ELECTRONIC SUPPLEMENTARY INFORMATION:

The other side of the superoxide radical anion: Its ability for chemically repairing DNA oxidized sites

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Calculation methodology: QM-ORSA

Geometry optimizations and frequency calculations have been carried out using the M05-2X functional[1] and the 6-31+G(d,p) basis set, in conjunction with the SMD continuum model,[2] using water as solvent. The M05-2X functional has been recommended for thermodynamic and kinetic calculations by their developers,[1] and it has been also successfully used by independent authors to that purposes.[3–7] Local minima and transition states were identified by the number of imaginary frequencies (NIMAG = 0 or 1, respectively). In addition, intrinsic reaction coordinate (IRC) calculations have been performed to confirm that the transition state properly connects reactants and products. All of the electronic calculations were performed with the Gaussian 09 package of programs.[8] Thermodynamic corrections at 298.15 K were included in the calculation of relative energies.

The rate constants (k) were calculated using conventional transition state theory (TST)[9–11] and 1 M standard state as

$$k = \sigma\kappa \frac{k_B T}{h} e^{-(\Delta G^{\neq})/RT}$$

where k_B and h are the Boltzmann and Planck constants, $\Delta G^{\ddagger}$ is the Gibbs free energy of activation, σ represents the reaction path degeneracy, accounting for the number of equivalent reaction paths, and κ accounts for tunneling corrections which were calculated using the zero curvature tunneling approach (ZCT).[12] For the electron transfer reactions $\Delta G^{\ddagger}$ was calculated using the Marcus theory[13,14] as

$$\Delta G^{\neq} = \frac{\lambda}{4}\left(1 + \frac{\Delta G}{\lambda}\right)^2$$

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where ΔG is the free energy of reaction and λ is a reorganization term. Some of the calculated rate constants (k) are close to the diffusion-limit. Accordingly, the apparent rate constant (k_{app}) cannot be directly obtained from TST calculations. In the present work the Collins–Kimball theory is used to that purpose[15]

$$k_{app} = \frac{k_D k_{act}}{k_D + k_{act}}$$

where k_{act} is the thermal rate constant, obtained from TST calculations (equation 1), and k_D is the steady-state Smoluchowski[16] rate constant for an irreversible bimolecular diffusion-controlled reaction

$$k_D = 4\pi R D_{AB} N_A$$

where R denotes the reaction distance, N_A is the Avogadro number, and D_{AB} is the mutual diffusion coefficient of the reactants A (damaged species) and B (repairing species). D_{AB} has been calculated from D_A and D_B according to reference [17], and D_A and D_B have been estimated from the Stokes–Einstein approach[18,19]
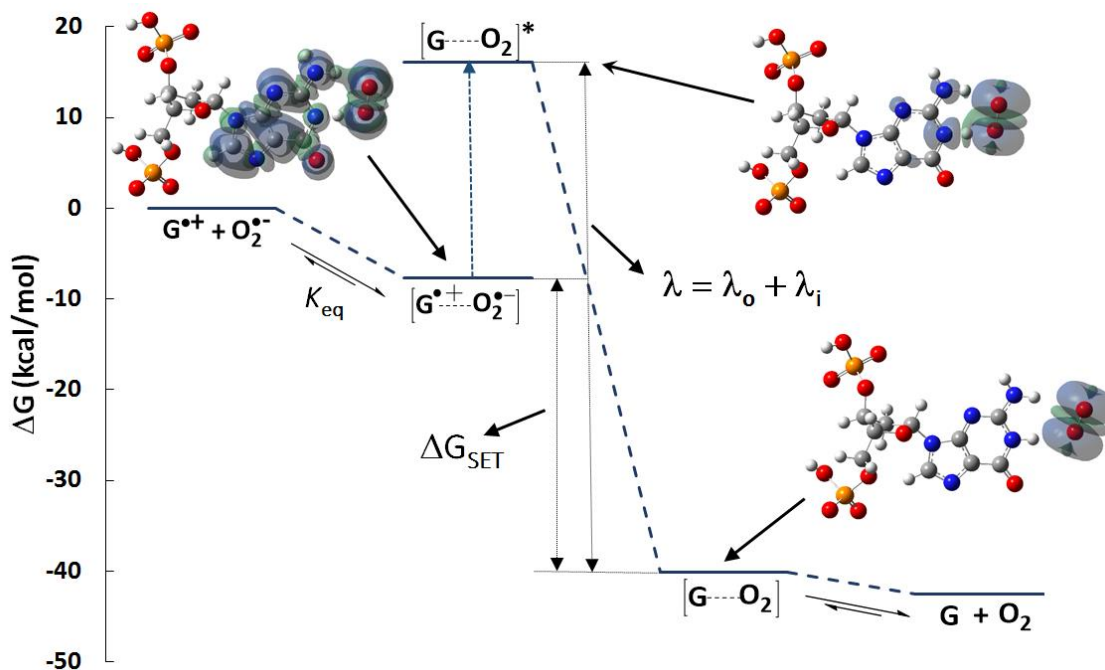
$$D = \frac{k_B T}{6\pi \eta a}$$

Figure S1. Pre-equilibrium reaction and parameters used in the kinetic analyses of the SPGET mechanism between $G^{\bullet+}$ and $O_2^{\bullet-}$. Structures and spin densities are shown. The first elementary (SPGET-1) corresponding to the protonation of $G_{(-H)}^{\bullet}$ is not included.
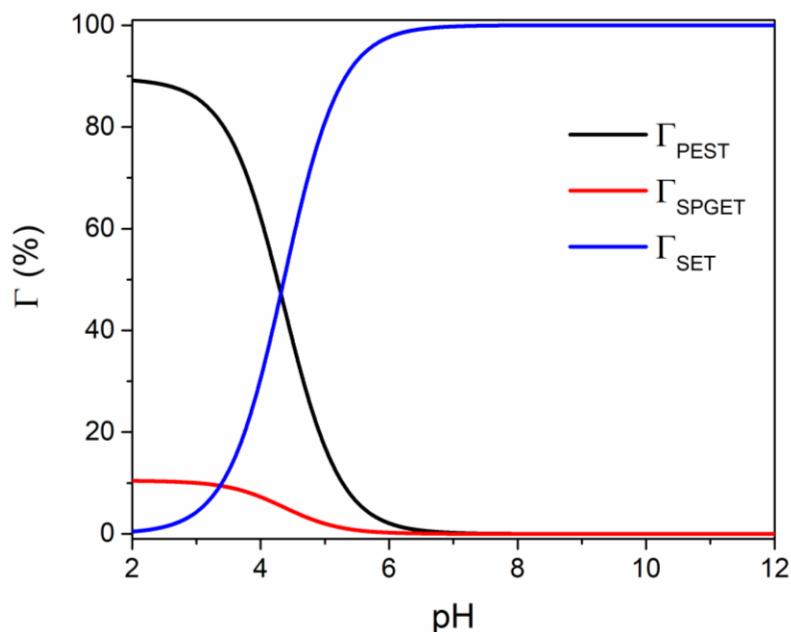

Figure S2. Branching ratios (Γ) of reactions mechanisms at different pH values.

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