

Low-energy electron-induced “oxygen fixation” to DNA SAMs studied by stimulated anion desorption

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Synopsis Reactions of $^{18}\text{O}_2$ with self-assembled monolayer films of thiolated DNA oligomers are studied by the electron stimulated desorption of anions. Electrons with energies < 20 eV initiate dehydrogenation of the DNA by resonant and non-resonant processes, to form radical sites for oxygenation. This damage mechanism may underlie the “oxygen fixation” process of radiobiology.

The binding of $^{18}\text{O}_2$ to self-assembled monolayers (SAMs) of single stranded DNA oligonucleotide (5'AAAGGACAAA-3' phosphothiolated at the 3' end) grafted onto gold, was studied by the electron-stimulated desorption (ESD) of anions. Dosing DNA SAMs with $^{18}\text{O}_2$ at 50 K, results in the enhancement of the $^{18}\text{O}^-$ and $^{18}\text{OH}^-$ ESD yields. Such signals persist to temperatures as high as 250 K [1]. “Pre-irradiating” the DNA SAMs with electrons (of energies 0–20 eV) prior to exposure to $^{18}\text{O}_2$, enhances the $^{18}\text{O}^-$ and $^{18}\text{OH}^-$ ESD proportionally to pre-irradiation fluence (Figure 1). Absent pre-irradiation, $^{18}\text{O}^-$ and $^{18}\text{OH}^-$ are undetected, indicating that these signals derive from the dissociation of species formed in the film when $^{18}\text{O}_2$ reacts with electron damaged DNA [1].

Further experiments show that a minimum pre-irradiation energy of ~5.5 eV is required to form damage sites in the DNA that will react with $^{18}\text{O}_2$, and that maximum $^{18}\text{O}^-$ yields are observed after pre-irradiation at ~8.5 eV. These energies closely correspond with those for production of H^- via dissociative electron attachment (DEA: $\text{RH} + \text{e}^- \rightarrow (\text{RH})^{\bullet-} \rightarrow \text{R}^\bullet + \text{H}^-$).

These results reveal that $^{18}\text{O}_2$ reacts with the radicals formed in the hydrocarbon sections (CH_{x-1}^\bullet) of the DNA film to form RCOO^\bullet and RCOOH species, from which the $^{18}\text{O}^-$ and $^{18}\text{OH}^-$ ESD signals originate. The current results indicate that “oxygen fixation” and the

radio-sensitization effect of O_2 known in radiobiology [2], may be initiated by electron induced damage of DNA.

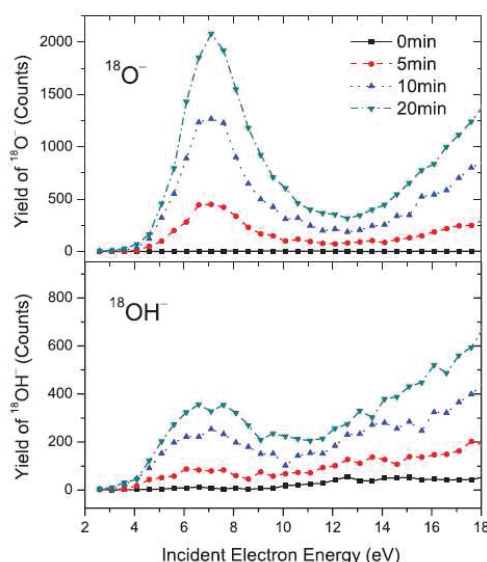


Figure 1. Anion yield functions for (a) $^{18}\text{O}^-$ and (b) $^{18}\text{OH}^-$ from SAM-DNA measured at 150 K after dosing with ~1 ML of $^{18}\text{O}_2$ at 50 K. The SAM-DNA films were irradiated with 0–18 eV electrons (at an incident current of 2 nA) for the indicated periods prior to exposure to $^{18}\text{O}_2$. [1].

References

- [1] Mirsaleh-Kohan N *et al* 2012 *J. Chem. Phys.* **136** 235104
- [2] Hall EJ and Giaccia AJ 2006 *Oxygen effect and reoxygenation in Radiobiology for the radiologist* (Philadelphia: Lippincott, Williams and Wilkins)

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