Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

A theoretical and shock tube kinetic study on hydrogen abstraction from phenyl formate

Hongbo Ning, [ab] Dapeng Liu, [c] Junjun Wu, [ab] Liuhao Ma, [ab] Wei Ren, [*ab] and Aamir Farooq [c]

[a] *Shenzhen Research Institute, The Chinese University of Hong Kong, New Territories, Hong Kong*

[b] *Department of Mechanical and Automation Engineering, The Chinese University of Hong Kong, New Territories, Hong Kong*

[c] *King Abdullah University of Science and Technology (KAUST), Clean Combustion Research Center, Physical Sciences and Engineering Division, Thuwal 23955, Saudi Arabia*

[*] Corresponding author. *E-mail address*: renwei@mae.cuhk.edu.hk (W. Ren)

Table S1 Relative energies (kcal mol^{-1}) for H-abstraction reactions PF + H/O/OH/HO_2 at the ROCBS-QB3//M06-2X/cc-pVTZ level.

Reactants	RCs	TS1	PCs	Products
H (0.0)		9.2		H_2 (-8.0)
O (0.0)		8.3		OH (-5.4)
PF + OH (0.0)	-1.5	0.9	-22.5	PFR1 + H_2O (-21.2)
HO_2 (0.0)[a]		16.5[a]		H_2O_2 (11.3)[a]
		TS2		
H (0.0)		15.8		H_2 (8.3)
O (0.0)		10.9		OH (10.9)
PF + OH (0.0)	-1.5	4.1	-4.6	PFR2 + H_2O (-4.9)
HO_2 (0.0)[a]		22.2[a]		H_2O_2 (26.1)[a]
		TS3		
H (0.0)		14.7		H_2 (7.6)
O (0.0)		9.9		OH (10.2)
PF + OH (0.0)	-2.1	4.0	-6.4	PFR3 + H_2O (-5.6)
HO_2 (0.0)[a]		23.9[a]		H_2O_2 (25.9)[a]
		TS4		
H (0.0)		15.2		H_2 (7.9)
O (0.0)		10.2		OH (10.5)
PF + OH (0.0)	-5.4	4.0	-5.4	PFR4 + H_2O (-5.3)
HO_2 (0.0)[a]		24.5[a]		H_2O_2 (26.4)[a]

Note: [a] at the M06-2X/cc-pVTZ level.

Table S2 Site-specific H-abstraction rate constants for reactions PF + H/O/OH/HO_2.

Reactions	A (cm^3 $molecule^{-1}$ s^{-1})	n	E (kcal mol^{-1})
PF + H = PFR1 + H_2	4.277×10^{-19}	2.46	5.23
= PFR2 + H_2	1.892×10^{-17}	1.98	13.88
= PFR3 + H_2	2.151×10^{-17}	2.01	12.48
= PFR4 + H_2	1.907×10^{-17}	1.93	12.93
PF + O = PFR1 + OH	9.681×10^{-20}	2.61	5.54
= PFR2 + OH	7.541×10^{-20}	2.64	9.41
= PFR3 + OH	3.197×10^{-18}	2.24	8.56
= PFR4 + OH	4.376×10^{-18}	2.22	8.83
PF + OH = PFR1 + H_2O	1.048×10^{-19}	2.50	-0.31
= PFR2 + H_2O	1.513×10^{-22}	3.32	1.57
= PFR3 + H_2O	3.365×10^{-21}	2.95	1.83
= PFR4 + H_2O	2.746×10^{-21}	2.94	1.77
PF + HO_2 = PFR1 + H_2O_2	3.533×10^{-24}	3.48	13.21
= PFR2 + H_2O_2	1.199×10^{-24}	3.41	20.37
= PFR3 + H_2O_2	3.073×10^{-23}	3.22	22.38
= PFR4 + H_2O_2	4.153×10^{-23}	3.15	22.82

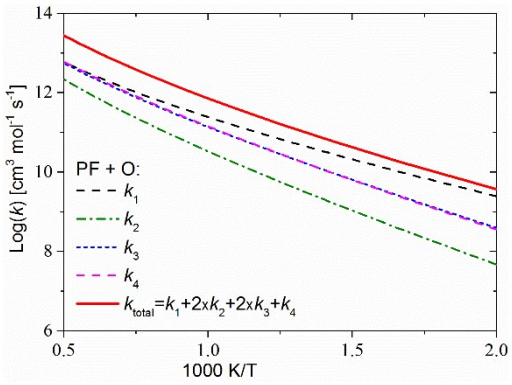

Fig. S1. Rate constants for PF + O determined in this work.