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As „Supporting Information“:

Experimental Section

Chemicals. Thioanisole, 3,4-dimethoxybenzaldehyde (veratrylaldehyde), potassium peroxydisulfate, thallium(I) sulfate, potassium hydrogenphosphate, sodium dihydrogenphosphate, sodium tetraborate, sodium hydroxide, potassium thiocyanate, perchloric acid and 2-methyl-2-propanol were of the highest commercial quality available. Milli-Q-filtered (Millipore) water was used for all solutions.

Reagents. Veratryl alcohol (VA) was purified by chromatography on a silica gel column. Veratryl alcohol methyl ether (VAME) was prepared by reaction of VA with methyl iodide and sodium hydride in anhydrous tetrahydrofuran. ^1H NMR (CDCl_3): δ 3.34 (s, 3H, OCH_3), 3.85 (s, 3H, ring OCH_3), 3.86 (s, 3H, ring OCH_3), 4.36 (s, 2H, CH_2), 6.78-6.87 (m, 3H, Ar). 1-(3,4-Dimethoxyphenyl)-2,2-dimethyl-1-propanol was prepared by reaction of 3,4-dimethoxybenzaldehyde with *t*-butylmagnesium bromide. ^1H NMR (CDCl_3): δ 0.89 (s, 3H, $\text{C}(\text{CH}_3)_3$), 1.86 (s, 1H, OH), 3.84 (s, 6H, 2OCH_3), 4.31 (s, 1H, CH), 6.76-6.85 (m, 3H, Ar). The purity of all reagents was > 99 %.

Product Analysis. Products were identified and quantitatively determined by HPLC (comparison with authentic samples).

γ -Irradiations were carried out with a panorama ^{60}Co γ -source (Nuclear Engineering) at dose rates of 0.3-0.9 Gy s^{-1} . In a typical experiment 5 ml of an argon saturated aqueous solutions containing the substrate (1.0 mM), potassium peroxydisulfate (0.5 mM) and 2-methyl-2-propanol (0.2 M) were irradiated at room temperature for the time necessary to obtain a 40% conversion with respect to peroxydisulfate. The oxidation of VA led to veratryl aldehyde as main reaction product, both in acid and basic solution. The oxidation of 1-(3,4-dimethoxyphenyl)-

2,2-dimethyl-1-propanol led to the formation of two products both in acid and neutral solution: veratryl aldehyde and the ketone $3,4-(\text{MeO})_2\text{C}_6\text{H}_3\text{C}(\text{O})\text{CMe}_3$, with the following aldehyde/ketone (a/k) ratios: pH = 4, a/k = 2. pH = 6.9 (buffer KH_2PO_4 10 mM - Na_2HPO_4 10 mM), a/k = 50 (see text).

The oxidation of 1-(3,4-dimethoxyphenyl)-2,2-dimethyl-1-propanol was also studied using potassium 12-tungstocobalt(III)ate ($\text{Co}(\text{III})\text{W}_{12}\text{O}_{40}^{5-}$, abbreviated as Co(III)W), as the oxidant. Co(III)W (0.0035 mmol) was added to 5 ml of an argon saturated aqueous solution (pH = 6.9: buffer KH_2PO_4 10 mM - Na_2HPO_4 10 mM), containing the substrate (0.0035 mmol), kept at $T = 25^\circ\text{C}$. After 90 min, the reaction mixture was analyzed by HPLC which showed the quantitative formation of 3,4-dimethoxybenzaldehyde.

Pulse Radiolysis. The pulse radiolysis experiments were performed using a 3 MeV van de Graaff accelerator which supplied 300-ns pulses with doses such that 0.3-3 μM radicals were produced. Both optical and conductivity detection were employed. The pulse radiolysis setup and the methods of data handling have been described elsewhere.⁵¹ For the optical experiments, dosimetry was performed with N_2O saturated 10 mM KSCN aqueous solutions, for which $G[(\text{SCN})_2^{\bullet-}] = 6.0 \times 10^{-7} \text{ mol J}^{-1}$ and $\epsilon[(\text{SCN})_2^{\bullet-}] = 7600 \text{ M}^{-1} \text{ cm}^{-1}$ at 480 nm.⁵²

Experiments were performed using argon saturated aqueous solutions containing the substrate (0.1-1.0 mM), potassium peroxydisulfate (1-10 mM) and 2-methyl-2-propanol (0.1 M). Alternatively, N_2O saturated aqueous solutions containing the substrate (0.1-0.2 mM) and thallium(I) sulfate (0.5-2.0 mM) were employed. The pH of the solutions was adjusted with NaOH or HClO_4 . The temperature of the solutions was kept constant at $25 \pm 0.2^\circ\text{C}$.

The second order rate constants for reaction of the radical cations with OH^- were obtained from the slopes of the plots of the observed rates (k_{obs}) vs the concentration of NaOH. For these experiments the solution containing 0.5 mM substrate, 10 mM potassium peroxydisulfate and 0.1 M 2-methyl-2-propanol was saturated with oxygen and 1 mM sodium tetraborate was added to avoid undesired pH variations upon

irradiation. Rate constants were obtained by averaging 8 to 14 values, each consisting of the average of 10 to 30 shots and were reproducible to within 3%.

For the determination of the reduction potentials of $VA^{\bullet+}$ and $VAME^{\bullet+}$, thioanisole (TA) was used as a redox standard. VA (VAME) (from 0.01 to 0.1 mM) was added to an argon saturated aqueous solution containing 1.4 mM TA, 5 mM potassium peroxydisulfate and 0.1 M 2-methyl-2-propanol, and absorbances at equilibrium of $TA^{\bullet+}$ and rates of buildup of $VA^{\bullet+}$ ($VAME^{\bullet+}$) were measured at 530 and 430 nm, respectively. The temperature of the solution was kept at 25 ± 0.2 °C and doses of ≤ 2 Gy/pulse were employed.

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