

Selective Gas-phase Ion–Molecule Reactions of the Benzoyl Ion

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Gas phase ion–molecule studies using ion trap mass spectrometry show that the benzoyl ion, $[\text{C}_6\text{H}_5\text{CO}]^+$, undergoes selective reactions with hydroxy functional groups; the formation of product ions $[\text{M} + 105]^+$, $[\text{M} - \text{H}]^+$ and $[\text{M} - \text{OH}]^+$ is characteristic of the hydroxy group environment.

Gas phase ion–molecule reactions involving hydroxy functional groups have been reported for the nitrosonium ion, NO^+ ,¹ the trimethylsilyl ion, Me_3Si^+ ,^{2,3} the boron-containing cations, $[\text{MeOBOMe}]^+$ and $[\text{MeBMe}]^+$,⁴ and the dimethyl ether derived ion, MeOCH_2^+ .⁵ However the selectivity of these ions for hydroxy groups is limited by their reactions with a variety of other functional groups, such as alkenes, ketones, ethers and acids.^{6–8} The benzoyl ion, $[\text{C}_6\text{H}_5\text{CO}]^+$, has been reported to form adduct ions when allowed to react with ammonia⁹ and simple amines.¹⁰ Its reactions with the hydroxy functional group have not previously been described. In this communication we report the surprising selectivity of the ion–molecule reactions of the $[\text{C}_6\text{H}_5\text{CO}]^+$ ion with the hydroxy group which allow different hydroxy environments to be distinguished by ion trap mass spectrometry.

The mass spectrum resulting from the reaction of the $[\text{C}_6\text{H}_5\text{CO}]^+$ ion with 2-methylpropan-2-ol is shown in Fig. 1. The spectrum shows a strong $[\text{M} + 105]^+$ adduct ion at m/z 179 (100%) and a weak $[\text{M} - \text{OH}]^+$ ion at m/z 57 (4%), arising from hydroxy abstraction. Both of these are characteristic product ions of reactions of the benzoyl ion with hydroxy groups. A fragmentation product of the adduct is observed at m/z 123, arising from loss of butene, which reacts further with water to yield an ion at m/z 141. The identity of these ions was confirmed by tandem mass spectrometry using collisionally activated dissociation with resonance excitation.¹¹ Scheme 1 illustrates these reaction processes. A protonated 2-methylpropan-2-ol dimer ion is also present in the spectrum at m/z 149, which yields a fragmentation product at m/z 93.

Ions in the spectrum at m/z 195, 177 and 139 arise from competing reactions of protonated acetophenone, $[\text{C}_6\text{H}_5\text{C}(\text{OH})\text{Me}]^+$, with 2-methylpropan-2-ol. Acetophenone is present in the trap as the precursor for the $[\text{C}_6\text{H}_5\text{CO}]^+$ ion, but undergoes self-CI,¹² followed by reaction with 2-methylpropan-2-ol. Introduction of acetophenone through a pulsed valve yields spectra free of these products of the protonated acetophenone ion.

Table 1 lists the reaction products of $[\text{C}_6\text{H}_5\text{CO}]^+$ with a selection of compounds containing hydroxy groups. Butan-2-ol reacts to produce the characteristic $[\text{M} + 105]^+$ adduct ion (55%) and an $[\text{M} - \text{H}]^+$ ion resulting from hydride abstraction (21%), but no reaction is observed with butan-1-ol. Cyclohexanol yields only the $[\text{M} - \text{H}]^+$ ion (100%) on reaction with $[\text{C}_6\text{H}_5\text{CO}]^+$. In contrast, the aromatic benzyl alcohol and

benzhydrol produce strong $[\text{M} - \text{OH}]^+$ hydroxy abstraction ions (100%), with no adduct formation or hydride abstraction observed, whilst phenol does not react with the benzoyl ion. These data show that reactivity is strongly dependent on the hydroxy environment.

The formation of benzoic acid from $[\text{C}_6\text{H}_5\text{CO}]^+$ is strongly exothermic (~ 999 kJ mol⁻¹ under standard conditions) and the reaction to form $[\text{M} - \text{OH}]^+$ from the neutral precursor might therefore be expected to be favoured if hydroxy abstraction is endothermic by less than this amount. Consequently, the $[\text{C}_7\text{H}_7]^+$ ion is observed as the only product for the reaction of the $[\text{C}_6\text{H}_5\text{CO}]^+$ ion with benzyl alcohol ($\Delta H_r = -24$ kJ mol⁻¹). However, the $[\text{C}_4\text{H}_9]^+$ ion is not formed from the reaction of the benzoyl ion with butan-1-ol ($\Delta H_r = +125$ kJ mol⁻¹), or butan-2-ol ($\Delta H_r = +62$ kJ mol⁻¹), since both these reactions are endothermic, as is that for phenol ($\Delta H_r = +292$ kJ mol⁻¹). A weak $[\text{t-C}_4\text{H}_9]^+$ ion is detected following the reaction with 2-methylpropan-2-ol (4%), even though the overall reaction is slightly endothermic ($\Delta H_r = +6$ kJ mol⁻¹). The reaction leading to the appearance of the $[\text{M} - \text{H}]^+$ (22%) from butan-2-ol, is also calculated to be endothermic by 8 kJ mol⁻¹, taking the formation of benzaldehyde from

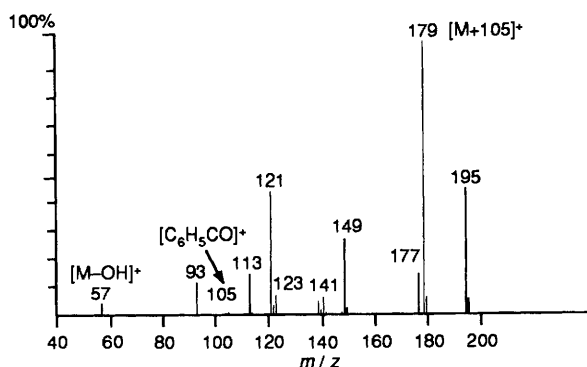
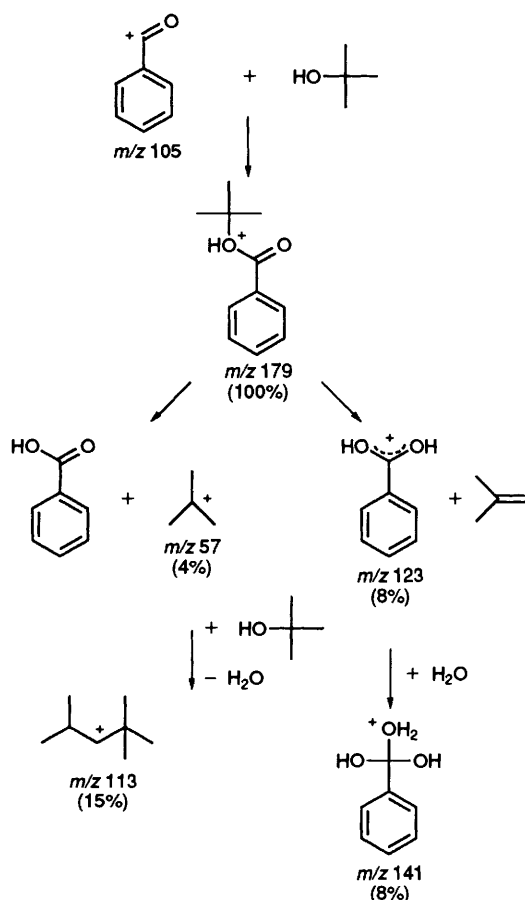


Fig. 1 The mass spectrum resulting from the reaction of the $[\text{C}_6\text{H}_5\text{CO}]^+$ ion with 2-methylpropan-2-ol



Scheme 1 The reaction of the $[\text{C}_6\text{H}_5\text{CO}]^+$ ion with 2-methylpropan-2-ol

Table 1 The reaction of $[C_6H_5CO]^+$ with selected alcohols (% intensity)

Compound	$[M + 105]^+$	$[M - OH]^+$	$[M - H]^+$	Other ions
2-Methylpropan-2-ol	179 (100%)	57 (4%)	—	113 (15%), 123 (8%) 141 (3%)
Butan-2-ol	179 (55%)	—	73 (21%)	123 (100%), 129 (23%) 147 (13%), 131 (11%)
Butan-1-ol	—	No reaction	—	—
Cyclohexanol	—	—	99 (100%)	—
Benzhydrol	—	167 (100%)	—	—
Benzyl alcohol	—	91 (100%)	—	197 (19%), 181 (17%) 169 (8%), 211 (6%)
Phenol	—	No reaction	—	—

$[C_6H_5CO]^+$ to be exothermic by 742 kJ mol^{-1} . It should be noted, however, that the effective temperature of an ion in the ion trap is a complex function of the trap temperature and the applied voltages and that this will influence the thermochemistry of these reactions.¹³

The behaviour of the $[C_6H_5CO]^+$ ion towards a number of acids, ethers, ketones and amines has been investigated. Amines are, as yet, the only other functional group which has been found to react with the benzoyl ion. These observations suggest that $[C_6H_5CO]^+$ reacts with compounds containing a hydroxy functional group in a specific and predictable way, which is determined by the nature of the alcohol, making it a potentially useful probe for establishing the presence and chemical environment of hydroxy groups.

Experiments were performed using a quadrupole ion trap mass spectrometer (ITMS) (Finnigan-Mat, San Jose, CA), operating at 120°C . Electron ionisation (70 eV) of acetophenone (Aldrich), introduced through a leak valve, followed by resonance hole isolation,¹⁴ was employed to isolate the $[C_6H_5CO]^+$ ions. $[C_6H_5CO]^+$ was then allowed to react for a reaction time of 100 ms with neutral sample vapour, introduced through a second leak valve system. Typical sample pressures were 5×10^{-6} torr. Helium-bath gas pressure was maintained at 1×10^{-3} torr. All thermochemical data were taken from refs. 15 and 16.

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