Insertion and abstraction mechanisms in collisions of O^- with H_2^+ and CH^+

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Our merged ion beams set-up [1] has been used to measure the total cross section of the reactions:

$$H_2^+ + O^- \to H_2 O^+ + e/OH^+ + H + e$$
 (1)/(2)

$$D_2^+ + O^- \to D_2 O^+ + e/OD^+ + D + e$$
 (3)/(4)

$$CH^+ + O^- \to HCO^+ + e/CO^+ + H + e$$
 (5)/(6)

Reactive cross sections (2),(4),(6) are found to be rather large at thermal energy (> 10^{-15} cm²), and exceed the AI cross sections by an order of magnitude for reactions (1) and (3), and about a factor of 4 for reaction (5). They all behave as 1/E as a result of Coulomb attraction between reactants. A clear isotope effect is observed when comparing reactions (2) and (4), probably because deuterated species have more time to rearrange and/or to undergo autoionisation in the reactive domain of the potential energy surface. As indicated by an early study of the D₂⁺+O(³P) reaction [2], the strong predominance of the reactive channel stems from the fact that the collinear approach corresponds to the asymmetric stretch of the complex and does not lead to water cation formation, which is only possible via an insertion mechanism [3,4]. On the other hand, all geometries are likely to contribute to the formation of HCO⁺ and its isomer, HOC⁺, undistinguishable in the present experiment.



References

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