On the Nature of the Tetrahedral Species in the Gas Phase Hydrolysis of Esters

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Ion cyclotron resonance techniques show that in the gas phase the oxygen exchange reaction in the system $OH^- + HC(^{18}O)(OMe)$ is at least 10^{-2} times slower than the hydrolysis reaction; this result, plus thermochemical estimates, suggest that the tetrahedral adduct $HC(OMe)(OH)O^-$ is more likely a local transition state rather than a stable intermediate.

Ester hydrolysis is one of the most ubiquitous reactions in organic chemistry for which mechanistic details are well understood. Yet, this same reaction in the gas phase exhibits important differences.[1,2]

For example, isotopic labelling experiments show that while reaction (1) in the gas phase proceeds primarily by an

$$OH^- + RCO_2Me \longrightarrow RCO_2^- + MeOH \qquad (1)$$

addition–elimination mechanism at the carbonyl centre

($B_{AC}2$), considerable contribution is also observed from an S_N2 type mechanism.[2] The reaction also displays no activation energy, and very large rate constants, *i.e.*, $k_1 = 5.0 \times 10^{11}$ dm^3 mol^{-1} s^{-1} for R = H at room temperature.[1]

The gas phase $B_{AC}2$ mechanism has been assumed, as in solution, to involve a tetrahedral intermediate. Nevertheless, the relative stability of this species and its location along the potential energy diagram remain controversial issues at present. It is generally agreed upon that reaction (1) can be represented by an energetic downhill potential surface with local minima corresponding to stable collision complexes or ionic moieties.[3] Direct detection of the species corresponding to a tetrahedral intermediate, *i.e.*, RC(OMe)(OH)O$^-$ for reaction (1), has seldom been achieved in the gas phase. In the cases where such observation has been possible, the mass spectrometric techniques utilized cannot unequivocally distinguish between a loose collision complex and a true tetrahedral intermediate.[4]

The present sets of experiments concern themselves with reactions (2) and (3). Hydroxide ions generated in an ion

$$OH^- + HC(^{18}O)(OMe) \rightarrow HC^{18}OO^- + MeOH \qquad (2)$$

$$\rightarrow {}^{18}OH^- + \underset{\text{exchange}}{HC(O)(OMe)} \qquad (3)$$

cyclotron resonance (i.c.r.) spectrometer from H_2O (maintained at 2.6×10^{-3} N m^{-2}) were allowed to react with varying amounts (1.3×10^{-4} to 1.3×10^{-3} N m^{-2}) of 10% oxygen-18 enriched HC(^{18}O)(OMe). We observed that (a) the HC^{18}OO$^-$ retained all of the oxygen-18 initially present in the ester and (b) reaction (3) was not detected within the dynamic range of i.c.r. spectroscopy. This implies that $(k_{ex}/k_2) < 0.01$.

The above results imply that either (i) the tetrahedral species represents a local transition state which does not allow for oxygen randomization or (ii) the forward reaction is so strongly favoured due to its large exothermicity (45 kcal mol^{-1}),† such that few collision complexes, whatever their nature, return to reagents. This latter contention is appropriate since the overall efficiency (fraction of collisions which result in products) for the OH$^-$–HCO$_2$Me system, including all reaction channels, amounts to 0.64.

The first alternative is reinforced by the estimated thermochemical stability of a tetrahedral HC(OMe)(OH)O$^-$, calculated on the basis of reasonable assumptions for the heat of formation of the HC(OMe)(OH)O• radical and for its electron affinity. This approach[3] places the tetrahedral intermediate of reaction (2) in the range of 1 to 7 kcal mol^{-1} *below* the energy of the reagents, considerably less than that expected even for loose collision complexes of highly exothermic reactions. By comparison, the free energy profile for the solution reaction places the tetrahedral intermediate, in a minimum, 4.3 kcal mol^{-1} *above* the reagents.[5]

The fact that the exchange reaction (3) is slow within the i.c.r. time scale, coupled with the thermochemical estimates, is consistent with a scheme in which reaction (2) proceeds initially by the formation of a loose collision complex. This collision complex either reverts to reagents without oxygen randomization, or evolves into products *via* a tetrahedral intermediate, a local transition state along the potential energy surface. The absence of a noticeable isotope exchange in the present case and the proposed scheme, are analogous to those previously encountered in gas phase S_N2 reactions.[6,7]

The question of the relative stability of such tetrahedral species is being investigated in systems of lower exothermicity and efficiency, and even for systems which have no exothermic channels available.

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† 1 kcal = 4.18 kJ.