Supporting Information for:

Speciation of the Products of and Establishing the Role of Water in the Reaction of TNT with Hydroxide and Amines: Structure, Kinetics, and Computational Results

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Table S1. Thermodynamic parameters for explored bases and conjugate acids calculated at the B3LYP/6-31G*//HF/6-311G** level of theory in vacuum.

Species	E° (kJ/mol)	G° (kJ/mol)	H° (kJ/mol)	S° (J/mol·K)
OH^-	-198800.88	-198818.23	-198766.98	171.87
H_2O	-200607.82	-200594.42	-200538.35	188.06
MeO^-	-302114.61	-302074.28	-302008.59	220.33
MeOH	-303804.09	-303727.93	-303656.21	240.55
NH_3	-148464.02	-148418.43	-148361.11	192.26
NH_4^+	-149372.42	-149282.88	-149227.57	185.49
EA	-354885.93	-354709.00	-354626.88	275.42
H^+-EA	-355849.87	-355632.36	-355549.64	277.42
DEA	-561308.42	-560991.27	-560893.68	327.33
H^+-DEA	-562313.12	-561955.24	-561857.15	328.99
TEA	-767734.80	-767274.25	-767165.83	363.64
H^+-TEA	-768758.73	-768256.17	-768147.38	364.89
TNT	-2323635.89	-2323372.85	-2323239.18	448.36
TNT^-	-2322240.20	-2322009.11	-2321877.65	440.89
TNT-OH^- C_1	-2522923.85	-2522626.67	-2522486.23	471.07
TNT-OH^- C_3	-2522897.48	-2522599.74	-2522459.25	471.22
TNT-OCH_3^- C_1	-2626098.64	-2625728.68	-2625583.02	488.53
TNT-OCH_3^- C_3	-2626101.98	-2625730.52	-2625585.54	486.27
TNT-NH_3 C_1	-2472083.14	-2471713.47	-2471572.26	473.60
TNT-NH_3 C_3	-2472070.00	-2471700.81	-2471559.24	474.80
$[NH_4^+][TNT^-]$	-2472034.25	-2471677.78	-2471530.46	494.10
TNT-EA C_1	-2678527.92	-2678013.89	-2677861.69	510.49
TNT-EA C_3	-2678514.90	-2678000.44	-2677848.37	510.02
$[H^+$-EA$][TNT^-]$	-2678479.61	-2677974.95	-2677818.63	524.32
TNT-DEA C_1	-2884907.43	-2884248.77	-2884085.42	547.90
TNT-DEA C_3	-2884914.24	-2884255.68	-2884092.69	546.69
$[H^+$-DEA$][TNT^-]$	-2884920.78	-2884270.09	-2884103.72	558.02
$[H^+$-TEA$][TNT^-]$	-3091314.59	-3090518.53	-3090341.18	594.81

Table S2. Structural parameters from TNT products optimized at the HF/6-311+G** level. Note that "B" refers to the bonding site of the nucleophile, and the nomenclature of parameters for C_1 adducts represents the nucleophile coming out of plane as shown in Scheme 1.

	Bond Lengths (Å)							
Species	B – C_1	C_1-C_7	C_1-C_2	C_1-C_6	C_2-C_3	C_5-C_6	C_3-C_4	C_4-C_5
TNT	-	1.513	1.395	1.395	1.378	1.378	1.376	1.376
TNT^-	-	1.335	1.489	1.489	1.355	1.353	1.401	1.402
$[NH_4^+][TNT^-]$	-	1.331	1.477	1.477	1.361	1.361	1.399	1.399
$[H^+$-EA$][TNT^-]$	-	1.331	1.478	1.478	1.361	1.360	1.399	1.399
$[H^+$-DEA$][TNT^-]$	-	1.331	1.478	1.478	1.360	1.360	1.399	1.400
$[H^+$-TEA$][TNT^-]$	-	1.332	1.481	1.481	1.348	1.376	1.414	1.382
TNT-OH^- C_1	1.408	1.543	1.536	1.528	1.355	1.342	1.397	1.414
TNT-OCH_3^- C_1	1.418	1.545	1.533	1.533	1.349	1.349	1.405	1.405
TNT-NH_3 C_1	1.541	1.542	1.519	1.519	1.360	1.360	1.392	1.392
TNT-EA C_1	1.540	1.545	1.522	1.522	1.359	1.359	1.393	1.393
TNT-DEA C_1	1.597	1.544	1.521	1.528	1.357	1.361	1.395	1.389
TNT-OH^- C_3	1.422	1.517	1.352	1.448	1.508	1.405	1.493	1.350
TNT-OCH_3^- C_3	1.420	1.516	1.374	1.430	1.509	1.411	1.494	1.344
TNT-NH_3 C_3	1.561	1.514	1.383	1.419	1.495	1.396	1.480	1.354
TNT-EA C_3	1.554	1.515	1.382	1.419	1.499	1.398	1.483	1.352
TNT-DEA C_3	1.584	1.515	1.392	1.413	1.496	1.403	1.486	1.349

	Bond Angles (°)					Dihedral Angles (°)		
Species	C_2-C_1-C_6	C_2-C_3-C_4	O-N-O (C_2)	O-N-O (C_6)	O-N-O (C_4)	C_1-C_2-C_3-C_4	C_7-C_1-C_2-C_3	B-C_1-C_2-C_3
TNT	114.00	118.09	125.60	125.60	125.73	1.26	174.56	-
TNT^-	110.38	120.91	122.20	122.28	122.49	4.90	162.29	-
$[NH_4^+][TNT^-]$	110.07	119.51	121.91	121.92	123.97	10.41	143.96	-
$[H^+$-EA$][TNT^-]$	110.14	119.63	122.02	122.07	123.89	10.22	144.94	-
$[H^+$-DEA$][TNT^-]$	110.16	119.67	122.09	122.13	123.83	10.18	145.20	-
$[H^+$-TEA$][TNT^-]$	110.33	119.73	123.04	120.98	123.77	8.07	149.96	-
TNT-OH^- C_1	106.59	120.86	121.66	122.59	122.31	3.67	112.27	124.86
TNT-OCH_3^- C_1	106.37	121.11	122.09	122.10	122.24	1.44	112.76	121.44
TNT-NH_3 C_1	107.88	121.24	122.72	122.72	124.22	4.74	91.70	126.68
TNT-EA C_1	107.81	121.25	122.57	122.57	124.11	4.49	115.00	127.84
TNT-DEA C_1	106.77	121.65	123.06	122.56	124.07	1.12	121.90	114.76
TNT-OH^- C_3	116.15	108.46	123.02	121.47	122.84	20.29	177.53	100.79
TNT-OCH_3^- C_3	116.24	107.64	121.83	121.47	122.67	29.28	159.57	90.78
TNT-NH_3 C_3	116.69	110.48	122.70	123.44	123.69	12.68	169.12	109.28
TNT-EA C_3	116.67	110.15	122.49	123.32	123.51	13.37	168.87	110.81
TNT-DEA C_3	116.57	109.06	122.43	123.29	123.74	24.13	164.56	97.53

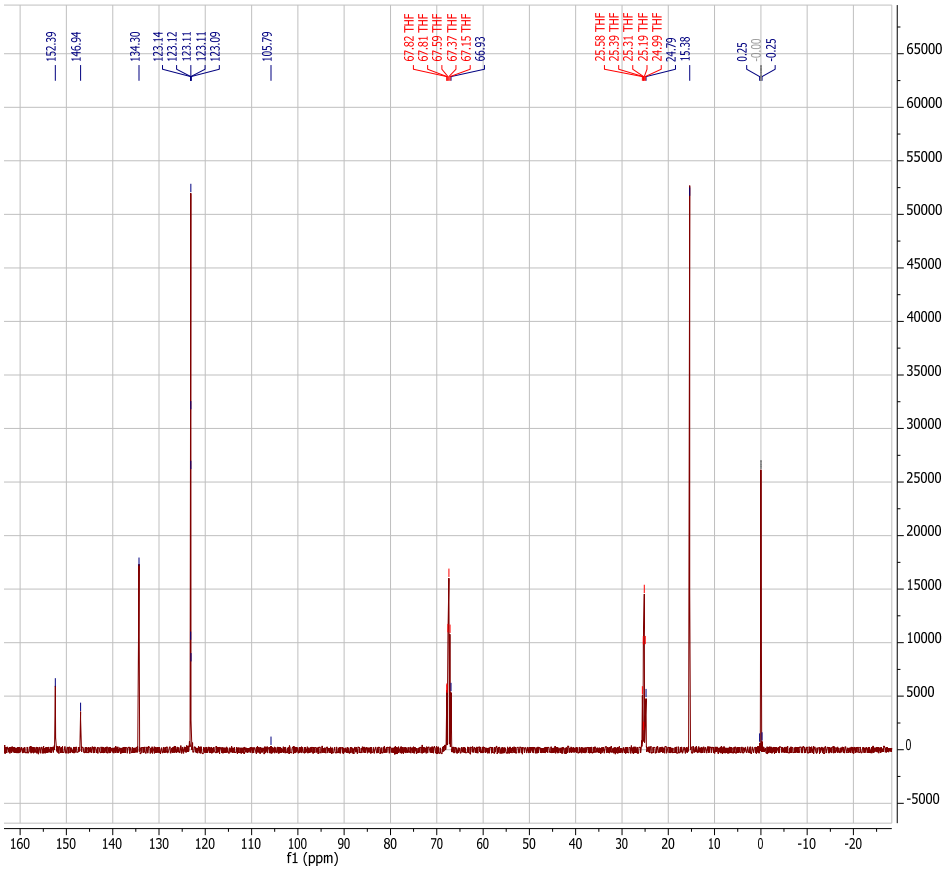

Figure S1. ^{13}C NMR spectrum of TNT in d_8-THF prior to addition of base.

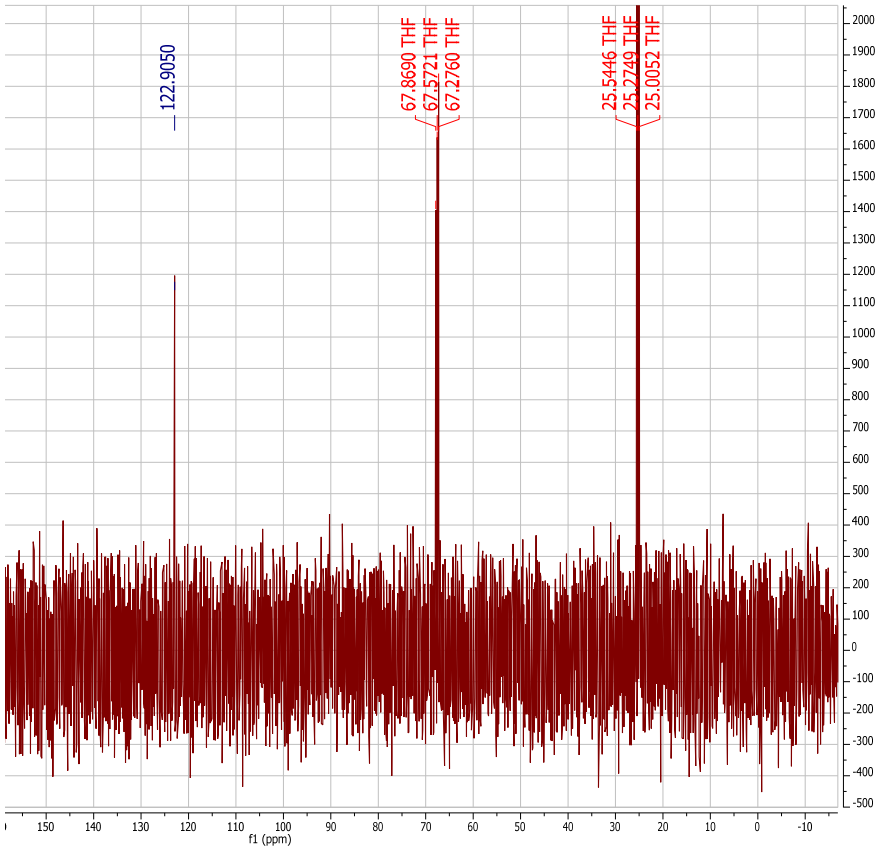

Figure S2. ^{13}C DEPT 135 spectrum of TNT + excess NaOD in d_8-THF followed by addition of excess DCl.

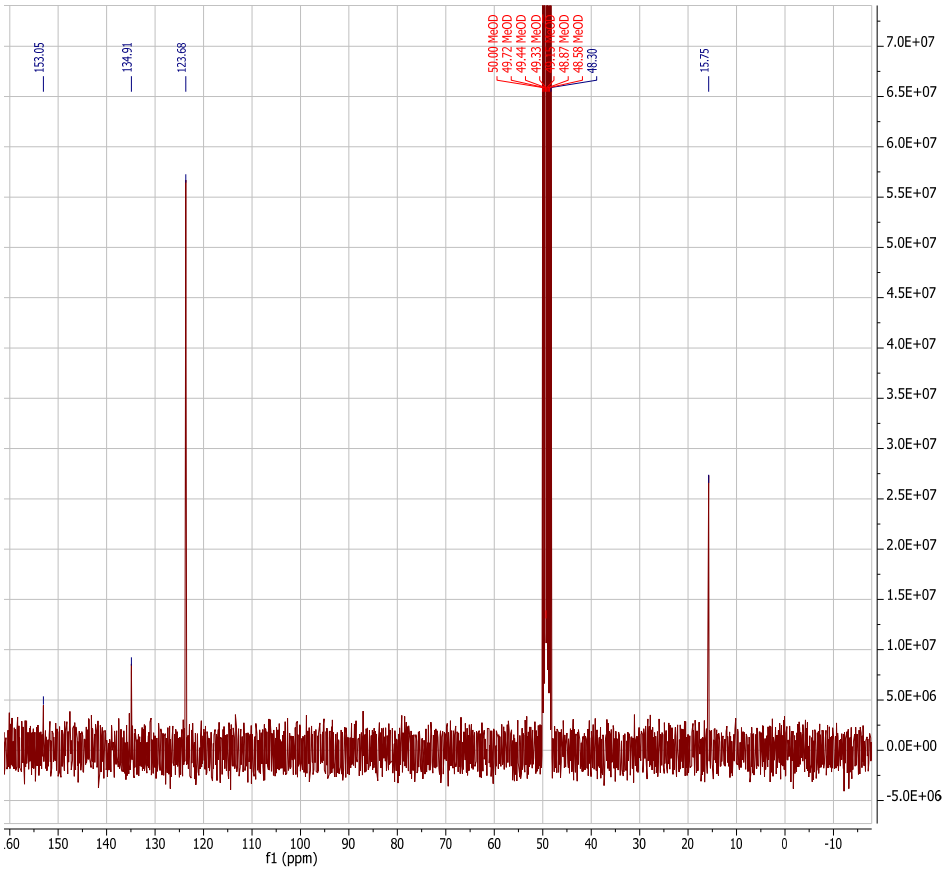

Figure S3. ^{13}C NMR spectrum of TNT in CD_3OD before addition of base.

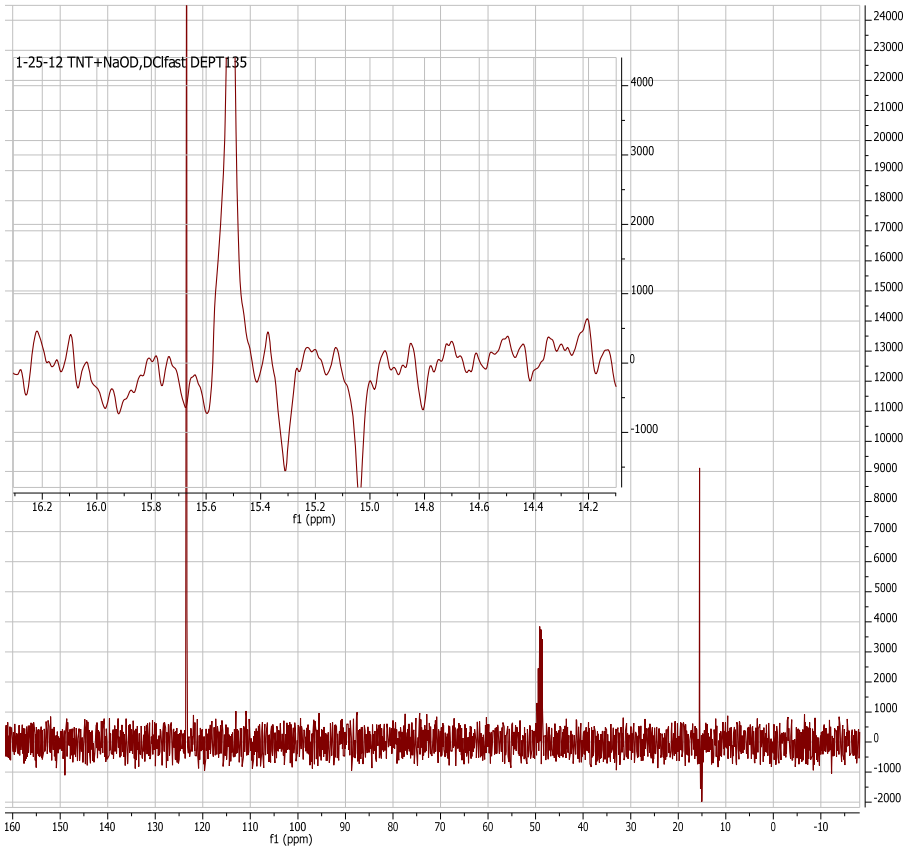

Figure S4. ^{13}C DEPT 135 spectrum of TNT + excess NaOD followed by addition of excess DCl in CD_3OD. The inset is a zoomed view of the 14 ppm to 17 ppm region, where negative features can be observed consistent with the deprotonation and re-deuteration of TNT.

Kinetic Model Derivation:

For the competing equilibrium reactions between TNT and hydroxide (or methoxide):

$$TNT(solv) + OH^-(solv) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} TNT^-(solv) + H_2O(solv) \qquad [S1]$$

$$TNT(solv) + OH^-(solv) \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} TNT - OH^-(solv) \qquad [S2]$$

We cannot assume one equilibrium is much faster than the other, because we observe both on a similar timescale. Therefore, they must be solved simultaneously.

The mass balance and charge balance conditions require:

$$[TNT]_o = [TNT] + [TNT^-] + [TNTOH^-] \qquad [S3]$$

$$[OH^-]_o + [H_2O]_o = [OH^-] + [H_2O] + [TNTOH^-] \quad [S4]$$

$$[OH^-]_o = [OH^-] + [TNT^-] + [TNTOH^-] \qquad [S5]$$

The latter two equations can be combined to show:

$$[H_2O] = [TNT^-] + [H_2O]_o \qquad [S6]$$

The differential equations are:

$$\frac{d[TNT^-]}{dt} = k_1[TNT][OH^-] - k_{-1}[TNT^-][H_2O] \qquad [S7]$$

$$\frac{d[TNTOH^-]}{dt} = k_2[TNT][OH^-] - k_{-2}[TNTOH^-] \qquad [S8]$$

Case 1: $[OH^-]_o >> [TNT]_o$, so that $[OH^-] \sim [OH^-]_o$

Using S3 and S6 gives:

$$\frac{d[TNT^-]}{dt} = k_1[OH^-]_o([TNT]_o - [TNT^-] - [TNTOH^-]) - k_{-1}[H_2O]_o[TNT^-] - k_{-1}[TNT^-]^2 \qquad [S9]$$

$$\frac{d[TNTOH^-]}{dt} = k_2[OH^-]_o([TNT]_o - [TNT^-] - [TNTOH^-]) - k_{-2}[TNTOH^-] \quad [S10]$$

Equation S4 and S6 is used to substitute for [TNTOH$^-$] and [H_2O], respectively, in S9 and S5 is used to substitute for [TNT$^-$] in S10:

$$\frac{d[TNT^-]}{dt} = k_1[OH^-]_o([TNT]_o - [TNT^-] - ([OH^-]_o + [H_2O]_o - [OH^-] - [TNT^-] - [H_2O]_o)) - k_{-1}[H_2O]_o[TNT^-] - k_{-1}[TNT^-]^2 \quad [S11]$$

$$\frac{d[TNTOH^-]}{dt} = k_2[OH^-]_o([TNT]_o - ([OH^-]_o - [OH^-] - [TNTOH^-]) - [TNTOH^-]) - k_{-2}[TNTOH^-] \quad [S12]$$

Collecting terms gives:

$$\frac{d[TNT^-]}{dt} = k_1[OH^-]_o([TNT]_o - [OH^-]_o + [OH^-]) - k_{-1}[H_2O]_o[TNT^-] - k_{-1}[TNT^-]^2 \quad [S13]$$

$$\frac{d[TNTOH^-]}{dt} = k_2[OH^-]_o([TNT]_o - [OH^-]_o + [OH^-]) - k_{-2}[TNTOH^-] \quad [S14]$$

$$\frac{d[TNT^-]}{dt} = k_1[OH^-]_o[TNT]_o - k_{-1}[H_2O]_o[TNT^-] - k_{-1}[TNT^-]^2 \quad [S15]$$

$$\frac{d[TNTOH^-]}{dt} = k_2[OH^-]_o[TNT]_o - k_{-2}[TNTOH^-] \quad [S16]$$

These solve to give

$$[TNT^-] = \frac{2k_1[OH^-]_o[TNT]_o}{k_{obs}(1+e^{-k_{obs}t}) + k_{-1}[H_2O]_o(1-e^{-k_{obs}t})}(1-e^{-k_{obs}t}) \qquad [S17]$$

$$[TNTOH^-] = \frac{k_2[OH^-]_o[TNT]_o}{k_{-2}}(1-e^{-k_{-2}t}) \qquad [S18]$$

where $k_{obs} = \sqrt{k_{-1}^2[H_2O]_o^2 + k_1k_{-1}[OH^-]_o[TNT]_o}$

in the case $k_{-1}^2[H_2O]_o^2 \gg k_1k_{-1}[OH^-]_o[TNT]_o$, which is always the case in this work S17 becomes

$$[TNT^-] = \frac{k_1[OH^-]_o[TNT]_o}{k_{obs}}(1-e^{-k_{obs}t}) \qquad [S19]$$

where $k_{obs} = k_{-1}[H_2O]_o$.

Case 2: $[TNT]_o \gg [OH^-]_o$, so that $[TNT^-] \sim [TNT]_o$

Using S3 to substitute for $[TNTOH^-]$ in S7, S4 to substitute for $[OH^-]$ in S7 and S8, S3 to substitute for $[H_2O]$ in S7 and collecting terms gives equations S15 and S16 and the same solutions as above.

TNT + NaOH in THF

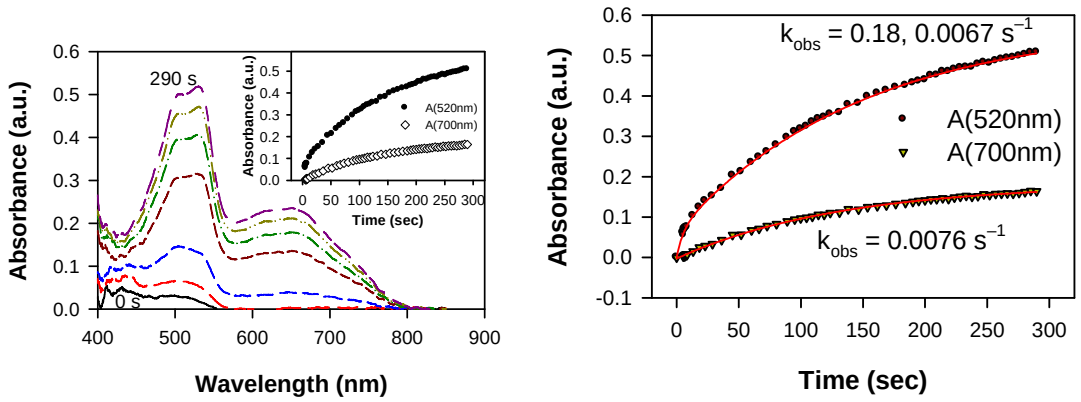

Figure S5. Absorbance evolution for the reaction of 1TNT + 100NaOH in THF, where [TNT] = 4.2×10^{-5} M and $[OH^-] = 4.2\times10^{-3}$ M. The left figure shows absorbance growth in the visible range comprised of two discernible products, TNT-OH^- and TNT^-. The right figure shows the absorbance data at 520 nm and at 700 nm as a function of time. The data have been fit to equations S18 and S19, with the observed rate constants indicated.

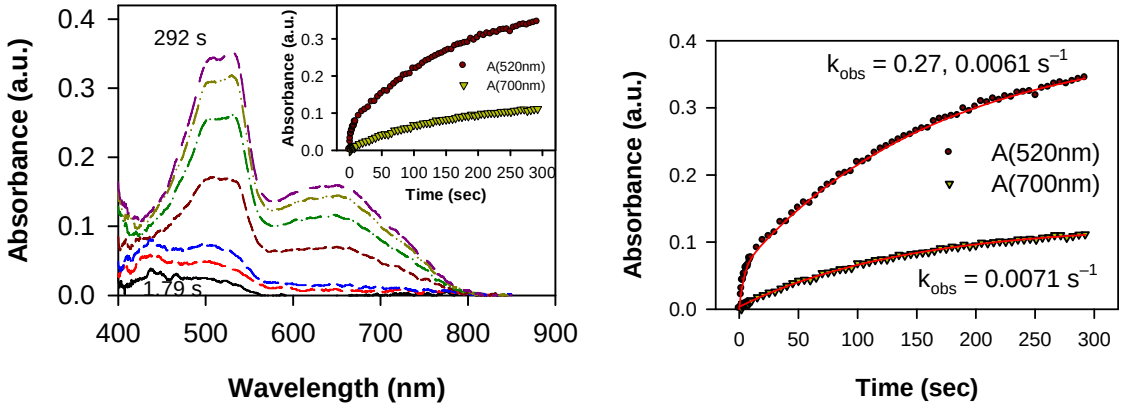

Figure S6. Absorbance evolution for the reaction of 1TNT + 100NaOH in THF, where [TNT] = 3.2×10^{-5} M and $[OH^-] = 3.2\times10^{-3}$ M. The left figure shows absorbance growth in the visible range comprised of two discernible products, TNT-OH^- and TNT^-. The right figure shows the absorbance data at 520 nm and at 700 nm as a function of time. The data have been fit to equations S18 and S19, with the observed rate constants indicated.

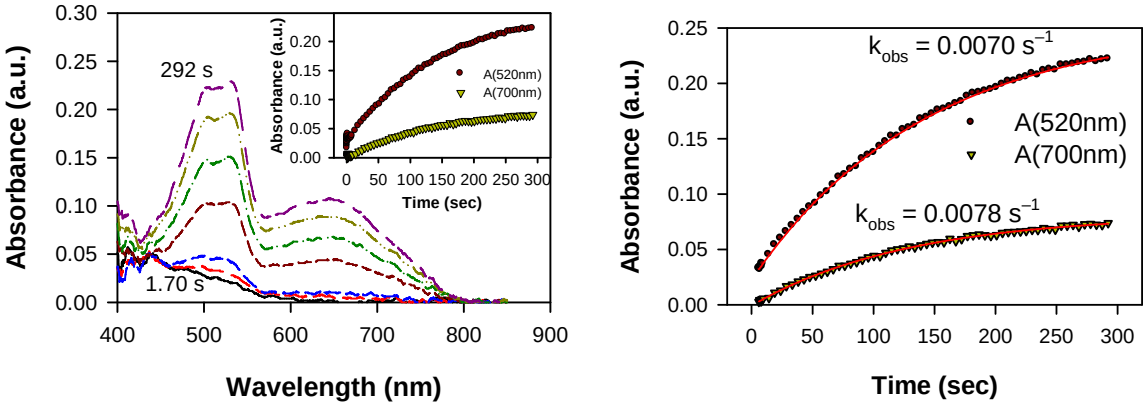

Figure S7. Absorbance evolution for the reaction of 1TNT + 100NaOH in THF, where [TNT] = 2.2×10^{-5} M and [OH^-] = 2.2×10^{-3} M. The left figure shows absorbance growth in the visible range comprised of two discernible products, TNT-OH^- and TNT^-. The right figure shows the absorbance data at 520 nm and at 700 nm as a function of time. The data have been fit to equations S18 and S19, with the observed rate constants indicated.

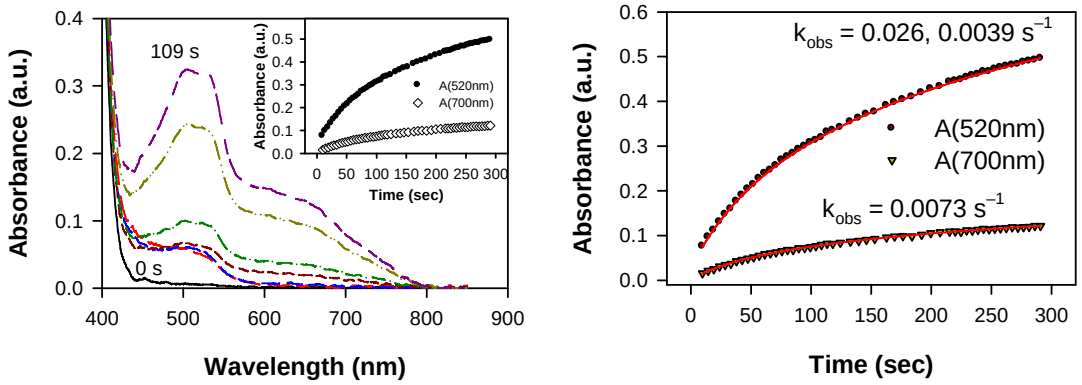

Figure S8. Absorbance evolution for the reaction of 100TNT + 1NaOH in THF, where [TNT] = 2.2×10^{-3} M and [OH^-] = 2.2×10^{-5} M. The left figure shows absorbance growth in the visible range comprised of two discernible products, TNT-OH^- and TNT^-. The right figure shows the absorbance data at 520 nm and at 700 nm as a function of time. The data have been fit to equations S18 and S19, with the observed rate constants indicated.

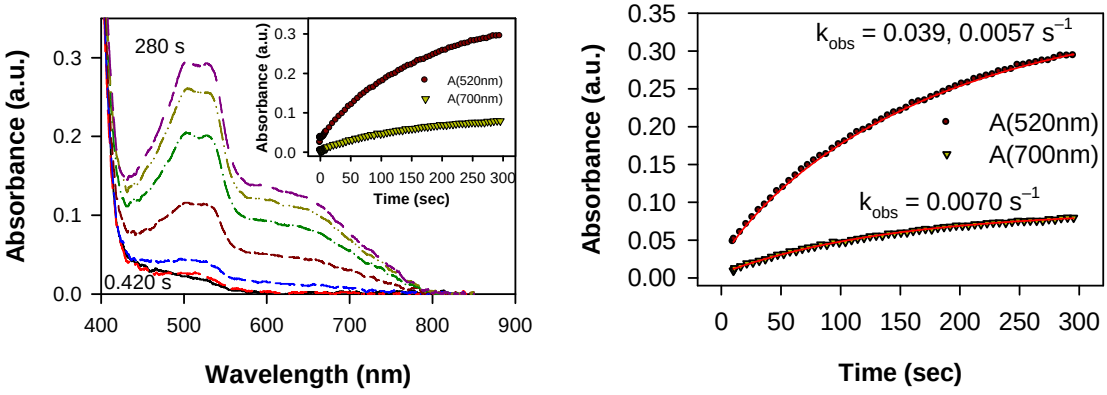

Figure S9. Absorbance evolution for the reaction of 100TNT + 1NaOH in THF, where [TNT] = 1.7×10^{-3} M and [OH^-] = 1.7×10^{-5} M. The left figure shows absorbance growth in the visible range comprised of two discernible products, TNT-OH^- and TNT^-. The right figure shows the absorbance data at 520 nm and at 700 nm as a function of time. The data have been fit to equations S18 and S19, with the observed rate constants indicated.

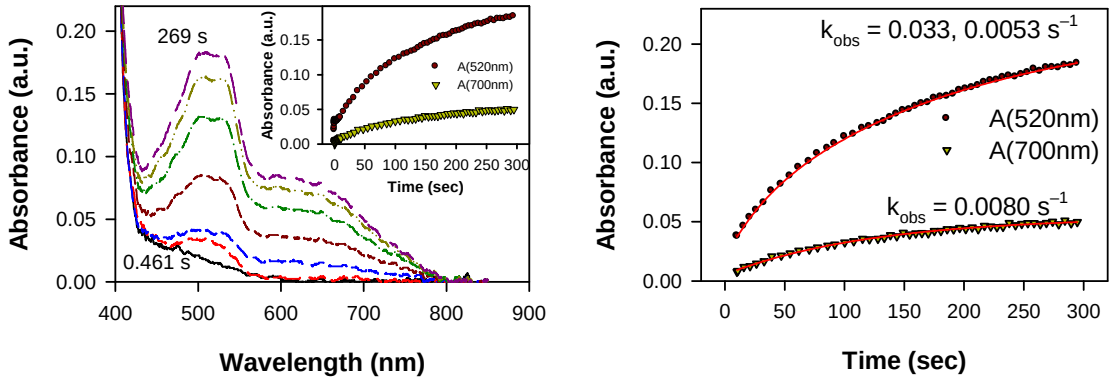

Figure S10. Absorbance evolution for the reaction of 100TNT + 1NaOH in THF, where [TNT] = 1.3×10^{-3} M and [OH^-] = 1.3×10^{-5} M. The left figure shows absorbance growth in the visible range comprised of two discernible products, TNT-OH^- and TNT^-. The right figure shows the absorbance data at 520 nm and at 700 nm as a function of time. The data have been fit to equations S18 and S19, with the observed rate constants indicated.

TNT + NaOH in MeOH

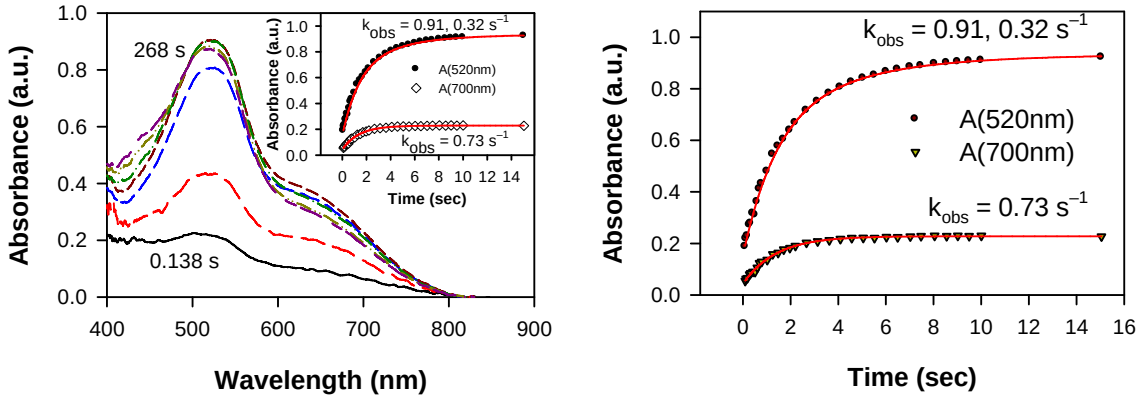

Figure S11. Absorbance evolution for the reaction of 1TNT + 100NaOH in MeOH, where [TNT] = 2.5×10^{-4} M and [OH^-] = 2.5×10^{-2} M. The left figure shows absorbance growth in the visible range comprised of two discernible products, TNT-OH^- and TNT^-. The left figure inset shows the phenomenological fit of the absorbance data at 520 nm and 700 nm over the first five minutes of reaction to a set of exponential rise and decay functions. The right figure shows the initial absorbance data at 520 nm and at 700 nm as a function of time. The data have been fit to equations S18 and S19, with the observed rate constants indicated.

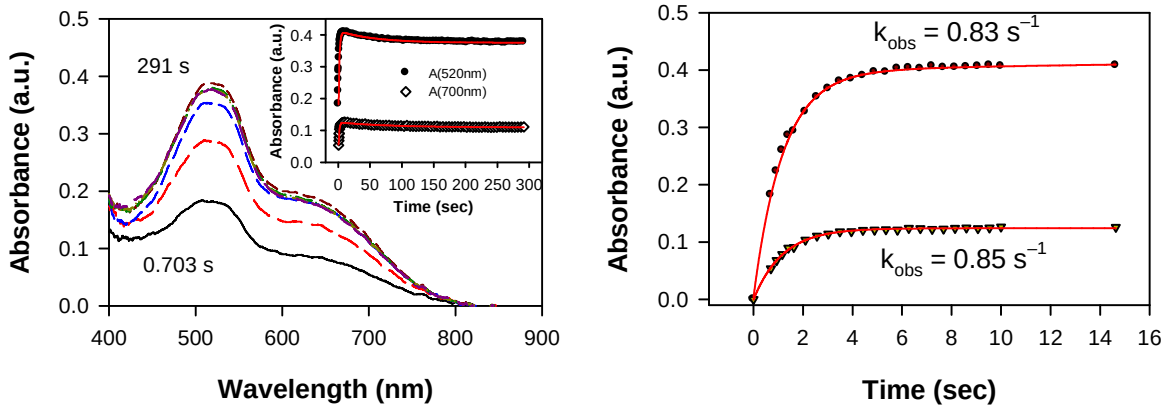

Figure S12. Absorbance evolution for the reaction of 1TNT + 100NaOH in MeOH, where [TNT] = 1.9×10^{-4} M and [OH^-] = 1.8×10^{-2} M. The left figure shows absorbance growth in the visible range comprised of two discernible products, TNT-OH^- and TNT^-. The left figure inset shows the phenomenological fit of the absorbance data at 520 nm and 700 nm over the first five minutes of reaction to a set of exponential rise and decay functions. The right figure shows the initial absorbance data at 520 nm and at 700 nm as a function of time. The data have been fit to equations S18 and S19, with the observed rate constants indicated.

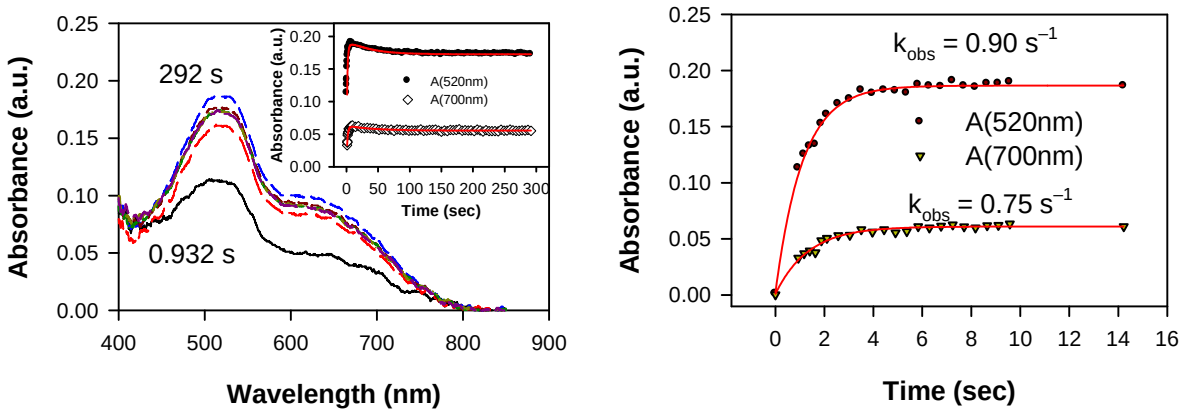

Figure S13. Absorbance evolution for the reaction of 1TNT + 100NaOH in MeOH, where [TNT] = 1.5×10^{-4} M and [OH^-] = 1.4×10^{-2} M. The left figure shows absorbance growth in the visible range comprised of two discernible products, TNT-OH^- and TNT^-. The left figure inset shows the phenomenological fit of the absorbance data at 520 nm and 700 nm over the first five minutes of reaction to a set of exponential rise and decay functions. The right figure shows the initial absorbance data at 520 nm and at 700 nm as a function of time. The data have been fit to equations S18 and S19, with the observed rate constants indicated.

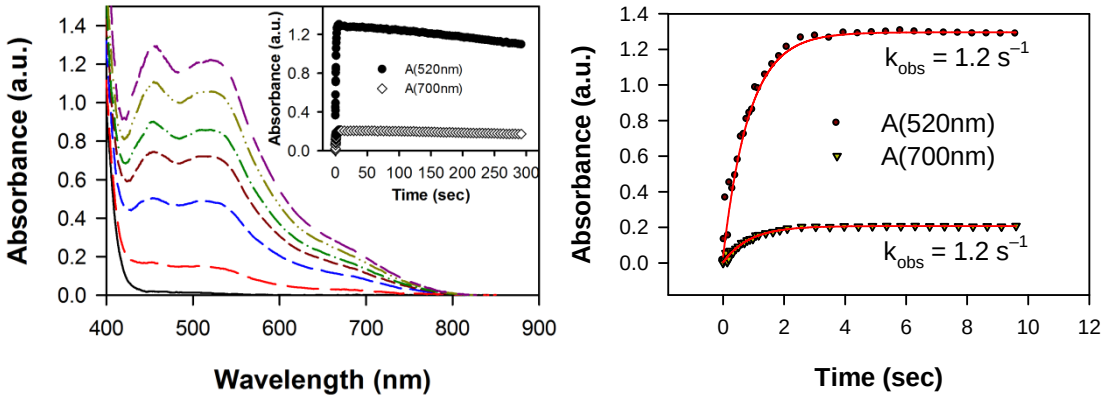

Figure S14. Absorbance evolution for the reaction of 100TNT + 1NaOH in MeOH, where [TNT] = 4.1×10^{-2} M, [OH^-] = 4.0×10^{-4} M. The left figure shows absorbance growth in the visible range comprised of two discernible products, TNT-OH^- and TNT^-. The left figure inset shows the absorbance data at 520 nm and 700 nm over the first five minutes of reaction. The right figure shows the initial absorbance data at 520 nm and at 700 nm as a function of time. The data have been fit to equations S18 and S19, with the observed rate constants indicated.

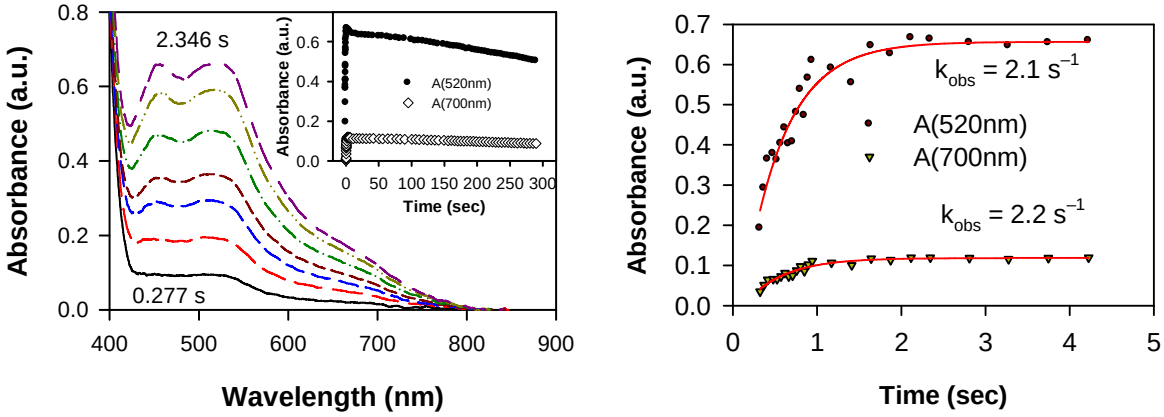

Figure S15. Absorbance evolution for the reaction of 100TNT + 1NaOH in MeOH, where [TNT] = 2.9×10^{-2} M, [OH^-] = 2.9×10^{-4} M. The left figure shows absorbance growth in the visible range comprised of two discernible products, TNT-OH^- and TNT^-. The left figure inset shows the absorbance data at 520 nm and 700 nm over the first five minutes of reaction. The right figure shows the initial absorbance data at 520 nm and at 700 nm as a function of time. The data have been fit to equations S18 and S19, with the observed rate constants indicated.

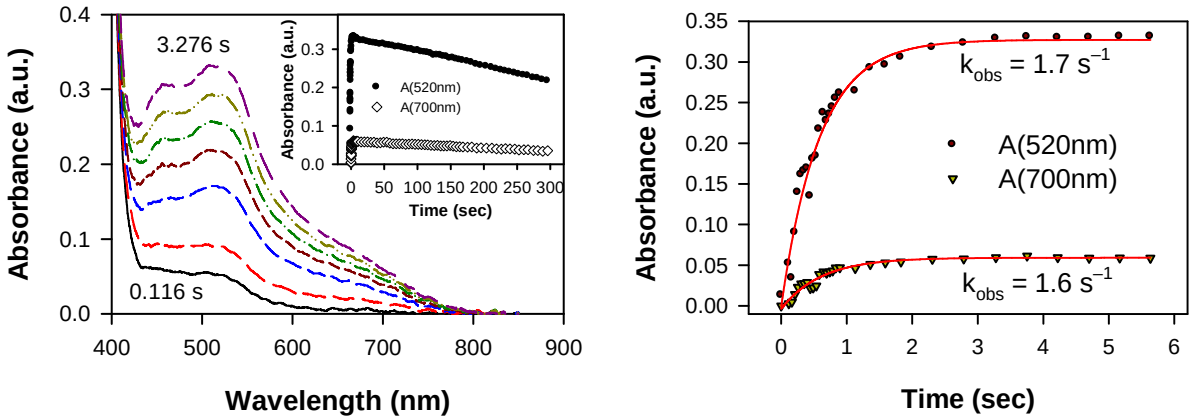

Figure S16. Absorbance evolution for the reaction of 100TNT + 1NaOH in MeOH, where [TNT] = 2.2×10^{-2} M, [OH^-] = 2.2×10^{-4} M. The left figure shows absorbance growth in the visible range comprised of two discernible products, TNT-OH^- and TNT^-. The left figure inset shows the absorbance data at 520 nm and 700 nm over the first five minutes of reaction. The right figure shows the initial absorbance data at 520 nm and at 700 nm as a function of time. The data have been fit to equations S18 and S19, with the observed rate constants indicated.

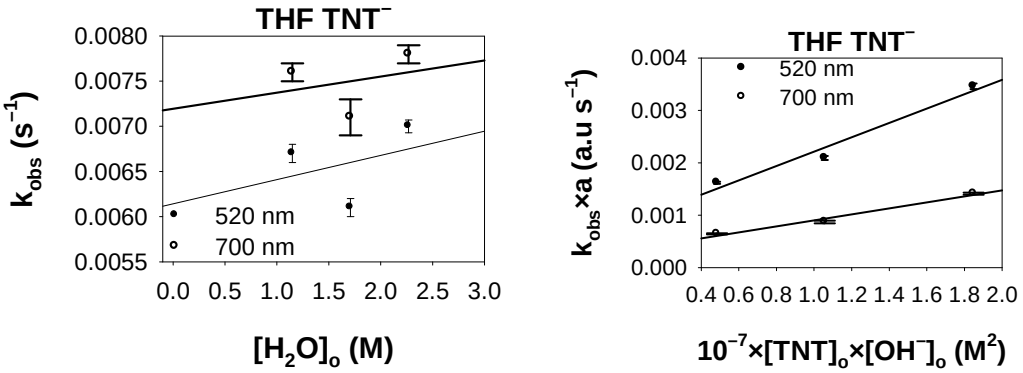

Figure S17. Plots of k_{obs} vs. $[H_2O]_o$ (left) (slopes = 2.7×10^{-4} $M^{-1}s^{-1}$ and 1.8×10^{-4} $M^{-1}s^{-1}$ for 520 nm and 700 nm, respectively) and $k_{obs}\times a$ vs. $[TNT]_o[OH^-]_o$ (right) (slopes = 1.3×10^4 a.u.$M^{-2}s^{-1}$ and 5.6×10^3 a.u.$M^{-2}s^{-1}$ for 520 nm and 700 nm, respectively) for the data for TNT^- in THF.

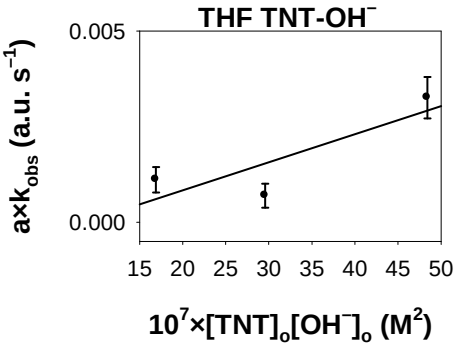

Figure S18. Plot k_{obs}×a vs. $[TNT]_o[OH^-]_o$ for the 520 nm data for TNT-OH^- in THF (slope = 7.3×10^2 a.u.$M^{-2}s^{-1}$).

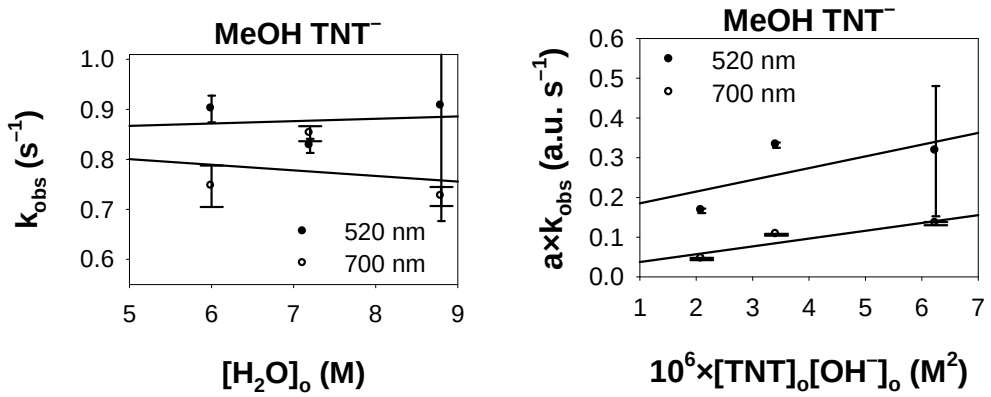

Figure S19. Plots of k_{obs} vs. $[H_2O]_o$ (left) (slope = 4.8×10^{-3} $M^{-1}s^{-1}$ for 520 nm) and k_{obs}×a vs. $[TNT]_o[OH^-]_o$ (right) (slopes = 3.0×10^5 a.u.$M^{-2}s^{-1}$ and 2.0×10^5 a.u.$M^{-2}s^{-1}$ for 520 nm and 700 nm, respectively) for the data for TNT^- in MeOH. The negative slope found in the plot of k_{obs} (700 nm) vs. $[H_2O]_o$ was not used in the determination of k_{-1}.

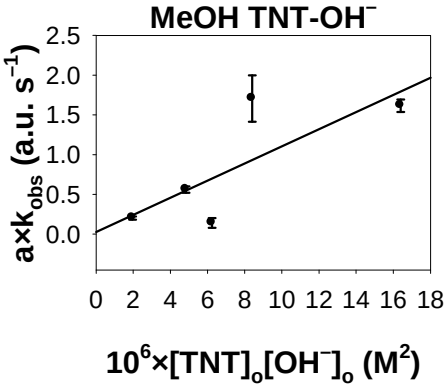

Figure S20. Plot k_{obs}×a vs. $[TNT]_o[OH^-]_o$ for the 520 nm data for TNT-OH^- in MeOH (slope = 1.1×10^5 a.u.$M^{-2}s^{-1}$).

Table S3. Energies for explored bases and conjugate acids calculated at the B3LYP/6-31G*//HF/6-311G** level of theory in implicit solvation models.

	E° (kJ/mol)							
Species	Vacuum	Hexane	THF	1-Propanol	MeOH	Formic Acid	Water	Formamide
OH^-	-198800.88	-198956.81	-199093.78	-199227.72	-199261.18	-199259.10	-199274.68	-199269.77
H_2O	-200607.82	-200618.97	-200628.84	-200638.52	-200641.18	-200635.38	-200644.50	-200640.00
MeO^-	-302114.61	-302260.67	-302384.27	-302460.37	-302479.42	-302475.78	-302484.96	-302481.80
MeOH	-303804.09	-303811.09	-303816.19	-303821.32	-303823.22	-303817.69	-303823.00	-303819.18
NH_3	-148464.02	-148468.54	-148474.84	-148479.16	-148480.51	-148482.03	-148481.64	-148478.99
NH_4^+	-149372.42	-149569.34	-149735.02	-149747.09	-149750.55	-149754.10	-149759.79	-149756.12
EA	-354885.93	-354895.74	-354898.52	-354902.63	-354904.09	-354903.69	-354901.48	-354900.23
H^+-EA	-355849.87	-356017.27	-356154.14	-356164.23	-356167.54	-356167.29	-356168.93	-356168.67
DEA	-561308.42	-561322.19	-561322.21	-561325.89	-561327.46	-561325.05	-561320.42	-561321.25
H^+-DEA	-562313.12	-562459.15	-562572.66	-562581.29	-562584.47	-562580.63	-562577.50	-562581.43
TEA	-767734.80	-767752.05	-767750.00	-767751.90	-767753.44	-767747.99	-767739.13	-767744.10
H^+-TEA	-768758.73	-768887.95	-768982.29	-768990.60	-768993.83	-768987.54	-768979.96	-768987.45

Table S4. Energies for TNT and related products calculated at the B3LYP/6-31G*//HF/6-311G** level of theory in implicit solvation models.

	E° (kJ/mol)							
Species	Vacuum	Hexane	THF	1-Propanol	MeOH	Formic Acid	Water	Formamide
TNT	-2323635.89	-2323669.69	-2323674.65	-2323669.65	-2323670.82	-2323647.18	-2323657.42	-2323651.65
TNT^-	-2322240.20	-2322333.57	-2322390.64	-2322414.85	-2322423.19	-2322401.50	-2322414.88	-2322407.29
TNT-OH^- C_1	-2522923.85	-2523018.15	-2523078.90	-2523107.75	-2523117.76	-2523094.80	-2523111.34	-2523102.47
TNT-OH^- C_3	-2522897.48	-2522897.48	-2523055.96	-2523087.80	-2523097.99	-2523073.86	-2523091.35	-2523082.65
TNT-OCH_3^- C_1	-2626098.64	-2626191.22	-2626249.79	-2626281.60	-2626291.90	-2626270.10	-2626283.26	-2626275.29
TNT-OCH_3^- C_3	-2626101.98	-2626195.03	-2626253.67	-2626284.05	-2626293.95	-2626271.32	-2626284.86	-2626277.19
TNT-NH_3 C_1	-2472083.14	-2472138.62	-2472169.52	-2472183.76	-2472188.94	-2472168.77	-2472181.22	-2472172.27
TNT-NH_3 C_3	-2472070.00	-2472129.43	-2472169.52	-2472176.57	-2472181.69	-2472161.26	-2472181.22	-2472165.34
$[NH_4^+][TNT^-]$	-2472034.25	-2472104.81	-2472149.06	-2472162.78	-2472168.75	-2472148.07	-2472161.34	-2472151.84
TNT-EA C_1	-2678527.92	-2678577.75	-2678597.24	-2678608.48	-2678613.61	-2678590.92	-2678598.44	-2678593.55
TNT-EA C_3	-2678514.90	-2678567.44	-2678588.43	-2678599.97	-2678604.99	-2678581.94	-2678589.34	-2678585.09
$[H^+$-EA$][TNT^-]$	-2678479.61	-2678544.97	-2678577.11	-2678589.98	-2678595.74	-2678571.97	-2678581.24	-2678575.42
TNT-DEA C_1	-2884907.43	-2884956.06	-2884971.72	-2884978.72	-2884983.53	-2884959.90	-2884963.91	-2884961.84
TNT-DEA C_3	-2884914.24	-2884966.44	-2884984.78	-2884992.25	-2884997.09	-2884973.06	-2884976.71	-2884914.24
$[H^+$-DEA$][TNT^-]$	-2884920.78	-2884981.74	-2885005.19	-2885015.03	-2885020.66	-2884994.38	-2884999.18	-2884997.35
$[H^+$-TEA$][TNT^-]$	-3091314.59	-3091380.26	-3091405.80	-3091416.06	-3091422.13	-3091395.38	-3091397.85	-3091397.62

Table S5. HOMO, LUMO, and TDDFT energies calculated at the B3LYP 6-311+G**/HF 6-311G+** level of theory.

Species	HOMO (eV)	LUMO (eV)	TDDFT wavelengths (nm)	TDDFT intensities
TNT	-8.77	-3.65	266.74 272.45 284.65 300.36 301.32 303.88	0.0001568 0.0022780 0.0000464 0.0365716 0.0058020 0.0000891
TNT^{-}	-2.31	0.50	304.14 312.09 312.98 316.58 406.61 511.20	0.0000655 0.3115760 0.0176902 0.0473531 0.2093510 0.1756960
TNT-NH_3 C1	-6.66	-3.45	297.16 302.00 308.92 310.46 331.57 410.45	0.00148740 0.00000038 0.00020381 0.00066509 0.18512400 0.32474500
TNT-EA C1	-6.51	-3.33	298.91 302.58 308.20 311.32 331.05 412.28	0.000468252 0.000000334 0.000068890 0.004977040 0.225500000 0.319937000

TNT-DEA C1	-6.42	-3.16	297.47	0.0001177
			299.91	0.0033573
			304.61	0.0001008
			312.53	0.0005805
			330.58	0.2240990
			409.40	0.2868690
TNT-OH^- C1	-2.73	0.41	289.90	0.01677940
			307.19	0.00021826
			309.47	0.00043647
			316.50	0.00480370
			347.89	0.34054600
			419.16	0.31516600
TNT-OCH_3^- C1	-2.67	0.54	305.71	0.0000092
			308.95	0.0018620
			313.39	0.0650377
			318.55	0.0569989
			349.00	0.2750790
			413.22	0.3118780
TNT-NH_3 C3	-6.65	-3.31	292.99	0.02793840
			297.03	0.00134577
			300.75	0.01030340
			307.64	0.01457890
			338.09	0.16099800
			403.32	0.28525500
TNT-EA C3	-6.50	-3.19	293.52	0.027287100
			296.61	0.000568472
			297.73	0.006270280
			307.70	0.005044890
			338.07	0.193170000
			405.32	0.284345000
TNT-DEA C3	-6.45	-3.07	288.73	0.01581700
			294.32	0.01266110
			299.02	0.01869990
			315.55	0.03954120
			336.43	0.17331700
			404.28	0.22514000
TNT-OH^- C3	-2.75	0.69	278.05	0.10748400
			301.55	0.01005880
			306.58	0.01753140
			309.04	0.01005180
			351.08	0.31112500
			401.08	0.23743800
TNT-OCH_3^- C3	-2.76	0.60	292.20	0.0851797
			304.71	0.0080981
			308.60	0.0184820
			324.51	0.0218973
			350.84	0.2646460
			395.75	0.2980620