

Examination of the chemical behavior of the quercetin radical cation towards some bases†

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It has been generally accepted that, due to high ionization potential values, single electron transfer followed by proton transfer (SET-PT) is not a plausible mechanism of antioxidant action in flavonoids. In this paper the SET-PT mechanism of quercetin (Q) was examined by revealing possible reaction paths of the once formed quercetin radical cation ($Q^{\bullet+}$) at the M0-52X/6311+G(d,p) level of theory. The deprotonation of $Q^{\bullet+}$ was simulated by examining its chemical behavior in the presence of three bases: methylamine (representative of neutral bases), the MeS anion (CH_3S^-) and the hydroxide anion (representative of anionic bases). It was found that $Q^{\bullet+}$ will spontaneously be transformed into Q in the presence of bases whose HOMO energies are higher than the SOMO energy of $Q^{\bullet+}$ in a given medium, implying that Q cannot undergo the SET-PT mechanism in such an environment. In the reaction with the MeS anion in both gaseous and aqueous phases and the hydroxide anion in the gaseous phase $Q^{\bullet+}$ accepts an electron from the base, and so-formed Q undergoes the hydrogen atom transfer mechanism. On the other hand, SET-PT is a plausible mechanism of Q in the presence of bases whose HOMO energies are lower than the SOMO energy of $Q^{\bullet+}$ in a given medium. In such cases $Q^{\bullet+}$ spontaneously donates a proton to the base, with energetic stabilization of the system. Our investigation showed that Q conforms to the SET-PT mechanism in the presence of methylamine, in both gaseous and aqueous phases, and in the presence of the hydroxide anion, in the aqueous solution.

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1 Introduction

To counteract the damaging effect of free radicals, the organisms rely on a variety of internal and external factors defying different defense mechanisms which prevent free radical damage. These factors include enzymes (such as superoxide dismutase and catalase),

copper and iron transport proteins, water-soluble and lipid-soluble antioxidants and dietary substances, such as flavonoids, vitamins C and E, hydroquinones and various sulfhydryl compounds.¹

Flavonoids are natural phenolic compounds recognized as potent external defense factors against oxidative damage. Their protective role correlates well with their antioxidant activity which is manifested through different actions, like direct radical scavenging, transition metal chelation, inhibition of certain enzymes, or removing oxidatively changed and damaged biomolecules. They can also manifest prooxidant, toxic effects involved in cytotoxicity, inhibition of mitochondrial respiration and mutagenicity, all closely related to their ability to oxidize in the presence of dissolved oxygen and to produce the superoxide anion which, in dismutation reaction, reacts with itself to produce oxygen and hydrogen peroxide which, through Fenton chemistry, gives a hydroxyl radical.^{2–6}

Due to their electron-rich and highly conjugated chemical structure flavonoids easily participate in electron and proton transfers, the fundamental processes in chemistry and biology, which are also considered among the major determinants influencing good antioxidant activity. In the radical scavenging

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† Electronic supplementary information (ESI) available: Tables listing the experimental and calculated geometrical parameters of Q and $Q^{\bullet+}$, plots of the HOMO of Q, NBO charges of Q and $Q^{\bullet+}$, the results of the IRC calculations for all TSs, tables presenting crucial bond distances of the participants in the examined reactions, spin density distribution of the participants in the investigated reactions, plots of $\ln k$ versus $1/T$ for all reactions of Q in the gaseous phase, and the energy profile for the reactions of the hydroxyl radical with different OH groups of Q in the gaseous phase. See DOI: 10.1039/c3cp44605k

