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A FOURIER TRANSFORM ION CYCLOTRON RESONANCE STUDY OF THE GAS PHASE NEGATIVE ION CHEMISTRY OF BENZALDEHYDE

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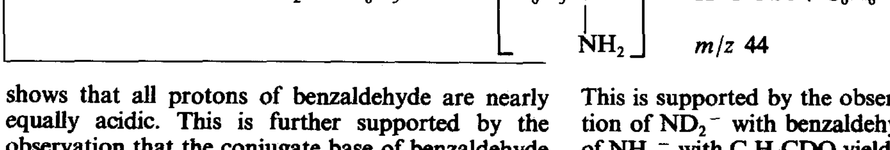
Abstract—Fourier transform ion cyclotron resonance mass spectrometry has been used to investigate some aspects of the gas phase negative ion chemistry of benzaldehyde. It is shown that all protons are nearly equally acidic. Exothermic proton abstraction from the aldehydic position by NH_2^- leads to the formation of $C_6H_5^-$ ions. Reactions of several nucleophiles and benzaldehyde are discussed. Some of them proceed via a tetrahedral intermediate. Arguments are put forward to show that one of the reactions of the conjugate base of benzaldehyde involves benzaldehyde–hydrate molecules formed in the inlet lines towards the cell.

The chemistry of negative ions in the gas phase has received considerable attention in the past few years as it may provide insight in the intrinsic properties of the chemical species involved,[1-3] which for example is of interest from a theoretical point of view.[4-7] Recently a paper describing molecular orbital calculations on the stability of several carbonyl anions $R{-}\bar{C}{=}O$ has appeared.[7] One of the examples discussed was the $C_6H_5{-}\bar{C}O$ ion. Its proton affinity (PA) was calculated[7] to be 1564.6 kJ mol^{-1}. This prompted us to investigate some gas phase reactions of benzaldehyde such as proton transfer and hydrogen/deuterium exchange[8-11] reactions, because these may provide insight in the relative acidities of the various protons of this molecule. During the course of this study performed by using Fourier transform ion cyclotron resonance (FT–ICR) mass spectrometry,[12,13] many other reactions of benzaldehyde and its conjugate base have been observed. Some of them will be discussed here.

RESULTS AND DISCUSSION

The gas phase acidity of benzaldehyde

The reaction of NH_2^- ($PA(NH_2^-) = 1689.8$ kJ mol^{-1})[14] with C_6H_5CDO yields $(M{-}H)^-$ ions (m/z 105) and $(M{-}D)^-$ ions (m/z 106) in a ratio of about 88:12 at short trapping times (~ 35 ms), which is not far from a statistical proton/deuteron abstraction (83:17) in the absence of an isotope effect. This shows that all protons of benzaldehyde are nearly equally acidic. This is further supported by the observation that the conjugate base of benzaldehyde incorporates up to five deuterium atoms in the reaction with D_2O[8-11] ($PA(OH)^- = 1636.2$).[14] CH_3O^- ($PA(CH_3O^-) = 1587.6$ kJ mol^{-1})[14] is observed not to abstract a proton from benzaldehyde. Instead, it transfers a hydride to benzaldehyde.[15] These observations place the gas phase acidity of benzaldehyde between that of water and methanol.

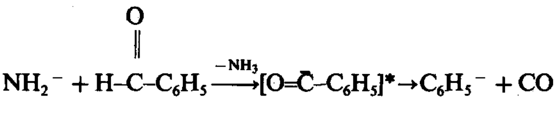


$$NH_2^- + C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}H \rightarrow \left[C_6H_5{-}\overset{O^-}{\overset{|}{\underset{NH_2}{\underset{|}{C}}}}{-}H \right]^* \rightarrow \underset{m/z\ 44}{H{-}\overset{O^-}{\overset{|}{C}}{=}NH} + C_6H_6 \qquad (2)$$

Reactions of NH_2^- *with benzaldehyde*

In addition to proton transfer (*vide supra*) the reaction of NH_2^- with benzaldehyde yields two product ions: ions m/z 77 and m/z 44.

The ions m/z 77 are probably due to dissociation of some of the ions formed by exothermic abstraction of the aldehydic proton:



$$NH_2^- + H{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5 \xrightarrow{-NH_3} [O{=}\bar{C}{-}C_6H_5]^* \rightarrow \underset{m/z\ 77}{C_6H_5^-} + CO \qquad (1)$$

This is supported by the reaction of ND_2^- with benzaldehyde and of NH_2^- with C_6H_5CDO which both almost exclusively yield $C_6H_5^-$ ions.

The ions m/z 77 are also observed if OH^- generated from water is used. They are absent, however, if OH^- generated by reaction of $O^{-\cdot}$ with n-hexane[16] is used. This discrepancy is most likely due to the presence of H^- in the former case. This is in line with thermodynamic considerations: the reactions of NH_2^- and H^- with benzaldehyde yielding $C_6H_5^-$ ions are calculated[17] to be *exo*thermic by 26 and 13 kJ mol^{-1}, respectively, whereas the reaction of OH^- is calculated[17] to be *endo*thermic by 28 kJ mol^{-1}. The formation of ions m/z 44 can be explained by the following mechanism:

This is supported by the observation that both reaction of ND_2^- with benzaldehyde as well as reaction of NH_2^- with C_6H_5CDO yields ions m/z 45, showing that the aldehydic proton and one of the protons originating from NH_2^- are retained in the production.

Similar observations have been made for the reaction of NH_2^- with formaldehyde which also yields ions m/z 44, although their abundance is low with respect to that of the other product ions formed, i.e. HCO^-, CH_3O^- and NH_4^-.[18]

Table 1. Distribution of some of the product ions of the reaction of $^{18}O^{-\cdot}$ with deuterated benzaldehydes

Reactant molecule	m/z	Product ion assigned composition	Product ion Distribution ratio[a)]
C_6D_5CHO	47	$HC^{18}OO^-$	7
	128	$D_5C_7{}^{18}OO^-$	22
	127	$D_4HC_7{}^{18}OO^-$	70 ✓
C_6H_5CDO	48	$DC^{18}OO^-$	8
	123	$H_5C_7{}^{18}OO^-$	21
	124	$H_4DC_7{}^{18}OO^-$	71 ✓

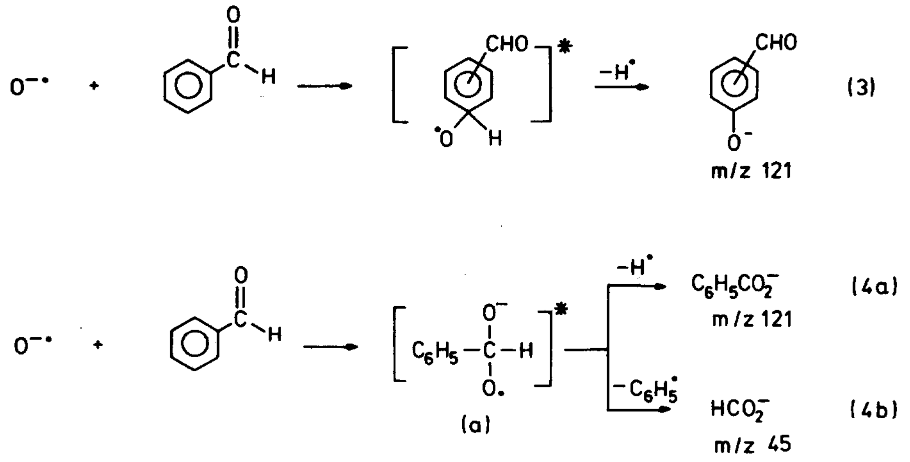
a) Percentage of the total sum of the three product ions given.

Reactions of $O^{-\cdot}$ *with benzaldehyde*

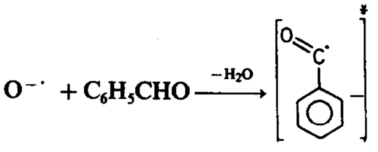
Proton transfer is only a minor pathway in the reactions of $O^{-\cdot}$ with benzaldehyde. The main product ion is observed at *m/z* 121. In addition ions *m/z* 45 are formed. Deuterium- and ^{18}O-labelling serve as an aid in determining the nature of these product ions (see Table 1).

On the basis of these observations the mechanisms as given in eqns 3, 4a and 4b can be put forward to explain the formation of these ions.

Similar reactions have been reported in the literature.[19–21] Formation of $C_6H_5^-$ ions (*m/z* 77) is observed as well. A mechanism equivalent to eqn (1) can be excluded on the basis of its calculated[17] endothermicity of approx. 72 kJ mol⁻¹. Probably these ions are formed via the reaction shown in eqn (4), either by dissociation of the intermediate ion a into $C_6H_5^-$ and $HCO_2^{\cdot}$ (calculated[17,22] exothermicity 15 kJ mol⁻¹) or by dissociation of the $C_6H_5CO_2^-$ ions into $C_6H_5^-$ and CO_2 (calculated[17] exothermicity 40 kJ mol⁻¹).



Another reaction channel is $H_2^{+\cdot}$ abstraction resulting in the formation of $(M–H_2)^{-\cdot}$ ions.[3,19,23–26] Reaction of $O^{-\cdot}$ with C_6H_5CDO shows that the stable $(M–H_2)^{-\cdot}$ ions are formed almost exclusively by abstraction of $H_2^{+\cdot}$ from the phenyl ring. Abstraction of $H_2^{+\cdot}$ containing the aldehydic hydrogen atom, however, might take place as can be concluded from the observed formation of $C_6H_4^{-\cdot}$ ions (*m/z* 76), probably due to dissociation of the unstable $(M–H_2)^{-\cdot}$ ions b:



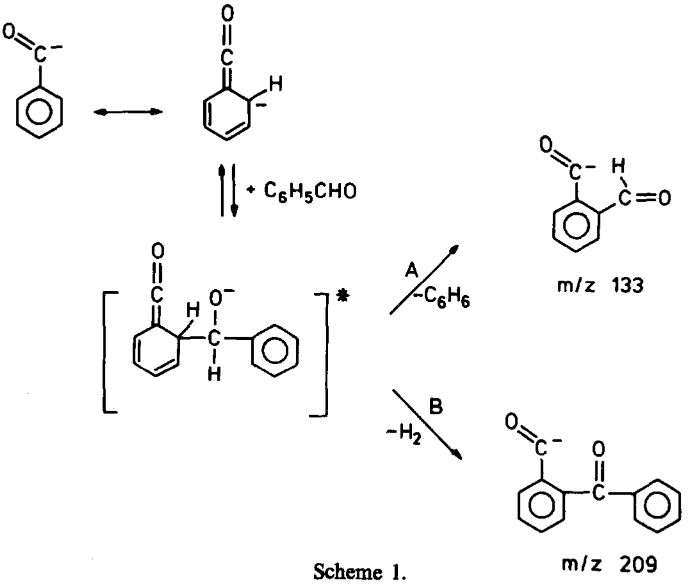
b

$\rightarrow C_6H_4^{-\cdot} + CO$
m/z 76 (5)

The actual position of the negative charge and the radical in ion b is not known. Reaction of $O^{-\cdot}$ with C_6H_5CDO yields ions $C_6H_4^{-\cdot}$ and not $C_6H_3D^{-\cdot}$ which is in agreement with the mechanism shown in eqn 5.

Reactions of the conjugate base of benzaldehyde

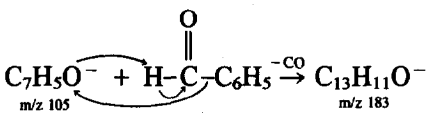
The $(M–H)^-$ ions of benzaldehyde, formed through proton abstraction by a suitable base (*vide supra*), are observed to react with neutral benzaldehyde yielding ions *m/z* 133 and 183 and to a



Scheme 1.

minor extent ions m/z 209 and 211. The latter can be explained as being $(2M{-}H)^-$ ions.[27] The formation of the ions m/z 133 can be explained by the mechanism shown in Scheme 1 (pathway A), which also presents a possible mechanism for the formation of the ions m/z 209 (pathway B).

Pathway A in Scheme 1 is supported by deuterium labelling: when using C_6H_5CDO mainly ions m/z 134 are formed, showing that only one of the two aldehydic protons is retained in the product ion. Moreover, ejection of all ions with the exception of the ^{13}C isotope of the $(M{-}H)^-$ ions shows that the ^{13}C isotope is retained in the formation of the product ion, i.e. almost exclusively ions m/z 134 are formed (see Fig. 1). This is in line with the proposed loss of the phenyl substituent originating from the neutral reactant (see Scheme 1).



$$\underset{m/z\ 105}{C_7H_5O^-} + H-\overset{\overset{O}{\|}}{C}-C_6H_5 \xrightarrow{-CO} \underset{m/z\ 183}{C_{13}H_{11}O^-} \qquad (6)$$

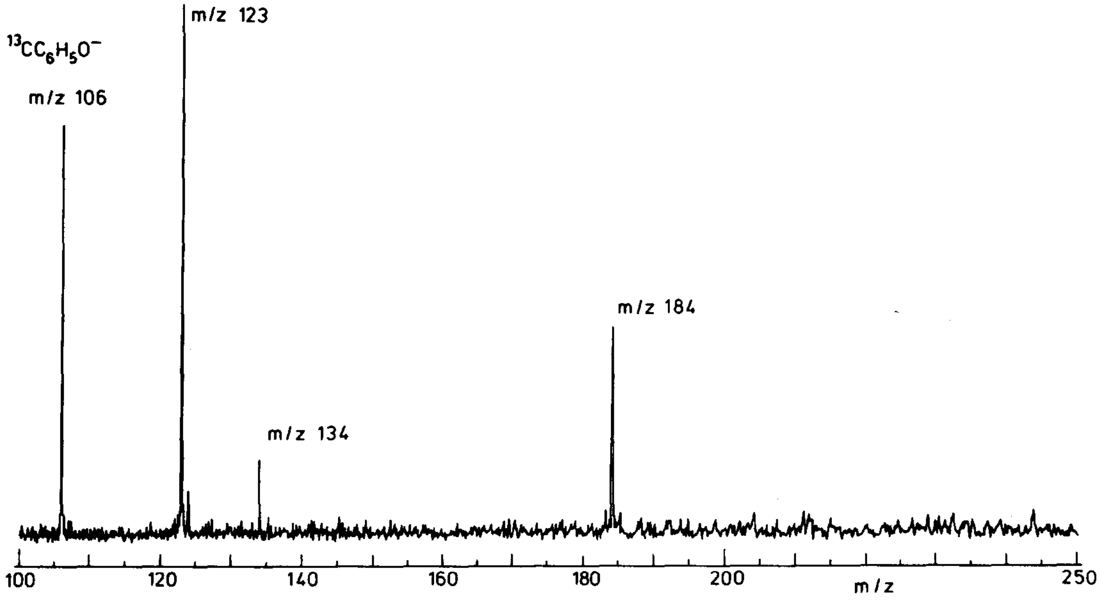


Fig. 1. FT-ICR spectrum of the $OH^-/H_2O/C_6H_5CHO$ system. Experimental conditions: $p(H_2O) = 40\ \mu Pa$, $p(C_6H_5CHO) = 50\ \mu Pa$, magnetic field strength = 1.4 T, electron energy = 1.6 eV, emission current = 250 nA. The spectrum is taken at a trapping time of 700 ms (i.e. 700 ms after the electron beam pulse started), 6300 transients accumulated. At 100 ms a pulse (amplitude 5 V peak to peak, duration 55 ms) is applied to eject all ions with the exception of the ions m/z 106: at the resonance frequency of the ions m/z 106 the phase is shifted by 180°. During the rest of the trapping period the ions m/z 105 are continuously ejected to avoid their reformation.

Table 2. Results of labelling studies on the ions m/z 123, $C_7H_7O_2^-$

System studied	ion(s) observed m/z	assigned composition
$OD^-/D_2O/C_6H_5CHO$	124	$C_7H_6DO_2^-$
$OH^-/H_2O/C_6H_5CDO$	124	$C_7H_6DO_2^-$
$OH^-/H_2O/C_6D_5CHO$	128	$C_7H_2D_5O_2^-$
$^{18}OH^-/H_2{}^{18}O/C_6H_5CHO$	125	$C_7H_7{}^{18}O^{16}O^-$
	127	$C_7H_7{}^{18}O_2^-$

Although the mechanism shown in eqn 6 (which bears some resemblance to the base induced carbon monoxide loss from alkyl formates reported by Riveros *et al.*[28,29]) might appear attractive to explain the formation of ions *m/z* 183, it is disproved by the results of ^{18}O-labelling. As will be discussed below, the (M–H)$^-$ ions of benzaldehyde incorporate ^{18}O in the presence of $H_2{}^{18}O$. It is observed that the ^{18}O enriched (M–H)$^-$ ions formed in this way react to give ions *m/z* 183 and hardly any ions *m/z* 185. This indicates that the carbonyl-group originating from the reactant (M–H)$^-$ ions is lost in the formation of the ions *m/z* 183. Furthermore, it is observed that mainly ions *m/z* 185 are formed if C_6H_5CDO is used, indicating that both aldehydic protons are retained in the product ion. In spite of these observations, no definite mechanism for the formation of the ions *m/z* 183 can be given at this stage.

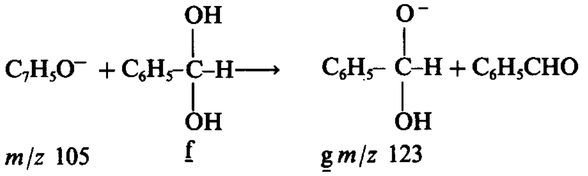
The formation of ions m/z 123

In addition to the ions discussed above, ions *m/z* 123 are formed in systems where water is present. Ejection experiments[30] show that mainly the (M–H)$^-$ ions are their precursors. However, ejection of all ions with the exception of the ^{13}C isotope of the (M–H)$^-$ ions shows that no ^{13}C isotope is retained in the formation of the ions *m/z* 123, i.e. no ions *m/z* 124 are formed (see Fig. 1). This excludes a clustering reaction as shown in eqn (7), which is also not very likely on the basis of the low pressures used in the FT–ICR instrument

$$\underset{m/z\ 105}{C_7H_5O^-} + H_2O \xrightarrow{\cdot M} \underset{m/z\ 123.}{C_7H_5O^- \cdot H_2O} \qquad (7)$$

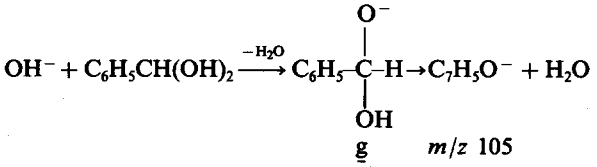
The results of labelling studies are listed in Table 2. Ejection experiments[30] show that the *m/z* 127 ions in the $^{18}OH^-/H_2{}^{18}O/C_6H_5CHO$ system are formed from the *m/z* 125 ions. This resembles a $^{16}O/^{18}O$-exchange reaction as has also been reported for the $CH_3{}^{16}O^{18}O^-$ ion generated in the $H_2{}^{18}O/CH_2O$ system.[16]

The results listed in Table 2 point to the formation of benzaldehyde–hydrate molecules (f) in the inlet lines towards the cell. Proton abstraction from these molecules by the conjugate base of benzaldehyde then yields the ions *m/z* 123



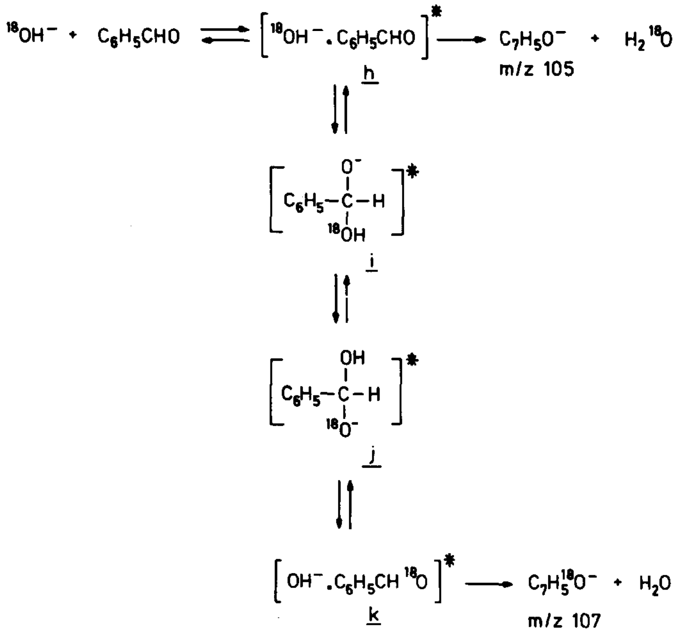
$$\underset{m/z\ 105}{C_7H_5O^-} + \underset{f}{C_6H_5\text{–}\overset{OH}{\underset{OH}{C}}\text{–}H} \longrightarrow \underset{g\ m/z\ 123}{C_6H_5\text{–}\overset{O^-}{\underset{OH}{C}}\text{–}H} + C_6H_5CHO \qquad (8)$$

Ejection[30] shows that only a small fraction of the ions *m/z* 123 is formed by a direct reaction of OH^-. Apparently, proton abstraction by OH^- is so exothermic that most of the formed deprotonated benzaldehyde–hydrate ions g then dissociate



$$OH^- + C_6H_5CH(OH)_2 \xrightarrow{-H_2O} \underset{g}{C_6H_5\text{–}\overset{O^-}{\underset{OH}{C}}\text{–}H} \rightarrow \underset{m/z\ 105}{C_7H_5O^-} + H_2O \qquad (9)$$

This also explains the observed incorporation of ^{18}O into the (M–H)$^-$ ions in the presence of $H_2{}^{18}O$. However, an additional route to the formation of these ^{18}O enriched (M–H)$^-$ ions must be operative as can be concluded from the reaction of $^{18}OH^-$-generated by reaction of $^{18}O^{-\cdot}$ with n-



Scheme 2.

hexane– which yields ions *m/z* 107 ($C_7H_5{}^{18}O^-$) for approximately 12% of the total $(M–H)^-$ abundance. Because no $H_2{}^{18}O$ and hence no ^{18}O-labelled benzaldehyde–hydrate is present—indeed, no ions *m/z* 125 are observed—this exchange must have taken place in the primary collision complex between $^{18}OH^-$ and benzaldehyde, probably involving a tetrahedral type of ion as presented in Scheme 2.

The actual mechanism of the rearrangement of ion i̲ to ion j̲ is not known, but study of the reactions of $^{18}OH^-$ with C_6H_5CDO and of $^{18}OD^-$ (generated by reaction of $^{18}O^{-\cdot}$ with d_{12}-cyclohexane) with benzaldehyde gave results obscured by the competing hydrogen/deuterium exchange in the complexes h̲ and k̲.

EXPERIMENTAL

The experiments described in this paper have been performed using a FT–ICR spectrometer made in our laboratory. Details concerning the essential hardware,[31] software[32] and main operating procedures[33,34] have been described elsewhere.

The total pressure was normally kept below 100 μPa. $NH_2{}^-$ and $O^{-\cdot}$ ions have been generated by dissociative electron attachment from NH_3 ($\sim$6 eV) and N_2O ($\sim$1.2 eV), respectively. During $NH_2{}^-$ formation from ammonia H^- was ejected by a radio-frequency pulse of 180 kHz applied to the trapping plates. OH^- ions have been generated (i) by dissociative electron attachment from water ($\sim$6 eV, OH^- is formed via H^-) or (ii) by reaction of $O^{-\cdot}$ with n-hexane, to avoid reactions with H_2O or of H^- (to generate OD^- d_{12}-cyclohexane was used).

Ejection of ions was performed in several ways. Ejection of one ion was achieved by applying a radio-frequency pulse of 0.5–1.0 V peak to peak amplitude at a frequency corresponding to the mass-to-charge ratio of the ion to be expelled. It is also possible to eject all ions with the exception of ions of only one specific mass-to-charge ratio by creation of a notch in the waveform of the excitation pulse, as has been described previously.[35,36]

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