Supplemental Information

for

C5’- and C3'- sugar radicals produced via photo-excitation of one-electron oxidized adenine in 2'-deoxyadenosine and its derivatives

By

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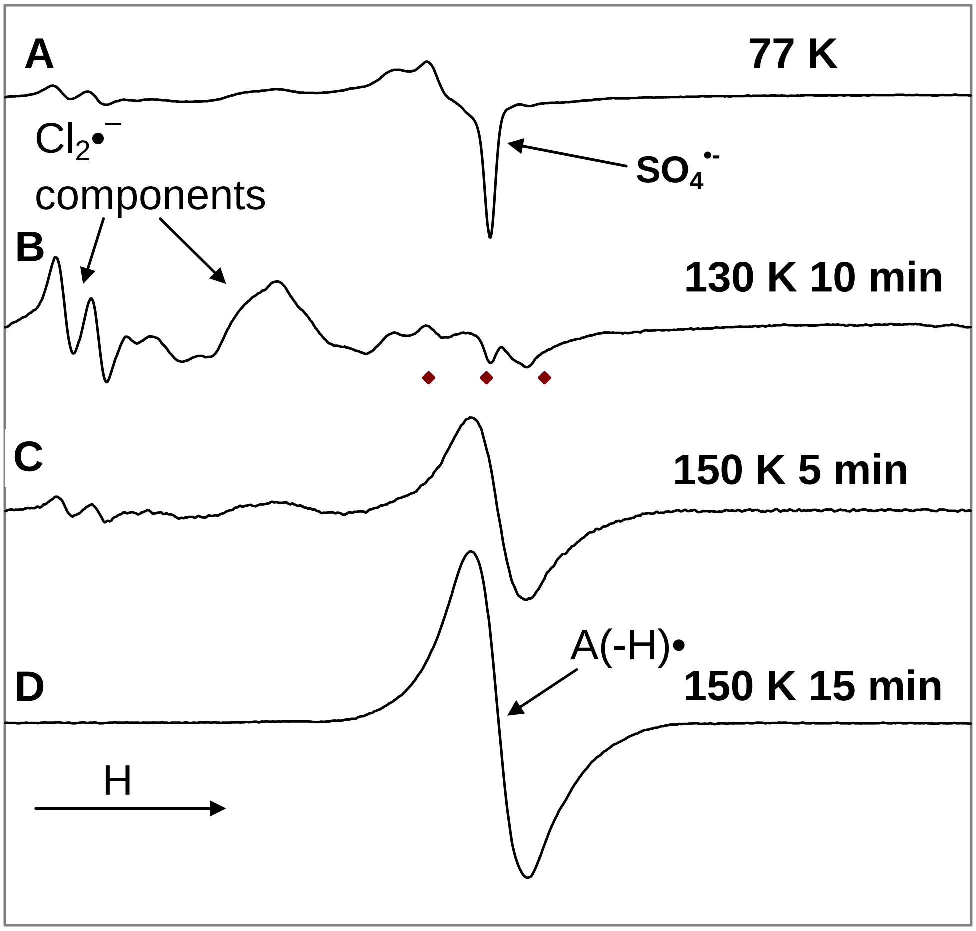
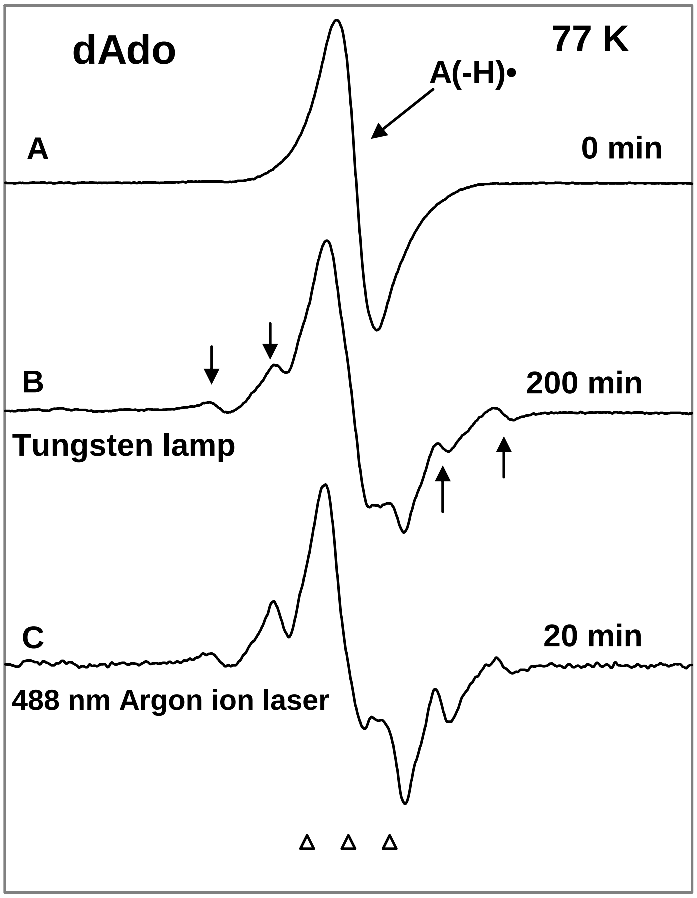
Supplementary Material:

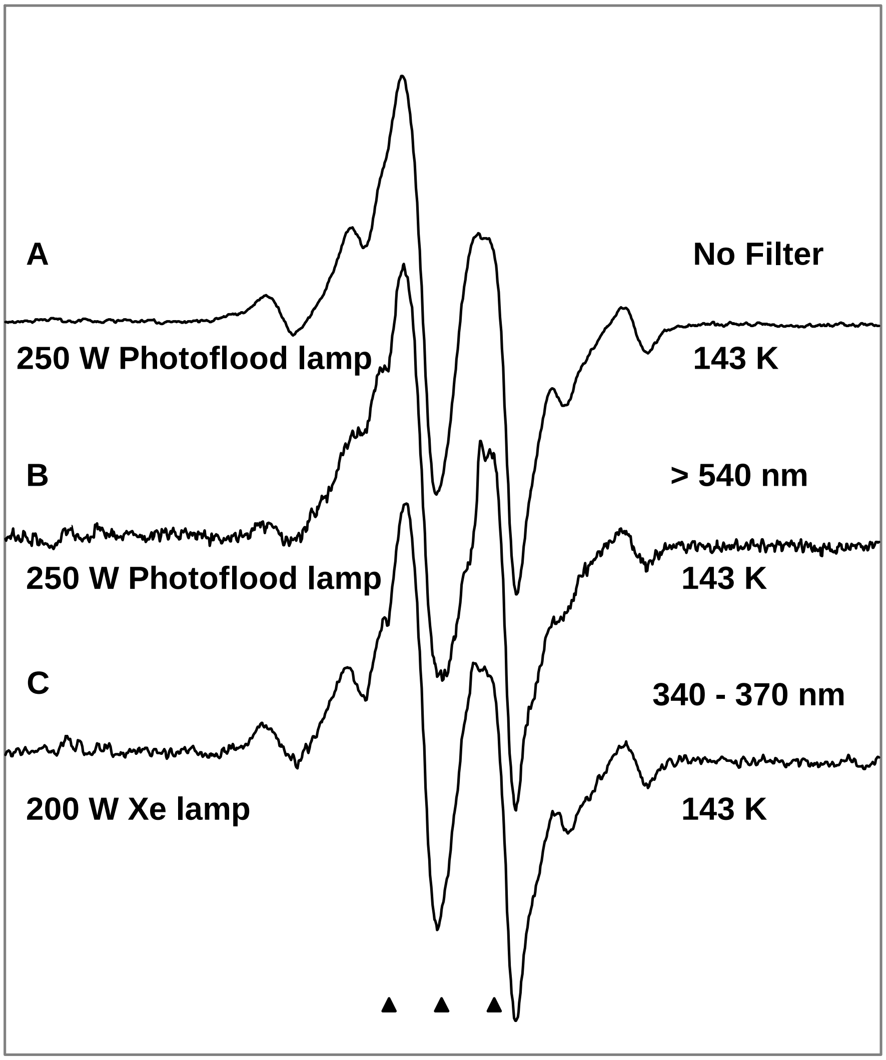
Figure S1
Figure S2
Figure S3
Figure S4



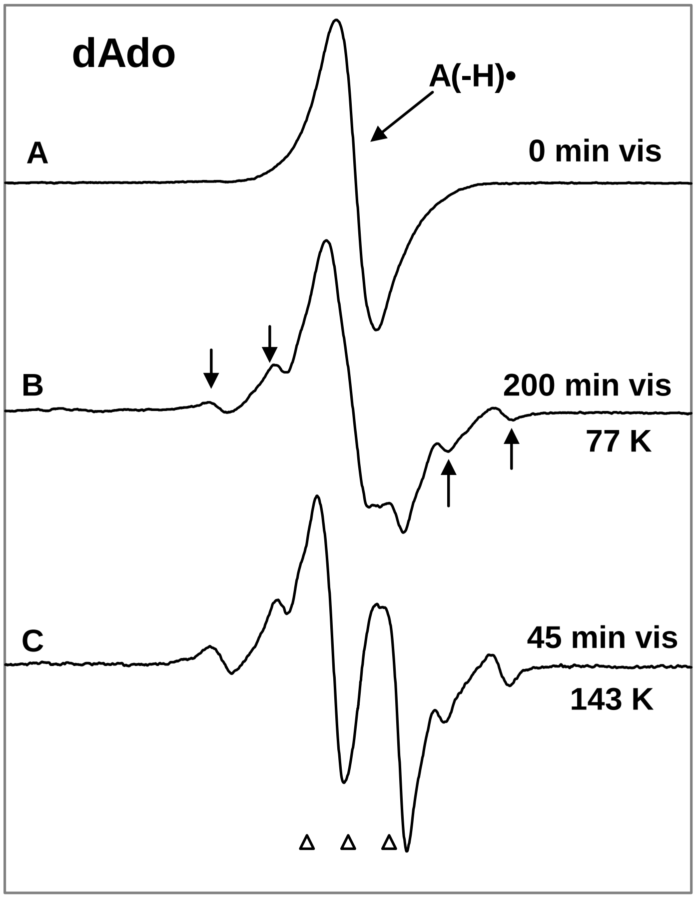
Supplemental Figure S1. Formation of A(-H)• via one-electron oxidation of dAdo. (A) ESR spectrum showing $SO_4^{\bullet -}$ and $Cl_2^{\bullet -}$ formation in a γ-irradiated (2.5 kGy) 7 *M* N_2-saturated LiCl/D_2O glass containing dAdo (3mg) and $K_2S_2O_8$ (5mg as an electron scavenger). No ESR single associated with the adenine electron adduct is found. (B) Spectrum of the sample in (A) after annealing to 130 K for 10 min. $SO_4^{\bullet -}$ reacts with Cl^- at this temperature to form $Cl_2^{\bullet -}$. Except for a residual amount of $SO_4^{\bullet -}$, $Cl_2^{\bullet -}$ is the only radical species at this point. (C) After further annealing at 150 K for 5 min where $Cl_2^{\bullet -}$ partially reacts with dAdo to form A(-H)• . (D) After annealing for another 10 min (i.e., total 15 min) at 150 K to complete the reaction. Only the spectrum of A(-H)• is observed at this point and no ESR single associated with the adenine electron adduct is found. All ESR spectra were recorded at 77 K. The three reference markers in this and in subsequent figures are Fremy's salt resonances (The central marker is at g = 2.0056 and each of three markers is separated from one another by 13.09 G).



Supplemental Figure S2. Comparison of tungsten lamp intensity with an Argon ion laser (488 nm, 800 mW). (A) Spectrum of A(-H)• in dAdo before illumination at 7 *M* N_2-saturated LiCl/D_2O glass. (B) After visible illumination at 77 K with a tungsten incandescent lamp (250 W). (C) Photo-excitation of an identical new sample of A(-H)• in dAdo using an Argon-ion laser (488 nm, 800 mW) at 77 K. Both visible and laser illuminations show conversion to sugar radicals with the laser about 10 times as effective owing to its greater fluence. Arrows indicate 4 outer line components from C3'• and a central doublet assigned to C5'• is present. All the spectra were also recorded at 77 K.



Supplemental Figure S3. Wavelength dependence of the production of sugar radicals by photo-excitation of A(–H)•. Samples of dAdo in a 7 *M* N_2-saturated LiCl/D_2O glass were photo-excited at 143K using light with different wavelengths indicated in the figure. A. For 45 min. B. For 1h. C. For 20 min. The remaining A(–H)• spectrum (ca. 50%) was subtracted from the original spectra to obtain spectra shown in Figures B and C. All the spectra were recorded at 77 K.



Supplemental Figure S4. Temperature dependence of sugar radical formation via photo-excitation of A(-H)•. (A) Spectrum of A(-H)• in dAdo in a 7 *M* N_2-saturated LiCl/D_2O glass before illumination; (B) After visible illumination at 77 K of A(-H)• in dAdo. Arrows indicate 4 outer line components from C3'•. (C) After visible illumination at 143 K of a new sample of A(-H)• in dAdo, showing a nearly complete conversion to sugar radicals (Table IV). A central doublet assigned to C5'• is present. All the spectra were recorded at 77 K.