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FORMATION OF SUBSTITUTED BENZENE RADICAL CATIONS VIA ION/MOLECULE REACTIONS WITH IODOBENZENE

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Ion/molecule reactions commonly occur in mass spectrometers. While in many cases such reactions are undesirable they can be useful for structure determination or for comparison of gas-phase chemistry with solution chemistry. In general, when an even electron ion reacts with a neutral molecule, the product ion formed is also an even electron ion due to the normally unfavorable energetics involved in electron unpairing. A notable exception to this is a system we have been studying, the reactions of iodobenzene with a variety of different even-electron ions.

As shown below, a variety of even-electron hydrocarbon ions react with iodobenzene to give alkyl benzene radical cations. The general reaction is

$$R^+ + \phi\text{-I} \rightarrow \phi\text{-R}^{+\bullet} + I^\bullet$$

Thus, an ion is observed at (R+77). Reactions are observed in cases in which the reactant ion is less than 15 kcal/mol or so more stable than the resulting alkylbenzene radical cation. The driving force for the reactions in which the odd-electron product ion is less stable than the even-electron reactant ion is the fairly unique situation of the radical product ($I^\bullet$) being about 15 kcal/mol more stable than the neutral reactant (iodobenzene).

We first observed the reaction of iodobenzene giving substituted benzene radical cations in the methane CI mass spectrum of iodobenzene. With the ion trap, selected reagent ion CI demonstrated that $C_2H_5^+$ gives an ion at m/z 106, $C_8H_{10}^{+\bullet}$, which is ethylbenzene. While the fact that this reaction occurs is interesting, the product can reasonably only be ethylbenzene. However, the next higher ion in the series, the propyl cation, has two possible structures *n*- or *i*-. Thus, m/z 43 was generated by electron ionization of isobutane. The spectrum obtained when m/z 43 is allowed to react for 100ms is shown in Figure 1. The major product ion is m/z 57 due to hydride abstraction from isobutane. The other two ions in the spectrum result from reactions of 43^+ with ϕ-I. The ion at m/z 205 is formed by the commonly observed proton transfer reaction while the species at m/z 120 corresponds to the substitution of $C_3H_7^+$ for $I^\bullet$ in ϕ-I. The thermochemistry of the system is that the proton transfer is exothermic by about 2 kcal/mol, *i*-$C_3H_7^+$ substitution is exothermic by about 5 kcal/mol and *n*-$C_3H_7^+$ substitution is exothermic by about 25 kcal/mol.

Figure 2 shows the MS^3 experiment in which the MS/MS spectrum of the reaction product at m/z 120 is obtained. From comparison of this spectrum with MS/MS spectra of the two isomeric propylbenzenes, it can be determined that the expected isopropylbenzene is the major product (giving the product ion at m/z 105) but that there is some *n*-propylbenzene also formed (giving product ions at m/z 91 and 78).

Continuing up in the series, $C_4H_9^+$ would not be expected to react if it is *t*-butyl but the other three isomers, *s*-,*i*-, and *n*-butyl should react. When m/z 57 is formed from 1 or 2-chlorobutane approximately 0.06% of the ions are reactive, giving m/z 134. The product ion spectrum of m/z 134 has only one ion, m/z 105, which is characteristic of *s*-butylbenzene.

The vinyl cation is an extremely reactive species which rarely is observed to form stable substitution products because of the high exothermicity of its reactions. However, when it reacts with ϕ-I the substitution product is observed. An MS^4 experiment was performed in which the MS/MS product ion spectrum was obtained on the vinyl cation reaction product with the vinyl cation being formed by CID of $C_3H_7^+$. This spectrum indicated that styrene is formed, as expected. This reaction is about 50 kcal/mol exothermic, which suggests that significant energy may be partitioned into translational energy of the products.

An ion with a higher degree of unsaturation than the vinyl cation, $C_4H_3^+$, which is a major fragment from phenyl cations, has also been studied. In addition to the product ion formed from the ϕ-I substitution reaction, the molecular ion and protonated molecule of ϕ-I are observed. The protonated species comes about as discussed above. The molecular ion is formed by charge exchange with $^{13}CC_3H_2^{+\bullet}$ isobar which is also present at m/z 51 when that m/z is selected from the mass spectrum. (Isobarically pure m/z 51 can be generated by MS/MS if so desired.) The MS/MS spectrum of the reaction product formed by $C_4H_3^+$ is shown in Figure 3. MS/MS experiments generating ^{13}C containing $C_4H_3^+$ suggest that the structure of m/z 128 is that of naphthalene. The MS/MS spectrum of the molecular ion of naphthalene was obtained and is identical to Fig. 3.

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During the course of the MS/MS experiments on the m/z 128 reaction product it was observed that the product ion at m/z 127 produced an ion at m/z 204. While this could be the molecular ion of ϕ-I, it is also (R+77) for R=127. An MS^5 experiment demonstrates that it is the later species which is formed.

The reaction of m/z 127 indicated that cyclic ions would also react in addition to the linear hydrocarbons. Figure 4 shows the reaction of the phenyl cation with ϕ-I. Not only is the substitution product observed but also the reaction intermediate, m/z 281. From a kinetics plot for the reaction m/z 77 the rate constant for this reaction in the ion trap was determined to be 2×10^{-9} cm^3-s/molecule, indicating that this is a very efficient reaction. The MS/MS spectrum of the reaction intermediate shows the expected dissociation, loss of I•. The MS/MS spectrum of the reaction product indicates that it is biphenyl.

We have observed this reaction with other halobenzenes. Crude bracketing of unknown heats of formation can be performed by observing if this reaction occurs with ϕ-I and the analogs, ϕ-Br and ϕ-Cl. The reaction will occur with ϕ-I if the difference in heats of formation of the reactant and product ion is less than 15 kcal/mol. For the reaction to occur with ϕ-Br the product ion must be at least as stable as the reactant, while for ϕ-Cl the product ion must be at least 15 kcal/mol more stable than the reactant.

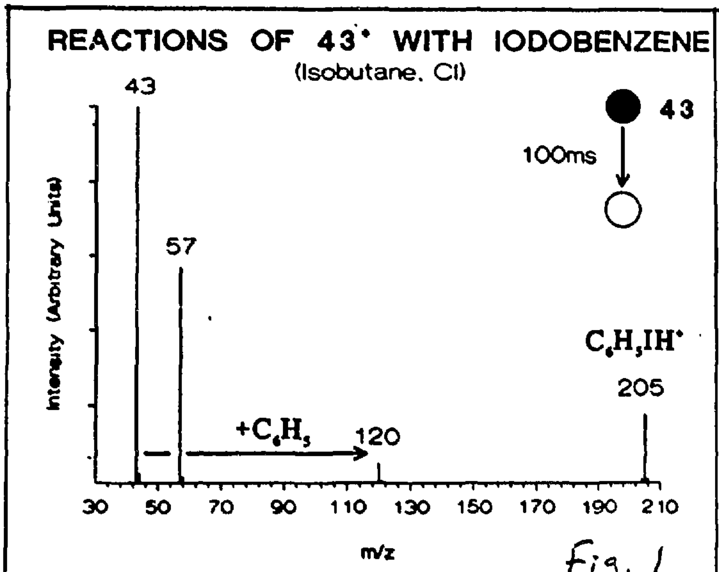
REACTIONS OF 43+ WITH IODOBENZENE
(Isobutane, CI)

Fig. 1

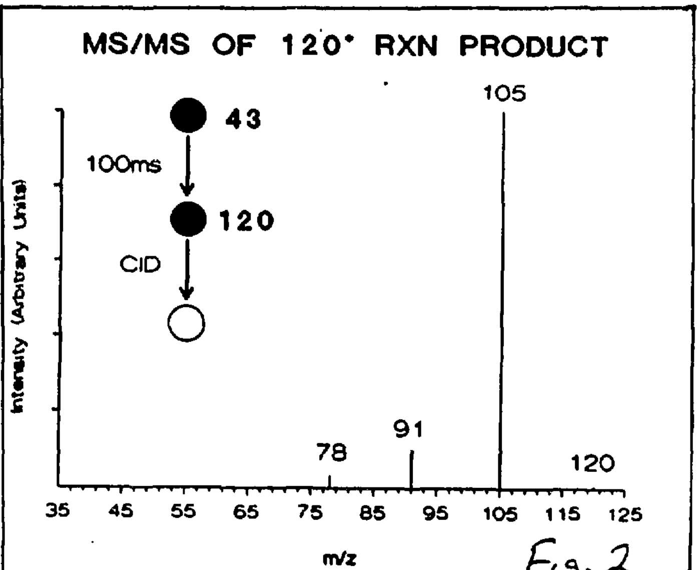
MS/MS OF 120+ RXN PRODUCT

Fig. 2

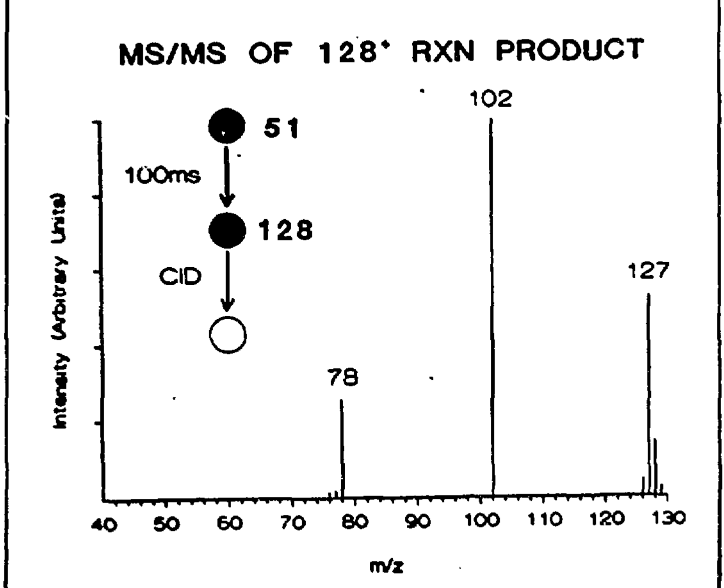
MS/MS OF 128+ RXN PRODUCT

Fig. 3

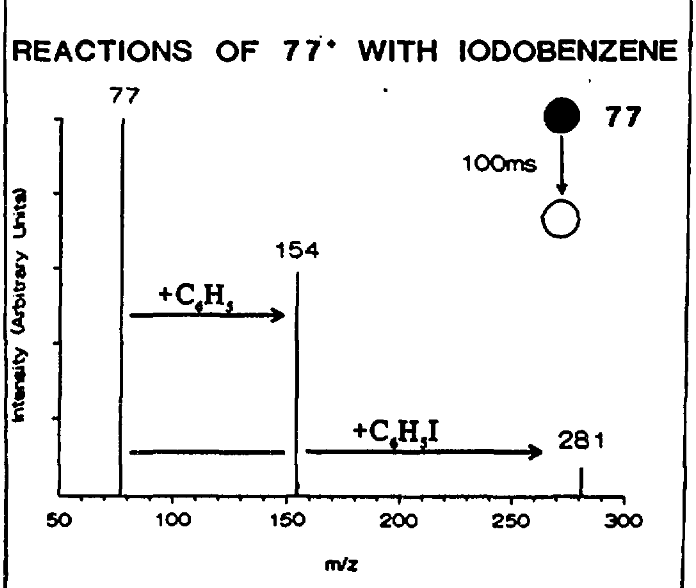
REACTIONS OF 77+ WITH IODOBENZENE

Fig. 4