

Electrophilic Aromatic Substitution: Comparison of Gas-phase and Solution Chemistry

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Reaction of $C_3H_5^+$ and $C_3H_7^+$ with benzene in the gas phase yields products with the structure of a 'Wheland intermediate' analogous to that in solution.

The electrophilic attack of organic cations upon aromatics is well known in solution and also has been studied in the gas phase using ion cyclotron resonance (i.c.r.)¹ and tandem mass

spectrometry.² Recently, Morrison *et al.*,^{3,4} using a triple sector quadrupole (t.s.q.), have investigated these reactions (see ref. 3 for experimental details). No adduct ions were observed;

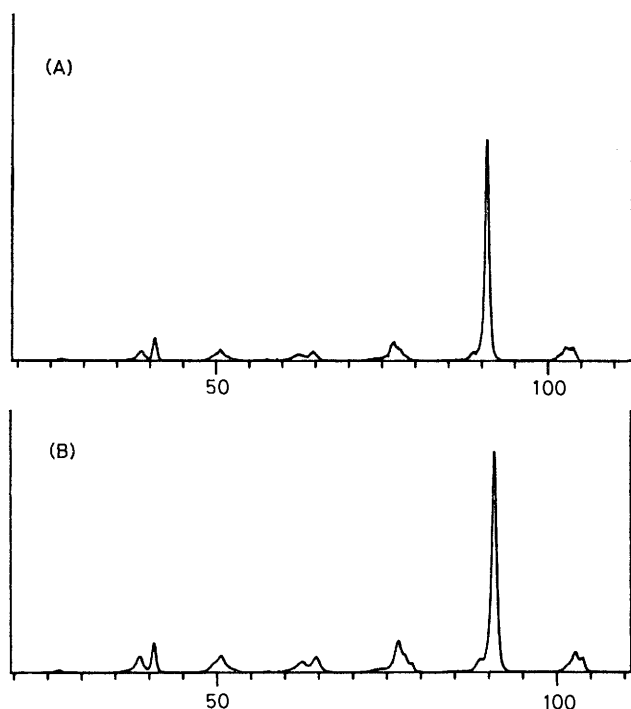


Figure 1. (A) C.i.d. spectrum of protonated allylbenzene, (B) c.i.d. spectrum of adduct formed in the reaction of allyl ion and benzene.

instead, charge exchange, hydrogen transfer, and disproportionation were found indicating that although all reactions except the charge exchange must proceed through an 'addition complex,' this was unlikely to have much resemblance to the 'Wheland intermediate' (or σ -complex) postulated for solution phase reactions.³

Normally, however, the chemistry of gas-phase ions bears a striking similarity to that of the corresponding ions in solution,⁵ and thus gas-phase studies have proven useful in understanding the solution phase.

We have been investigating electrophilic aromatic substitution reactions by using a different technique, m.s./m.s. with a triple analyser mass spectrometer equipped with a high-pressure (chemical ionization) source.⁶ The reactions were conducted in the ion source where the reaction intermediate is collisionally stabilized. Following acceleration from the source, the intermediate is selected by mass analysis using a double-focusing mass spectrometer, collisionally activated, and a collision-induced decomposition (c.i.d.) spectrum taken by scanning the final analyser, an electrostatic analyser. Without the collisional activation, the unimolecular dissociations of the product ions were also observed.

The reactions discussed below were also examined in a Fourier transform mass spectrometer⁷ at low pressures (no collisional stabilization). The reacting species were found to be the electrophiles by using double resonance, but no adducts could be observed.

The adduct ion production in the reaction of allyl ion with benzene was observed at high pressure in the source of the triple analyser, and its c.i.d. spectrum was taken. The spectrum was nearly identical to that of protonated allylbenzene (see Figure 1) indicating identical ion structures. The only unimolecular dissociation was loss of C_2H_4 to give $C_7H_7^+$ as was observed at low pressure in the F.t.m.s. experiments. The correspondence between the unimolecular chemistry observed

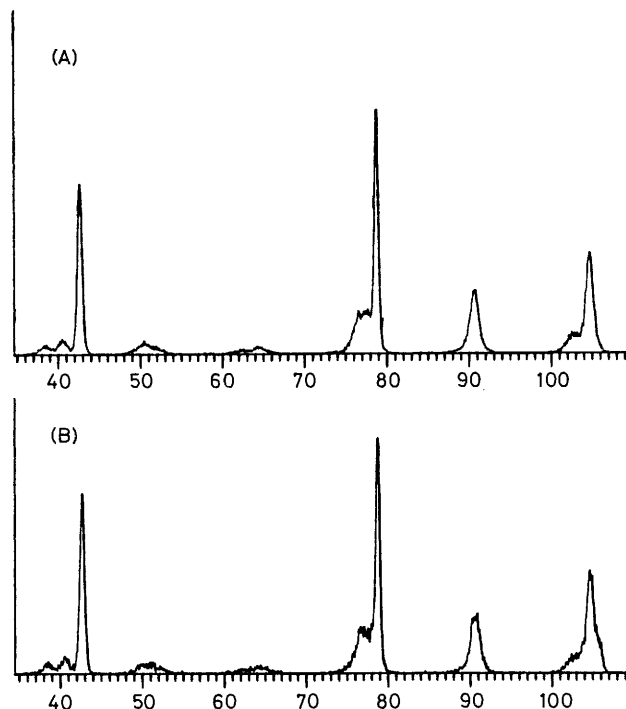
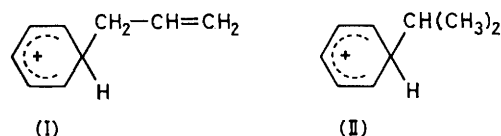


Figure 2. (A) C.i.d. spectrum of protonated isopropylbenzene, (B) c.i.d. spectrum of adduct formed in the reaction of isopropyl ion and benzene.



in the F.t.m.s. and the triple analyser indicates that the ion-molecule reaction intermediates were the same in both experiments, and that the intact adduct ion was not seen in the F.t.m.s. because of the absence of collisional stabilization.

The $C_9H_{13}^+$ formed in the reaction of benzene and $i-C_3H_7^+$ from propane was also studied. Its c.i.d. spectrum is nearly identical to that of isopropylbenzene protonated with $C_4H_9^+$ (Figure 2), but significantly different from that of protonated n-propylbenzene.

The successful detection of the intact adduct in these gas-phase reactions carried out at the higher pressures (ca. 0.1 Torr) available for the m.s./m.s. experiment is a result of collisional stabilization of the adduct. We postulate that the same structure is formed in the F.t.m.s. experiments, but, without collisional stabilization, the adduct undergoes unimolecular dissociation. However, a change in mechanism may occur if the translational energy of the reactant ions is increased as in the t.s.q. experiments conducted by Morrison *et al.*³ For example, these authors observed $C_7H_6^+$ in the reaction of allyl ion and benzene, but this ion was not found in either the low- or high-pressure experiments we have conducted. Instead, we observed $C_7H_7^+$.

In view of established analogies for solution and gas-phase acidities,⁸ we postulate that protonated allylbenzene and isopropylbenzene and the $C_9H_{11}^+$ and $C_9H_{13}^+$ produced in the gas-phase electrophilic substitution reactions have the structure of

'Wheland intermediates'; *i.e.* (I) and (II) respectively. This interpretation is consistent with other gas-phase/solution analogies^{5,8} and serves as another demonstration that a smooth mechanistic continuum is followed for reactions occurring in both media. In the case of electrophilic substitution, a 'Wheland intermediate' forms under conditions involving thermal reactant ions; the difference between low- and high-pressure conditions is that at low pressure the energy released causes it to undergo unimolecular dissociation.

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