Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information: Influence of Uranyl Complexation on the Reaction Kinetics of the Dodecane Radical Cation with Used Nuclear Fuel Extraction Ligands (TBP, DEHBA, and DEH*i*BA)

Cristian Celis-Baros, Corey D. Pilgrim, Andrew R. Cook, Travis S. Grimes, Stephen P. Mezyk, and Gregory P. Horne

Kinect Figures

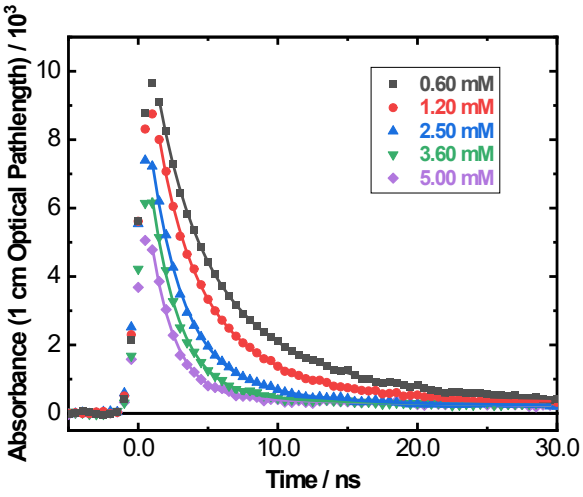

Fig. S1. Double-exponential fitting for $RH^{\bullet+}$ decays at 800 nm with $[UO_2(NO_3)_2(DEHBA)_2]$ in 0.5 M DCM/*n*-dodecane solution.

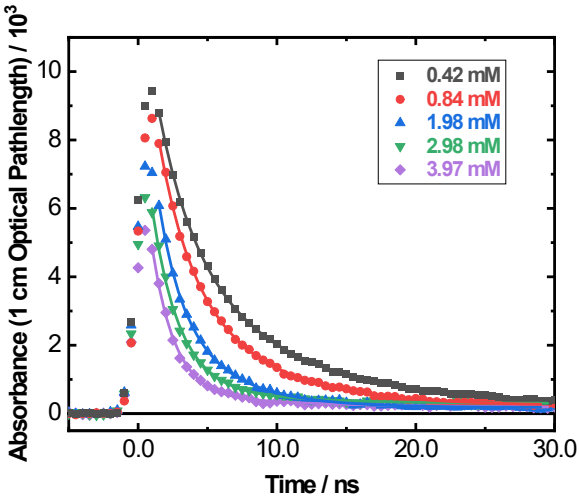

Fig. S2. Double-exponential fitting for $RH^{\bullet+}$ decays at 800 nm with $[UO_2(NO_3)_2(DEHiBA)_2]$ in 0.5 M DCM/*n*-dodecane solution.

Computational Figures and Tables

Table S1. Electronic structure calculation free energy (ΔG) values for the reaction of $RH^{\bullet+}$ with TBP, DEHBA, and DEH*i*BA for electron/hole transfer and proton transfer scenarios, without dispersion corrections in the geometries or energies.

Ligand	$\Delta G_{electron/hole\ transfer}$ (eV)	$\Delta G_{proton\ transfer}$ (eV)
TBP	0.33	-0.43
DEHBA	-1.03	-0.61
DEH*i*BA	-1.01	-0.61

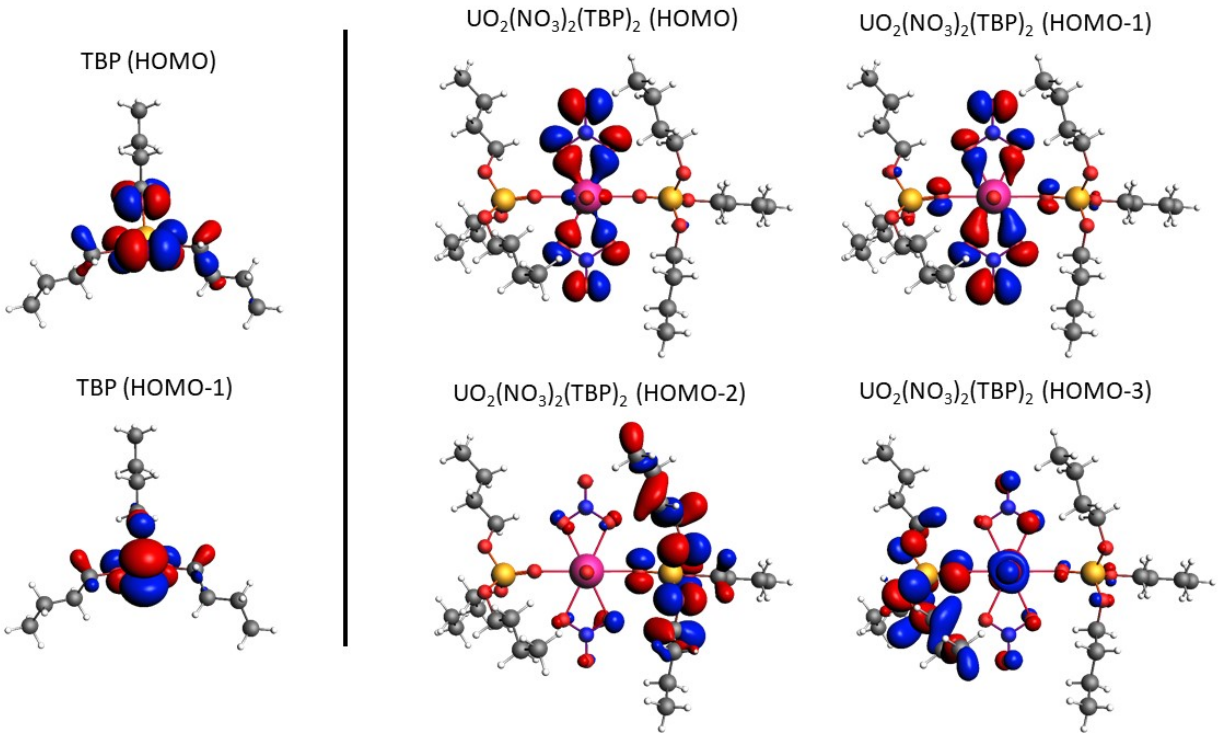

Fig. S3. Selected molecular orbitals of TBP (left panel) and the complexed uranyl compound (right panel).

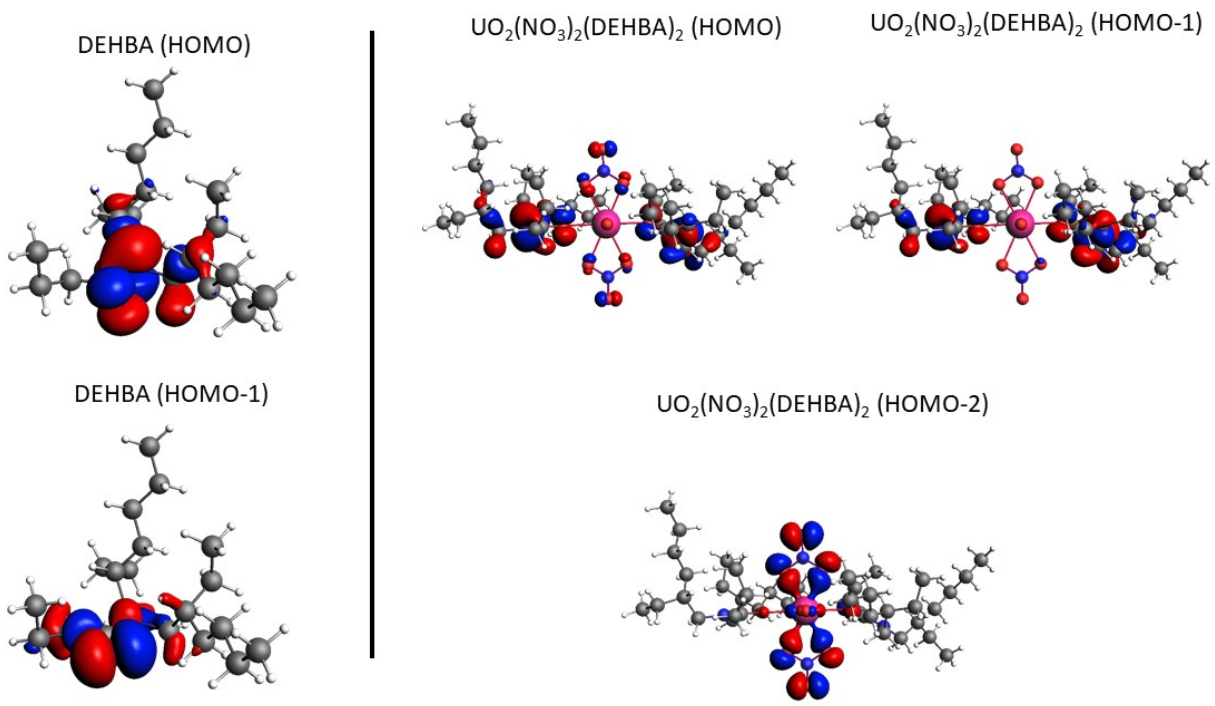

Fig. S4. Selected molecular orbitals of DEHBA (left panel) and the complexed uranyl compound (right panel).

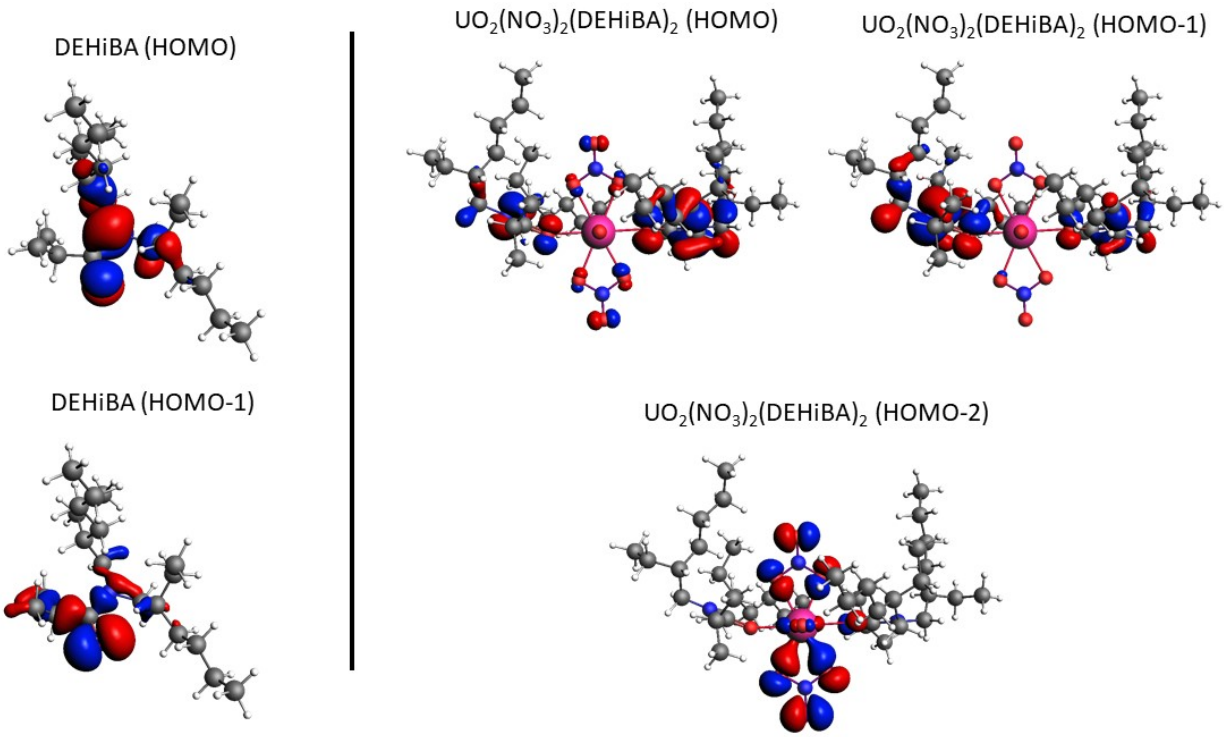

Fig. S5. Selected molecular orbitals of DEH*i*BA (left panel) and the complexed uranyl compound (right panel).

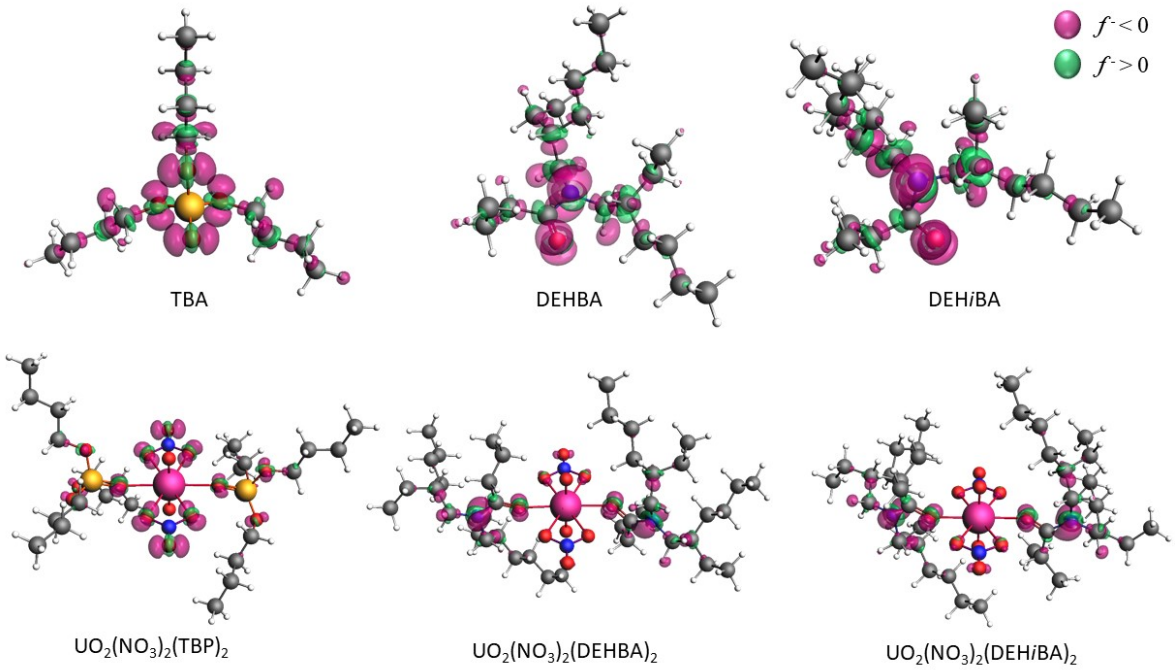

Fig. S6. Global electrophilic Fukui function (f^-) plots. The violet surfaces correspond to the regions where the Fukui function is negative while green surfaces to positive values. Uranium atoms are depicted in pink, carbon in grey, nitrogen in blue, sulfur in orange, and hydrogen in white.

Table S2. Selected bond lengths of the TBP-derived structures. All distances are given in Å.

	TBP	**TBP$^{\bullet+}$**	**$[UO_2(NO_3)_2(TBP)_2]$**		**$[UO_2(NO_3)_2(TBP)_2]^{\bullet+}$**	
			TBP1	**TBP2**	**TBP1**	**TBP2**
$P–O_{TBP}$	1.482	1.501	1.496	1.500	1.522	1.523
$P–OR1_{TBP}$	1.613	1.611	1.594	1.592	1.591	1.590
$P–OR2_{TBP}$	1.619	1.604	1.592	1.595	1.576	1.579
$P–OR3_{TBP}$	1.614	1.574	1.605	1.607	1.578	1.579
$P–OR_{avg}$	1.615	1.596	1.597	1.598	1.582	1.583
$U–O_{TBP}$	-	-	2.456	2.495	2.435	2.361
$U–O1_{YL}$	-	-	1.800		1.791	
$U–O2_{YL}$	-	-	1.795		1.786	
$U–O1_{NO3(a)}$	-	-	2.536		2.601	
$U–O2_{NO3(a)}$	-	-	2.524		2.595	
$U–O1_{NO3(b)}$	-	-	2.544		2.695	
$U–O2_{NO3(b)}$	-	-	2.521		2.687	

Table S3. Selected bond lengths of DEHBA-derived structures. All distances are given in Å.

	DEHBA	DEHBA$^{\bullet+}$	$[UO_2(NO_3)_2(DEHBA)_2]$		$[UO_2(NO_3)_2(DEHBA)_2]^{\bullet+}$	
			DEHBA1	DEHBA2	DEHBA1	DEHBA2
C=O	1.234	1.217	1.261	1.268	1.262	1.261
N–C	1.383	1.468	1.359	1.355	1.376	1.376
C–C_{pr}	1.532	1.510	1.516	1.514	1.509	1.509
U–O_{DEHBA}	-	-	2.426	2.431	2.455	2.452
U–$O1_{YL}$	-	-	1.808		1.800	
U–$O2_{YL}$	-	-	1.807		1.801	
U–$O1_{NO3(a)}$	-	-	2.533		2.529	
U–$O2_{NO3(a)}$	-	-	2.531		2.533	
U–$O1_{NO3(b)}$	-	-	2.523		2.523	
U–$O2_{NO3(b)}$	-	-	2.524		2.525	

Table S4. Selected bond lengths of DEH*i*BA-derived structures. All distances are given in Å.

	DEH*i*BA	DEH*i*BA$^{\bullet+}$	$[UO_2(NO_3)_2(DEHiBA)_2]$		$[UO_2(NO_3)_2(DEHiBA)_2]^{\bullet+}$	
			DEH*i*BA1	DEH*i*BA2	DEH*i*BA1	DEH*i*BA2
C=O	1.243	1.212	1.265	1.269	1.258	1.262
N–C	1.385	1.493	1.356	1.357	1.378	1.380
C–C_{ipr}	1.548	1.518	1.526	1.533	1.518	1.527
U–O_{DEHiBA}	-	-	2.429	2.425	2.446	2.448
U–$O1_{YL}$	-	-	1.809		1.802	
U–$O2_{YL}$	-	-	1.807		1.801	
U–$O1_{NO3(a)}$	-	-	2.511		2.514	
U–$O2_{NO3(a)}$	-	-	2.515		2.525	
U–$O1_{NO3(b)}$	-	-	2.543		2.527	
U–$O2_{NO3(b)}$	-	-	2.549		2.527	

Table S5. Condensed electrophilic Fukui function and electrophilic softness values of key atoms in TBP and $[UO_2(NO_3)_2(TBP)_2]$. L1 and L2 refer to ligands (TBP, O_{yl}, or NO_3).

	f_k^-			s_k^-		
	TBP	**$[UO_2(NO_3)_2(TBP)_2]$**		**TBP**	**$[UO_2(NO_3)_2(TBP)_2]$**	
		L1	**L2**		**L1**	**L2**
$O_{P=O}$	**0.136**	0.016	0.018	**0.430**	0.131	0.147
O_{OBu} (1)	0.121	0.026	0.014	0.383	0.212	0.114
O_{OBu} (2)	0.106	0.031	0.029	0.335	0.253	0.237
O_{OBu}(3)	0.093	0.021	0.025	0.294	0.171	0.204
$P_{O=P}$	0.032	0.019	0.020	0.101	0.155	0.163
O_{yl}	-	0.031	0.032	-	0.253	0.261
O_{NO3} (1)	-	0.067	0.063	-	0.539	0.506
O_{NO3} (2)	-	0.066	0.059	-	0.531	0.482
O_{NO3} (3)*	-	**0.106**	**0.100**	-	**0.857**	**0.808**
N_{NO3}	-	0.021	0.019	-	0.171	0.155

* O_{NO3} (3) corresponds to the nitrate's non-complexed oxygen atom.

Table S6. Condensed electrophilic Fukui function and electrophilic softness values of key atoms in DEHBA and $[UO_2(NO_3)_2(DEHBA)_2]$. L1 and L2 refer to ligands (DEHBA, O_{yl}, or NO_3).

	f_k^-			s_k^-		
	DEHBA	**$[UO_2(NO_3)_2(DEHBA)_2]$**		**DEHBA**	**$[UO_2(NO_3)_2(DEHBA)_2]$**	
		L1	**L2**		**L1**	**L2**
$O_{C=O}$	**0.167**	0.051	0.046	**0.639**	0.490	0.442
$C_{O=C}$	0.121	0.008	0.008	0.383	0.077	0.077
N_{DEHBA}	0.106	**0.068**	**0.069**	0.335	**0.653**	**0.662**
C_{propyl}	0.093	-0.006	-0.006	0.294	-0.058	-0.058
O_{yl}	-	0.016	0.021	-	0.154	0.202
O_{NO3} (1)	-	0.007	0.014	-	0.067	0.134
O_{NO3} (2)	-	0.000	0.015	-	0.000	0.144
O_{NO3} (3)*	-	0.041	0.046	-	0.394	0.442
N_{NO3}	-	0.006	0.007	-	0.058	0.067

* O_{NO3} (3) corresponds to the nitrate's non-complexed oxygen atom.

Table S7. Condensed electrophilic Fukui function and electrophilic softness values of key atoms in DEH*i*BA and $[UO_2(NO_3)_2(DEHiBA)_2]$. L1 and L2 refer to ligands (DEH*i*BA, O_{yl}, or NO_3).

	f_k^-			s_k^-		
	DEH*i*BA	**$UO_2(DEHiBA)_2(NO_3)_2$**		**DEH*i*BA**	**$UO_2(DEHiBA)_2(NO_3)_2$**	
		L1	**L2**		**L1**	**L2**
$O_{C=O}$	**0.171**	0.049	0.048	0.658	0.482	0.472
$C_{O=C}$	0.121	0.005	0.008	0.039	0.059	0.079
N_{DEHiBA}	0.106	**0.070**	**0.066**	**0.700**	**0.689**	**0.649**
C_{propyl}	0.093	-0.006	-0.011	-0.070	-0.059	-0.108
O_{yl}	-	0.015	0.019	-	0.148	0.187
O_{NO3} (1)	-	0.015	0.005	-	0.148	0.049
O_{NO3} (2)	-	0.009	0.007	-	0.089	0.069
O_{NO3} (3)*	-	0.047	0.035	-	0.462	0.344
N_{NO3}	-	0.007	0.007	-	0.069	0.069

* O_{NO3} (3) corresponds to the nitrate's non-complexed oxygen atom.

Table S8. Composition of natural localized molecular orbitals (NLMOs) in terms of natural hybrid orbitals (NHOs). The selected NLMOs correspond to the most relevant for the chemical bond based on their natural localized bond order (BO) contributions

	$[UO_2(NO_3)_2(TBP)_2]$			**$[UO_2(NO_3)_2(DEHBA)_2]$**			**$[UO_2(NO_3)_2(DEHiBA)_2]$**		
	BO	**Type**	**Composition**	**BO**	**Type**	**Composition**	**BO**	**Type**	**Composition**
$^aU–O_{yl}$	0.44	π	22% U (38 6d + 62 5f) 78% O (2p)	0.43	π	22% U (38 6d + 62 5f) 78% O (2p)	0.43	π	22% U (38 6d + 62 5f) 78 O (2p)
	0.44	π	22% U (39 6d + 61 5f) 78% O (2p)	0.43	π	22% U (39 6d + 61 5f) 78% O (2p)	0.43	π	22% U (39 6d + 61 5f) 78 O (2p)
	0.58	σ	29% U (18 6d + 82 5f) 70% O (2p)	0.57	σ	29% U (18 6d + 82 5f) 70% O (2p)	0.56	σ	29% U (18 6d + 82 5f) 70% O (2p)
$^aU–O_L$	0.07	σ	4% U (10 7s + 52 6d + 37 5f) 96 % TBP	0.15	σ	8% U (11 7s + 55 6d + 34 5f) 92 % DEHBA	0.15	σ	8% U (11 7s + 53 6d + 36 5f) 92 % DEHBA
	0.07	σ	4% U (10 7s + 50 6d + 40 5f) 96 % TBP	0.05	π	2% U (5 7s + 37 6d + 58 5f) 98 % DEHBA	0.04	π	2% U (1 7s + 34 6d + 65 5f) 98 % DEHBA

[a] Average values.