Electronic Supplementary Information (ESI)

for

Radiolytic degradation of selective actinide extractants from bis-1,2,4-triazine family in cyclohexanone solutions

Adrian Sulich,*a,b Jan Grodkowski,††b and Krzysztof Bobrowskib

*E-mail: sulich@ifpan.edu.pl.

^aInstitute of Physics, Polish Academy of Sciences, Aleja Lotnikow 32/46 PL 02 668 Warsaw, Poland.

^bInstitute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland.

^{††}Professor Jan Grodkowski died before this article was written, but he is mentioned as a co-author due to his significant contribution to the reported research, related to doctoral studies began by Adrian Sulich under his scientific supervision and finished under the scientific supervision of Professor Krzysztof Bobrowski.

Contents

Fig. S1. Structural formulas of the investigated extracting ligands	p.2
Fig. S2. Stationary UV-VIS absorption spectra of cyclohexanone	p.2
Fig. S3. Stationary UV-VIS absorption spectra of solutions containing 0.1 mM in cyclohexanone	of ligands p.2
Tab. ST1. Properties of the transient species derived from cyclohexanone radiolysis	during its p.3
Fig. S4. Transient absorption spectra recorded at different time points after a	n electron

- pulse during radiolysis of Ar-saturated samples of pure cyclohexanone and cyclohexanone pre-equilibrated with 1M HNO₃ p.3 Fig. S5. Transient absorption spectra of Ar saturated solutions of 200 mM benzonbenone
- Fig. S5. Transient absorption spectra of Ar-saturated solutions of 200 mM benzophenonein cyclohexanone, pre-equilibrated with 1M HClO4 or HNO3p.4



Figure S1. Structural formulas of the investigated extracting ligands: (a) 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-[1,2,4-]triazin-3-yl)-[2,2'] bipyridine (CyMe4-BTBP), (b) 2,6-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-[1,2,4]triazin-3-yl)pyridine (CyMe₄-BTP).



Figure S2. Stationary UV-VIS absorption spectra of cyclohexanone: (a) pure, (b) pre-equilibrated with water, (c) pre-equilibrated with 1M HNO₃. The samples were not saturated with inert gas - they remained in equilibrium with air.



Figure S3. Stationary UV-VIS absorption spectra of solutions containing 0.1 mM of ligands in cyclohexanone: (a) $CyMe_4$ -BTP, (b) $CyMe_4$ -BTBP. The samples were not saturated with inert gas - they remained in equilibrium with air.

Transient species from cyclohexanone	Properties	Reference
triplet states of cyclohexanone ³ (c-Hex)	absorption band with λ_{max} at 280-320 nm, low intensity	J.C. Dalton, N.J. Turro, Annual Review of Physical Chemistry, 1970, 21, 499- 560
anion radicals of cyclohexanone (c-Hex)•-	absorption band with λ_{max} in the vicinity of 580 nm, too short lifetime at room temperature, absorption spectrum was recorded only at 77K	S. Arai, M. Hoshino and M. Imamura, The Journal of Physical Chemistry, 1975, 79, 702-707
neutral ketyl radicals of cyclohexanone (c-Hex)•	absorption band with λ_{max} at 230 nm	M. Simic, P. Neta and E. Hayon, The Journal of Physical Chemistry, 1969, 73, 3794-3800

Table ST1. Properties of the transient species derived from cyclohexanone during its radiolysis.



Figure S4. Transient absorption spectra recorded at different time points after an electron pulse during radiolysis of Ar-saturated samples: (a) pure cyclohexanone and (b) cyclohexanone pre-equilibrated with 1M HNO₃. Dose: 20 Gy/pulse.



Figure S5. Transient absorption spectra of Ar-saturated solutions of 200 mM benzophenone in cyclohexanone, pre-equilibrated with: (a) $1M \text{ HClO}_4$ and (b) $1M \text{ HNO}_3$. Dose: 20 Gy/pulse.