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Supporting Information

Table 1. Values of electron affinities (*EA*), ionization potentials (*IP*), exothermicities ($-\Delta H_r$) and Hammett σ_p. For the notations see Figures 1 and 2

Alkene (R_1, R_2)	EA[a,b]	IP[a,b]	$-\Delta H_r$[a,c]	σ_p[e]
H, CN	–20.26	1053	139	0.66
Me, Ph	–22.19	790.2	139	–0.18
H, Ph	–24.12	813.3	143	–0.01
H, COOMe	–47.28	955.2	118	0.45
Cl, Cl	–73.32	944.5	119	0.46
H, $Si(OEt)_3$	–107.1	970.6		0.19[f]
H, $Si(Me)_3$	–110.0	916.6	102	–0.07
H, OCOMe	–114.8	886.7	97	0.31
H, CH_2CN	–126.4	984.1		0.01
Me, Cl	–138.9	941.6	96	0.06
Me, OCOMe	–145.7	878.0	117	0.14
H, $CH_2Si(Me)_3$	–165.9	868.3		–0.21
H, tBu	–166.9	911.7	104[d]	–0.20
H, OEt	–216.1	849.0	106	–0.24
Me, OMe	–239.3	833.6	109	–0.44

[a]Values are in kJ/mol, and are measured at 298 K.

[b]Ref. 1a.

[c]Ref. 17.

[d]Estimated from the value for 1-butene.

[e]Ref. 40 unless indicated otherwise.

[f]Estimated from the value for the $Si(OMe)_3$ substituent.

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Table 2. Values of experimental rate constants[a] for reaction (1). For the notations see Figures 1 and 2

Alkene (R_1, R_2)	HP[b]	tBu[c]	HM[d]	MeOBz[c]	FBz[c]	MeBz[c]	Me[f]	Bz[g]
H, CN	$1.0\ 10^8$	$1.0\ 10^6$	$1.1\ 10^6$	1800	3250	2100	$6.1\ 10^5$	2200
Me, Ph	$4.0\ 10^8$	$6.79\ 10^4$	$2.8\ 10^4$				$3\ 10^5$	850
H, Ph	$2.2\ 10^6$	$1.32\ 10^5$	$2.3\ 10^4$	2300	2400	2300	$2.6\ 10^5$	1100
H, COOMe	$1.0\ 10^7$	$1.04\ 10^6$	$7.1\ 10^5$	2450	1200	3000	$3.4\ 10^5$	430
Cl, Cl	$2.15\ 10^5$	$3.50\ 10^5$	$5.3\ 10^4$	1050	810	490	$2.3\ 10^5$	460
H, $Si(OEt)_3$	$8.26\ 10^4$	$2.75\ 10^4$						44
H, $Si(Me)_3$	$2.49\ 10^4$	9600	2060				$2.4\ 10^4$	33
H, OCOMe	7500	4200	590	36	27	25	$1\ 10^4$	15
H, CH_2CN	$2.33\ 10^4$	$1.12\ 10^4$		28	8	10		3[c]
Me, Cl	$2.22\ 10^4$	$1.14\ 10^4$	2110				$3.5\ 10^4$	43
Me, OCOMe	4850	1700	680				$1.2\ 10^4$	46
H, $CH_2Si(Me)_3$	1300	1120						56[c]
H, tBu	1070	150	300[e]	15	25	49	7600[e]	18
H, OEt	320	390	180	12	18	32	$1.4\ 10^4$	14
Me, OMe	1080	220	230				$1.2\ 10^4$	21

Supporting information. Table 2 (continued)

Alkene (R_1, R_2)	CNBz[c]	CP[c]	BCM[h]	CM[h]	TOS[i]	$PhSO_2$[j]	MA[l]
H, CN	1400	2020	$5.40\ 10^5$	$1.1\ 10^5$	0.19	0.006	$1.49\ 10^5$
Me, Ph		2310	$3.9\ 10^6$	$6.6\ 10^5$		3.21	$1.33\ 10^6$
H, Ph	3400	2410	$1.9\ 10^6$	$3.8\ 10^5$	14.8	1	$1.15\ 10^6$
H, COOMe	680	367	$4.9\ 10^5$	$1.1\ 10^5$	0.35	0.012	$1.12\ 10^5$
Cl, Cl	890	603	$2.7\ 10^5$	$3.3\ 10^4$			$3.88\ 10^5$
H, $Si(OEt)_3$		323	$6.7\ 10^4$				
H, $Si(Me)_3$		75	$8.9\ 10^4$	$1.3\ 10^4$			$2.23\ 10^5$
H, OCOMe	20	41	$6.5\ 10^4$	$1.3\ 10^4$	0.3	0.008	$3.95\ 10^5$
H, CH_2CN	10	88	$4.4\ 10^4$		0.067		
Me, Cl		120	$1.6\ 10^5$	$1.6\ 10^4$			$9.20\ 10^5$
Me, OCOMe		79	$8.8\ 10^4$	$5.2\ 10^4$			$5.84\ 10^5$
H, $CH_2Si(Me)_3$		47	$9.5\ 10^4$				
H, tBu	57	87	$3.5\ 10^4$	$1.1.10^4$[e]	0.58	0.02[k]	$1.92\ 10^5$
H, OEt	260	108	$1.5\ 10^5$	$4.3\ 10^4$			$3.02\ 10^5$
Me, OMe		82	$1.4\ 10^5$	$3.5\ 10^4$			$4.00\ 10^5$

[a]All rate constant values are in $dm^3.mol^{-1}.s^{-1}$, and are measured at 296 K, except for the values for CP measured at 315 K.
[b]Ref. 6. [c]Ref. 1a. [d]Ref. 7. [e]Estimated from the value for 1-butene. [f]Ref. 17.
[g]Ref. 34 unless indicated otherwise. [h]Ref. 20. [i]Ref. 29. [j]Ref. 22.
[k]Estimated from the value for 1-hexene. [l]Ref. 33.

Supporting Information

Table 3. Values of theoretical barrier heights (E_a) and reaction enthalpies (ΔH_r) for reaction (1), as well as electron affinities (*EA*), ionization potentials (*IP*), exothermicities ($-\Delta H_{r,PCA}$) and Hammett σ_p. For the notations see Figures 1 and 2

Alkene (R_1, R_2)	E_aMe[a]	E_aHM[a]	E_aCM[a]	E_atBu[b]	ΔH_rMe[a]	ΔH_rHM[a]	ΔH_rCM[a]	ΔH_rtBu[b]
H, F	39.8	35.0	42.3	21.6	–94.2	–87.5	–63.2	–89.5
H, H	38.9	32.7	42.5	21.4	–93.5	–87.1	–63.3	–87.8
H, NH_2	36.3	32.5	30.7	17.9	–100.2	–91.4	–72.1	–95.7
H, Cl	32.5	24.6	35.9	13.6	–105.9	–97.8	–74.5	–99.1
H, CHO	28.7	18.3	33.9	6.5	–120.7	–118.6	–92.9	–120.5
H, CN	24.3	11.7	32.6	1.9	–129.3	–123.7	–93.4	–124.5

Alkene (R_1, R_2)	*EA*[c,d]	*IP*[c,d]	$-\Delta H_{r,PCA}$[f]	σ_p[g]
H, F	–1.62	10.37	0.89177	0.06
H, H	–1.86	10.58	0.93516	0.00
H, NH_2	–1.92	8.18	0.46661	–0.66
H, Cl	–1.28[e]	9.98	0.17157	0.23
H, CHO	0.03	10.21	–1.08306	0.42
H, CN	–0.23	10.98	–1.38205	0.66

[a]Ref. 10. [b]Ref. 11. [c]Values are in eV. [d]Ref. 10,11 unless indicated otherwise.
[e]Taken from Burrow, P. D.; Modelli, A.; Chiu, N. S. and Jordan, K. D. *Chem. Phys. Lett.* **1981**, *82*, 270–276.
[f]Obtained using PCA of the reaction enthalpy data. [g]Ref. 40.

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Table 4. Variances accounted for by the individual principal components in *data sets 1a, 2a, 3a*

	Data set 1a[a]		*Data set 2a*[b]		*Data set 3a*[c]	
Principal component	variance accounted for	percent of total variance	variance accounted for	percent of total variance	variance accounted for	percent of total variance
C1	6.89873	76.653	11.27709	75.181	3.46272	86.568
C2	1.48159	16.462	3.20417	21.361	0.53149	13.287
C3	0.34012	3.779	0.31482	2.099	0.00537	0.134
C4	0.13349	1.483	0.20392	1.359	0.00041	0.010
C5	0.08287	0.921	0.00000	0.000		
C6	0.04918	0.546				
C7	0.00989	0.110				
C8	0.00304	0.034				
C9	0.00109	0.012				

[a]*Data set 1a* includes 9 radicals and 12 alkenes, therefore 9 principal components were obtained.

[b]*Data set 2a* includes 15 radicals and 5 alkenes, therefore 5 principal components were obtained.

[c]*Data set 3a* includes 4 radicals and 6 alkenes, therefore 4 principal components were obtained.

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Table 5. Variances accounted for by the individual principal components in *data sets 1b, 2b, 3b*

	Data set 1b[a]		*Data set 2b*[b]		*Data set 3b*[c]	
Principal component	variance accounted for	percent of total variance	variance accounted for	percent of total variance	variance accounted for	percent of total variance
C1	12.50663	78.166	13.11221	72.846	5.35612	76.516
C2	2.32629	14.539	4.09046	22.725	1.50455	21.494
C3	0.54901	3.431	0.48250	2.681	0.12941	1.849
C4	0.35340	2.209	0.31483	1.749	0.00874	0.125
C5	0.17726	1.108	0.00000	0.000	0.00118	0.017
C6	0.08741	0.546			0.00000	0.000
C7	0.00000	0.000				

[a]*Data set 1b* includes 13 radicals + 3 descriptors, as well as 7 alkenes, therefore 7 principal components were obtained.

[b]*Data set 2b* includes 15 radicals + 3 descriptors, as well as 5 alkenes, therefore 5 principal components were obtained.

[c]*Data set 3b* includes 4 radicals + 3 descriptors, as well as 6 alkenes, therefore 6 principal components were obtained.

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Table 6. Values of component loadings for the first two principal components for *data sets 1a*, *2a*, *3a*. Dimensionalities are given in parentheses. For the notations see Figures 1 and 2

Radical	*Data set 1a* (9 × 12)		*Data set 2a* (15 × 5)		*Data set 3a* (4 × 6)	
	A1	*A2*	*A1*	*A2*	*A1*	*A2*
tBu	0.89009	–0.32475	0.90667	–0.31476	0.98866	–0.13742
HP	0.95673	–0.06244	0.93929	–0.32088		
MeOBz			0.98426	–0.07581		
FBz			0.99629	–0.06035		
Bz	0.98113	–0.06500	0.98239	–0.07241		
MeBz			0.97656	–0.09139		
CP	0.95241	0.14084	0.94125	0.14351		
BCM	0.90950	0.36334	0.96381	0.23225		
CNBz			0.96911	0.15536		
HM	0.90129	–0.41808	0.88058	–0.47032	0.96785	–0.24938
CM	0.83714	0.40238	0.96657	0.24538	0.75091	0.66039
Me	0.97886	–0.15540	0.97946	–0.20139	0.99231	–0.11959
TOS			0.34252	0.92957		
$PhSO_2$			0.38028	0.91252		
MA	0.15143	0.92483	0.08753	0.92829		

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Table 7. Values of component loadings for the first two principal components for *data sets 1b*, *2b*, *3b*. Dimensionalities are given in parentheses. For the notations see Figures 1 and 2

Radical	*Data set 1b* {(13 + 3) × 7}		*Data set 2b* {(15 + 3) × 5}		*Data set 3b*[a] {(4 + 3) × 6}	
	A1	*A2*	*A1*	*A2*	*A1*	*A2*
tBu	0.92859	–0.20478	0.90674	–0.29293	0.99886	0.02616
HP	0.95161	–0.23672	0.94354	–0.31499		
MeOBz	0.97427	–0.03704	0.98064	–0.05709		
FBz	0.99523	–0.02169	0.99779	–0.05738		
Bz	0.99010	–0.02793	0.98700	–0.07751		
MeBz	0.97572	–0.04314	0.97103	–0.07897		
CP	0.93911	0.19813	0.94707	0.12796		
BCM	0.90168	0.38192	0.96137	0.24555		
CNBz	0.88902	0.28957	0.96778	0.15335		
HM	0.92632	–0.36159	0.88088	–0.45863	0.98915	–0.08570
CM	0.84379	0.40936	0.96271	0.25712	0.62916	0.77398
Me	0.98504	–0.09764	0.98028	–0.19395	0.99144	0.04567
TOS			0.33330	0.93390		
$PhSO_2$			0.37104	0.91628		
MA	0.02961	0.90827	0.08960	0.92692		
EA	0.91643	–0.07532	0.96592	–0.03442	0.94066	–0.18446
(*–IP*)	–0.40447	0.86676	–0.21683	0.93090	–0.35693	0.92758
$(-\Delta H_r)$	0.91474	0.25514	0.93123	0.18359	0.99446	0.03118

[a]In this case (*–EA*), *IP* and $(-\Delta H_{r,PCA})$ were applied as descriptors (see text).

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Table 8. Values of component scores for the first two principal components for *data sets 1a, 2a, 3a*. Dimensionalities are given in parentheses. For the notations see equation (1)

Alkene (R_1, R_2)	*Data set 1a* (9 × 12)		*Data set 2a* (15 × 5)		*Data set 3a* (4 × 6)	
	C1	*C2*	*C1*	*C2*	*C1*	*C2*
H, CN	1.35574	–1.38290	0.76814	–0.94449	–1.43182	0.50429
Me, Ph	1.42251	1.63752				
H, Ph	1.17588	1.30888	0.87399	1.55908		
H, COOMe	0.92540	–1.59912	0.53100	–0.80263		
Cl, Cl	0.54254	–0.56948				
H, $Si(Me)_3$	–0.59112	–0.75205				
H, OCOMe	–0.91622	–0.13978	–1.04875	0.00656		
Me, Cl	–0.37797	0.49445				
Me, OCOMe	–0.63460	0.56045				
H, tBu	–1.17236	–0.48009	–1.12439	0.18147		
H, OEt	–0.86378	0.38322				
Me, OMe	–0.86602	0.53892				
H, F					1.10906	0.53744
H, H					0.99930	0.74257
H, NH_2					0.23703	–1.96751
H, Cl					–0.10482	–0.00214
H, CHO					–0.80876	0.18535

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Table 9. Values of component scores for the first two principal components for *data sets 1b*, *2b*, *3b*. Dimensionalities are given in parentheses. For the notations see equation (1)

Alkene (R_1, R_2)	*Data set 1b* {(13 + 3) × 7}		*Data set 2b* {(15 + 3) × 5}		*Data set 3b* {(4 + 3) × 6}	
	C1	*C2*	*C1*	*C2*	*C1*	*C2*
H, CN	1.10367	–1.00818	0.81403	–1.02442	–1.42781	0.32451
H, Ph	0.96088	1.89420	0.86579	1.56322		
H, COOMe	0.69519	–0.87345	0.48647	–0.70015		
Cl, Cl	0.35732	–0.12432				
H, OCOMe	–1.01452	–0.15019	–1.03480	0.03772		
H, tBu	–1.11477	–0.39835	–1.13150	0.12362		
H, OEt	–0.98777	0.66028				
H, F					0.93751	0.75850
H, H					0.90824	0.88676
H, NH_2					0.55727	–1.87694
H, Cl					–0.00208	–0.10043
H, CHO					–0.97312	0.00760