Proton Exchange between Arenium Ions and Arenes in the Gas Phase**

By Dietmar Kuck,* Steen Ingemann, Leo J. de Koning, Hans-Friedrich Grützmacher, and Nico M. M. Nibbering

Proton transfer reactions are known to be extremely fast in general. In the gas phase, they can be studied by modern, time-resolved mass spectrometry. Thus, MIKE spectroscopy of metastable ions (time scale $10^{-5}$ to $10^{-4}$ s) is used for the investigation of intramolecular hydrogen migration reactions, e.g., the proton exchange in protonated a,o-diphenylalkanes [Eq. (1a)], while, for intermolecular exchange reactions, Fourier transform ion cyclotron resonance (FT-ICR) spectrometry is becoming increasingly important (time scale $10^{-7}$ to $10^{-5}$ s). We report here on the intermolecular proton exchange [Eq. (1b)] between simple arenium ions and arenes in the cell of a FT-ICR mass spectrometer (Ar, Ar'= aryl).

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We generated the benzenium ions $\text{C}_6\text{H}_5^\oplus$ and $\text{C}_6\text{HD}_5^\oplus$ by electron-impact ionization of a mixture of benzene, $\text{D}_2$-benzene, and methane at $10^{-4}$ Pa (Fig. 1a).[7a] All ions except $\text{C}_6\text{H}_5^\oplus$ (m/z 79) were then removed from the ICR cell by “notch ejection” (Fig. 1b); subsequently, the ion-molecule reactions of the benzenium ions isolated in this way with the $\text{C}_6\text{H}_5/\text{C}_6\text{D}_5$ mixture were followed as a function of time ($t_i$). Figures 1c and 1d show all ions present in the cell at $t_i=190$ and 6290 ms, respectively; Figure 2 displays the dependence of the relative abundance of the product ions $\text{C}_6\text{H}_5(\text{H,D})$ on $t_i$.

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\[2\] D. K. thanks the Deutscher Akademischer Austauschdienst, Bonn, and the Ministerium voor Onderwijs en Wetenschappen, The Hague, for a grant.

\[3\] Experimental procedure: 2: 30\% H$_2$O$_2$ (11.3 g, 100 mmol) was added with stirring to ethyl pyruvate (17.3 g, 150 mmol) at $-10$ to $0\,^\circ$C [3]. This solution was then added with stirring and cooling (5 to $0\,^\circ$C) to a mixture of 1 (10 mmol), conc. H$_2$SO$_4$ (3 g), H$_2$O (8 g), FeSO$_4$·7H$_2$O (28 g, 100 mmol), and CH$_3$Cl (150 mL). After 15 min of further stirring, the resulting mixture was poured into ice water, the phases were separated, and the aqueous phase was exhaustively extracted with CH$_3$Cl. After drying over anhydrous Na$_2$SO$_4$, the solvent and excess ethyl pyruvate were removed in vacuo. The spontaneously crystallizing, colorless needles were recrystallized from diethyl ether: Yield: 1.4 g (81\%)

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**Fig. 1. a) FT-ICR mass spectrum of a mixture of $\text{C}_6\text{H}_5$, $\text{C}_6\text{H}_5$, and $\text{C}_6\text{D}_5$ [7a]; b) after ejection of all ions except $\text{C}_6\text{H}_5^\oplus$ (m/z 79) at the time $t_i=0$; c) after $t_i=190$ ms, and d) after $t_i=6290$ ms.

**Fig. 2. Relative abundances of the product ions in the system $\text{C}_6\text{H}_5^\oplus$/ $\text{C}_6\text{H}_5$/$\text{C}_6\text{D}_5$ as a function of the reaction time $t_i$ given relative to the sum of all product ions and corrected for naturally occurring $^{13}\text{C}$.

The measurements allow two conclusions to be drawn:
1. The proton exchange between benzenium ions and benzene is a surprisingly slow process (cf., for example, the system $\text{D}_2\text{O}^\ominus$/ $\text{C}_6\text{H}_5$[47]). For short reaction times $t_i$ (under
ChHD₂, a radiofrequency pulse with an amplitude of 2.5 V peak-to-peak was used.

2. The proton exchange occurs not only by consecutive ion-molecule reactions, but also within the collision complexes (e.g., [C₆H₆·C₆D₆]⁺). This follows from extrapolation of the relative abundances of the product ions to tᵣ = 0; The exchange products C₆H₆D⁺ (m/z 80) and C₆H₃D⁵⁺ (m/z 84) are already present there (Fig. 2).

Similar results are obtained from the corresponding investigation of the reaction of isolated C₆H₅D⁺ ions with the C₆H₆/C₆D₆ mixture. A further experiment allows a clear distinction to be made between these two exchange processes (Scheme 1). If the ions C₆H₅D⁵⁺ (m/z 85) are continuously removed from the cell for the entire reaction time, the formation of all further C₆D₆H⁵⁺ ions is suppressed to the extent that they are formed via C₆H₅D⁵⁺ (Scheme 1a). In contrast, C₆D₆H⁵⁺ ions that arise via H⁻/D⁺ exchange within the collision complexes [C₆H₆·C₆D₆]⁺ are not suppressed (Scheme 1b).

In Table 1 the relative abundances of the ions present in the cell after tᵣ = 790 ms—with and without continuous removal of the ions m/z 85—are compared.

![Scheme 1](image)

Table 1. Ion abundances in the system C₆H₅/C₆H₆/C₆D₆ after tᵣ = 790 ms without (+) and with (−) continuous removal of the ions C₆H₅D⁵⁺ (m/z 85) [a]

<table>
<thead>
<tr>
<th>m/z</th>
<th>78</th>
<th>79</th>
<th>80</th>
<th>81</th>
<th>82</th>
<th>83</th>
<th>84</th>
<th>85</th>
<th>86</th>
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<tbody>
<tr>
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<td>30</td>
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<td>49</td>
<td>8.6</td>
<td>7.9</td>
<td>14.3</td>
<td>70</td>
<td>168</td>
<td>15.8</td>
</tr>
<tr>
<td>(+)</td>
<td>30</td>
<td>1000</td>
<td>49</td>
<td>6.4</td>
<td>4.2</td>
<td>10.4</td>
<td>62</td>
<td>0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

[a] ¹³C-corrected values. The absolute abundance of the ions C₆H₅⁺ (= 1000) was constant in both experiments. In order to continuously remove the ions C₆H₅D⁵⁺, a radiofrequency pulse with an amplitude of 2.5 V peak-to-peak was used.

The data confirm that the proton exchange takes place within the collision complex: even upon ejection of the ions m/z 85, all C₆(H,D)⁵⁺ isotopomers are formed, albeit in lower absolute abundances. Thus, for example, the abundance of the ions C₆H₅D⁵⁺ (m/z 80) decreases by only a relative 19%; in contrast, the formation of the ions C₆D₅⁺ (m/z 86), which are formed exclusively by consecutive ion-molecule reactions (Scheme 1a), is completely suppressed.

The proton exchange between toluenium ions and toluene (C₆H₅/C₆D₅/C₆D₆) is even slower than that between the lower homologues. Here, too, the exchange takes place partly within the collision complexes (e.g., [C₆D₅⁺·C₆H₅⁺]). Thus, a fraction of the C₆(H,D)⁶⁺ isotopomers are still formed despite continuous removal of the ions C₆H₆D⁺. A possible reason is that the proton exchange in the collision complex [C₆H₅⁺·C₆H₃⁺] only occurs between positions having the same proton affinity (primarily para<para'), which must lead to a considerable slowing of the reaction compared with the exchange in the collision complex [C₆H₅⁺·C₆H₆⁺].

In fact, no proton exchange is observed for non-degenerate proton-transfer reactions, such as in the system benzene/toluene/methane. Accordingly, solely proton transfer is observed at all tᵣ in the exothermic direction of the reaction [Eq. (2a)], and no other toluene isotopomers are formed in the endothermic direction of the reaction [Eq. (2b)].

\[
\text{C₆D₅⁺} + \text{C₆H₅} \rightarrow \text{C₆D₆} + \text{C₆H₆D} \\
\text{C₆H₅⁺} + \text{C₆D₆} \rightarrow \text{C₆H₆D} + \text{C₆H₅D} 
\]

These observations can be explained qualitatively by a symmetrical (Ar=Ar') or an asymmetrical (Ar≠Ar') double-minimum energy profile.[12] According to our results, the activation barrier between the minima [ArH⁺·Ar'H] and [ArH⁺·Ar'H⁺] must be relatively high. This is especially noteworthy in comparison with the extremely fast intramolecular proton exchange in protonated a,a-diphenylalkanes and related arenium ions.[13]

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of further heteroatoms. Reactions of ethylene oxide and sulfur dioxide in the presence of catalysts have been well documented.[2] Ethylene sulfite is formed. We have now found that the reaction of ethylene oxide and sulfur dioxide in the presence of catalysts have been well documented.[2] Ethylene sulfite is formed. We have now found that the reaction of ethylene oxide and sulfur dioxide in the presence of catalysts have been well documented.[2] Ethylene sulfite is formed. We have now found that the reaction of ethylene oxide and sulfur dioxide in the presence of catalysts have been well documented.[2] Ethylene sulfite is formed.