Supporting Information for

Quantitative Evaluation of the Actual Hydrogen Atom Donating Activities of O-H bonds in Phenols: Structure-Activity Relationship

Yan-Hua Fu,*[†] Yanwei Zhang,[†] Fang Wang,[†] Ling Zhao,[†] Guang-Bin Shen,*[§] Xiao-Qing Zhu*[‡]

[†] *College of Chemistry and Environmental Engineering, Anyang Institute of Technology, Anyang, Henan, 455000, China*

[§] *School of Medical Engineering, Jining Medical University, Jining, Shandong, 272000, P. R. China.*

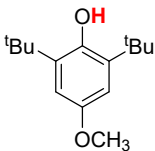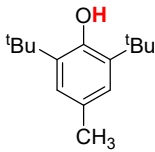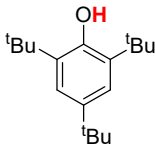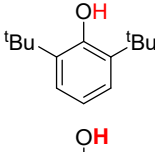[‡] *Department of Chemistry, Nankai University, Tianjin, 300071, China*
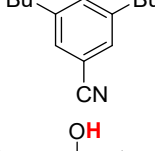
E-mail:20180031@ayit.edu.cn; gbshen@mail.jnmc.edu.cn; xqzhu@nankai.edu.cn

SI. Kinetic studies of the HAT reactions from XH to Y in literatures

The second-order rate constants k_2 and activation free energies $\Delta G^{\neq}_{XH/Y}$ of HATs are listed in Table S1.
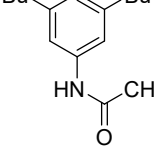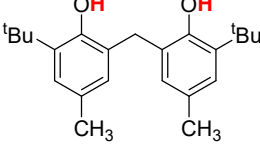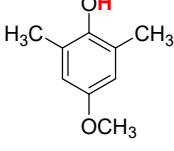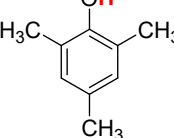
Table S1. Second-order rate constants (k_2), activation free energies ($\Delta G^{\neq}_{XH/Y}$) of HAT reactions (XH/CumO•) and the references in CH$_3$CN at 298 K.

XH	Y	k_2 (M^{-1}s^{-1}) [a]	$\Delta G^{\neq}_{XH/Y}$(kcal/mol) [b]	ref.
	PINO	8.00×10^4	10.76	S2
	PINO	6.00×10^3	12.29	S2
	PINO	4.80×10^3	12.43	S2
	PINO	1.50×10^3	13.11	S2
	DPPH	5.00×10^{-2}	19.22	S4
	PINO	3.60×10^4	11.23	S2
	DPPH	1.50×10^4	11.75	S5
	PINO	2.70×10^6	8.68	S2
	PINO	1.40×10^5	10.43	S2

Substrate	Oxidant	k	BDE	Ref
	PINO	1.60×10^4	11.71	S2
	DPPH	8.60×10^{-2}	18.90	S4
	PINO	1.00×10^4	11.99	S2
	DPPH	1.10×10^{-2}	20.12	S4
	PINO	1.20×10^6	9.16	S2
	DPPH	1.90×10^{-2}	19.79	S4
	DPPH	5.00	16.49	S1
	DPPH	6.40×10^{-2}	19.07	S4
	DPPH	3.40×10^{-2}	19.45	S4
	DPPH	1.20×10^3	13.25	S1

(structure)	DPPH	2.34×10^3	12.85	S1
(structure)	DPPH	2.80×10^2	14.11	S1
(structure)	PINO	1.20×10^5	10.52	S3
(structure)	PINO	8.20×10^4	10.74	S3
(structure)	PINO	2.50×10^8	5.99	S3
(structure)	DPPH	4.90×10^2	13.78	S6
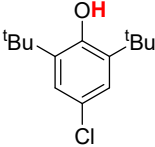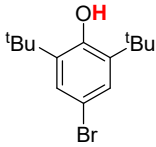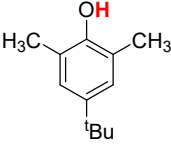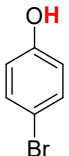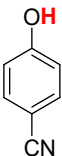
[a] The uncertainty of date is smaller than 5%.　[b] The date of $\Delta G^{\neq}_{XH/Y}$ are derived from Eyring equation $k_2 = (k_B T/h)\exp(-\Delta G^{\neq}/RT)$.

SII. ΔG^o(XH) determined by theoretical calculation in this work

In order to obtain the electronic effects of the substituents at position 4, the changes of bond dissociation free energy $\Delta\Delta G^o$ between H-substituted phenols (4H, 10H and 15H) and other substituents in the 2, 6-di-*tert*-butylphenol series, 2, 6-di-methylphenol series and 4-substituted phenols respectively, are compared in Table 2. The ΔG^o(XH) values of some 2, 6-di-*tert*-butylphenol series, 2, 6-di-methylphenol series and 4-substituted phenols determined by theoretical calculation in this work are listed in Table S2.
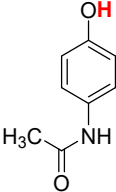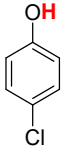
Table S2. ΔG^o(XH) of O-H bonds in phenols in CH_3CN at 298 K determined by the *i*BonD HM method in this work.

XH	ΔG^o(XH) (kcal/mol) [a]	XH	ΔG^o(XH) (kcal/mol) [a]

2,6-di-tBu-4-Cl-phenol (OH)	77.50
2,6-di-tBu-4-Br-phenol (OH)	76.70
2,6-dimethyl-4-tBu-phenol (OH)	78.60
N-(4-hydroxyphenyl)acetamide (OH)	80.90
4-Cl-phenol (OH)	85.40
4-Br-phenol (OH)	83.70
4-CN-phenol (OH)	87.80

[a] ΔG^o(XH) values are obtained by the *i*BonD HM method in this work.

SIII. Calculation process

$\Delta G^{\neq o}$(CumOO$^\bullet$) = -41.63 kcal/mol, $\Delta G^{\neq o}$(XH) of antioxidants should be within the scope of 44.35 ~49.80 kcal/mol, the calculation process is provided below.

$$XH + CumOO^\bullet \quad \rightarrow \quad X^\bullet + CumOO\text{-}H \tag{1}$$

$$\Delta G^{\neq}_{XH/CumOO}{}^\bullet = \Delta G^{\neq o}(XH) + \Delta G^{\neq o}(CumOO^\bullet) \tag{2}$$

The magnitude of second-order rate constant for equation 1 is $10 \sim 10^5$ M^{-1}s^{-1}, as it is easy and accurate to determine the rate constant by stopped-flow method. According to Eyring equation:

$$k_2 = (k_B T/h)\exp(-\Delta G^{\neq}/RT) \tag{3}$$

When T = 298 K, we substitute the constants into the eq 3 to obtain the relationship between the activation free energy $\Delta G^{\neq}$ and the second-order rate constant k_2.

$$\Delta G^{\neq} = 1.36373 \times (12.7926 - \lg k_2) \tag{4}$$

When $k_2 = 10$ M^{-1}s^{-1}, $\Delta G^{\neq}_{XH/CumOO}{}^\bullet = 16.08$ kcal/mol,

$\Delta G^{\neq o}$(XH) = $\Delta G^{\neq}_{XH/CumOO}{}^\bullet$ - $\Delta G^{\neq o}$(CumOO$^\bullet$) = 49.80 kcal/mol

When $k_2 = 10^5$ M^{-1}s^{-1}, $\Delta G^{\neq}_{BNAH/Y} = 10.63$ kcal/mol,

$\Delta G^{\neq o}$(XH) = $\Delta G^{\neq}_{XH/CumOO}{}^\bullet$ - $\Delta G^{\neq o}$(CumOO$^\bullet$) = 44.35 kcal/mol

References

S1 R. Amorati, S. Menichetti, C. Viglianisib, M. C. Foti, *Chem. Commun.,* 2012*,* **48***,* 11904-11906.

S2 C. D' Alfonso, M. Bietti, G. A. DiLabio, O. Lanzalunga, M. Salamone, *J. Org. Chem.*, 2013, **78**, 1026-1037.

S3 M. Mazzonna, M. Bietti, G. A. DiLabio, O. Lanzalunga, M. Salamone, *J. Org. Chem.*, 2014, **79**, 5209-5218.

S4 G. Litwinienko, K. U. Ingold, *J. Org. Chem.*, 2003, **68**, 3433-3438.

S5 G. Litwinienko, K. U. Ingold, *J. Org. Chem.*, 2005, **70**, 8982-8990.

S6 L. Valgimigli, J. T. Banks, J. Lusztyk, K. U. Ingold, *J. Org. Chem.*, 1999, **64**, 3381-3383.