The Formyloxyl Radical: Electrophilicity, C-H Bond Activation and Anti-Markovnikov Selectivity in the Oxidation of Aliphatic Alkenes

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Electronic Supplementary Information

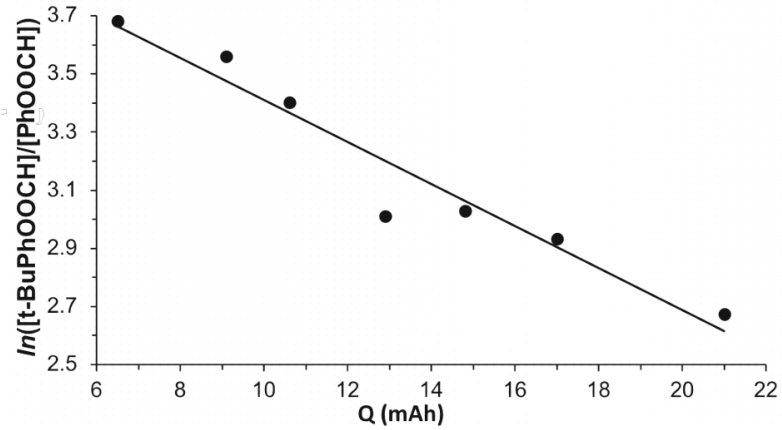


Figure S1. Ratio of pseudo-first-order rates as a function of the charge transferred Q for *t*-butylbenzene/benzene.

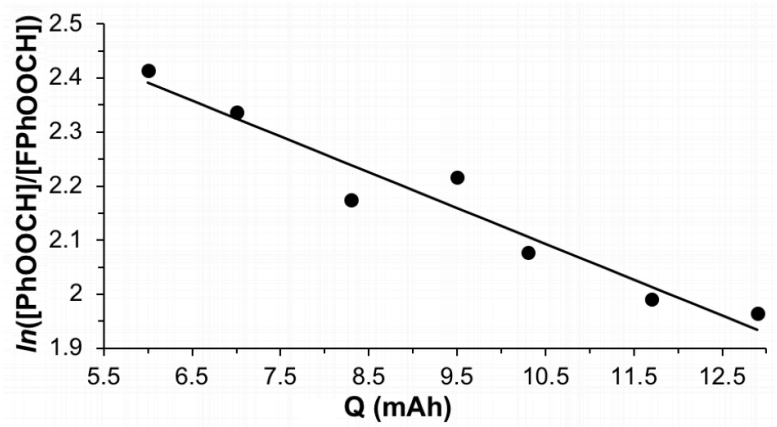


Figure S2. Ratio of pseudo-first-order rates as a function of the charge transferred Q for benzene/fluorobenzene.

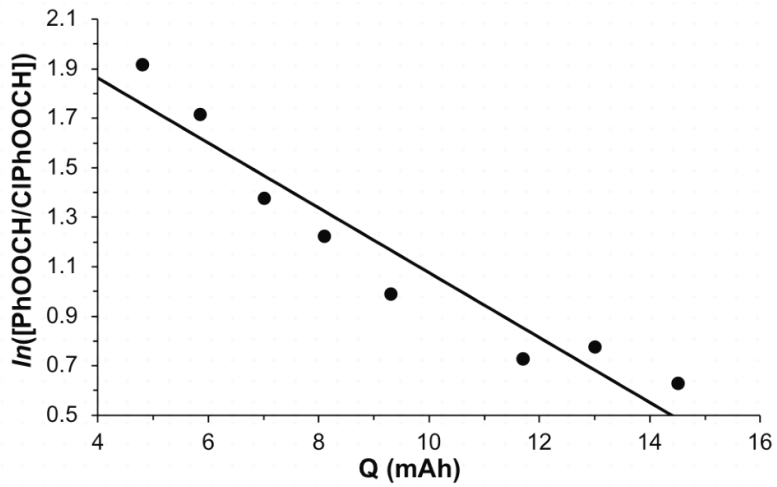


Figure S3. Ratio of pseudo-first-order rates as a function of the charge transferred Q for benzene/chlorobenzene.

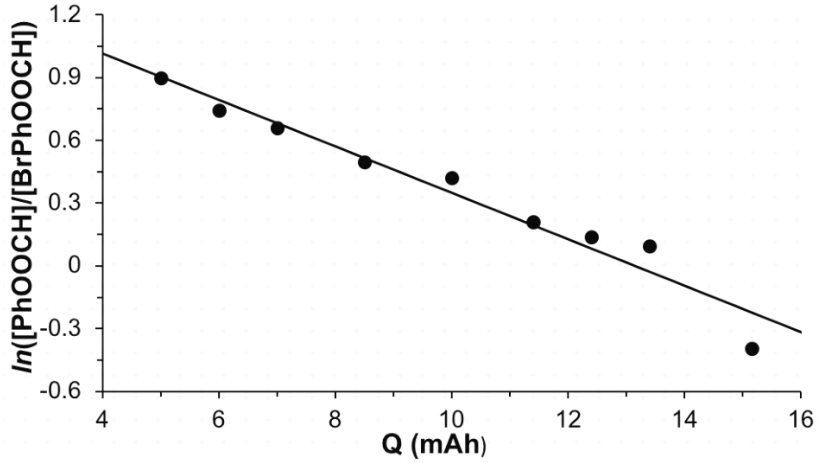


Figure S4. Ratio of pseudo-first-order rates as a function of Q for benzene/bromobenzene.

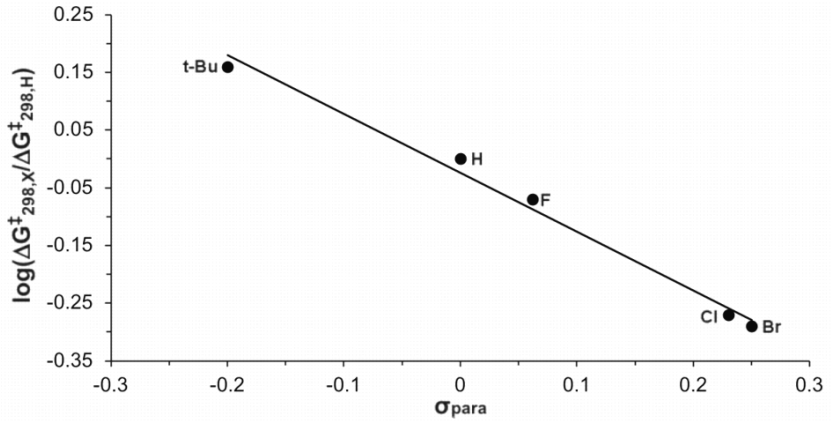


Figure S5. Hammett plot for reaction of the formyloxy radical with substituted benzenes derived from DFT-calculated free energies of activation for substitution at the *para* position. The ρ value calculated is an underestimation since other isomers with higher barriers are also formed in the experiment.

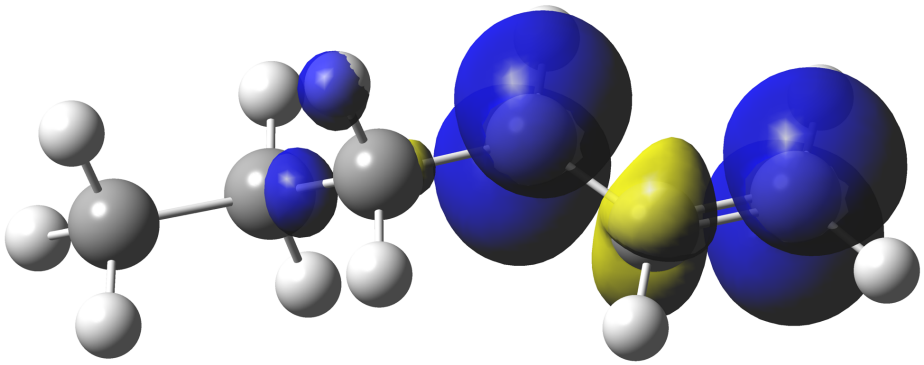
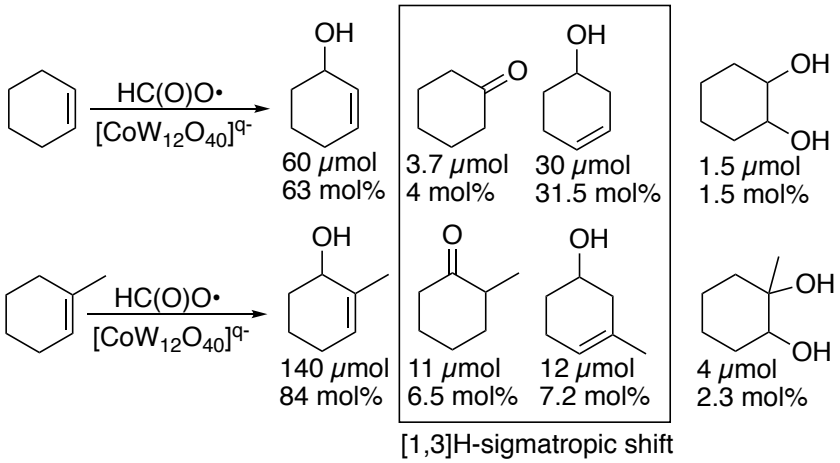


Figure S6. PW6B95D3BJ/def2-SVP spin density for the hexallyl radical.



Scheme S1. Oxidation of cyclic alkenes. Reaction conditions: 1 mmol cyclic alkene, 3 mL 1:1 HCOOH–CH_3CN, 70 mg LiOCOH, 35 mg $K_5Co^{III}W_{12}O_{40}$. Working electrode – Pt net, Reference electrode – Pt wire, counter electrode – Pt; 1.8 V vs SHE in an undivided cell; t = 1.5 h; RT. Product analyses were carried out as described in the Experimental section. Product yields and selectivities are shown in the Scheme.

Table S1. Reaction of 1-hexene with formyloxy radicals at different temperatures.

	22 °C		**0 °C**		**-10 °C**	
Product	**Yield, μmol**	**Selectivity mol %**	**Yield, μmol**	**Selectivity mol %**	**Yield, μmol**	**Selectivity mol %**
n-hexanal	8.7	50	9	43	7.8	45
trans-2-hexen-ol	2.8	15	4.3	20.5	3.6	20.5
2-hexanone	1.2	6.2	1.5	7.0	1.2	7
3-hexanone	0.4	1.8	0.3	1.5	0.3	1.5
1,2-hexanediol	1.3	7.5	2.5	12.5	1.9	11
n-pentanal	3.7	20	3.3	15.5	2.7	15.5
3-hydroxy hexanal	<0.1	–	<0.1	–	<0.1	–

Reaction conditions: 1 mmol 1-hexene, 3 mL 1:1 HCOOH–CH_3CN, 70 mg LiOCOH, 35 mg $K_5Co^{III}W_{12}O_{40}$. Working electrode – Pt net, Reference electrode – Pt wire, counter electrode –Pt; 1.8 V vs SHE in an undivided cell; t = 1.5 h; T = 22, 0 and -10 °C.

Table S2. Reaction of 1-hexene with formyloxy radicals at different potentials.

	1.4 V vs SHE		1.6 V vs SHE		1.8 V vs SHE		2.0 V vs SHE		2.2 V vs SHE	
Product	**Yield, µmol**	**Selectivity mol %**	**Yield, µmol**	**Selectivity mol %**	**Yield, µmol**	**Selectivity mol %**	**Yield, µmol**	**Selectivity mol %**	**Yield, µmol**	**Selectivity mol %**
n-hexanal	7.3	33	17.6	43	8.7	50	9	60	9	57
trans-2-hexen-ol	4.5	20	7.5	18	2.8	15	2.4	16	2.5	15.5
2-hexanone	1.4	6.4	3.0	6	1.2	6.2	1.27	8.2	1.5	9.3
3-hexanone	0.6	2.6	1.0	2	0.4	1.8	0.43	2.8	0.5	3.2
1,2-hexanediol	6.5	30	6.1	15	1.3	7.5	–	–	–	–
n-pentanal	1.7	8	6.8	16	3.7	20	2	13	2.4	15

Reaction conditions: 1 mmol 1-hexene, 3 mL 1:1 HCOOH–CH_3CN, 70 mg LiOCOH, 35 mg $K_5Co^{III}W_{12}O_{40}$. Working electrode – Pt net, Reference electrode – Pt wire, counter electrode – Pt; 1.4 to 2.2 V vs SHE in an undivided cell; t = 1.5 h; T – 22 °C.

Table S3. Reaction of 1-hexene with formyloxy radicals with added water and/or higher temperature.

	22 °C				40 °C			
	10% H_2O		20% H_2O		10% H_2O		20% H_2O	
Product	**Yield, µmol**	**Selectivity mol %**	**Yield, µmol**	**Selectivity mol %**	**Yield, µmol**	**Selectivity mol %**	**Yield, µmol**	**Selectivity mol %**
n-hexanal	12	56	13.6	55.7	13.5	54	21	55.8
trans-2-hexen-ol	3	14	2.5	10	3.5	14	3.4	9
2-hexanone	2.2	10.3	2.3	9.5	2.1	8.4	4.2	11.2
3-hexanone	0.7	3.2	0.7	2.8	0.75	3	1.2	3.2
1,2-hexanediol	0.3	1.5	–	–	–	–	–	–
n-pentanal	3.2	15	5.4	22	5.4	21.6	7.8	20.8

Reaction conditions: 1 mmol 1-alkene, 70 mg LiOCOH, 35 mg $K_5Co^{III}W_{12}O_{40}$. Working electrode – Pt net, Reference electrode – Pt wire, counter electrode – Pt; 1.8 V vs SHE in an undivided cell; t = 1.5 h; T – 22 and 40 °C. Solvent: "10% H_2O" = 1.35 mL HCOOH, 1.35 mL CH_3CN and 0.3 mL H_2O; "20% H_2O" = 1.2 mL HCOOH, 1.2 mL CH_3CN and 0.6 mL H_2O.

Complete Reference 21

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, GAUSSIAN 16, REVISION B.01, Gaussian, Inc.: Wallingford, CT, 2016.