Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts

Supplementary Information for

One electron oxidation potential as a predictor of rate constants of N-containing compounds with carbonate radical and triplet excited state organic matter

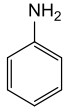
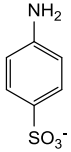
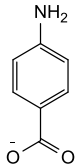
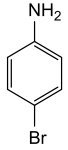
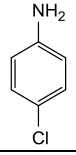
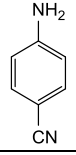
William A. Arnold[†,*]

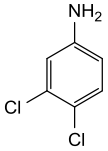
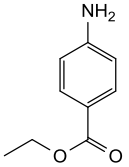
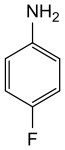
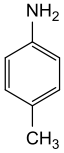
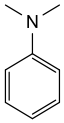
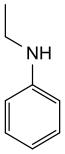
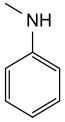
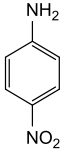
[†]Department of Civil Engineering, University of Minnesota, 500 Pillsbury Dr. SE, Minneapolis, MN 55455

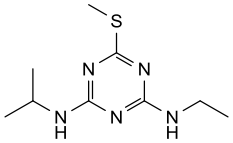
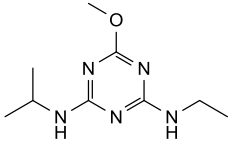
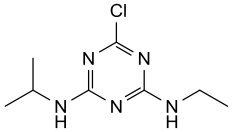
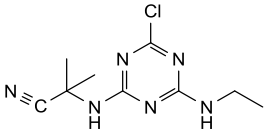
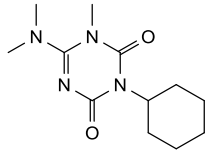
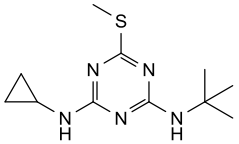
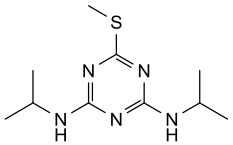
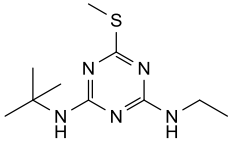
*Author to whom correspondence should be addressed.
Phone: (612) 625-8582; Fax: (612) 626 7750; Email: arnol032@umn.edu

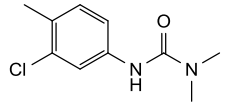
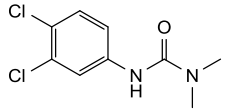
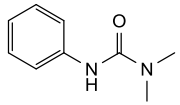
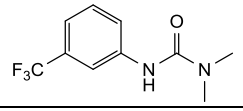
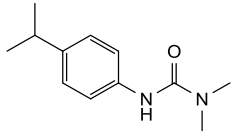
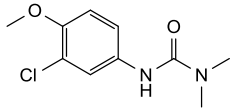
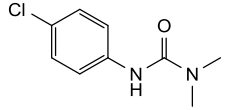
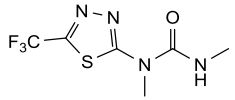
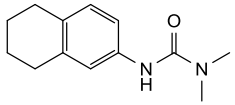
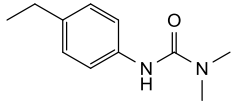
Additional information for compounds listed in Tables 2 and 3

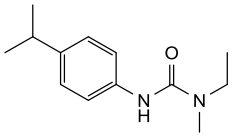
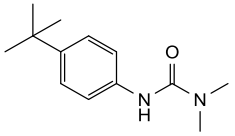
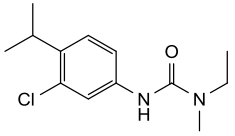
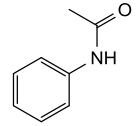
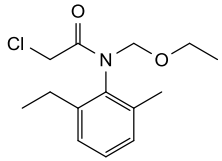
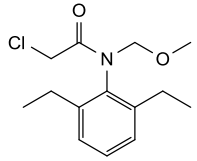
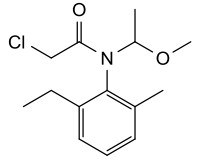
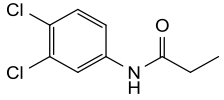
Table S1. Carbonate radical reaction rate constants, triplet excited state reaction rate constants, E_1 values, and spin densities of the reactive nitrogen atom for compounds where the radial cation is resonance stabilized.

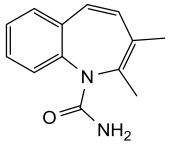
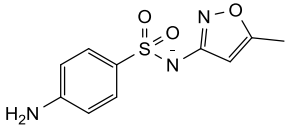
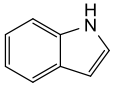
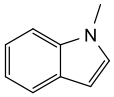
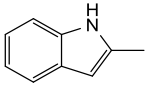
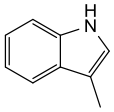
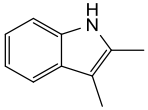
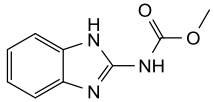
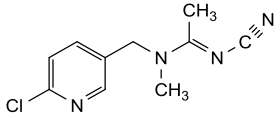
Name	CAS No.	Structure	$k_{CO_3^{\bullet-}}$ ($M^{-1}s^{-1}$)	Average $\log k_{CO_3^{\bullet-}}$ [j]	$k_{^3NOM^*}$ ($M^{-1}s^{-1}$)	E_1 (V)	spin density on oxidized N atom
anilines							
aniline	62-53-3		6.1×10^8 [a] 5×10^8 [b] 6×10^8 [b] 5.4×10^8 [b]	8.75		-1.12	0.41
4-amino-benzenesulfonate	121-57-3		8.7×10^7 [a]	7.94		-1.25	0.42
4-amino-benzoate	150-13-0		2×10^8 [b]	8.30		-1.15	0.39
4-bromoaniline	106-40-1		3.8×10^8 [b]	8.58		-1.21	0.4
4-chloroaniline	106-47-8		6.2×10^8 [a] 4.3×10^8 [b]	8.71		-1.17	0.4
4-cyanoaniline	873-74-5		1.2×10^8 [a]	8.08		-1.50	0.42

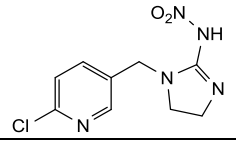
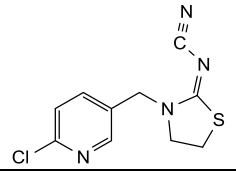
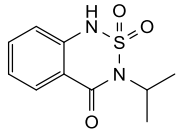
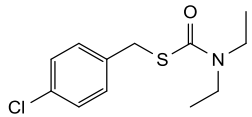
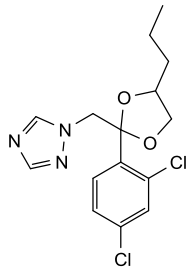
3,4-dichloroaniline	95-76-1		4.1×10^{8} [a]	8.61		-1.34	0.4
ethyl 4-aminobenzoate (benzocaine)	94-09-7		2×10^{8} [b]	8.30		-1.39	0.42
4-fluoroaniline	371-40-4		6.2×10^{8} [b]	8.79		-1.07	0.41
4-methylaniline	106-49-0		1.15×10^{9} [a] 9.1×10^{8} [b]	9.01		-0.94	0.38
N,N-dimethylaniline	121-69-7		1.85×10^{9} [a] 1.4×10^{9} [b] 1.8×10^{9} [b]	9.22		-0.95	0.5
N-ethylaniline	103-69-5		2.2×10^{9} [a]	9.34		-0.93	0.46
N-methylaniline	100-61-8		2.25×10^{9} [a] (flash) 1.8×10^{9} [b]	9.30		-0.97	0.45
4-nitroaniline	100-01-6		6.3×10^{7} [a] 7.3×10^{7} [b]	7.83		-1.74	0.45

triazines							
ametryn	834-12-8		7.4×10^{6} [a]	6.87		-2.23	0.52
atraton	1610-17-9		4.3×10^{6} [a]	6.63		-2.23	0.56
atrazine	1912-24-9		3.70×10^{6} [a] 4×10^{6} [c] 5×10^{6} [d]	6.62	1.2×10^{9} [d]	-2.41	0.59
cyanazine	21725-46-2		8.8×10^{6} [d]	6.94	4.5×10^{8} [d]	-2.47	0.69
hexazinone	51235-04-2		2.4×10^{5} [c]	5.38		-2.25	0.699
irgarol	28159-98-0		7.3×10^{6} [a]	6.86		-1.68	0.46
prometryn	7287-19-6		6.1×10^{6} [a]	6.79		-2.21	0.44
terbutryn	866-50-0		4.9×10^{6} [a]	6.69		-2.17	0.55

ureas							
chlorotoluron	15545-48-9		1.7×10^{7} [a]	7.23	2.7×10^{9} [h] 2.7×10^{8} [i]	-1.57	0.34
diuron	330-54-1		8.3×10^{6} [a] 8.1×10^{6} [d]	6.91	5.2×10^{8} [h] 9.0×10^{6} [i] 7.8×10^{9} [d]	-1.72	0.36
fenuron	101-42-8		6×10^{6} [a]	6.78	2.0×10^{9} [h] 8.1×10^{7} [i]	-1.59	0.37
fluometuron	2164-17-2		4×10^{6} [a] 4.2×10^{6} [c]	6.61	7.1×10^{8} [h] 8.0×10^{6} [i]	-1.74	0.41
isoproturon	34123-59-6		3×10^{7} [a] 2.8×10^{7} [d]	7.46	3.2×10^{9} [h] 8.2×10^{8} [i] 9.7×10^{9} [d]	-1.36	0.32
metoxuron	19937-59-8		1.1×10^{8} [a] 7.5×10^{7} [d]	7.96	3.1×10^{9} [h] 2.0×10^{9} [i] 9.7×10^{9} [d]	-1.24	0.26
monuron	150-68-2		1.5×10^{7} [a]	7.18		-1.55	0.35
thiazafluron	25366-23-8		3.6×10^{5} [c]	5.56		-2.57	0.47
GCA 24482					3.7×10^{9} [h] 1.9×10^{9} [i]	-1.24	0.27
CGA 16519					3.4×10^{9} [h] 9.5×10^{8} [i]	-1.36	0.29

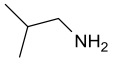
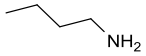
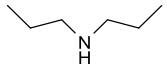
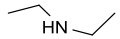
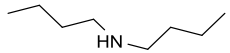
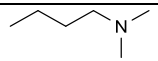
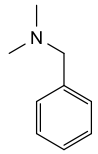
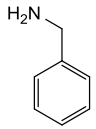
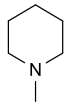
CGA 17667					3.8×10^{9} [h] 8.5×10^{8} [i]	-1.43	0.29
CGA 17092					3.3×10^{9} [h] 8.4×10^{8} [i]	-1.40	0.30
CGA 18414					2.8×10^{9} [h] 1.8×10^{8} [i]	-1.53	0.30
amides							
acetanilide	103-84-4		3.2×10^{8} [b]	5.51		-1.90	0.28
acetochlor	34256-82-1		1.1×10^{6} [d]	6.04	6.1×10^{8} [d]	-2.19	0.008
alachlor	15972-60-8		9.7×10^{6} [d]	6.99	6.9×10^{8} [d]	-2.25	0.015
metolachlor	51218-45-2		6.2×10^{6} [d]	6.79	9.8×10^{8} [d]	-2.40	0.48
propanil	709-98-8		1.4×10^{7} [a]	7.15		-1.96	0.27

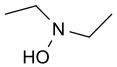
carbamazepine	298-46-4		2.3×10^{6} [g]	6.36		-1.95	0.36
sulfmethoxazole anion	723-46-6		4.4×10^{8} [g]	8.64		-1.18	0.52
indoles and imidazoles							
indole	120-72-9		3×10^{8} [b] 4.1×10^{8} [b] 3.2×10^{8} [b]	8.53		-1.39	0.112
1-methylindole	603-76-9		8.5×10^{8} [b]	8.93		-1.30	0.157
2-methylindole	95-20-5		1.4×10^{9} [b]	9.15		-1.19	0.048
3-methylindole	83-34-1		1.5×10^{9} [b]	9.18		-1.17	0.15
2,3-dimethylindole	91-55-4		2.5×10^{9} [b]	9.40		-0.96	0.07
carbendazim	10605-21-7		6×10^{6} [e]	6.78		-1.69	0.14
neonicotinoids							
acetamiprid	135410-20-7		1.5×10^{5} [f]	5.18		-2.44	0.46

imidacloprid	138261-41-3		4.0×10^{6} [f]	6.60		-2.51	0.59
thiacloprid	111988-49-9		2.8×10^{5} [f]	5.45		-2.67	0.59
other structures							
bentazon	25057-89-0		2.5×10^{7} [d]	7.40	9.7×10^{8} [d]	-2.23	0.23
benthiocarb	28249-77-6		2.8×10^{5} [c]	5.45		-2.15	0.55
propicanozole	60207-90-1		2.5×10^{6} [d]	6.40	1.3×10^{8} [d]	-2.78	0.015

[a] From ref. [1]; [b] From ref. [2]; [c] From ref. [3]; [d] From ref. [4] ; [e] From ref. [5]; [f] From ref. [6]; [g] From ref. [7]; [h] From ref. [8], with benzophenone as the triplet sensitizer; [i] From ref. [8], with 3'-methoxyacetophenone as the triplet sensitizer; [j] When multiple values are reported, "Average log$k_{CO_3^{-\bullet}}$" was determined by taking the log of each reported rate constant, and then averaging these log$k$ values.

Table S2. Carbonate radical reaction rate constants, E_1 values, and spin densities of the reactive nitrogen atom for compounds where the radical cation product is not resonance stabilized.

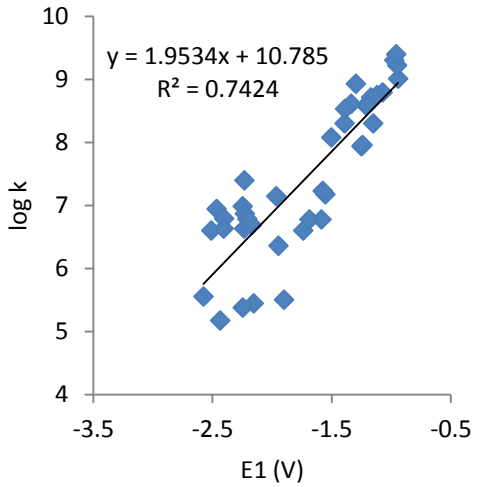
Name	CAS No.	Structure	$k_{CO_3^{\bullet-}}$ ($M^{-1}s^{-1}$)[a]	log $k_{CO_3^{\bullet-}}$	E_1 (V)	spin density on oxidized N atom
isobutylamine	78-81-9		4.0×10^5	5.60	-1.59	0.91
butylamine	109-73-9		4.0×10^5	5.60	-1.61	0.9
t-butylamine	75-64-9		5.8×10^4	4.76	-1.68	0.89
isopropylamine	75-31-0		5.0×10^5	5.70	-1.65	0.89
dipropylamine	142-84-7		4.5×10^6	6.65	-1.18	0.87
diethylamine	109-89-7		3.8×10^6	6.58	-1.17	0.85
piperidine	110-89-4		3.30×10^6	6.52	-1.23	0.82
cyclohexylamine	108-91-8		7.20×10^5	5.86	-1.60	0.82
dibutylamine	111-92-2		5.0×10^6	6.70	-1.17	0.82
N,N-dimethylbutylamine	927-62-8		3.0×10^6	6.48	-0.83	0.81
N,N-dimethylbenzylamine	103-83-3		3.40×10^6	6.53	-1.09	0.79
benzylamine	100-46-9		7.50×10^6	5.88	-1.75	0.79
N-methylpiperidine	626-67-5		2.60×10^6	6.41	-0.85	0.77

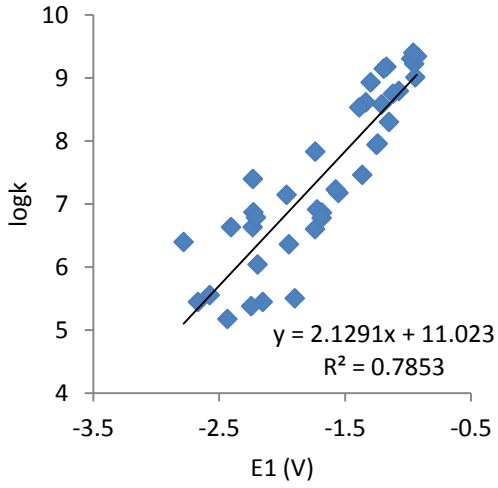
N,N-diethylhydroxylamine	3710-84-7		4.3×10^7	7.63	-1.00	0.69
1,4-Diazabicyclo[2.2.2]octane	280-57-9		1.70×10^7	7.23	-0.65	0.32 (on each N)
imidazole	288-32-4		5.50×10^5	5.74	-1.88	-0.1 (on each N)

[a]Rate constants from ref. [2]

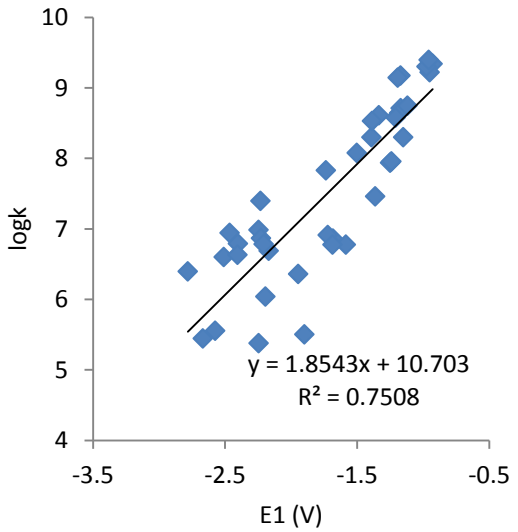
Regressions of training sets and results from validation sets for carbonate radical rate constant prediction

Compound Name	**E_1 (V)**	**log*k* (exp)**	**log*k* (pred)**	**Unsigned error**
		Set 1		
N-ethylaniline	-0.93	9.34	8.97	0.37
irgarol	-1.68	6.86	7.50	0.63
nitroaniline	-1.74	7.83	7.39	0.44
diuron	-1.72	6.91	7.42	0.51
isoproturon	-1.36	7.46	8.12	0.66
3-methylindole	-1.17	9.18	8.50	0.68
2-methylindole	-1.19	9.15	8.45	0.69
acetochlor	-2.19	6.04	6.50	0.46
thiacloprid	-2.67	5.45	5.57	0.13
propicanozole	-2.78	6.40	5.35	1.05
			MUE	**0.56**
		Set 2		
cyanazine	-2.47	6.94	5.77	1.17
terbutryn	-2.17	6.69	6.40	0.29
metolachlor	-2.40	6.79	5.91	0.88
4-cyanoaniline	-1.50	8.08	7.82	0.26
ethyl 4-aminobenzoate	-1.39	8.30	8.06	0.24
4-chloroaniline	-1.17	8.71	8.53	0.18
fenuron	-1.59	6.78	7.65	0.87
alachlor	-2.25	6.99	6.24	0.75
imidacloprid	-2.51	6.60	5.68	0.92
sulfmethoxazole anion	-1.18	8.64	8.51	0.14
			MUE	**0.57**

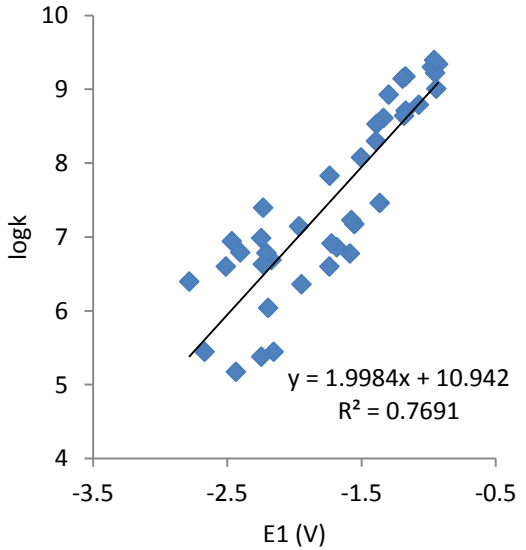




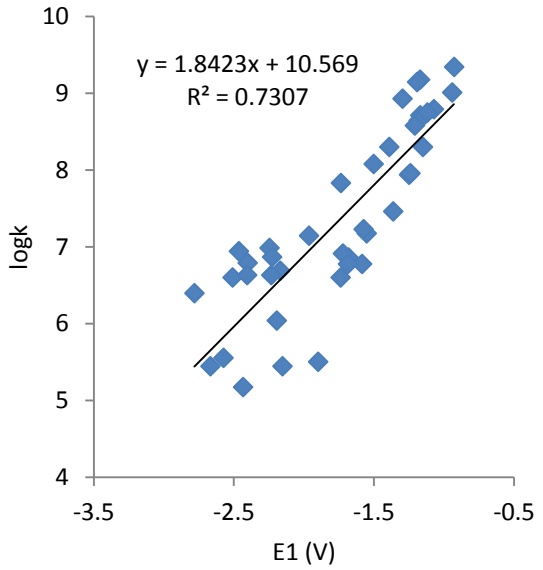
Set 3				
atraton	-2.23	6.63	6.56	0.07
4-fluoroaniline	-1.07	8.79	8.71	0.08
fluometuron	-1.74	6.60	7.48	0.88
4-methylaniline	-0.94	9.01	8.96	0.05
monuron	-1.55	7.18	7.82	0.65
chlorotoluron	-1.57	7.23	7.78	0.55
propanil	-1.96	7.15	7.06	0.09
1-methylindole	-1.30	8.93	8.30	0.63
benthiocarb	-2.15	5.45	6.71	1.26
acetamiprid	-2.44	5.18	6.19	1.01
			MUE	**0.52**



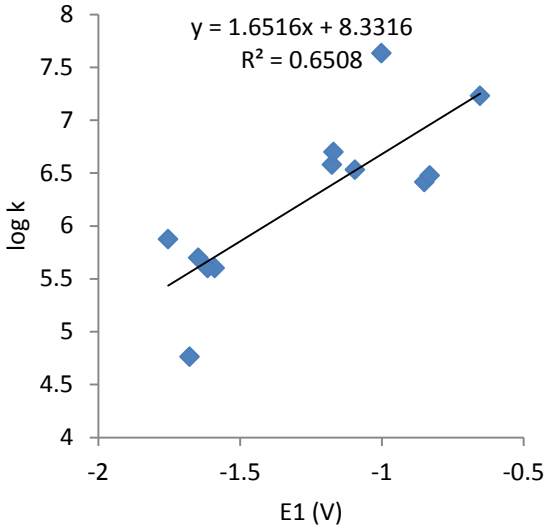
Set 4				
carbendazim	-1.69	6.78	7.57	0.79
atrazine	-2.41	6.63	6.13	0.50
ametryn	-2.23	6.87	6.49	0.38
4-NH_2benzenesulfonate	-1.25	7.94	8.44	0.50
aniline	-1.12	8.75	8.71	0.04
4-bromooaniline	-1.21	8.58	8.53	0.05
4-amino-benzoate	-1.15	8.30	8.64	0.34
acetanilide	-1.90	5.51	7.15	1.64
metoxuron	-1.24	7.96	8.46	0.50
thiazafluron	-2.57	5.56	5.80	0.24
			MUE	**0.50**



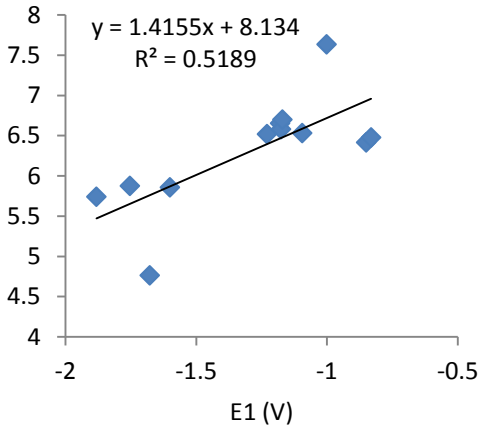
Set 5				
N,N-dimethylaniline	-0.95	9.22	8.82	0.41
N-methylaniline	-0.97	9.30	8.77	0.53
prometryn	-2.21	6.79	6.50	0.28
3,4-dichloroaniline	-1.34	8.61	8.11	0.50
carbamazepine	-1.95	6.36	6.98	0.62
indole	-1.39	8.53	8.01	0.52
2,3-dimethylindole	-0.96	9.40	8.80	0.59
hexazinone	-2.25	5.38	6.43	1.05
bentazon	-2.23	7.40	6.46	0.94
			MUE	**0.61**



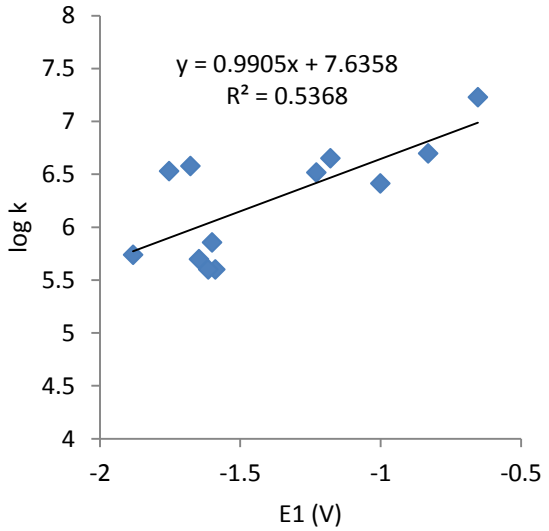
Compound Name	E_1 (V)	log*k* (exp)	log*k* (pred)	Unsigned error
	Set 1			
dipropylamine	-1.18	6.65	6.38	0.27
piperidine	-1.23	6.52	6.30	0.22
cyclohexylamine	-1.60	5.86	5.69	0.17
imidazole	-1.88	5.74	5.22	0.52
			MUE	**0.29**



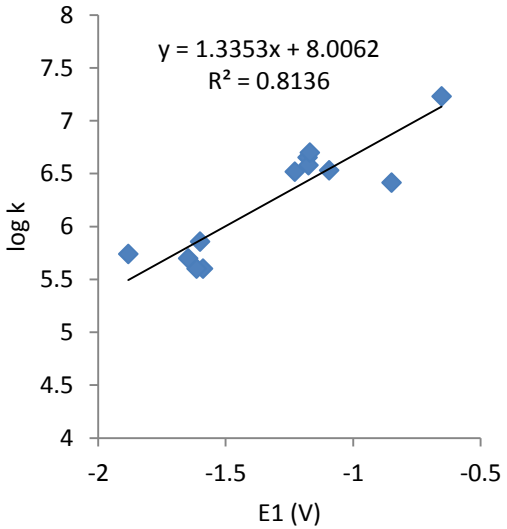
	Set 2			
isobutylamine	-1.59	5.60	5.88	0.28
butylamine	-1.61	5.60	5.85	0.25
isopropylamine	-1.65	5.70	5.80	0.10
1,4-Diazabicyclo[2.2.2]octane	-0.65	7.23	7.21	0.02
			MUE	**0.16**



Set 3				
diethylamine	-1.18	6.58	6.47	0.11
dibutylamne	-1.17	6.70	6.48	0.22
N,N-dimethylbenzylamine	-1.09	6.53	6.55	0.02
N-methylpiperidine	-0.85	6.41	6.79	0.38
			MUE	**0.18**



Set 4				
t-butylamine	-1.68	4.76	5.77	1.00
N,N-dimethylbutylamine	-0.83	6.48	6.90	0.42
benzylamine	-1.75	5.88	5.66	0.21
N,N-diethylhydroxylamine	-1.00	7.63	6.67	0.96
			MUE	**0.65**



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