The Impact of Phase Modification on the Equilibrium and Kinetics of Lanthanide(III) Extraction from Nitric Acid Media by TODGA

Supplementary Information

Wyatt S. Nobley[1], Mark P. Jensen[1,2]*

[1] Chemistry Department, Colorado School of Mines, Golden, Colorado, USA

[2] Nuclear Science and Engineering Program, Colorado School of Mines, Golden, Colorado, USA

*Corresponding author E-mail: mjensen@mines.edu

ORCiD – Wyatt S. Nobley – 0009-0008-9657-4143

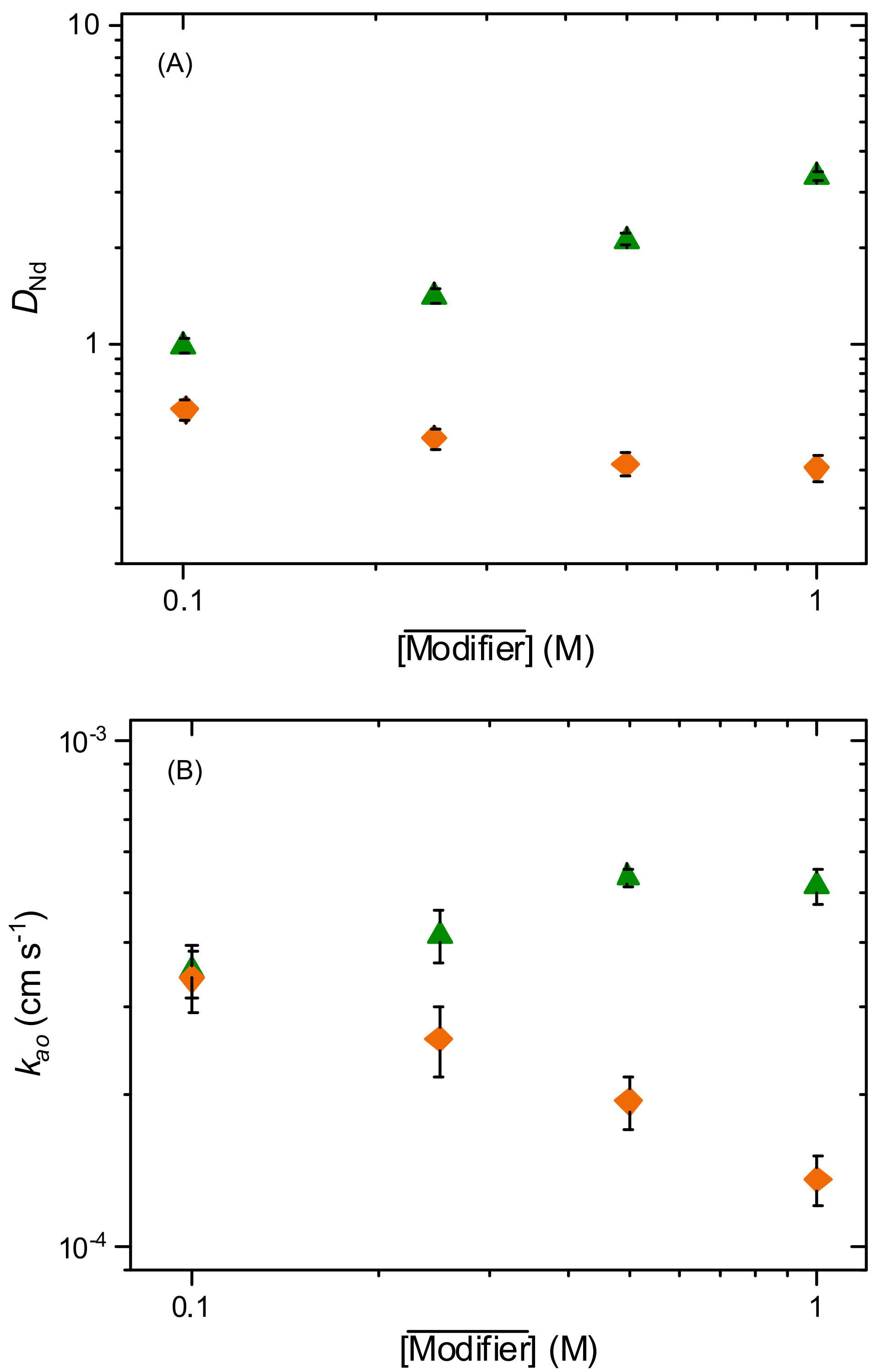
ORCiD – Mark P. Jensen – 0000-0003-4494-6693

Synthesis of TODGA

Synthesis of *N,N,N',N'*-tetra(*n*-octyl)diglycolamide (TODGA) was adapted from a published diglycolamide synthesis procedure.[1] Di(*n*-octyl)amine (0.33 mol) and triethylamine (0.35 mol) were dissolved in ~400 mL of methylene chloride (DCM) and stirred vigorously in a round bottom flask in an ice bath. Diglycolyl chloride (0.18 mol) was added dropwise while the reaction was flushed with argon gas. The reaction was allowed to progress at room temperature for 1-2 hours. The organic phase was washed with equal volumes of DI H_2O twice, 1 M HCl twice, and brine solution two or three times until it was clear. The DCM, containing TODGA and impurities, was dried over $MgSO_4$, filtered using a Büchner funnel and filter paper, and then removed under reduced pressure using a rotary evaporator. The crude product, with ~90% crude yield, was purified using column chromatography. Columns were packed with silica gel wet with 10% ethyl acetate (EtOAc) in hexanes. Crude product was loaded, and 10% EtOAc was used to elute the initial impurity band, then a gradient of 10-50% EtOAc in hexanes was used to elute purified TODGA from the column. The final product, at ~70% yield and 99+% purity, was concentrated under reduced pressure and characterized using ^{1}H NMR. (500 MHz, $CDCl_3$ δ 7.260, 20.4 °C, 64 scans), δ 0.874 (12H, m), δ 1.268 (40H, s), δ 1.513 (8H, m), δ 3.172 (4H, t), δ 3.285 (4H, t), δ 4.306 (4H, s).

Synthesis of DHOA

Synthesis of *N,N*-di(*n*-hexyl)octanamide (DHOA) was adapted from a published diglycolamide synthesis procedure.[2] Di(*n*-hexyl)amine (0.16 mol) and triethylamine (0.17 mol) were dissolved in ~200 mL of chloroform ($CHCl_3$) and stirred vigorously in a round bottom flask in an ice bath. Octanoyl chloride (0.16 mol) was added dropwise under an argon atmosphere at a slow rate to keep the reaction below 10 °C. The reaction was refluxed for 3 hours, then washed with equal volumes of 10 % sodium bicarbonate twice, 1 M HCl twice, DI water twice, and brine solution once. The $CHCl_3$, containing DHOA and impurities, was dried over $MgSO_4$, filtered through a filter paper in a Büchner funnel under light vacuum, and removed from the product under reduced pressure. The crude product (>95% yield) was purified using vacuum distillation. Impurities were collected initially at 100 °C and 3 torr. Purified, clear DHOA was collected at 175 °C and 2 torr with a condenser temperature of 25 °C due to the product solidifying at lower temperatures. The final product, at >80% yield and 99.5+% purity, was characterized using ^1H NMR. (500 MHz, $CDCl_3$ δ 7.260, 20.4 °C, 64 scans), δ 0.881 (9H, m), δ 1.283 (20H, d), δ 1.506 (4H, m), δ 1.625 (2H, m), δ 2.266 (2H, t), δ 3.190 (2H, t), δ 3.278 (2H, t).



(A)
10
1
D_Nd
0.1
1
[Modifier] (M)
(B)
10^-3
10^-4
k_ao (cm s^-1)
0.1
1
[Modifier] (M)

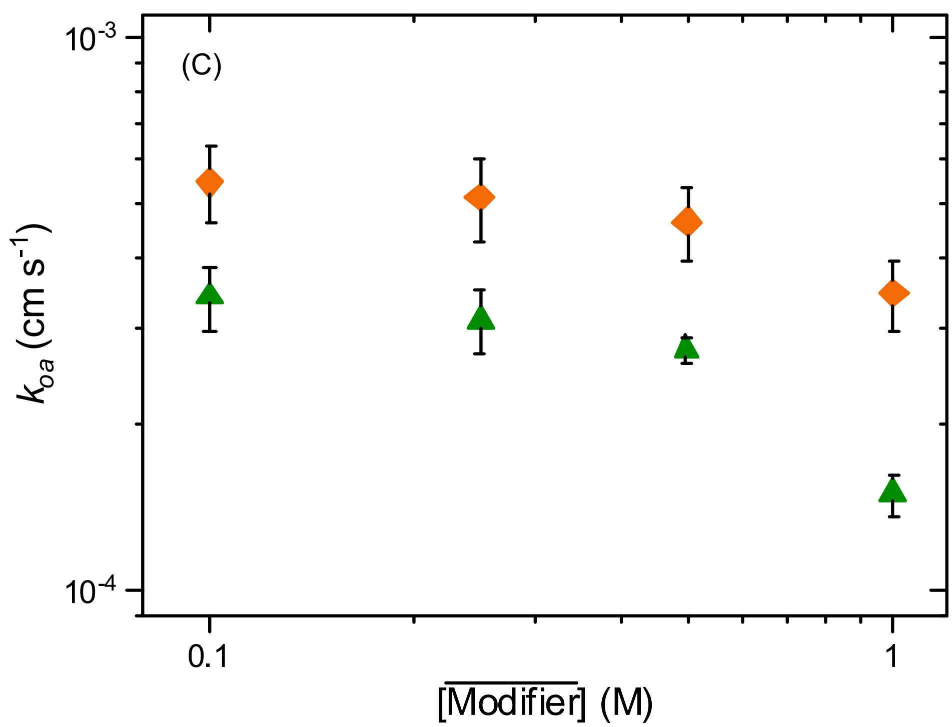


Figure S1. The logarithmic dependence of (A) the distribution ratio of Nd(III) D_{Nd}, (B) the absolute extraction rate constant k_{ao}, and (C) the absolute stripping rate constant k_{oa} on the organic DHOA (orange diamonds) or TBP (green triangles) concentration. Data collected from the solvent extraction of 4.90 mM Nd(III) in 0.50 M HNO_3 by solution of 0.10 M TODGA/PM/*n*-dodecane. The phase modifier concentration was varied from 0.10 – 1.0 M.

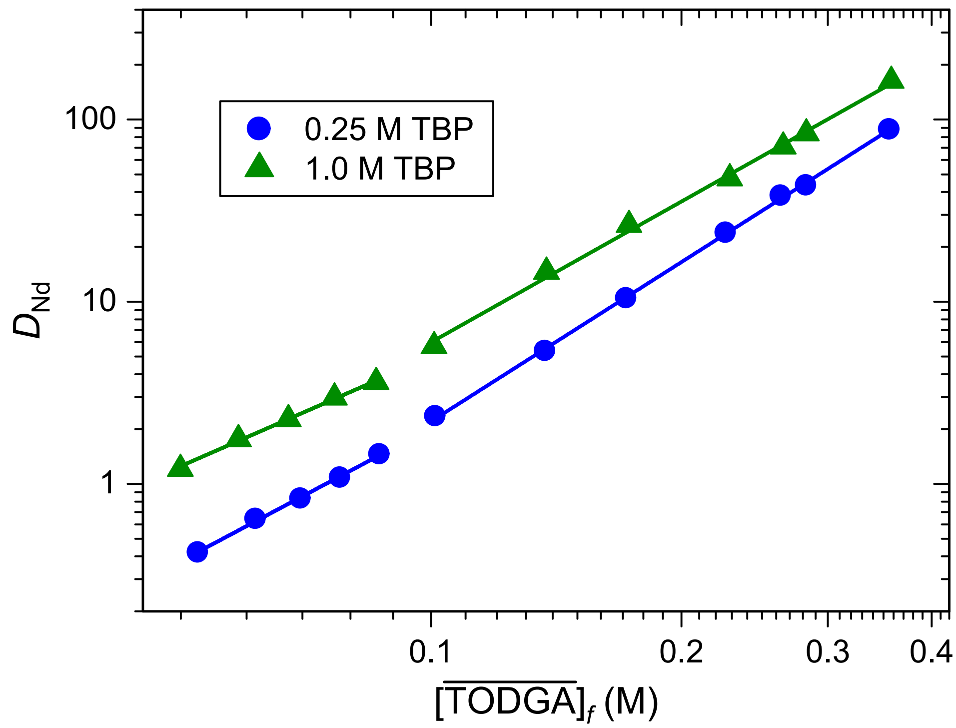


Figure S2. Dependence of D_{Nd} on free TODGA concentration with linear regions across 0.060 – 0.10 M initial TODGA and 0.12 – 0.40 M initial TODGA; (blue circles) 0.25 M TBP and (green triangles) 1.0 M TBP in *n*-dodecane.

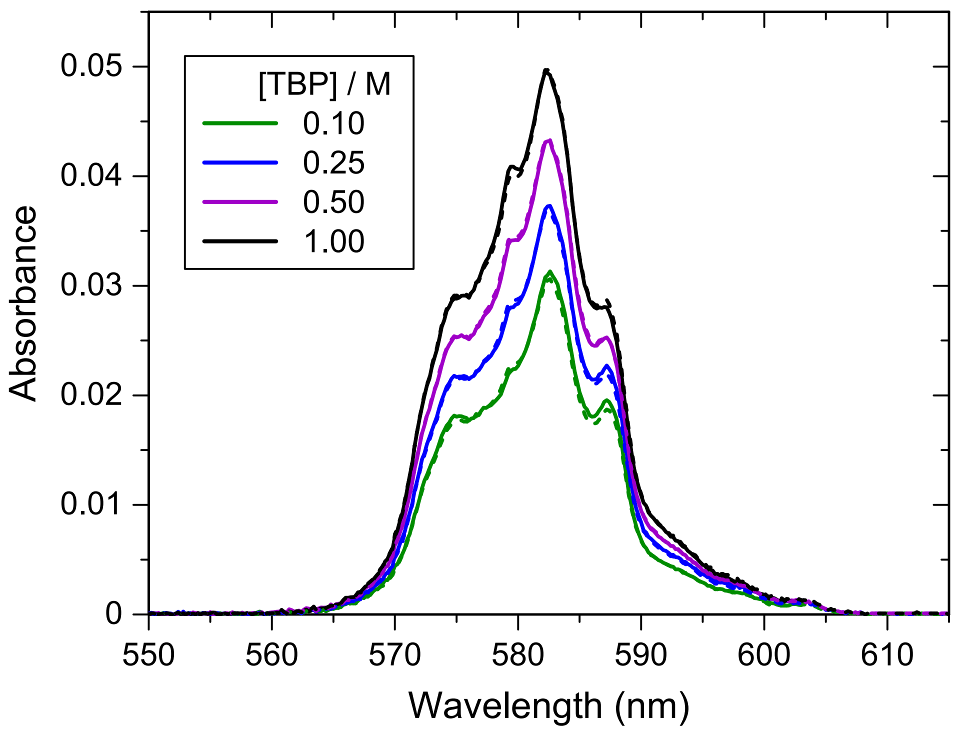


Figure S3. A comparison of the experimental organic phase spectra (solid lines) and the spectra calculated by SQUAD (dashed lines) using the best fitting equilibrium constant and molar absorptivities. The organic phases were 0.10 M TODGA + 0.10, 0.25, 0.50, 1.00 M TBP in *n*-dodecane. The aqueous phase was 4.90 mM Nd(III) in 0.50 M HNO_3.

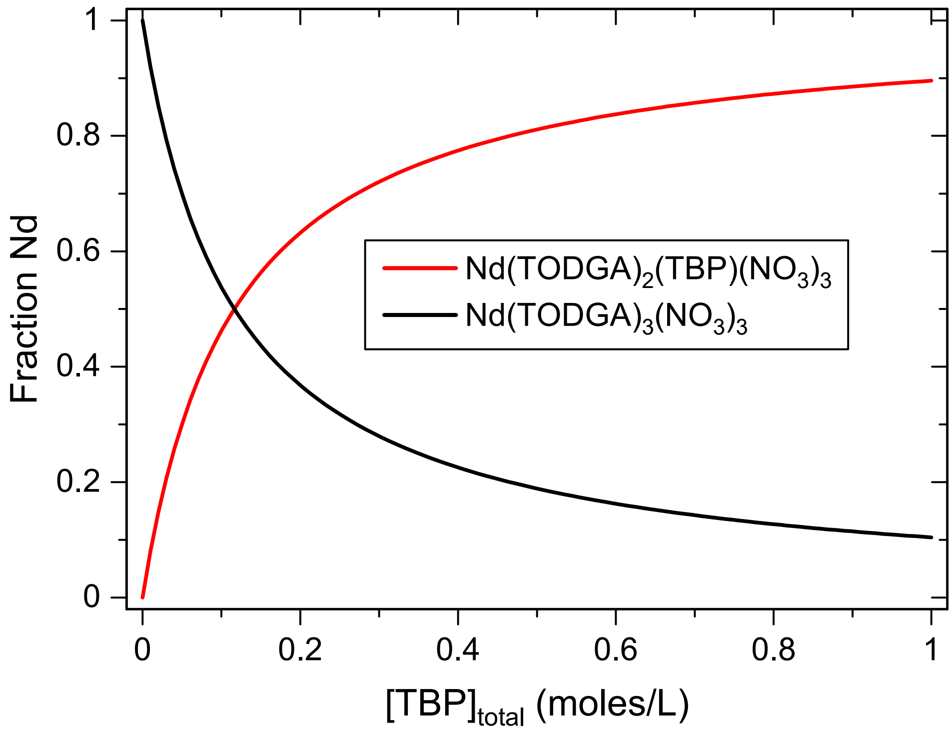


Figure S4. Speciation diagram of Nd complexes when adding TBP to 0.10 M TODGA in equilibrium with 0.50 M HNO_3 with K = 0.752 ± 0.043.

Correcting D_{Nd} *for Aqueous Activity and Free Extractant Concentration*

It is important to account for the consumption of TODGA by extracted nitric acid and neodymium(III), in order to obtain the amount of free TODGA, $TODGA_f$, which is the reactant in the equilibrium expression,

$$Nd^{3+} + l\,\overline{TODGA}_f + m\,H^+ + (n+m)\,NO_3^- \rightleftharpoons \overline{Nd(TODGA)_l(NO_3)_n \cdot m\,HNO_3} \tag{S1}$$

defined by the extraction constant, K_{ex}, which is a function of the activities of all the reactants and products involved,

$$K_{ex} = \frac{\{\overline{Nd(TODGA)_l(NO_3)_n \cdot (HNO_3)_m}\}}{\{Nd^{3+}\}\{\overline{TODGA}\}_f^{\,l}\{NO_3^-\}^{n+m}\{H^+\}^m} \tag{S2}$$

The activity coefficients of all the organic phase species are assumed to be constant since the composition of the organic phase varies little in the nitrate dependence experiments and are assigned a value of unity. The dissociation of HNO_3, aqueous phase activities, and free cation concentrations are treated in a similar manner as our previously published work.[3,4]

Although the activities in the organic phase are not used, the TODGA extractant is only available to extract Nd^{3+} if it is not bound to HNO_3 or Nd(III) in the organic phase. Therefore, the concentration of free TODGA, $[\overline{TODGA}]_f$, was calculated following the work of McLachlan et al. who found TODGA-HNO_3 adducts were present in TBP/*n*-dodecane solutions with 1:1 and 1:2 TODGA:HNO_3 ratios, while 1:3 and 1:4 complexes became important only at high acidities.[5] The extraction of HNO_3 in various ratios *x*:*y* was considered according to the equations

$$x\,\overline{TODGA}_f + y\,H^+ + y\,NO_3^- \rightleftharpoons \overline{(TODGA)_x(HNO_3)_y} \tag{S3}$$

and

$$\beta_{xy} = \frac{\overline{(TODGA)_x(HNO_3)_y}}{[\overline{TODGA}]_f^{\,x}\{H^+\}^y\{NO_3^-\}^y} \tag{S4}$$

Solving Equation S4 for $[\overline{TODGA}]_f$, using McLachlan's formation constants, the aqueous nitrate anion and proton activities, and the TODGA:Nd(III) stoichiometry in the extracted complex provided the free extractant concentration.

Table S1. Distribution ratio results reported in Figure 1.

[TODGA] (M)	D_{Nd} 0.25 M DHOA	2σ 0.25 M DHOA	D_{Nd} 1.0 M DHOA	2σ 1.0 M DHOA
0.061	0.127	0.018		
0.071	0.232	0.020	0.165	0.019
0.080	0.326	0.031	0.247	0.023
0.090	0.409	0.030	0.294	0.028
0.10	0.566	0.034	0.402	0.031
0.12	1.02	0.04	0.669	0.036
0.16	2.62	0.08	1.66	0.06
0.20	6.00	0.17	3.61	0.10
0.26	11.9	0.3	9.01	0.26
0.30	20.1	0.5	16.0	0.4
0.32	25.8	0.7	19.5	0.6
0.40	57.6	1.7	46.4	1.4

Table S2. Rate constant results reported in Figure 4A.

[TODGA] (M)	k_{ao} (cm s^{-1}) 0.25 M DHOA	2σ k_{ao} 0.25 M DHOA	k_{ao} (cm s^{-1}) 1.0 M DHOA	2σ k_{ao} 1.0 M DHOA
0.061	5.76×10^{-5}	1.69×10^{-5}		
0.071	1.05×10^{-4}	1.6×10^{-5}	5.32×10^{-5}	9.6×10^{-6}
0.080	1.65×10^{-4}	4.1×10^{-5}	7.88×10^{-5}	9.4×10^{-6}
0.090	2.19×10^{-4}	2.6×10^{-5}	1.08×10^{-4}	1.3×10^{-5}
0.10	2.96×10^{-4}	2.4×10^{-5}	1.38×10^{-4}	2.3×10^{-5}
0.12	4.60×10^{-4}	3.3×10^{-5}	2.22×10^{-4}	3.5×10^{-5}
0.16	7.23×10^{-4}	5.5×10^{-5}	3.93×10^{-4}	3.2×10^{-5}
0.20	9.35×10^{-4}	9.6×10^{-5}	5.61×10^{-4}	4.4×10^{-5}
0.26	9.39×10^{-4}	1.17×10^{-4}	7.24×10^{-4}	1.00×10^{-4}
0.30	1.04×10^{-3}	6×10^{-5}	6.95×10^{-4}	2.0×10^{-5}
0.32	1.10×10^{-3}	1.3×10^{-4}	7.45×10^{-4}	6.5×10^{-5}
0.40	1.09×10^{-3}	1.3×10^{-4}	8.81×10^{-4}	1.45×10^{-4}

Table S3. Rate constant results reported in Figure 4B.

[TODGA] (M)	***k_{oa}* (cm s^{-1}) 0.25 M DHOA**	**2σ *k_{oa}* 0.25 M DHOA**	***k_{oa}* (cm s^{-1}) 1.0 M DHOA**	**2σ *k_{oa}* 1.0 M DHOA**
0.061	4.41 x 10^{-4}	1.43 x 10^{-4}		
0.071	4.10 x 10^{-4}	7.1 x 10^{-5}	3.20 x 10^{-4}	6.8 x 10^{-5}
0.080	5.06 x 10^{-4}	1.35 x 10^{-4}	3.17 x 10^{-4}	4.8 x 10^{-5}
0.090	5.33 x 10^{-4}	7.5 x 10^{-5}	3.66 x 10^{-4}	5.6 x 10^{-5}
0.10	5.22 x 10^{-4}	5.3 x 10^{-5}	3.43 x 10^{-4}	6.2 x 10^{-5}
0.12	4.52 x 10^{-4}	3.8 x 10^{-5}	3.26 x 10^{-4}	5.4 x 10^{-5}
0.16	2.63 x 10^{-4}	2.2 x 10^{-5}	2.41 x 10^{-4}	2.1 x 10^{-5}
0.20	1.55 x 10^{-4}	1.6 x 10^{-5}	1.54 x 10^{-4}	1.3 x 10^{-5}
0.26	7.73 x 10^{-5}	9.8 x 10^{-6}	7.33 x 10^{-5}	1.03 x 10^{-5}
0.30	5.18 x 10^{-5}	3.5 x 10^{-6}	4.77 x 10^{-5}	1.9 x 10^{-6}
0.32	4.25 x 10^{-5}	5.1 x 10^{-6}	4.19 x 10^{-5}	3.9 x 10^{-6}
0.40	1.89 x 10^{-5}	2.2 x 10^{-6}	2.01 x 10^{-5}	3.3 x 10^{-6}

Table S4. Distribution ratio results reported in Figure 5.

$\{NO_3^-\}$	***D_{Nd}* 0.25 M DHOA**	**2σ 0.25 M DHOA**	***D_{Nd}* 1.0 M DHOA**	**2σ 1.0 M DHOA**
0.23	0.136	0.021	0.099	0.024
0.27	0.244	0.030	0.129	0.027
0.31	0.330	0.028	0.170	0.026
0.37	0.566	0.034	0.402	0.031
0.44	1.12	0.04	0.724	0.037
0.59	3.58	0.11	2.19	0.07
0.75	10.6	0.3	6.29	0.21
1.2	109	3	39.3	1.3
1.6	286	7	70.0	3.1
1.8	409	17	96.0	4.7
2.2	708	26	140.	9
2.7	1020	85	183	10

Table S5. Rate constant results reported in Figure 6A.

$\{NO_3^-\}$	k_{ao} (cm s^{-1}) 0.25 M DHOA	2σ k_{ao} 0.25 M DHOA	k_{ao} (cm s^{-1}) 1.0 M DHOA	2σ k_{ao} 1.0 M DHOA
0.23	7.65×10^{-5}	1.56×10^{-5}	2.91×10^{-5}	8.6×10^{-6}
0.27	1.20×10^{-4}	1.9×10^{-5}	4.77×10^{-5}	9.8×10^{-6}
0.31	1.69×10^{-4}	2.5×10^{-5}	6.75×10^{-5}	1.46×10^{-5}
0.37	2.96×10^{-4}	2.4×10^{-5}	1.38×10^{-4}	2.3×10^{-5}
0.44	4.79×10^{-4}	6.0×10^{-5}	2.26×10^{-4}	1.9×10^{-5}
0.59	7.54×10^{-4}	9.3×10^{-5}	4.62×10^{-4}	3.5×10^{-5}
0.75	9.20×10^{-4}	1.10×10^{-4}	6.69×10^{-4}	4.6×10^{-5}
1.2	1.28×10^{-3}	1.2×10^{-4}	7.39×10^{-4}	8.8×10^{-5}
1.6	1.30×10^{-3}	1.1×10^{-4}	7.04×10^{-4}	8.1×10^{-5}
1.8	1.36×10^{-3}	2.0×10^{-4}	7.50×10^{-4}	7.8×10^{-5}
2.2	1.31×10^{-3}	1.9×10^{-4}	8.23×10^{-4}	1.42×10^{-4}
2.7	1.40×10^{-3}	1.9×10^{-4}	6.86×10^{-4}	1.00×10^{-4}

Table S6. Rate constant results reported in Figure 6B.

$\{NO_3^-\}$	k_{oa} (cm s^{-1}) 0.25 M DHOA	2σ k_{oa} 0.25 M DHOA	k_{oa} (cm s^{-1}) 1.0 M DHOA	2σ k_{oa} 1.0 M DHOA
0.23	5.10×10^{-4}	1.30×10^{-4}	2.94×10^{-4}	1.13×10^{-4}
0.27	4.94×10^{-4}	9.9×10^{-5}	3.58×10^{-4}	1.04×10^{-4}
0.31	5.10×10^{-4}	8.9×10^{-5}	3.58×10^{-4}	9.5×10^{-5}
0.37	5.22×10^{-4}	5.3×10^{-5}	3.43×10^{-4}	6.2×10^{-5}
0.44	4.25×10^{-4}	5.6×10^{-5}	3.11×10^{-4}	3.0×10^{-5}
0.59	2.01×10^{-4}	2.5×10^{-5}	2.09×10^{-4}	1.7×10^{-5}
0.75	8.50×10^{-5}	1.05×10^{-5}	1.05×10^{-4}	8×10^{-6}
1.2	1.16×10^{-5}	1.1×10^{-6}	1.86×10^{-5}	2.3×10^{-6}
1.6	4.99×10^{-6}	4.5×10^{-7}	1.11×10^{-5}	1.4×10^{-6}
1.8	3.32×10^{-6}	5.1×10^{-7}	7.56×10^{-6}	8.7×10^{-7}
2.2	2.01×10^{-6}	3.0×10^{-7}	5.82×10^{-6}	1.06×10^{-6}
2.7	1.51×10^{-6}	2.4×10^{-7}	3.75×10^{-6}	5.8×10^{-7}

Table S7. Distribution ratio results reported in Figure 7 and Figure S2.

[TODGA]$_f$ (M) 0.25 M TBP	**D_{Nd} 0.25 M TBP**	**2σ 0.25 M TBP**	**[TODGA]$_f$ (M) 1.0 M TBP**	**D_{Nd} 1.0 M TBP**	**2σ 1.0 M TBP**
0.052	0.420	0.032	0.050	1.21	0.06
0.062	0.643	0.036	0.059	1.76	0.06
0.070	0.831	0.039	0.067	2.27	0.07
0.078	1.08	0.05	0.077	2.98	0.09
0.087	1.45	0.08	0.086	3.62	0.11
0.10	2.35	0.15	0.10	5.70	0.15
0.14	5.36	0.31	0.14	14.6	0.4
0.17	10.5	0.3	0.17	26.4	0.7
0.23	23.9	0.7	0.23	47.5	1.3
0.26	38.2	1.3	0.265	71.0	2.3
0.28	43.4	1.6	0.28	84.0	2.6
0.36	88.2	2.9	0.36	163	7

Table S8. Rate constant results reported in Figure 9A.

[TODGA]$_f$ (M) 0.25 M TBP	**k_{ao} (cm s^{-1}) 0.25 M TBP**	**2σ k_{ao} 0.25 M TBP**	**[TODGA]$_f$ (M) 1.0 M TBP**	**k_{ao} (cm s^{-1}) 1.0 M TBP**	**2σ k_{ao} 1.0 M TBP**
0.052	1.71×10^{-4}	2.7×10^{-5}	0.050	3.29×10^{-4}	2.6×10^{-5}
0.062	2.40×10^{-4}	2.0×10^{-5}	0.059	4.03×10^{-4}	3.3×10^{-5}
0.070	2.94×10^{-4}	4.0×10^{-5}	0.067	4.45×10^{-4}	3.3×10^{-5}
0.078	3.56×10^{-4}	3.8×10^{-5}	0.077	5.06×10^{-4}	4.1×10^{-5}
0.087	4.46×10^{-4}	5.8×10^{-5}	0.086	5.23×10^{-4}	3.7×10^{-5}
0.10	5.35×10^{-4}	7.5×10^{-5}	0.10	6.12×10^{-4}	2.6×10^{-5}
0.14	6.89×10^{-4}	7.3×10^{-5}	0.14	6.67×10^{-4}	4.7×10^{-5}
0.17	7.89×10^{-4}	1.03×10^{-4}	0.17	7.38×10^{-4}	1.15×10^{-4}
0.23	7.69×10^{-4}	7.9×10^{-5}	0.23	8.14×10^{-4}	5.8×10^{-5}
0.26	9.38×10^{-4}	$9.6\ 10^{-5}$	0.265	8.34×10^{-4}	5.7×10^{-5}

0.28	9.15 x 10^{-4}	6.5 x 10^{-5}	0.28	8.24 x 10^{-4}	9.7 x 10^{-5}
0.36	9.54 x 10^{-4}	8.4 x 10^{-5}	0.36	8.52 x 10^{-4}	6.8 x 10^{-5}

Table S9. Rate constant results reported in Figure 9B.

[TODGA]$_f$ (M) 0.25 M TBP	**k_{oa} (cm s^{-1}) 0.25 M TBP**	**2σ k_{oa} 0.25 M TBP**	**[TODGA]$_f$ (M) 1.0 M TBP**	**k_{oa} (cm s^{-1}) 1.0 M TBP**	**2σ k_{oa} 1.0 M TBP**
0.052	3.98 x 10^{-4}	7.2 x 10^{-5}	0.050	2.66 x 10^{-4}	2.4 x 10^{-5}
0.062	3.72 x 10^{-4}	3.7 x 10^{-5}	0.059	2.28 x 10^{-4}	2.0 x 10^{-5}
0.070	3.51 x 10^{-4}	5.1 x 10^{-5}	0.067	1.97 x 10^{-4}	1.6 x 10^{-5}
0.078	3.30 x 10^{-4}	3.8 x 10^{-5}	0.077	1.65 x 10^{-4}	1.4 x 10^{-5}
0.087	2.99 x 10^{-4}	4.0 x 10^{-5}	0.086	1.48 x 10^{-4}	1.1 x 10^{-5}
0.10	2.25 x 10^{-4}	3.3 x 10^{-5}	0.10	1.06 x 10^{-4}	5 x 10^{-6}
0.14	1.15 x 10^{-4}	1.3 x 10^{-5}	0.14	4.52 x 10^{-5}	3.4 x 10^{-6}
0.17	7.34 x 10^{-5}	9.8 x 10^{-6}	0.17	3.07 x 10^{-5}	4.8 x 10^{-6}
0.23	3.62 x 10^{-5}	3.8 x 10^{-6}	0.23	1.51 x 10^{-5}	1.1 x 10^{-6}
0.26	2.41 x 10^{-5}	2.5 x 10^{-6}	0.265	1.16 x 10^{-5}	9 x 10^{-7}
0.28	2.10 x 10^{-5}	1.7 x 10^{-6}	0.28	9.05 x 10^{-6}	1.10 x 10^{-6}
0.36	1.18 x 10^{-5}	1.1 x 10^{-6}	0.36	5.74 x 10^{-6}	5.2 x 10^{-7}

Table S10. Distribution ratio results reported in Figure 10.

$\{NO_3^-\}$	**D_{Nd} ± 2σ 0.25 M TBP**	**D_{Nd} ± 2σ 1.0 M TBP**	**D_c ± 2σ 0.25 M TBP**	**D_c ± 2σ 1.0 M TBP**
0.16	0.156 ± 0.022	0.694 ± 0.036	4.33 x 10^{2} ± 6.0 x 10^{1}	9.81 x 10^{2} ± 5.1 x 10^{1}
0.23	0.333 ± 0.030	1.49 ± 0.06	1.10 x 10^{3} ± 1.0 x 10^{2}	2.67 x 10^{3} ± 1.0 x 10^{2}
0.30	0.727 ± 0.037	2.75 ± 0.09	2.58 x 10^{3} ± 1.3 x 10^{2}	5.32 x 10^{3} ± 1.7 x 10^{2}
0.37	1.45 ± 0.05	3.60 ± 0.11	6.06 x 10^{3} ± 2.2 x 10^{2}	7.83 x 10^{3} ± 2.4 x 10^{2}
0.45	2.58 ± 0.08	8.45 ± 0.22	1.24 x 10^{4} ± 4 x 10^{2}	2.06 x 10^{4} ± 5 x 10^{2}
0.59	7.13 ± 0.18	18.3 ± 0.5	4.11 x 10^{4} ± 1.1 x 10^{3}	5.16 x 10^{4} ± 1.3 x 10^{3}
0.75	21.4 ± 0.6	42.2 ± 1.2	1.59 x 10^{5} ± 4 x 10^{3}	1.52 x 10^{5} ± 4 x 10^{3}
1.2	158 ± 5	117 ± 3	2.14 x 10^{6} ± 7 x 10^{4}	7.71 x 10^{5} ± 1.9 x 10^{4}
1.6	353 ± 9	223 ± 7	1.15 x 10^{7} ± 3 x 10^{5}	3.53 x 10^{6} ± 1.1 x 10^{5}
1.8	459 ± 18	290. ± 12	2.60 x 10^{7} ± 1.0 x 10^{6}	7.95 x 10^{6} ± 3.2 x 10^{5}

2.2	795 ± 35	382 ± 13	$9.65 \times 10^7 \pm 4.2 \times 10^6$	$2.20 \times 10^7 \pm 8 \times 10^5$
2.7	1130 ± 45	470. ± 18	$3.63 \times 10^8 \pm 1.5 \times 10^7$	$7.07 \times 10^7 \pm 2.7 \times 10^6$

Table S11. Rate constant results reported in Figure 11A.

$\{NO_3^-\}$	**k_{ao} (cm s^{-1}) 0.25 M TBP**	**2σ k_{ao} 0.25 M TBP**	**k_{ao} (cm s^{-1}) 1.0 M TBP**	**2σ k_{ao} 1.0 M TBP**
0.16	7.84×10^{-5}	1.52×10^{-5}	2.01×10^{-4}	1.7×10^{-5}
0.23	1.59×10^{-4}	2.4×10^{-5}	3.25×10^{-4}	1.2×10^{-5}
0.30	2.91×10^{-4}	2.3×10^{-5}	4.54×10^{-4}	1.5×10^{-5}
0.37	4.46×10^{-4}	5.8×10^{-5}	5.23×10^{-4}	3.7×10^{-5}
0.45	5.40×10^{-4}	1.8×10^{-5}	6.37×10^{-4}	2.7×10^{-5}
0.59	7.10×10^{-4}	4.1×10^{-5}	7.83×10^{-4}	3.3×10^{-5}
0.75	7.18×10^{-4}	8.7×10^{-5}	8.28×10^{-4}	5.9×10^{-5}
1.2	8.57×10^{-4}	1.58×10^{-4}	9.85×10^{-4}	7.0×10^{-5}
1.6	8.62×10^{-4}	1.58×10^{-4}	1.01×10^{-3}	8×10^{-5}
1.8	9.59×10^{-4}	7.8×10^{-5}	9.93×10^{-4}	8.8×10^{-5}
2.2	8.57×10^{-4}	1.16×10^{-4}	9.95×10^{-4}	8.9×10^{-5}
2.7	9.70×10^{-4}	1.21×10^{-4}	9.97×10^{-4}	8.3×10^{-5}

Table S12. Rate constant results reported in Figure 11B.

$\{NO_3^-\}$	**k_{oa} (cm s^{-1}) 0.25 M TBP**	**2σ k_{oa} 0.25 M TBP**	**k_{oa} (cm s^{-1}) 1.0 M TBP**	**2σ k_{oa} 1.0 M TBP**
0.16	5.03×10^{-4}	1.20×10^{-4}	2.89×10^{-4}	2.8×10^{-5}
0.23	4.53×10^{-4}	8.0×10^{-5}	2.16×10^{-4}	1.1×10^{-5}
0.30	4.01×10^{-4}	3.8×10^{-5}	1.69×10^{-4}	8×10^{-6}
0.37	2.99×10^{-4}	4.0×10^{-5}	1.48×10^{-4}	1.1×10^{-5}
0.45	2.10×10^{-4}	1.0×10^{-5}	7.87×10^{-5}	3.9×10^{-6}
0.59	9.96×10^{-5}	6.3×10^{-6}	4.13×10^{-5}	2.0×10^{-6}
0.75	3.64×10^{-5}	4.5×10^{-6}	2.16×10^{-5}	1.7×10^{-6}
1.2	5.98×10^{-6}	1.12×10^{-6}	8.26×10^{-6}	6.2×10^{-7}

1.6	2.67 x 10^{-6}	4.9 x 10^{-7}	4.98 x 10^{-6}	4.3 x 10^{-7}
1.8	2.10 x 10^{-6}	1.9 x 10^{-7}	3.76 x 10^{-6}	3.6 x 10^{-7}
2.2	1.18 x 10^{-6}	1.7 x 10^{-7}	2.87 x 10^{-6}	2.8 x 10^{-7}
2.7	8.65 x 10^{-7}	1.14 x 10^{-7}	2.12 x 10^{-6}	1.9 x 10^{-7}

Table S13. Distribution ratio and rate constant results reported in Figure S1.

[Modifier] (M)	D_{Nd} **± 2σ**	k_{ao} **± 2σ (cm s^{-1})**	k_{oa} **± 2σ (cm s^{-1})**
0.10 DHOA	0.615 ± 0.042	3.39 x 10^{-4} ± 4.7 x 10^{-5}	5.48 x 10^{-4} ± 8.4 x 10^{-5}
0.25 DHOA	0.499 ± 0.040	2.57 x 10^{-4} ± 3.9 x 10^{-5}	5.14 x 10^{-4} ± 8.9 x 10^{-5}
0.50 DHOA	0.416 ± 0.039	1.94 x 10^{-4} ± 2.2 x 10^{-5}	4.65 x 10^{-4} ± 6.9 x 10^{-5}
1.0 DHOA	0.401 ± 0.038	1.36 x 10^{-4} ± 1.5 x 10^{-5}	3.46 x 10^{-4} ± 5.1 x 10^{-5}
0.10 TBP	0.984 ± 0.049	3.52 x 10^{-4} ± 4.2 x 10^{-5}	3.40 x 10^{-4} ± 4.4 x 10^{-5}
0.25 TBP	1.41 ± 0.06	4.14 x 10^{-4} ± 4.9 x 10^{-5}	3.09 x 10^{-4} ± 3.9 x 10^{-5}
0.50 TBP	2.12 ± 0.09	5.39 x 10^{-4} ± 2.2 x 10^{-5}	2.73 x 10^{-4} ± 1.6 x 10^{-5}
1.0 TBP	3.36 ± 0.12	5.17 x 10^{-4} ± 4.0 x 10^{-5}	1.49 x 10^{-4} ± 1.3 x 10^{-5}

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