

## OMS Letters

Dear Sir

**Reactions of the  $\beta$ -Distonic Ion  $^+\text{CH}_2\text{OCH}_2\text{CH}_2^{\cdot}$  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.<sup>1</sup> In a previous publication<sup>2</sup> we discussed the unimolecular and bimolecular reactions of the  $\beta$ -distonic ion  $^+\text{CH}_2\text{OCH}_2\text{CH}_2^{\cdot}$  (*a*). Using the deuterated ions  $^+\text{CH}_2\text{OCD}_2\text{CD}_2^{\cdot}$  (*b*) and  $^+\text{CD}_2\text{OCH}_2\text{CH}_2^{\cdot}$  (*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.*<sup>3</sup> The structural integrity of  $^+\text{CH}_2\text{OCH}_2\text{CH}_2^{\cdot}$  revealed by these reactions is attributed to the unique thermodynamic stability of  $\beta$ -distonic ions.<sup>4</sup> However, a second abundant reaction of *a* is the transfer of a proton to acetonitrile and pyridine, respectively,<sup>2</sup> and from *b* as well as from *c*  $\text{H}^+$ - and  $\text{D}^+$ -transfer is observed. Obviously, each of the hydrogen atoms of *a* 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  $k_{\text{H}}/k_{\text{D}}$ . However, we did not succeed in obtaining consistent quantitative data for the reaction of *b* and *c* with  $\text{CH}_3\text{CN}$  because the intensity ratio  $[\text{CH}_3\text{CNH}^+]/[\text{CH}_3\text{CND}^+]$  increased continuously with the reaction time. It is very likely that the ion mixture in  $\text{CH}_3\text{CN}$  contained some unknown impurities which we were not able to remove. Here we report the results for the reaction of *a* with *n*-butyronitrile showing that *a* indeed loses its structure prior to the transfer of a proton.

The  $\beta$ -distonic ion *a* was generated by electron-impact induced fragmentation of 1,4-dioxane<sup>3</sup> in the external ion source of a Spectrospin CMS 47X Fourier transform-ion cyclotron resonance (FT-ICR) spectrometer. The resulting ions were transferred into the ICR cell filled with *n*- $\text{C}_3\text{H}_7\text{CN}$  at a pressure of  $4 \times 10^{-8}$  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.<sup>2,3</sup> 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 *n*- $\text{C}_3\text{H}_7\text{CN}$  are observed at  $m/z$  57 ( $\text{C}_3\text{H}_5\text{O}$ , [*a* - H], by high resolution),  $m/z$  69 ( $\text{C}_4\text{H}_7\text{N}$ ),  $m/z$  70 ( $\text{C}_4\text{H}_8\text{N}$ ) and  $m/z$  97 ( $\text{C}_6\text{H}_{11}\text{N}$ ). Figure 1 shows the mass spectra for the reaction of *b* and *c* after a reaction time of 1.5 s. The product ions  $m/z$  97 remain at this  $m/z$  value for *c* but are mass shifted to  $m/z$  101 for *b*. Therefore, these ions arise from  $\text{C}_2\text{H}_4^+$  ( $\text{C}_2\text{D}_4^+$ ) transfer to *n*-butyronitrile, a reaction well known from the reaction of *a* with acetonitrile<sup>2,3</sup> and proceeding without any H/D scrambling in *b* and *c*. In the case of *n*-butyronitrile, however, the  $\text{C}_2\text{H}_4^+$  adduct ions fragment further by loss of  $\text{C}_2\text{H}_4$  to yield an ion  $\text{C}_4\text{H}_7\text{N}^+$  isomeric to *n*-butyronitrile. This is clearly seen by the mass shift of the ion  $m/z$  69 to  $m/z$  73 in the spectrum of *b* indicating that  $\text{C}_2\text{H}_4$  is eliminated from the original

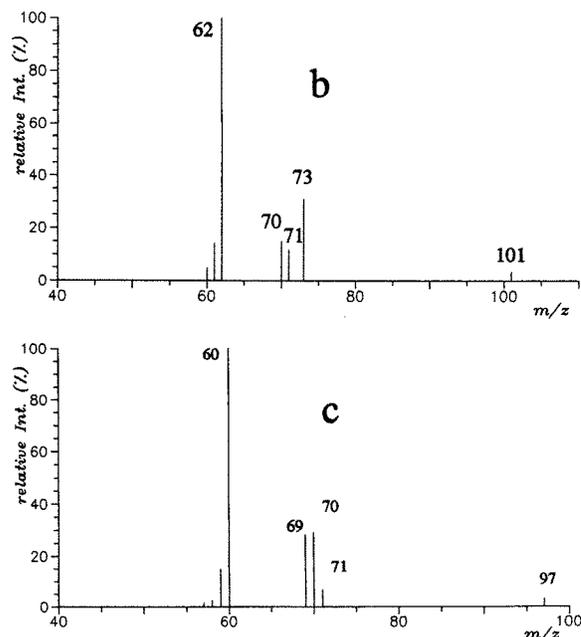
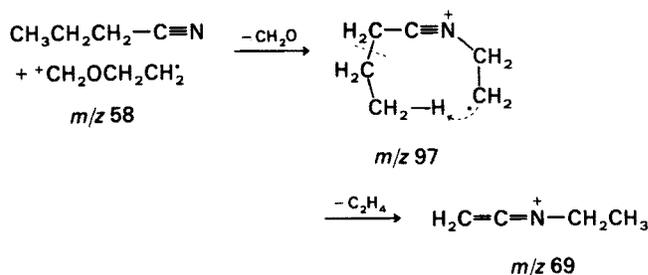


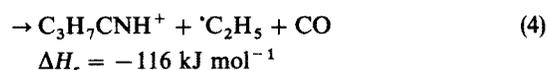
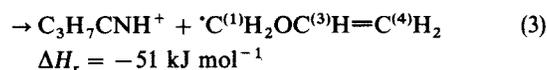
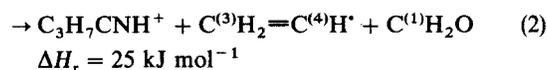
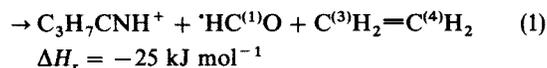
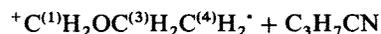
Figure 1. Mass spectra of *b* and *c* after a reaction time of 1.5 s.

*n*- $\text{C}_3\text{H}_7$  group of butyronitrile, probably by the rearrangement shown below:



The product ions  $m/z$  70 arise from proton transfer from *a* to butyronitrile, and part of the intensity for these ions appears at  $m/z$  71 in the spectra of *b* and *c*, indicating  $\text{D}^+$  as well as  $\text{H}^+$  transfer. Contrary to the experiments with  $\text{CH}_3\text{CN}$ ,  $[\text{C}_3\text{H}_7\text{CNH}^+]/[\text{C}_3\text{H}_7\text{CND}^+]$  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  $k_{\text{H}}/k_{\text{D}} = 2.24 \pm 0.10$  and  $2.33 \pm 0.10$ , respectively, identical within the experimental error.

The following reactions (1)–(4) can be envisaged for a protonation of *n*-butyronitrile by *a*. The heats of reaction,  $\Delta H_r$ , were calculated by using  $\Delta H_f(a) = 842 \text{ kJ mol}^{-1}$ <sup>4</sup> and  $\Delta H_f(\text{CH}_2\text{OCH}=\text{CH}_2) = 71 \text{ kJ mol}^{-1}$ .<sup>5</sup> The  $\Delta H_f$  of the other species were taken from the compilation of Lias *et al.*<sup>6</sup>



**Table 1. Stabilization energy (kJ mol<sup>-1</sup>) of the complex between *a* and nitrile**

<i>r</i> (Å)	3.6	3.7	3.8	3.9	4.0	4.1	4.2	4.3	4.4	4.5
CH <sub>3</sub> CN	112	105	99	93	87	82	78	74	70	66
C <sub>3</sub> H <sub>7</sub> CN	126	117	110	103	97	91	86	81	76	72

Reaction (2) corresponds to deprotonation from C<sup>(4)</sup> (or probably C<sup>(3)</sup>) but is excluded because of its endothermicity. The exothermic reactions (1) and (3) correspond to specific proton transfer from C<sup>(1)</sup> and C<sup>(3)</sup>, respectively. Hence, in view of the inactive C<sup>(4)</sup>H<sub>2</sub> 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<sub>3</sub>H<sub>7</sub>CNH<sup>+</sup>]/[C<sub>3</sub>H<sub>7</sub>CND<sup>+</sup>] 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<sub>2</sub>H<sub>5</sub><sup>•</sup>, 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<sub>2</sub>H<sub>6</sub><sup>+</sup>.<sup>2</sup> Obviously, this fragmentation is also induced by the electrostatic activation of *a* in the encounter complex with a base, for example a nitrile molecule. The sum of Δ*H*<sub>f</sub>(C<sub>2</sub>H<sub>6</sub><sup>+</sup>) and of Δ*H*<sub>f</sub>(CO) exceeds Δ*H*<sub>f</sub>(*a*) by 91 kJ mol<sup>-1</sup>. This amount of energy can be released by the electrostatic attraction (solvation) between *a* and the nitrile in the encounter complex. The stabilization energy is estimated from the classical equation for ion-dipole and ion-induced-dipole interaction<sup>7</sup> using the dipole moment μ = 4.05 D<sup>8</sup> and the polarizability α = 8.56 Å<sup>2</sup><sup>9</sup> for *n*-butyronitrile and μ = 3.92 D and α = 5.99 Å<sup>2</sup> for acetonitrile. The results are shown in Table 1 as a function of the distance *r* between the components of the encounter complex.

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<sub>2</sub>H<sub>6</sub><sup>+</sup>, in analogy to the decomposition induced by high-energy collisions with Ar.<sup>2</sup> Hence, some of the ions *a* form an intermediate 'three-body ion/two neutral complex' on a thermal collision with a nitrile molecule consisting of C<sub>2</sub>H<sub>6</sub><sup>+</sup>, CO and the nitrile molecule. Within the complex

C<sub>2</sub>H<sub>6</sub><sup>+</sup> delivers any of the 6H atoms to the nitrile in a fast exothermic proton transfer, resulting in a dissociation of the intermediate complex.

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