Dear Sir

Reactions of the β-Distonic Ion \(^{13} \text{CH}_2\text{OCH}_2\text{CH}_2^+\) with Butyronitrile: Evidence for an Intermediate Three-body Ion-Neutral Complex during Deprotonation

Distonic ions are reactive intermediates of organic gas-phase reactions exhibiting very interesting properties. In a previous publication we discussed the unimolecular and bimolecular reactions of the β-distonic ion \(^{13} \text{CH}_2\text{OCH}_2\text{CH}_2^+\) (a). Using the deuterated ions \(^{13} \text{CH}_2\text{OCD}_2\text{CD}_2^+\) (b) and \(^{13} \text{CD}_2\text{OCH}_2\text{CH}_2^+\) (c), it was shown that a transfers a \(\text{C}_2\text{H}_4^+\) unit and a \(\text{CHO}^-\) unit to acetonitrile and pyridine, respectively, without any H/D scrambling, corroborating in the case of the \(\text{C}_2\text{H}_4^+\) transfer earlier observations of Baumann et al. The structural integrity of \(^{13} \text{CH}_2\text{OCH}_2\text{CH}_2^+\) revealed by these reactions is attributed to the unique thermodynamic stability of β-distonic ions. However, a second abundant reaction of a is the transfer of a proton to acetonitrile and pyridine, respectively, and from b as well as from c \(\text{H}^+\)- and \(\text{D}^+\)-transfer is observed. Obviously, each of the hydrogen atoms of a and b is transferred with a certain probability. This may be due either to parallel proton transfers from each of the different positions of a or a H/D scrambling in a prior to the proton transfer, the latter explanation being in conflict with the structural integrity of a in the other ion-molecule reactions. Both possibilities can be distinguished by a quantitative analysis of H- and D-transfer from the isotopomers b and c, because only in the case of a H/D scrambling (unit preference factor for all positions) are the experimental data described by a single isotope effect \(k_p/k_d\). However, we did not succeed in obtaining consistent quantitative data for the reaction of b and c with \(\text{CH}_2\text{CN}\) because the intensity ratio \([\text{CH}_2\text{CNH}^+]/[\text{CH}_2\text{CND}^+]\) increased continuously with the reaction time. It is very likely that the ion mixture in \(\text{CH}_2\text{CN}\) contained some unknown impurities which we were not able to remove. Here we report the results for the reaction of a with \(\text{n-butyronitrile}\) showing that a indeed loses its structure prior to the transfer of a proton.

The β-distonic ion a was generated by electron-impact induced fragmentation of 1,4-dioxane in the external ion source of a Spectrosin CMS 47X Fourier transform-ion cyclotron resonance (FT-ICR) spectrometer. The resulting ions were transferred into the ICR cell filled with \(\text{n-C}_3\text{H}_7\text{CN}\) at a pressure of \(4 \times 10^{-9}\) mbar. In order to study the reactions of b and c, 2,2,3,3-tetradeutero-1,2-dioxane was ionized in the external ion source. The ions a, b and c, respectively, were isolated by removing all other ions using broad-band ejection and specific rf-pulses of low amplitude ('soft single shots') in the mass range of a, b and c. The isolated ions were thermalized by collisions with the reagent gas for 1.5 s, and any ions formed besides those to be studied were again ejected by single shots. Subsequently, mass spectra were obtained at intervals of 0.5 s during a total reaction time of ca. 5 s.

Products of the reaction of a with \(\text{n-C}_3\text{H}_7\text{CN}\) are observed at \(m/z\) 57 (\(\text{C}_2\text{H}_3\text{O}\), [a - H], by high resolution), \(m/z\) 69 (\(\text{C}_3\text{H}_7\text{N}\), \(m/z\) 70 (\(\text{C}_4\text{H}_8\text{N}\)) and \(m/z\) 97 (\(\text{C}_6\text{H}_{10}\text{N}\)). Figure 1 shows the mass spectra for the reaction of b and c after a reaction time of 1.5 s. The products ions \(m/z\) 71 arise from proton transfer from a to butyronitrile, and part of the intensity for these ions was ionized [\(\text{C}_3\text{H}_7\text{CNH}^+\)]/[\(\text{C}_3\text{H}_7\text{CND}^+\)] is constant over the total reaction time corresponding to \(1.12 \pm 0.05\) for b and \(4.66 \pm 0.18\) for c. Assuming participation of all 2H and 4D of b and all 4H and 2D of c, this results in an isotope effect \(k_p/k_d = 2.24 \pm 0.10\) and \(2.33 \pm 0.10\), respectively, identical within the experimental error.

The following reactions (1)-(4) can be envisaged for a protonation of \(\text{n-butyronitrile}\) by a. The heats of reaction, \(\Delta H_r\), were calculated by using \(\Delta H(a) = 842 \text{kJ mol}^{-1}\) and \(\Delta H(\text{C}_3\text{H}_7\text{OC}^{(3)}\text{H}_2\text{C}^{(4)}\text{H}_2) = 71 \text{kJ mol}^{-1}\). The \(\Delta H_r\) of the other species were taken from the compilation of Lias et al.

\[
\begin{align*}
+^{13} \text{CH}_2\text{OCH}_2\text{CH}_2^+ &\rightarrow \text{C}_2\text{H}_4\text{CNH}^+ + \text{H}^+ + \text{C}_3\text{H}_7\text{C}^{(3)}\text{H}_2\text{C}^{(4)}\text{H}_2 \\
\Delta H_r &= -25 \text{kJ mol}^{-1} \\
+^{13} \text{CH}_2\text{OCH}_2\text{CH}_2^+ &\rightarrow \text{C}_2\text{H}_4\text{CNH}^+ + \text{C}_3\text{H}_7\text{H}^{(3)}\text{H}^{(4)} + \text{C}_3\text{H}_7\text{O} \\
\Delta H_r &= -25 \text{kJ mol}^{-1} \\
+^{13} \text{CH}_2\text{OCH}_2\text{CH}_2^+ &\rightarrow \text{C}_2\text{H}_4\text{CNH}^+ + \text{C}_3\text{H}_7\text{OC}^{(3)}\text{H}^{(4)} = \text{C}_3\text{H}_7\text{H}^{(3)}\text{H}^{(4)} \\
\Delta H_r &= -51 \text{kJ mol}^{-1} \\
+^{13} \text{CH}_2\text{OCH}_2\text{CH}_2^+ &\rightarrow \text{C}_2\text{H}_4\text{CNH}^+ + \text{C}_3\text{H}_7\text{H}^{(3)}\text{H}^{(4)} + \text{CO} \\
\Delta H_r &= -116 \text{kJ mol}^{-1}
\end{align*}
\]

Figure 1. Mass spectra of b and c after a reaction time of 1.5 s.

Received 17 February 1992
Accepted 17 February 1992
Table 1. Stabilization energy (kJ mol$^{-1}$) of the complex between a and nitrile

<table>
<thead>
<tr>
<th>r (Å)</th>
<th>3.6</th>
<th>3.7</th>
<th>3.8</th>
<th>3.9</th>
<th>4.0</th>
<th>4.1</th>
<th>4.2</th>
<th>4.3</th>
<th>4.4</th>
<th>4.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CN</td>
<td>112</td>
<td>105</td>
<td>99</td>
<td>93</td>
<td>87</td>
<td>82</td>
<td>78</td>
<td>74</td>
<td>70</td>
<td>66</td>
</tr>
<tr>
<td>C$_2$H$_5$CN</td>
<td>126</td>
<td>117</td>
<td>110</td>
<td>103</td>
<td>97</td>
<td>91</td>
<td>86</td>
<td>81</td>
<td>76</td>
<td>72</td>
</tr>
</tbody>
</table>

Reaction (2) corresponds to deprotonation from C$^{4+}$ (or probably C$^{3+}$) but is excluded because of its endothermicity. The exothermic reactions (1) and (3) correspond to specific proton transfer from C$^{3+}$ and C$^{2+}$, respectively. Hence, in view of the inactive C$^{4+}$H$_2$ group a parallel deprotonation by reactions (1) and (3) involves only 2H and 2D for $b$ as well as for $c$. This does not agree with the very different ratios $[C_3H,CNH^+]/[C,H,CND]^+$ experimentally observed for $b$ and $c$. However, the exothermic reaction (4) includes a participation of the 6H atoms at all positions of $a$, because hydrogen rearrangements have to accompany the formation of the radical C$_2$H$_5^+$, and the origin of the proton transferred is not specified.

A hint to the possible mechanism of the proton transfer from $a$ by reaction (4) is the observation that collisional activation of $a$ results in the formation of CO and C$_2$H$_6^+$.

At distances of 3.8 Å and 4.1 Å between $a$ and the nitrile molecule, where the repulsive interactions ignored by the classical attraction potential are still very weak, the excitation energy of the complex is already sufficient to fragment $a$ into CO and C$_2$H$_6^+$, in analogy to the decomposition induced by high-energy collisions with Ar.

C$_2$H$_6^+$ delivers any of the 6H atoms to the nitrile in a fast exothermic proton transfer, resulting in a dissociation of the intermediate complex.

Acknowledgements. We thank the Deutsche Forschungsgemeinschaft for the FT-ICR spectrometer and for financial help of this work. Additional financial assistance by the Fonds der Chemischen Industrie is gratefully acknowledged.

Yours,

DORIS WITTNEBEN and
HANS-FRIEDRICH GRÜTZMACHER
Fakultät für Chemie,
Universität Bielefeld,
Postfach 8640,
D-4800 Bielefeld,
Germany

References
5. $\Delta H_a(\text{CH}_3\text{CN} = \text{CH}_2) = 71$ kJ mol$^{-1}$ was estimated from the isodesmic reaction CH$_2$OCH = CH$_2$ (-100.4) + CH$_2$OCH$_2$ (-12.6) → CH$_3$OCH$_2$ (-184.0) + CH$_2$OCH = CH$_2$, all $\Delta H_a(\text{kJ mol}^{-1})$ from Ref. 6.