Supplementary Information: Radiolytic evaluation of a new technetium redox control reagent for advanced used nuclear fuel separations

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ADDITIONAL CHEMICAL KINETICS

HYDRATED ELECTRON

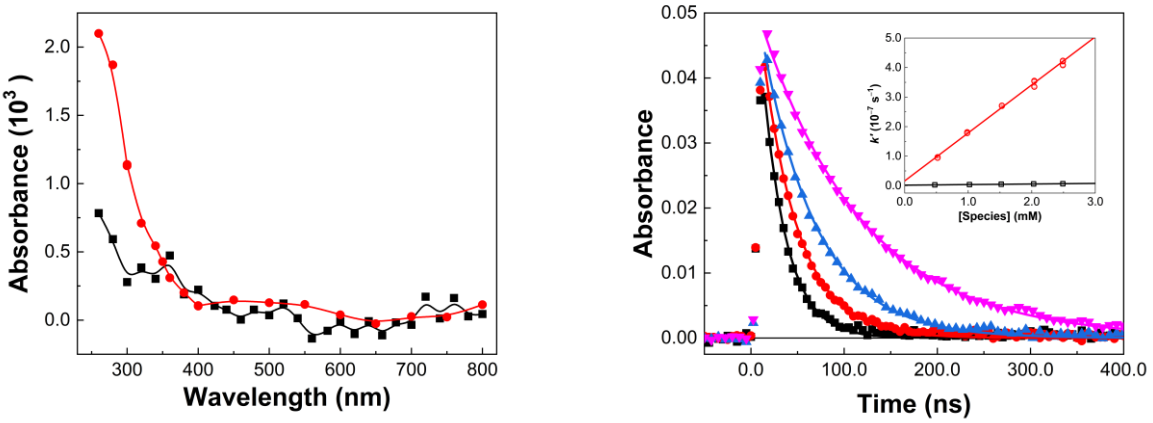

Fig. S1. Transient absorption spectra for e_{aq}^- reaction in Ar-saturated 2.49 mM DAG (■) and 2.49 mM 1:1 [DAG:ReO_4] (●) in 10 mM phosphate buffered pH 6.95 solution containing 0.50 M t-butanol at 22.4 ± 0.1 ºC. Data obtained from final limiting absorbance values fitted using single-exponential fit to measured kinetics. **(B)** Transient kinetics measured at 720 nm for Ar-saturated 2.49 (■), 1.53 (●), 0.98 (▲) and 0.52 (▼) mM 1:1 [DAG·ReO_4]. Solid lines correspond to single-exponential fits, with fitted values of k' = (4.21 ± 0.04), (2.70 ± 0.02), (1.79 ± 0.01), and (0.95 ± 0.01) × 10^7 s^{-1}, respectively. *Inset:* Second-order rate coefficient determination for DAG (■) and [DAG·ReO_4] (●) in the same respective solutions. The solid lines are weighted linear fits, corresponding to a second-order rate coefficient of $k(e_{aq}^- + DAG)$ = (1.97 ± 0.06) × 10^8 M^{-1} s^{-1}, and $k(e_{aq}^- + [DAG·ReO_4])$ = (1.62 ± 0.03) × 10^{10} M^{-1} s^{-1} , R^2 = 0.98 and 0.99, respectively.

HYDROGEN ATOM

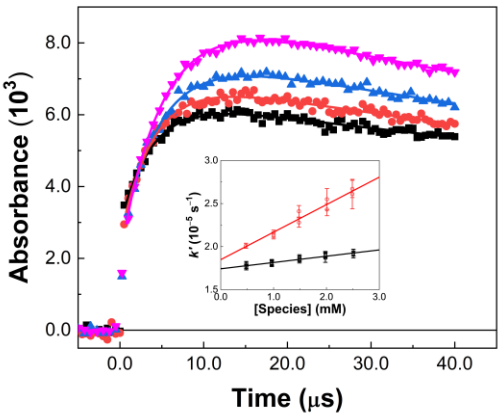

Fig. S2. Transient kinetics measured at 360 nm for H• atom reaction in N_2-saturated 2.49 (■), 1.48 (●), 1.00 (▲), and 0.48 (▼) mM 1:1 [DAG·ReO_4] in 10 mM phosphate buffer, pH 3.06 solution containing 102.5 μM pCBA at 22.7 ± 0.1 ºC. Solid lines correspond to exponential growth and decay function fits, with fitted growth values of k' = (2.67 ± 0.10), (2.41 ± 0.07), (2.15 ± 0.04), and (2.01 ± 0.03) × 10^5 s^{-1}, respectively. *Inset:* Second-order rate coefficient determination for DAG (■) and [DAG·ReO_4] (●) in the same respective solutions. The solid lines are weighted linear fits, corresponding to a second-order rate coefficient of k(H• + DAG) = (7.25 ± 0.23) × 10^6 M^{-1} s^{-1} and k(H• + [DAG·ReO_4]) = (3.19 ± 0.23) × 10^7 M^{-1} s^{-1}, R^2 = 0.94 and 0.96, respectively.

NITRATE RADICAL

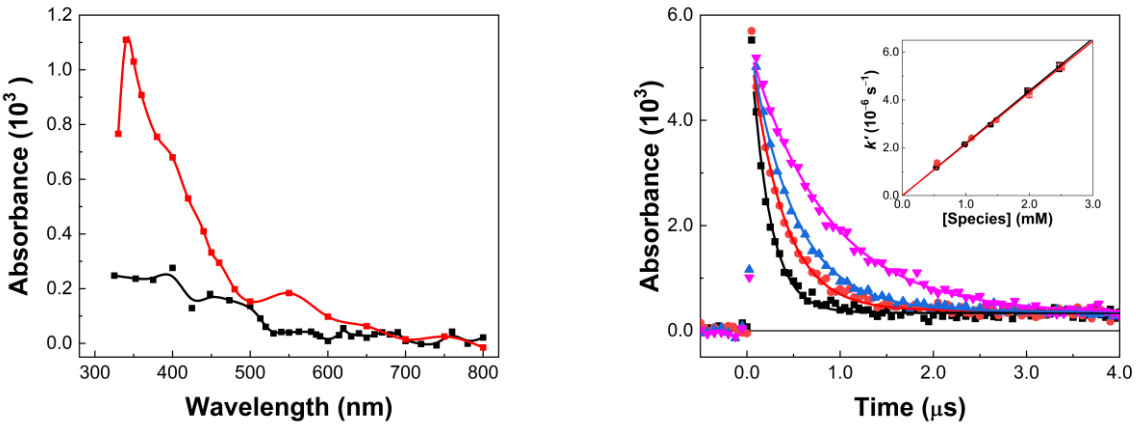

Fig. S3. (A) Transient absorption spectra for NO_3• radical reaction in N_2O-saturated 2.47 mM DAG (■) and 2.51 mM 1:1 [DAG:ReO_4] (●) at pH 3.02 in 5.0 M $NaNO_3$/1.0 mM $HClO_4$ at 22.8 ± 0.1 ºC. Data obtained from final limiting absorbance values fitted using single-exponential fit to measured kinetics. **(B)** Transient kinetics measured at 640 nm for N_2O-saturated 2.47 (■), 1.39 (●), 0.98 (▲), and 0.54 (▼) mM DAG. Solid lines correspond to single-exponential fits, with fitted values of k' = (5.29 ± 0.10), (2.96 ± 0.04), (2.15 ± 0.02), and (1.15 ± 0.01) × 10^6 s^{-1}, respectively. *Inset:* Second-order rate coefficient determination for DAG (■) and [DAG·ReO_4] (●) in the same respective solutions. The solid lines are weighted linear fits, corresponding to a second-order rate coefficient of k(NO_3• + DAG) = (2.19 ± 0.03) × 10^9 M^{-1} s^{-1} and k(NO_3• + [DAG·ReO_4]) = (2.06 ± 0.03) × 10^9 M^{-1} s^{-1}, R^2 = 0.99 and 0.99, respectively

NON-NORMALIZED DAG CONCENTRATIONS VS. ABSORBED GAMMA DOSE

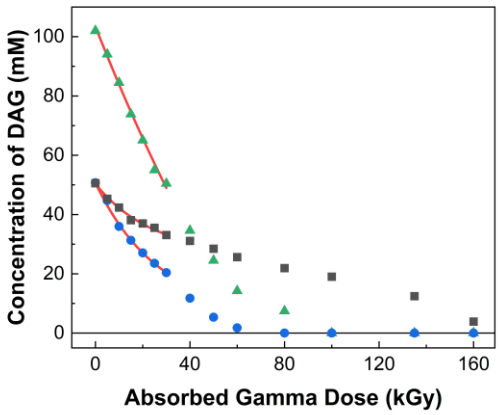

Fig. S4. Concentration of DAG as a function of absorbed dose from the gamma irradiation of formerly: 50 mM DAG in water (■); 50 mM DAG in 2.0 M HNO_3 (●); and 100 mM DAG in 2.0 M HNO_3:1.5 M DEH*i*BA/*n*-dodecane (▲) under ambient irradiator temperature conditions. Solid lines are first-order exponential fits to data for dose constant calculation.