

Supplementary Information

Picosecond Time-Resolved Investigation of NO_3^\bullet in PUREX Solvent

Amel Zorai,^{*a} Daniel Adjei,^a Mireille Benoît,^a Sergey Denisov,^a Philippe Moisy,^b Jacqueline Belloni,^a and Mehran Mostafavi ^{*a}

Amel Zorai,^{*a} Daniel Adjei,^a Mireille Benoît,^a Sergey Denisov,^a Philippe Moisy,^b Jacqueline Belloni,^a and Mehran Mostafavi ^{*a}

^a Institut de Chimie Physique, UMR CNRS/UPS 8000, Université Paris-Saclay, Rue Michel Magat, 91405 Orsay, France.

^b CEA, DES, ISEC, DMRC, Université de Montpellier, Bagnols-sur-Cèze 30207, France

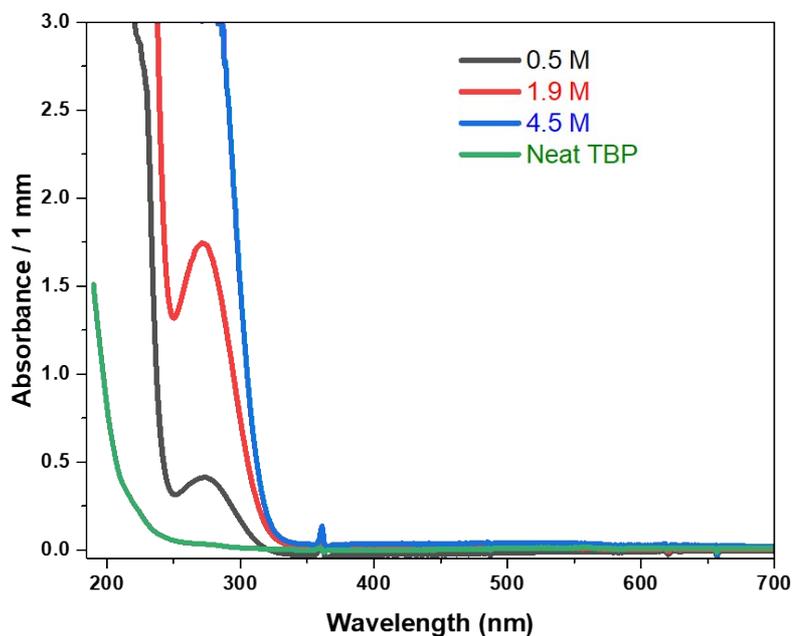


Fig. SI 1. Optical absorption spectra of neat TBP and of various solutions of nitric acid (0.5, 1.9 and 4.5 M), ($\lambda_{\text{max}} = 300$ nm), TBP and water (Table SI 1) before irradiation. Optical path: 1 mm.

Table SI 1. Dependence of the dose absorbed by the mixture components on their concentration (Series 1).

[HNO₃] (M)	0	0.5	1.9	4.5
Vol (%)	0	2.25	8.5	20.3
Electrons (M)	0	16	60.8	144
Dose (HNO₃) (J L⁻¹)	0	2.9	11	26.1
<i>f</i>(HNO₃)		0.029	0.11	0.251
[H₂O] (M)	0.8			1.5
Vol (%)	1.5			3
Electrons (M)	8			15
Dose (H₂O) (J L⁻¹)	1.5			2.6
<i>f</i>(H₂O)	0.015			0.025
TBP Vol (%)	98.5	96.25	90.1	76.7
[TBP] (M)	3.65	3.52	3.3	2.81
Electrons (M)	538	524	492	419
Dose (TBP) (J L⁻¹)	97.8	95.3	89.4	76
<i>f</i>(TBP)	0.984	0.955	0.875	0.726
Dose (Total) (J L⁻¹)	99.3	99	101.9	104.7

Table SI 2. Determination of absorbances and yields of e^-_{TBP} and NO_3^\bullet radical, and of 440 nm absorbance at the HNO_3 concentrations of 0.5 and 1.9 M.

[HNO_3] (0.5 M) [TBP] (3.5 M) [H_2O] (0.8 M)	440 nm	640 nm	670 nm	780 nm
$A(\text{Total})_{5 \text{ ps}}$ 0.5 cm	0.035	0.027	0.025	0.017
$A(e^-)_{5 \text{ ps}}$ (0.5 cm) ₅	0.006	0.011	0.012	0.017
$G(e^-)_{5 \text{ ps}}$ ($10^{-7} \text{ mol J}^{-1}$)	0.35			
$A(\text{NO}_3^\bullet)_{5 \text{ ps}}$ (0.5 cm)		0.016	0.013	0
$G(\text{NO}_3^\bullet)_{5 \text{ ps}}$ ($10^{-7} \text{ mol J}^{-1}$)	-	2.4	2.4	
$A(440 \text{ nm})_{5 \text{ ps}}$ (0.5 cm)	0.029	-	-	-

[HNO_3] (1.9 M) [TBP] (3.5 M) [H_2O] (0.8 M)	440 nm	640 nm	670 nm	780 nm
$A(\text{Total})_{5 \text{ ps}}$ 0.5 cm	0.029	0.029	0.0255	0.0122
$A(e^-)_{5 \text{ ps}}$ (0.5 cm)	0.0042	0.0077	0.0085	0.012
$G(e^-)_{5 \text{ ps}}$ ($10^{-7} \text{ mol J}^{-1}$)	0.24			
$A(\text{NO}_3^\bullet)_{5 \text{ ps}}$ (0.5 cm)	-	0.0213	0.0174	0
$G(\text{NO}_3^\bullet)_{\text{Total}, 5 \text{ ps}}$ ($10^{-7} \text{ mol J}^{-1}$)	-	3.2	3.2	-
$A(440 \text{ nm})_{5 \text{ ps}}$ (0.5 cm)	0.025	-	-	-

Table SI 3. Dependence of the dose absorbed by the components and f factor on the TBP and dodecane concentrations (2.5 M HNO₃/0.8 M H₂O) (Series 2).

[HNO ₃] (M)	2.5		
Vol (%)	11.5		
Electron (M)	80		
Dose (HNO ₃) (J L ⁻¹)	14.5		
f (HNO ₃)	0.15		
[H ₂ O] (M)	1.5		
Vol (%)	3		
Electrons (M)	15		
Dose (H ₂ O) (J L ⁻¹)	2.5		
f (H ₂ O)	0.025		
[TBP] (M)	3.1	2.6	2.2
TBP Vol (%)	86	73	61.7.
Electrons (M)	476	392	338
Dose TBP (J L ⁻¹)	83.3	67	57.4
f (TBP)	0.84	0.724	0.624
Vol (C ₁₂ H ₂₆) (%)	0	13	25.3
[C ₁₂ H ₂₆] (M)	0	0.61	1.11
Electrons (M)	0	60	110
Dose (C ₁₂ H ₂₆) (J/L)	0	11	20
f (C ₁₂ H ₂₆)	0	0.114	0.215
Dose (Total) (J L ⁻¹)	100.3	96.5	93.4