Nitric Acid Radiolysis: Effect of Alpha Rays on H₂ and HNO₂ Yields.

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Supporting Information

A validation of the analytical method was required prior to irradiations. In this sense, solutions of 2 M HNO₃ were irradiated at a dose rate of 0.1 Gy/s. One solution was irradiated for 7200 s, and the gas atmosphere was sampled every 1200 s. Another solution was irradiated for 14400 s, and the gaseous atmosphere sampled every 20 minutes, starting after 7200 s. The sampled volume does not induce any disturbance in the measurement, as can be seen in Figure 1S: the two set of data show good coherence, and the point at 835 J/Kg (7200 s), match within the measurement error. Therefore, this analytical method is validated, as the sampling of the gaseous atmosphere does not affect the measurements.



Figure 1S: H_2 production in 2 M HNO₃ solutions irradiated at a dose rate of 0.1 Gy/s. Coherence between data sampled every 1200 s for samples irradiated 7200 s (in black) and every 1200 s for samples irradiated 14400 s, sampling starting after 7200 s (in red).



Figure 2S: The SRIM evaluated dose deposition rate vs the penetration depth of the alpha particles.

Prior to all irradiation, an *in-situ* dosimetry is performed using the super Fricke chemical dosimeter. The concentration of ferric ions is followed by monitoring the absorption at 304 nm (ϵ =2197 M⁻¹·cm⁻¹). The evolution of the absorbed dose in time, calculated according to equation 2 is presented in Figure 2S, and from the slope of these lines we can determine the dose rate.



Figure 3S: Dose evolution as a function of time for the chosen current intensities.

Figure 4S shows the literature data on the variation of the dissociation degree as a function of the HNO_3 concentration.



Figure 4S: Literature values for the dissociation degree of HNO₃ showing a decreased dissociation at higher acid concentrations.^{1–}

REFERENCES

(1) Redlich, O.; Bigeleisen, J. The Ionization of Strong Electrolytes. I. General Remarks, Nitric Acid. J. Am. Chem. Soc. **1943**, 65 (10), 1883–1887.

(2) Redlich, Otto. The Dissociation of Strong Electrolytes. Chem. Rev. 1946, 39 (2), 333–356.

(3) Hood, G. C.; Redlich, O.; Reilly, C. A. Ionization of Strong Electrolytes. III. Proton Magnetic Resonance in Nitric, Perchloric, and Hydrochloric Acids. *J. Chem. Phys.* **1954**, *22* (12), 2067–2071.

(4) Hood, G. C.; Reilly, C. A. Ionization of Strong Electrolytes. VIII. Temperature Coefficient of Dissociation of Strong Acids by Proton Magnetic Resonance. *J. Chem. Phys.* **1960**, *32* (1), 127–130.

(5) Davis, W.; De Bruin, H. J. New Activity Coefficients of 0–100 per Cent Aqueous Nitric Acid. J. Inorg. Nucl. Chem. **1964**, 26 (6), 1069– 1083.

(6) Redlich, O.; Duerst, R. W.; Merbach, A. *Ionization of Strong Electrolytes XI. The Molecular States of Nitric Acid and Perchloric Acid*; UCRL-18049; Lawrence Berkeley National Laboratory: USA, 1968.

(7) Querry, M. R.; Tyler, I. L. Reflectance and Complex Refractive Indices in the Infrared for Aqueous Solutions of Nitric Acid. *J. Chem. Phys.* **1980**, 72 (4), 2495–2499.

(8) Ruas, A.; Pochon, P.; Simonin, J.-P.; Moisy, P. Nitric Acid: Modeling Osmotic Coefficients and Acid–Base Dissociation Using the BIMSA Theory. *Dalton Trans.* **2010**, *39* (42), 10148.

(9) Lewis, T.; Winter, B.; Stern, A. C.; Baer, M. D.; Mundy, C. J.; Tobias, D. J.; Hemminger, J. C. Does Nitric Acid Dissociate at the Aqueous Solution Surface? *J. Phys. Chem. C* **2011**, *115* (43), 21183–21190.

(10) Lewis, T.; Winter, B.; Stern, A. C. .; Baer, M. D.; Mundy, C. J.; Tobias, D. J.; Hemminger, J. C. Dissociation of Strong Acid Revisited: X-Ray Photoelectron Spectroscopy and Molecular Dynamics Simulations of HNO3 in Water. *J. Phys. Chem. B* **2011**, *115* (30), 9445–9451.

(11) McKenzie, H.; MacDonald-Taylor, J.; McLachlan, F.; Orr, R.; Woodhead, D. Modelling of Nitric and Nitrous Acid Chemistry for Solvent Extraction Purposes. *Procedia Chem.* **2016**, *21*, 481–486.