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Young Scientist Feature

The gas-phase methylation of benzene and toluene[☆]

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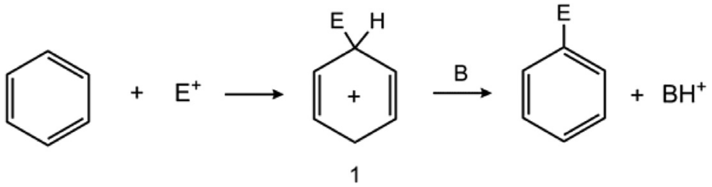
ABSTRACT

The reactions of the methyl cation with benzene and toluene in the gas phase have been examined using the flowing afterglow-selected ion flow-drift tube technique. With benzene four product ions are formed, $C_6H_6^+$ by electron transfer, $C_6H_5^+$ by addition and loss of CH_4, $C_7H_7^+$ by addition and loss of H_2, and an adduct $C_7H_9^+$. Deuterium and carbon-13 labeling experiments were carried out to provide mechanistic insights. In agreement with earlier work, deuterium labeling (CD_3^+ with C_6H_6 or CH_3^+ with C_6D_6) shows that partial H/D scrambling between the methyl group and the ring occurs during the formation of $C_6H_5^+$ and $C_7H_7^+$. However, in contrast to earlier work, no carbon-13 scrambling was observed between the methyl and ring carbons, thus ruling out a ring expansion and contraction mechanism to account for the H/D scrambling. Nor did we find H/D scrambling in the electron transfer product ion, $C_6H_6^+$. When collision-induced dissociation (CID) was carried out on the adduct ion, extensive H/D and carbon-13 scrambling was found, indicating that at least some ring expansion occurs during its formation. Reaction of $C_6H_5^+$ with methane at room temperature exclusively forms the adduct ion, but addition followed by loss of CH_4 and addition with loss of H_2 were also observed when the ion was given kinetic energy in a drift field. Mechanisms are proposed which account for our results, and these are supported by *ab initio* calculations. Similar studies were carried out with toluene as the neutral reagent. Besides the four analogous product ions, we found hydride transfer from the methyl group of toluene to be a major reaction channel and addition with loss of ethylene to be a minor channel.

1. Introduction

The Friedel-Crafts reaction (Eq. (1)), in which an electrophilic aromatic substitution occurs by way of an initial adduct (the so-called Wheland intermediate **1**) [1–4] is one of the most studied mechanistically in organic chemistry, and it is therefore a natural target in the gas phase, where the reactions of a cation, unencumbered by solvent and counterions, can be investigated [5–7].



(1)

[☆] Dedicated to Professor Terrance B. McMahon on the occasion of his 70th birthday and in recognition of his outstanding contributions to gas-phase ion chemistry and for many years of valued friendship.

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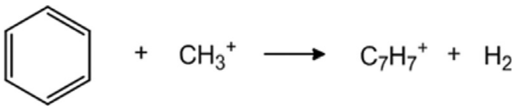
The gas phase chemistry of the methyl cation with benzene has been explored for more than four decades. Experimental studies of this reaction and related systems have been carried out by several groups, including Bursey et al. [8], Beauchamp [9], Morrison et al. [10,11] and Cacace and Giacomello [12]; in particular, a comprehensive and insightful series of investigations have been reported by Kuck and co-workers [13–19], including detailed mechanistic studies. These experiments reveal a rich and intriguing chemistry.

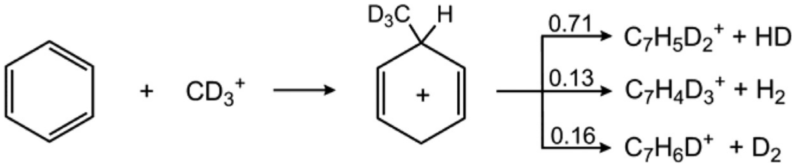
The first study of the methylation of benzene in the gas phase was carried out in an ion cyclotron resonance (ICR) spectrometer [8]. Simple substitution is not observed since there is no base present to remove the proton, and when an exothermic addition reaction takes place in the gas phase at low pressure, the exothermicity remains within the adduct and is often dissipated by fragmentation. In these ICR experiments an ion $C_7H_7^+$ was observed as a product, a result that corresponds to addition of a methyl group to benzene and loss of molecular hydrogen (Eq. (2)).



(2)

If one assumes that the reaction proceeds by initial formation of the Wheland intermediate, there are three obvious paths by which the two hydrogen atoms could be lost (Scheme 1) [13–15,20,21]. In the most straightforward pathway there is a 1,2-loss of H_2 across the initially formed C—C bond (path A) to form the benzyl cation. A second possible path (B) proceeds by way of a rapid proton migration around the ring followed by a 1,1-loss of H_2 to form a tolyl cation. A third possibility (path C) is that H_2 loss is preceded by skeletal rearrangement to a seven-membered ring. Of course even more complicated schemes can be devised. Williams and Hvistendahl [21] indicated that 1,1-H_2 loss giving $C_7H_7^+$ (Path B) would not occur in the case of the $C_7H_9^+$ ions. Instead, they suggested that protonated cycloheptatriene would form *via* ring expansion (Path C), with loss of H_2 to form the tropylium ion. Kuck et al. [13] proposed that the H_2 molecule could be expelled by a 1,2-elimination involving the $H_3C—C_\alpha$ bond to form the benzyl cation (Path A), agreeing with their "composite scrambling" model. Path A is further supported by Schröder et al. [22] who experimentally showed that the $C_7H_7^+$ ions generated possess the benzyl structure.

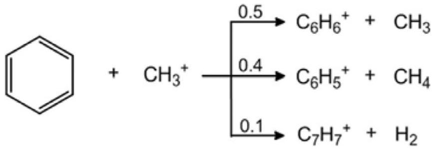
These three paths lead to different product ions and, in principle, these alternative paths can also be distinguished by labeling experiments. If, for example, CD_3^+ is used as the electrophile, one would expect HD to be lost if path A occurs, H_2 if path B occurs and, since the protons should rearrange rapidly in a ring-expanded ion [13], a random or near-random loss of H_2, HD, and D_2 if path C is followed. However, when this experiment was carried out in an ICR mass spectrometer [9], a mixture of ions corresponding primarily to loss of HD (71%) but with significant losses of H_2 (13%) and D_2 (16%) was observed (Eq. (3)).



(3)

These results suggest that the overall reaction is more complicated than any single path predicts.

In a later study, a triple quadrupole instrument was used to investigate this same reaction [10,11] and two additional product ions were identified. In these experiments the methyl cation was generated by electron impact on nitromethane and selected in the first quadrupole. Benzene vapor was introduced into the second quadrupole, where reactions occurred. The product ions were identified by mass separation in the third quadrupole. In addition to the $C_7H_7^+$ ion observed by ICR, $C_6H_6^+$ (the ion which would be produced by electron transfer) and $C_6H_5^+$ (the ion which would be produced by hydride transfer) were also observed in the relative amounts shown in Eq. (4).



(4)

When these reactions were repeated using CD_3^+ as the electrophile, scrambling of hydrogen and deuterium was found in all three product ions, again indicating that the mechanism is more complicated than is apparent from the unlabeled experiment. In particular, the results show that $C_6H_6^+$ and $C_6H_5^+$ are not formed by simple, long range electron and hydride transfer, and that each of these ions most probably arise from an initially formed Wheland adduct.

An extensive mechanistic investigation of the fragmentation of the Wheland intermediate was carried out with a double focusing mass spectrometer by Kuck et al. [13–19] In a seminal study [13], a series of isotopically labeled dihydrotoluic acids were synthesized and subjected to ionization in the mass spectrometer source. The initial fragmentation occurs by loss of COOH to produce protonated toluene, an isomer of the initial adduct of the methyl cation with benzene. Assuming that the protons of the ring rapidly equilibrate by a series of 1,2-H migrations these two species will fragment analogously, and in fact loss of molecular hydrogen and methane are observed in the metastable ion spectrum (Eq. (4)).