

OMS Letters

Dear Sir

FT-ICR STUDY OF THE REACTION OF EXTERNALLY GENERATED AMMONIA RADICAL CATIONS WITH CHLOROBENZENE

The spatial separation of ion generation and ion detection in ICR spectrometry is known to have many advantages. The pressure in the ICR cell can be maintained at very low values, which enhances resolution and sensitivity. Furthermore, ionization techniques like CI and FAB become feasible¹.

Little attention has been focused on the advantages of an external ionization concerning the study of ion-molecule reactions. Ionization of the reactant gas within the ICR cell is avoided and the temperature of the neutral gas is kept at room temperature. The most important advantage is, however, that the ions, generated in the external ion source, cannot react with their neutral precursors after transfer into the ICR cell.

We have examined the reaction of NH_3^+ ions, generated in the external ion source of a Bruker CMS 47X FT-ICR spectrometer, after transfer into the ICR cell with chlorobenzene. It can be seen from figures 1 and 2 that exclusively charge exchange occurs (reaction (1)), beside very little loss of a chlorine atom from chlorobenzene radical cations (m/z 112 \rightarrow m/z 77).

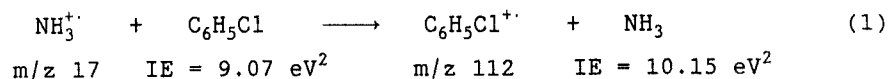


Figure 1: Reaction of NH_3^+ ions with chlorobenzene ($p = 5.0 \cdot 10^{-8}$ mbar), 1.5 ms after isolation of NH_3^+ , m/z 17, and after 1.4 s reaction time

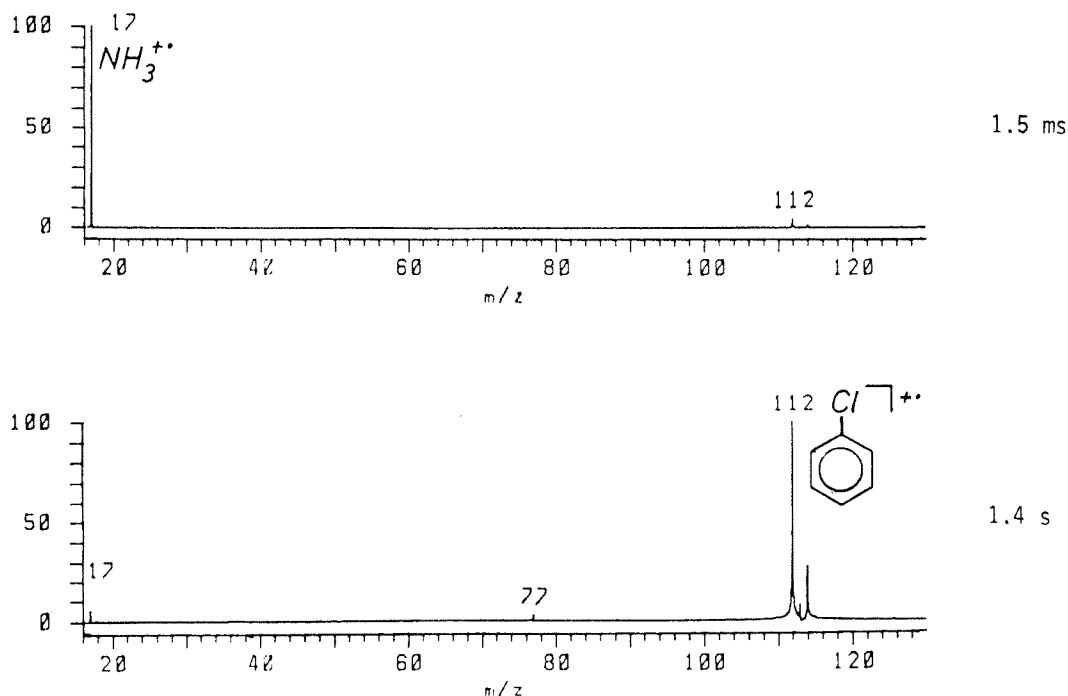
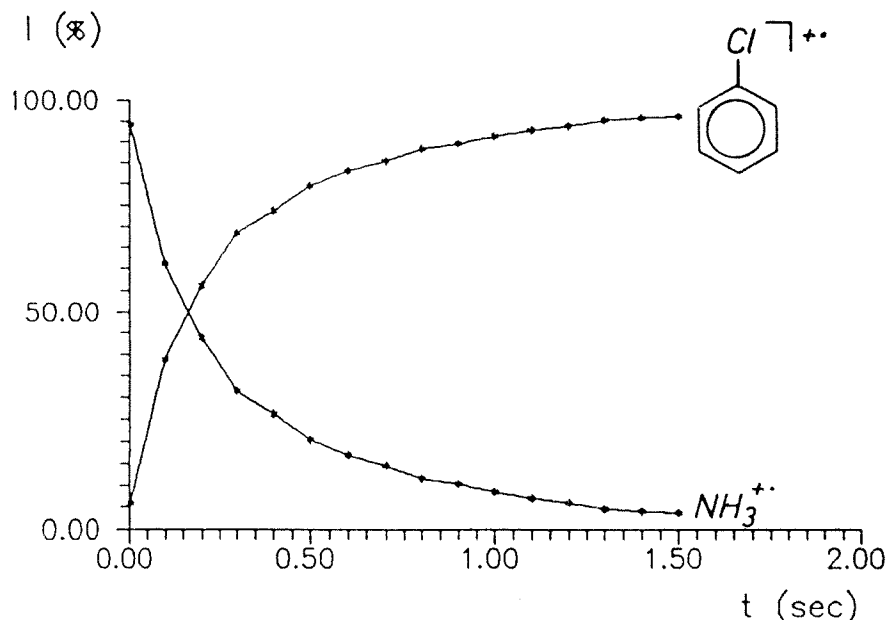
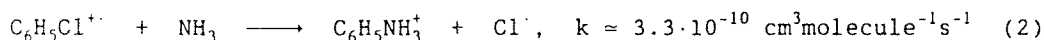


Figure 2: Time dependence of reaction (1), $p(\text{chlorobenzene}) = 5.0 \cdot 10^{-8}$ mbar, the intensities are normalized to sum of all ions = 100%



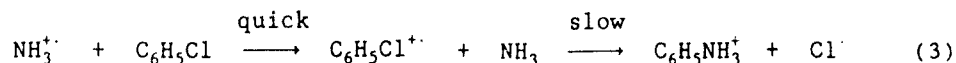
Evaluation of the reaction rate (1) shows that the reaction precedes collision controlled, $k_{\text{ADO}}^3 = 2.75 \cdot 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

In an ICR spectrometric study with conventional internal ionization, W.J. van der Hart et al.⁴ showed that anilinium ions are formed in an ipso-substitution by reaction (2).

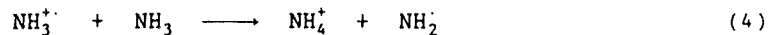


We could confirm this observation. Evaluation of the kinetics of reaction (2) showed that it possesses a strong negative temperature dependence⁵. The reaction rate decreases dramatically, if the ions possess kinetic energy. External ionization and transfer into the ICR cell may impart some kinetic energy to the ions because of imperfect deceleration at the end of the transfer line. Despite this it is possible to get the thermal rate constant of the reaction of the ions by just waiting a few hundred milliseconds until the ions are collisionally deactivated. The rate constant obtained in our experiments ($k = (3.0 \pm 0.3) \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is in excellent agreement with the data of van der Hart⁴. This shows that ICR spectrometry with external generation of ions is as well suited for the determination of reaction rates as ICR spectrometry using internal ionization.

Van der Hart et al. deduced from their experimental data that ammonia radical cations also react with chlorobenzene by substitution. Our investigations now show that this is *not* the case. The observation of anilinium ions during the reaction of internally generated ammonia radical cations with chlorobenzene is due to charge exchange and subsequent substitution reaction of chlorobenzene radical cations with ammonia (3).



External ionization avoids these problems, because the pressure of ammonia in the ICR cell is so small that the second part of reaction (3) does not take place. This is also true for reaction (4), which competes with reaction (3) in the case of internal ionization.



Ammonia radical cations were generated by electron impact (70 eV) in the external ion source. Ejection of ions was achieved by RF excitation. Chlorobenzene (purity > 99%) was steadily introduced into the ICR cell, the pressure was measured by an ionization gauge connected close to the turbo pump and is not corrected.

Yours

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