

The exciting aqueous chemistry of the simplest radical – proton-coupled electron transfer in the reactions of hydrogen atom

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We present our latest theoretical and experimental studies on the reactions of the simplest radical – the hydrogen atom – with a series of halogenated organics in neutral aqueous solutions. The investigated compounds are: monohaloacetates¹ (chloroacetate, bromoacetate, and iodoacetate) and a modified nucleobase, 5-bromouracil. The reactions are studied using density functional theory (M06-2X) in combination with the polarizable continuum model as an implicit description of the water solvent. We also study the effects of the presence of basic buffer anions, such as bicarbonate and hydrogen phosphate, on the reaction mechanisms and rates. The H atoms are generated as primary radicals of the water radiolysis and ionic chromatography is used to measure the yields of halide anions. These systems exhibit a variety of possible reaction mechanisms such as: halogen atom abstractions, H atom additions, H atom abstractions, and the proton-coupled electron transfer (PCET). The latter mechanism is of vast importance to biochemistry, electrochemistry and energy conversion.² The possibility of the PCET is especially interesting because, in cases when the proton and electron acceptor sites are spatially distinct, the PCET implies the disintegration of the H atom to the constituting proton and electron thereby representing the most fundamental instance of the process. The addition of the HCO_3^- or HPO_4^{2-} buffer anions, both of which are good proton acceptors, has a potential to accelerate the PCET. The calculations indicate that the PCET, which effectively involves a one-electron reduction of the substrates and hence causes their dehalogenation, is in close competition with the H atom abstraction (chloroacetate) and the direct halogen atom abstraction (bromoacetate). Since most of these processes are dominated by the light particle tunneling, for computing the reaction rate constants we use the variational transition state theory with the semi-classical tunneling corrections in the small curvature regime (SCT).

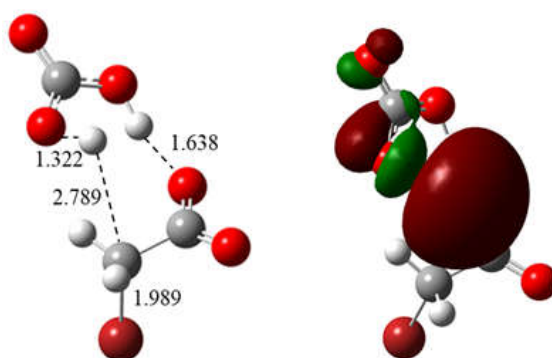


Figure 1: PCET transition state structure and its singly occupied molecular orbital (SOMO) in the reaction of H^\bullet with bromoacetate in the presence of bicarbonate (distances in Å).

References

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