

Redox processes in a complex of iron(III) and phenanthraquinone

Petr Milko^{a)} and Jana Roithová^{b)}

^{a)} Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nám. 2, 16610 Praha 6, Czech Republic

^{b)} Department of Organic Chemistry, Faculty of Sciences, Charles University in Prague, Hlavova 8, 12843 Prague 2, Czech Republic

Phenanthraquinone (PQ), one of the most abundant compounds occurring in diesel exhaust particles, interacts with iron-containing enzymes such as NADPH-cytochrome P450 reductase or cytochrome *bc₁* complex.^[1-3] The interaction leads to production of reactive oxygen species (ROS) $O_2^{\bullet-}$ which is responsible for a damage of the essential macromolecules. We can generate the $[FeCl(PQ)(CH_3O)]^+$ complex in the gas-phase and examine its structure as well as reactivity by means of mass spectrometry and IRMPD spectroscopy. Further, the reactivity is studied by DFT with triple-zeta basis set to get detail insight to the mechanism. The experiment and calculations show that CH_3O^- is oxidized to formaldehyde, which is associated with a transfer of one electron and proton to PQ producing phenanthrasemihydroquinone and the second electron migrates to iron. Previous study shows that presence of 1,10-phenanthroline (phen) protects against adverse effects of PQ.^[2] The $[FeCl(phen)(CH_3O)]^+$ complex follows the same dissociation pathways as the $[FeCl(PQ)(CH_3O)]^+$ complex, however, the mechanism shows classic two state reactivity of the iron complex instead of the single state reactivity for the PQ complex. Finally, effect of the coordination of phenanthroline to the iron-PQ complex is studied as well to show that the mixed complex $[FeCl(PQ)(phen)(CH_3O)]^+$ loses either PQ or CH_2O . Interestingly, the addition of phen facilitates producing of phenanthrasemihydroquinone and the reactivity of the mixed complex corresponds with the reactivity of the $[FeCl(PQ)(CH_3O)]^+$ complex. However iron binds phenanthroline much more strongly, consequently it weakens a bond between iron and phenanthraquinone. In conclusion, the protection by the phen ligand is based on its stronger affinity towards iron which leads to a displacement of PQ or a blockage of an iron center for the interaction with PQ.

Literature:

- [1] J. L. Bolton, M. A. Trush, T. M. Penning, G. Dryhurst, T. J. Monks, *Chem. Res. Toxicol.* **2000**, 13, 135-160.
- [2] R. Sugimoto, Y. Kumagi, Y. Nakai, T. Ishii, *Free Radic. Biol. Med.* **2005**, 38, 388-395.
- [3] S. Dröse, U. Brant, *J. Biol. Chem.* **2008**, 283, 21649-21654.