fluorine costs energy of over 2 eV indicates that the extra energy left in the intermediate is small when a light source of 340 nm (3.65 eV) is used. The calculations are in agreement with the experimental observation of Mg^+ and MgF^+ cations. However, with the small extra energy left in the fluorobenzyl radical or cation, ring-opening and hydrogen shifts in these intermediates are impossible.²⁸

In a study of photoionization and fragmentation of $o\text{-}, m\text{-},$ and $p\text{-}$ dibromobenzenes, Moini and Leroi concluded that all three systems led to the formation of the same $\text{C}_6\text{H}_4^{+\bullet}$ structure.²¹ That is, substituent isomerization occurs in $\text{C}_6\text{H}_4\text{Br}_2^{+\bullet}$ prior to dissociation to form either $\text{C}_6\text{H}_4\text{Br}^{+\bullet}$ or $\text{C}_6\text{H}_4^{+\bullet}$, which requires energy of about 3 eV. Is it possible that there is also substituent isomerization (scrambling) in excited $\text{Mg}^+(o\text{-}, m\text{-}, \text{ and } p\text{-C}_6\text{H}_4\text{F}_2)$ complexes before MgF_2 elimination so that $o\text{-C}_6\text{H}_4^{+\bullet}$ is formed in all three cases. We note that in all three complexes, the cation is centered at the Mg instead of at the benzene ring. It is quite unlikely for F to acquire a positive charge, which is required for scrambling.²⁹ The threshold for the formation of $\text{C}_6\text{H}_4^{+\bullet}$ from these complexes is about 2 eV. The isomerization of the $o\text{-}$ dichlorobenzene radical cation to the $p\text{-}$ dichlorobenzene

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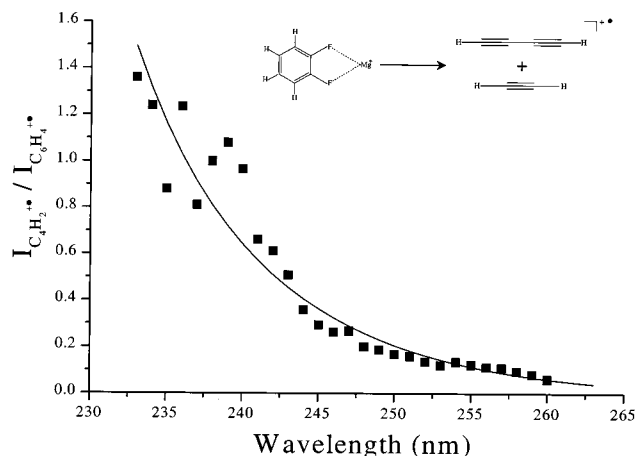


Figure 2. The relative yield of $C_4H_2^{+\bullet}$ ($I(C_4H_2^{+\bullet})/I(C_6H_4^{+\bullet})$) as a function of laser wavelength.

radical cation needs about 2.6 eV of energy.²⁹ It is expected that fluorine rearrangement would require much higher energy, because of a much stronger C–F bond than C–Cl and C–Br bonds. In addition, $C_6H_4F^{+\bullet}$ was not detected in all three photolysis reactions as shown in the left panel of Figure 1. Therefore, it is unlikely that scrambling would occur in the current experiments. This is supported by the fact that the $C_6H_4^{+\bullet}$ formation from $Mg^+(o-C_6H_4F_2)$ is much more efficient than that from $Mg^+(m- \text{ and } p-C_6H_4F_2)$. Thus, the $C_6H_4^{+\bullet}$ mass peaks shown in the left panel of Figure 1 most likely represent the *o*-, *m*-, and *p*-benzyne radical cations.

As the photolysis laser is tuned to short wavelengths (~ 250 nm), the difference mass spectra change, but again to a different extent for $Mg^+(o-C_6H_4F_2)$ and for $Mg^+(m-, p-C_6H_4F_2)$ (Figure 1, right panel). First, some more fragments appear from the photolysis of $Mg^+(m-, p-C_6H_4F_2)$, including $C_6H_4F_2^{+\bullet}$, $C_6H_4F^{+\bullet}$, and $C_4H_2^{+\bullet}$, whereas only $C_6H_4F_2^{+\bullet}$ and $C_4H_2^{+\bullet}$ are the extra fragments from photolysis of $Mg^+(o-C_6H_4F_2)$. Second, the relative intensity of $MgF^{+\bullet}$ increases in all mass spectra, but this increase is much more significant in the photolysis of $Mg^+(m-, p-C_6H_4F_2)$. As we know, the two F atoms are farther away in $Mg^+(m-, p-C_6H_4F_2)$, therefore $Mg^{+\bullet}$ has to pick up the F atoms one at a time, leading to the possible formation of $C_6H_4F^{+\bullet}$ and the more significant increase in $MgF^{+\bullet}$ in the photolysis of $Mg^+(m-, p-C_6H_4F_2)$ at short wavelengths. However, the proximity of $Mg^{+\bullet}$ to both F atoms in $Mg^+(o-C_6H_4F_2)$ renders the facile formation of MgF_2 . Last, the fragment $C_4H_2^{+\bullet}$ is much more prominent in the photolysis of $Mg^+(o-C_6H_4F_2)$ than of $Mg^+(m-, p-C_6H_4F_2)$. Laser fluence dependence of this fragment showed that it is from a one-photon process. In addition, the $C_4H_2^{+\bullet}$ peak appears to be broadened and asymmetric, and becomes narrower with decreasing wavelength, suggesting that it results from metastable decay, probably of $C_6H_4^{+\bullet}$.

Plotted in Figure 2 is the relative yield of $C_4H_2^{+\bullet}$ as a function of the photolysis laser wavelength for $Mg^+(o-C_6H_4F_2)$. Clearly, the relative yield gradually increases with decreasing wavelength from 285 nm until ~ 250 nm, where a sharper increase occurs toward the ultraviolet region. We believe that the initial photoinduced reaction which leads to the formation of $C_6H_4^{+\bullet}$ is fast with most of the available energy deposited on this species. However, further decomposition of $C_6H_4^{+\bullet}$ to $C_4H_2^{+\bullet}$ is likely to be slow due to the metastable nature of the $C_4H_2^{+\bullet}$ mass peak. The determination of the energy threshold (E_0) for

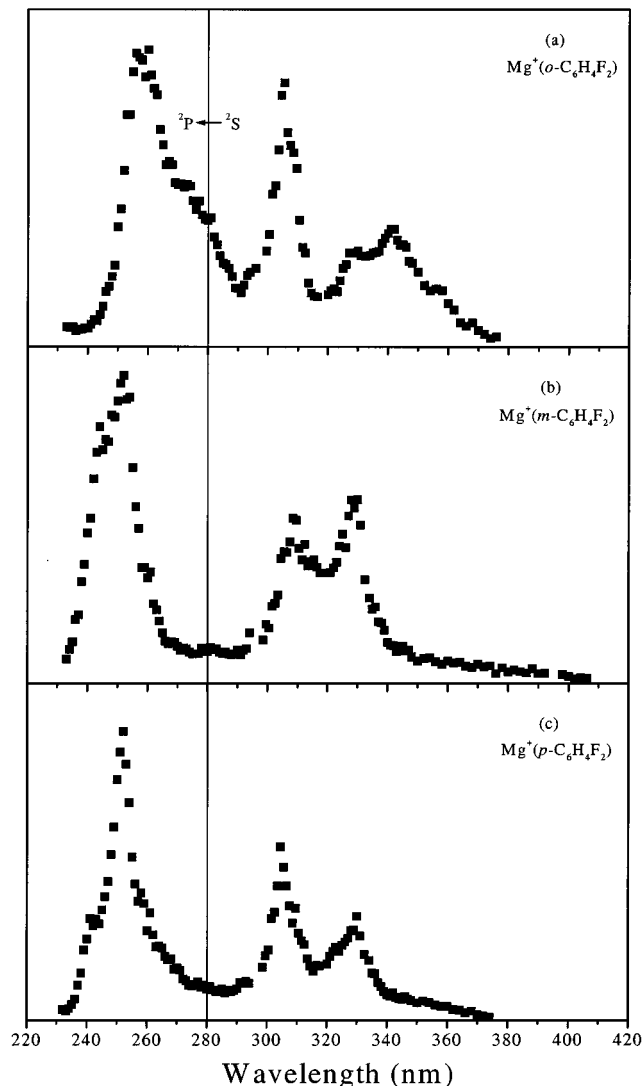


Figure 3. Action spectra of $Mg^+(o-, m-, p-C_6H_4F_2)$. The vertical axis represents the relative yield of all the photolysis products. The solid line indicates the atomic transition of Mg^+ ($^2P \leftarrow ^2S$), and the broken lines show the calculated excitation spectra.

the metastable decomposition of $C_6H_4^{+\bullet}$ calls for theories of unimolecular decay. A naive application of the RRRK theory gives the dissociation energy of about 1.7 eV. The solid line in Figure 2 is the result of the RRRK fitting according to $k = \nu(E/(E - E_0))^{s-1} \propto \ln\{[I(C_4H_2^{+\bullet}) + I(C_6H_4^{+\bullet})]/I(C_6H_4^{+\bullet})\}$, where ν is a constant, s is approximated as 12,³⁰ and E is taken as $(h\nu - 2.0)$ because the first step from $Mg^+(o-C_6H_4F_2)$ to $o-C_6H_4^{+\bullet}$ is calculated to cost 1.98 eV. Considering the crudeness of the model, the arbitrary assignment of s , and the multistep decomposition process, the value of 1.7 eV can only be regarded as a lower limit of the dissociation energy. The upper limit of the dissociation energy can be estimated by subtracting the energy cost in the first photolysis step (~ 2 eV) from the lowest photon energy at which the fragment $C_4H_2^{+\bullet}$ starts to appear (4.35 eV at 285 nm), i.e., 2.35 eV. This dissociation energy is still somewhat smaller than that from our calculated value of 2.56 eV. This is understandable because

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thermal energy present in the complex may have a substantial contribution. For example, at room temperature, the complex $\text{Mg}^+(o\text{-C}_6\text{H}_4\text{F}_2)$ may have an internal energy as high as 0.8 eV. Although the internal energies of the complexes from our pick-up source are probably below room temperature, they are likely to be well above 100 K.

The total yields of the photofragments, when plotted as a function of the excitation laser wavelength, constitute the action spectra. Such action spectra of $\text{Mg}^+(o\text{-}, m\text{-}, p\text{-C}_6\text{H}_4\text{F}_2)$ are displayed in Figure 3. Three main features arise in the action spectrum of $\text{Mg}^+(o\text{-C}_6\text{H}_4\text{F}_2)$ at ~ 260 , ~ 305 , and ~ 340 nm, respectively (Figure 3a). The action spectra of $\text{Mg}^+(m\text{-C}_6\text{H}_4\text{F}_2)$ (Figure 3b) and $\text{Mg}^+(p\text{-C}_6\text{H}_4\text{F}_2)$ (Figure 3c) are very similar with three main peaks at ~ 252 , ~ 305 , and ~ 330 nm, respectively. The only obvious difference between the two action spectra is the relative intensities of the three peaks. The action spectra of $\text{Mg}^+(o\text{-}, m\text{-}, p\text{-C}_6\text{H}_4\text{F}_2)$ presented above are all different from those of $\text{Mg}^+\text{-C}_6\text{H}_5\text{X}$ ($\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}$),^{22b} in which only two main features were observed. One possible explanation is that Mg^+ is linked to the F atoms in $\text{Mg}^+(o\text{-}, m\text{-}, p\text{-C}_6\text{H}_4\text{F}_2)$, whereas it is on the benzene ring in $\text{Mg}^+\text{-C}_6\text{H}_5\text{X}$. The three main peaks in the action spectra of $\text{Mg}^+(o\text{-}, m\text{-}, p\text{-C}_6\text{H}_4\text{F}_2)$ are ascribed to the splitting of the $^2\text{P} \leftarrow ^2\text{S}$ atomic transition of Mg^+ due to the presence of $\text{C}_6\text{H}_4\text{F}_2$. In each action spectrum, the shortest wavelength peak is blue shifted from the $^2\text{P} \leftarrow ^2\text{S}$ transition of Mg^+ (280 nm), while the other two peaks result from red shifts. Overall, the striking similarity of the action spectra of $\text{Mg}^+(m\text{-}, p\text{-C}_6\text{H}_4\text{F}_2)$ and their substantial difference from that of $\text{Mg}^+(o\text{-C}_6\text{H}_4\text{F}_2)$ suggest that $\text{Mg}^+(m\text{-}, p\text{-C}_6\text{H}_4\text{F}_2)$ possess a similar structure that is quite different from that of $\text{Mg}^+(o\text{-C}_6\text{H}_4\text{F}_2)$ (Scheme 1).

The action spectra of the complexes described above suggest that the optical excitation is centered on Mg^+ . This Mg^+ -centered excitation triggers a remarkable sequence of events involving electron shuffling, atomic transfer, and energy partitioning, leading eventually to the formation of the benzyne radical cations. The energy partitioning in the photolysis of $\text{Mg}^+(o\text{-C}_6\text{H}_4\text{F}_2)$ seems to be so specific that almost all the available energy is deposited on the fragment $o\text{-C}_6\text{H}_4^{\bullet+}$ and that this

energy-rich fragment in turn dissociates further to $\text{C}_4\text{H}_2^{\bullet+}$ and C_2H_2 .

Cernisharo et al. reported recently the first observation of C_4H_2 , C_6H_2 , and benzene along with C_2H_2 in the circumstellar medium in the direction of the protoplanetary nebula CRL 618.²⁹ The abundances of C_4H_2 and C_6H_2 are surprisingly high, only a factor of 2–4 lower than that of C_2H_2 . Noticing that $\text{C}_4\text{H}_2^{\bullet+}$ can be generated by ionization of C_4H_2 after the absorption of UV photons coming from the hot central star, we speculate that the reaction of $\text{C}_4\text{H}_2^{\bullet+}$ with C_2H_2 might be one of the possible pathways for the formation of benzene in the circumstellar medium. This [4+2] scheme is plausible because such a reaction is barrierless and is favorable in the circumstellar medium.

Conclusion

In summary, distonic $o\text{-}$, $m\text{-}$, and $p\text{-}$ benzyne radical cations can be formed readily by photolysis of a complex of Mg^+ with $o\text{-}$, $m\text{-}$, and $p\text{-C}_6\text{H}_4\text{F}_2$. The energy required for the formation of these radical cations is within 2.2 eV. The formation of the $o\text{-}$ benzyne cation is most facile due to the chelating nature of the complex. If the benzyne radical cations carry sufficient internal energy, they further decompose to give C_2H_2 and $\text{C}_4\text{H}_2^{\bullet+}$ as the major products. The whole process involves only a single photon, and is very efficient. The calculated energy threshold for the formation of $\text{C}_4\text{H}_2^{\bullet+}$ from the $\text{Mg}^+(o\text{-C}_6\text{H}_4\text{F}_2)$ complex is 4.6 eV, quite comparable with the experimental estimate. This study opens up a window for the isolation, characterization, and investigation of the chemical reactivity of these distonic benzyne radical cations.

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Supporting Information Available: Tables of experimental data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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