

OMS Letters

Dear Sir,

Reactions Between Doubly Charged $[C_6H_6]^{2+}$ Ions and Self-assembled Monolayer Surfaces

Self-assembled monolayer films prepared on gold surfaces have been used extensively in recent ion-surface collision experiments.¹⁻⁵ A portion of the kinetic energy of the projectile is converted into ion internal energy on collision and this energy transfer leads to dissociation of the projectile. This process is referred to as surface-induced dissociation (SID). In addition to dissociation, another interesting feature of these experiments is the detection of ions corresponding to reactions between the projectile ion and the monolayer films. Addition of H or CH_3 to singly charged benzene^{2,5,6} and pyrazine^{1,3} molecular ions from alkanethiolate monolayers ($n-C_nH_{2n+1}SAu$, $n = 4, 18$) have been observed, in addition to analogous reactions involving D and CD_3 additions from perdeuterioeicosanethiolate monolayer^{1,3,5} ($n-C_{20}D_{41}SAu$) and F and CF_3 additions from a 2-(perfluorooctyl)ethanethiolate monolayer^{2,5} [$CF_3(CF_2)_7CH_2CH_2SAu$]. Another competitive process is charge exchange between the projectile and the surface. The neutralization of singly charged benzene (manifested in chemical sputtering and the current measured on the surface) has recently been investigated.⁵ A partial reduction of doubly charged to singly charged ions has been observed for benzene,⁶ toluene⁷ and C_{60} .⁸ This process could provide an alternative electron-capture-induced decomposition (ECID) method. For a recent application of 'conventional' ECID for $[C_6H_6]^{2+}$ isomer ions, see Ref. 9.

Because addition reactions have been reported for singly charged projectiles, we investigated whether similar reactions could take place with doubly charged cations. This work deals mainly with the addition reactions that occur on collisions of doubly charged benzene, benzene- d_6 and hexa-2,4-diyne with self-assembled monolayers prepared on vapour-deposited gold by using n -alkanethiols [$CH_3(CH_2)_nSH$, $n = 1, 17$], perdeuterioeicosanethiol [$CD_3(CD_2)_{19}SH$] and 2-(perfluorooctyl)ethanethiol [$CF_3(CF_2)_7CH_2CH_2SH$]. For comparison, the ion-surface collision spectra obtained for the singly charged ions are also discussed.

We used a tandem quadrupole mass spectrometer that has been described previously.⁹ The collision energy was varied from 15 to 60 eV. Singly and doubly charged molecular ions were produced by 70 eV electron impact ionization. The pressure in the analyser region was kept within the range 5.0×10^{-7} – 5.5×10^{-7} Torr (1 Torr = 133.3 Pa). (For further details of surface preparations and instrument parameters, see Refs 5 and 10.)

Figure 1 shows the ion-surface collision spectra obtained by colliding (a) singly charged benzene, (b) doubly charged benzene, (c) singly charged hexa-2,4-diyne and (d) doubly charged hexa-2,4-diyne at 30 eV collision energy with a surface prepared from $CF_3(CF_2)_7CH_2CH_2SH$ on vapour-deposited gold. Spectra obtained with alkanethiolate surfaces are not shown owing to space limitations, but are discussed below.

Unfortunately, the ions selected at m/z 39 contain both singly charged m/z 39 ($[C_3H_3]^+$) and doubly charged m/z 78 ($[C_6H_6]^{2+}$) ions. However, the collision of this beam with the hydrocarbon, deuterocarbon and fluorocarbon monolayers [see, e.g., Figs 1(b) and (d)] yields peaks in the range m/z 40–78, which can be explained by reduction of the doubly charged ions (m/z 78) and to subsequent fragmentations (e.g.

m/z 75, 52, 51, 50). The intensities of these peaks are about 1.0–3.5% of the selected beam (m/z 39) in the 30 eV ion-surface collision spectra of the doubly charged benzene on the fluorocarbon surface [Fig. 1(b)]. In principle, these ions could also originate from reactions between the singly charged $[C_3H_3]^+$ cation (m/z 39) and the monolayers. However, the intensities of these peaks are less than 0.3% of the main beam (m/z 39) in the corresponding 30 eV ion-surface collision spectra of a 'pure' $[C_3H_3]^+$ ion formed in the ion source from the molecular ion of benzonitrile. [In this case, the doubly charged molecular ion (m/z 51.5) does not contribute to the ion beam of $[C_3H_3]^+$ at m/z 39.] The spectrum for the doubly charged benzene shows enhanced fragmentation of the singly charged ion formed by charge exchange at the surface in comparison with the singly charged ions formed in the source [compare Fig. 1(b) and Fig. 1(a)]. The singly charged hexa-2,4-diyne ion (m/z 78) was not detectable in the 30 eV ion-surface collision spectra of the doubly charged ion obtained with the fluorocarbon surface, and only a very weak peak was observed at m/z 78 in the corresponding spectrum obtained on the octadecanethiolate surface. This ion has also not been observed at 42 eV collision energy with a stainless-steel surface.⁶ We suggest, therefore, that the singly charged molecular ion of the hexa-2,4-diyne isomer ion formed by charge-exchange process with the surface is less stable than that of benzene. Note that the ions at m/z 31, 45, 57 and 70 in the ion-surface collision spectra shown in Fig. 1 are presumably F-containing ions with the formulae $[CF]^+$, $[C_2H_2F]^+$, $[C_3H_2F]^+$ and $[C_4H_3F]^+$, respectively.

Peaks at m/z values higher than 78 indicate reactions between projectile ions and monolayers. The spectra for singly and doubly charged deuterobenzene (C_6D_6) confirm that, similarly to the singly charged spectra,^{2,5} the peaks at m/z 96 and 95 are due to an F-addition reaction with benzene ions followed by subsequent H and H_2 losses, respectively [Figs 1(a) and (b)]. (The peaks at m/z 96 and 95 are shifted to m/z 101 and 99, respectively.) Although deuterated hexa-2,4-diyne was not available to us, it is reasonable to assume that the peaks at m/z 96 and 95 in the singly charged spectrum [Fig. 1(c)] originate also from an initial F addition. The peaks at m/z 96 and 95 are not observed in the spectrum of the doubly charged hexa-2,4-diyne ion [Fig. 1(d)]. However, peaks at m/z 94, 93 and 92 (together with, e.g., m/z 74) appear in the spectrum when the ion at m/z 37 is selected from the ion source. This suggests that an ion $[C_6H_2]^{2+}$ (m/z 37) is also formed in the ion source. This doubly charged ion undergoes charge exchange with the surface forming the ion at m/z 74 and reacts with the fluorocarbon surface, forming e.g. $[C_6HF]^{++}$ (m/z 92) and $[C_6H_2F]^+$ (m/z 93).

A peak at m/z 91 appears in the ion-surface collision spectra of both the singly and doubly charged C_6H_6 ions obtained with alkanethiolate surfaces. This peak results from CH_3 addition followed by H_2 loss, as supported by the reactions with the perdeuterioeicosanethiolate surface. In the case of the deuterated surface, three peaks are observed at m/z 94, 93 and 92, which correspond to CD_3 addition and the subsequent loss of H_2 (m/z 94), HD (m/z 93) and D_2 (m/z 92). The relative abundances of the ions corresponding to F addition remain roughly the same in comparison with the total ion abundances for both the singly and doubly charged ions of benzene; the intensities of the 'methyl addition' peaks are significantly lower for the doubly charged ions of both isomers.

Additional experiments are in progress to obtain more information on the isomeric $[C_6H_6]^{2+}$ structures and the

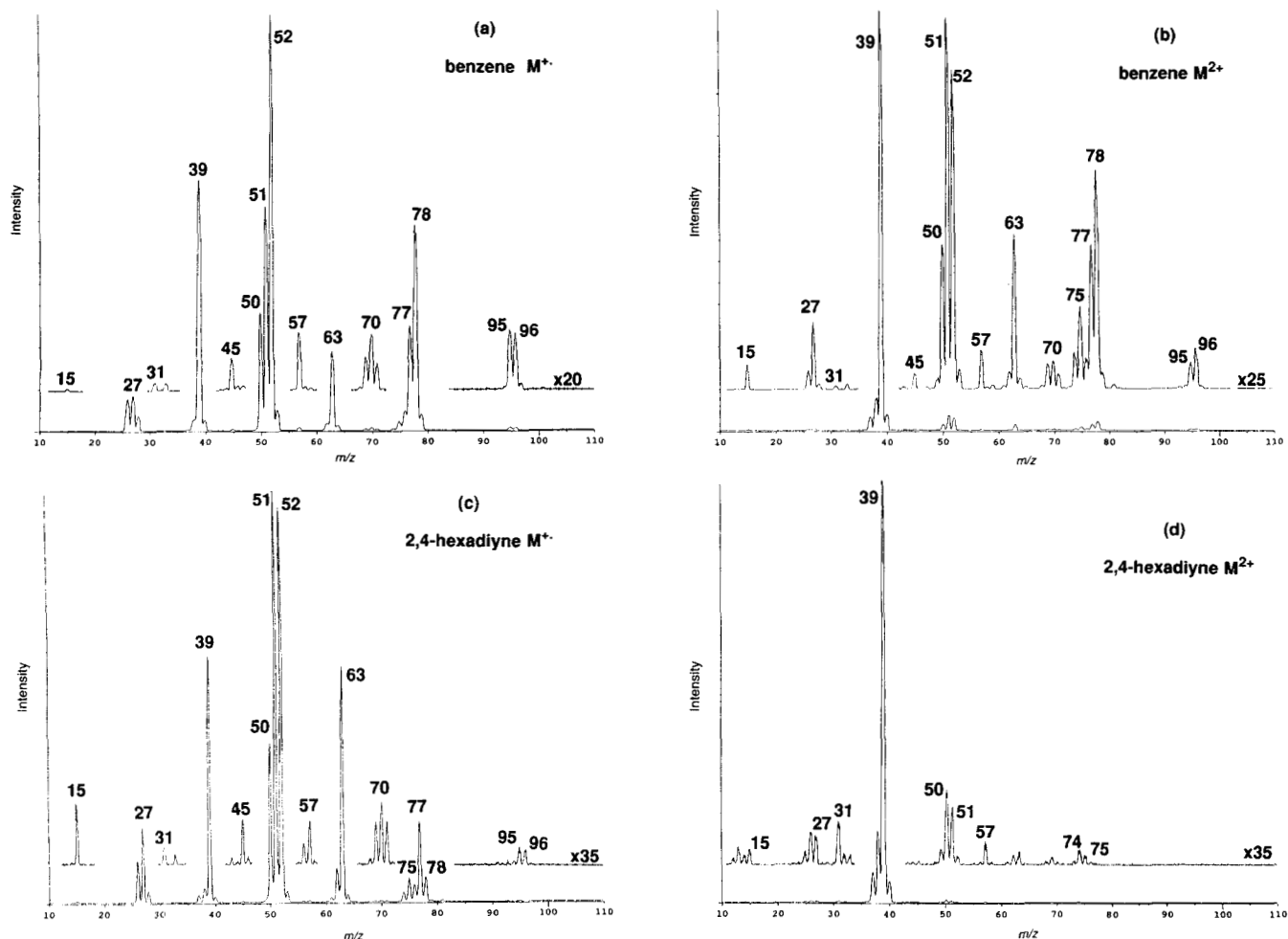


Figure 1. Ion-surface collision spectra obtained by colliding (a) singly charged benzene,⁵ (b) doubly charged benzene, (c) singly charged hexa-2,4-diyne and (d) doubly charged hexa-2,4-diyne at 30 eV collision energy with a surface prepared from $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{SH}$ on vapour-deposited gold.

energetics of the ion-surface reactions. Our preliminary results are in better agreement with the assumption of a closed-ring (but not necessarily planar¹¹) form of the doubly charged benzene, although a mixture of isomer ions may be present.

Yours

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