Supporting Information

Enhanced formation of trihalomethane disinfection byproducts from halobenzoquinones under combined UV/chlorine conditions

He Zhao[a,b], Ching-Hua Huang[b,*], Chen Zhong[a], Penghui Du[a,c], Peizhe Sun[b,d]

[a] *Beijing Engineering Research Center of Process Pollution Control, Division of Environment Technology and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China*

[b] *School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States*

[c] *State Environmental Protection Key Laboratory of Integrated Surface Water-Groundwater Pollution Control, School of Environmental Science and Engineering, Southern University of Science and Technology, Shenzhen 518055, China*

[d] *School of Environmental Science and Engineering, Tianjin University, Tianjin 300072, China*

***Corresponding author**

Email: ching-hua.huang@ce.gatech.edu (C.-H. Huang)

Tel: 1-404-894-7694; Fax: 1-404-385-7087

I. Methods

Stock preparation:

The stock solutions of individual HBQs (10 mM, with 0.1% formic acid) were prepared using methanol as solvent, and were stored at -20°C. The stock solutions were diluted by DI water before use.

DFT calculations:

In this study, the reactivity of HBQs as a whole was determined by the global nucleophilicity index (N, eV) and the global electrophilicity index (ω, eV) using Multiwfn software (Pérez et al. 2002, Chamorro et al. 2003, Lu et al. 2012). The highest occupied molecular orbital (HOMO) energy was used to describe the global nucleophilicity index, namely

$$N = E_{HOMO(Nu)}(eV) - E_{HOMO(TCE)}(eV)$$

Where tetracyanoethylene (TCE) is taken as a reference because it has the lowest HOMO energy in a series of molecule, giving us a positive nucleophilicity value (De Vleeschouwer et al. 2007).

The global electrophilicity index ω was calculated using the following equations:

$$\omega = \frac{\mu^2}{2\eta}$$

$$\mu \approx \frac{1}{2}(E_{HOMO} + E_{LUMO})$$

$$\eta = \left(\frac{\partial \mu}{\partial N}\right)_{v(r)} \cong (E_{LUMO} - E_{HOMO})$$

where μ was the electronic chemical potential, and η was the chemical hardness (Chattaraj et al. 2011).

Fukui function is an important concept in conceptual density functional theory, it has been widely used in prediction of reactive site of electrophilic and nucleophilic attacks (Parr et al. 1984). Fukui function is defined as

$$f(\mathrm{r}) = \left[\frac{\partial \rho(\mathrm{r})}{\partial N}\right]_V$$

where $\rho(\mathrm{r})$ is the electron density at a point r in space, *N* is electron number in present system, the constant term *v* in the partial derivative is external potential. In the condensed version of Fukui function, atomic population number is used to represent the amount of electron density distribution around an atom. The condensed Fukui function can be calculated unambiguously for three situations:

Nucleophilic attack: $f_k^+ = q_N^k - q_{N+1}^k$

Electrophilic attack: $f_k^- = q_{N-1}^k - q_N^k$

Radical attack: $f_k^0 = (q_{N-1}^k - q_{N+1}^k)/2$

where q^k is the atom charge of atom K at corresponding state, the reactive sites usually have larger value of CFF than other regions. In this study, Hirshfeld charge was used to study reactive site as it is considered to be one of the most suitable methods to calculate CFF (Olah et al. 2002).

The local nucleophilicity index (N_k, e*eV) and the local electrophilic index (ω_k, e*eV) have also been proposed to provide the local information of a particular atomic site in a molecule being prone to nucleophilic and electrophilic attack, respectively.

$$N_k = N\, f_k^-$$

$$\omega_k = \omega f_k^+$$

where $f^-(k)$ and $f^-(k)$ are the Fukui functions for electrophilic attack and nucleophilic attack, respectively (Roy et al. 2005). This Fukui function is condensed to atoms to calculate the Fukui index.

II. Hydroxylated products of HBQs

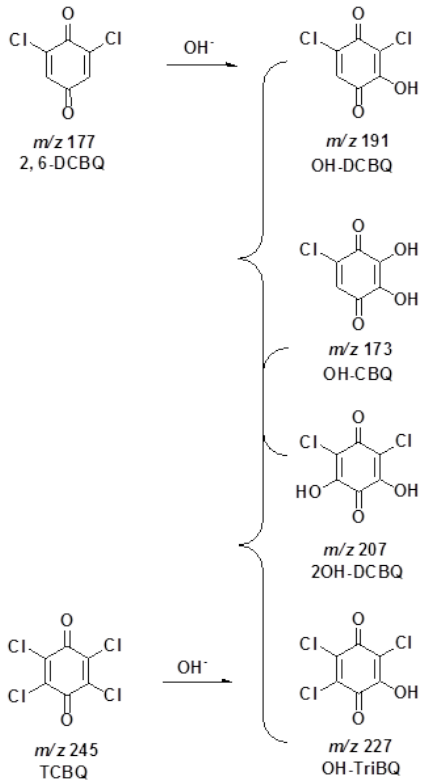


Figure S1. Possible hydroxylated products of 2,6-DCBQ and TCBQ (Qian et al., 2013).

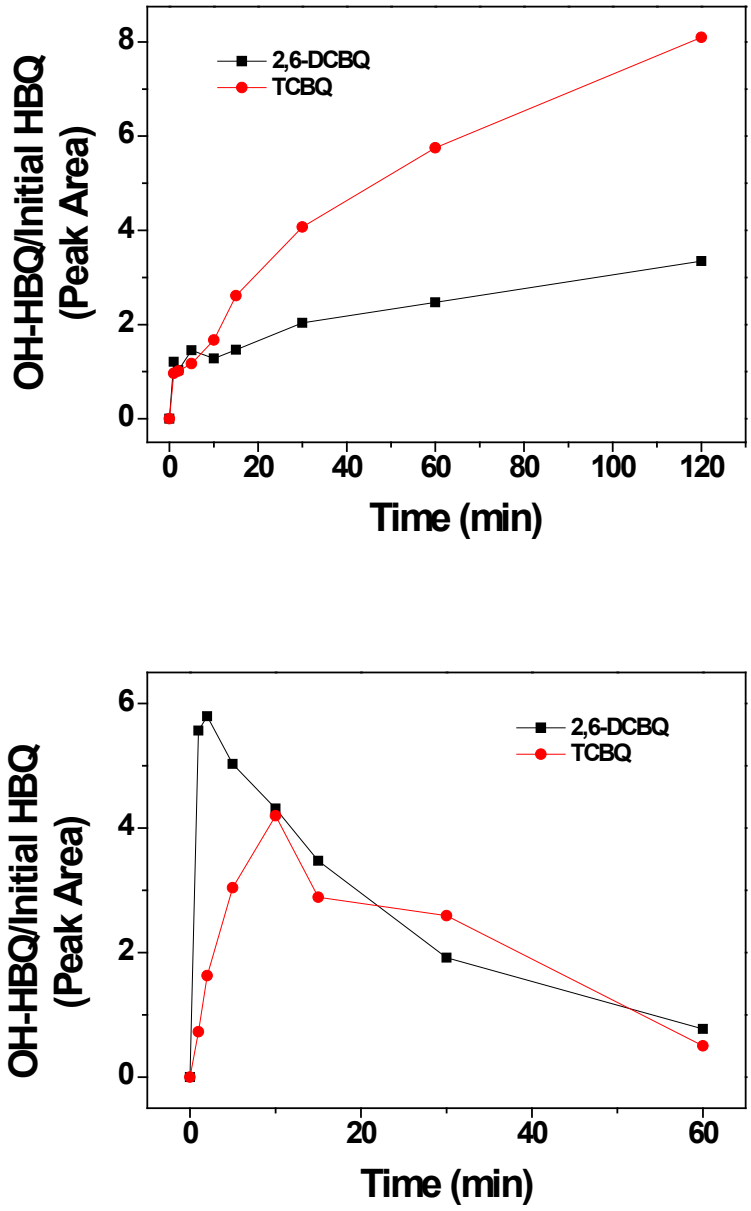


Figure S2. Variation of the peak area ratio of OH-HBQ products and the initial HBQs with time, a) at pH 8.0 without UV irradiation; and b) at pH 7.0 with UV = 3.9×10^{-6} Einstein/(L·s). ($[HBQ]_0 = 20$ μM)

III. Effect of UV on the stability of THMs

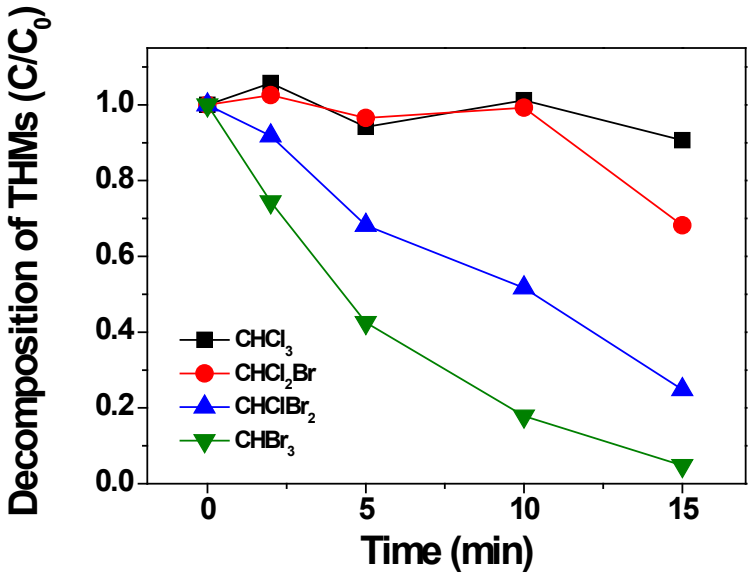
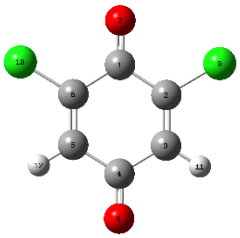


Figure S3. Decomposition of THMs species under UV irradiation. ($[THM]_0$ = 20 μM, pH = 7.0, UV = 3.9×10^{-6} Einstein·L^{-1}·s^{-1})

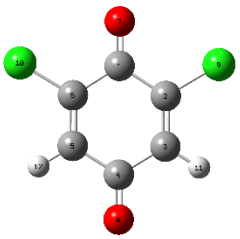
IV. The DFT calculation results of HBQs and OH-HBQs.

Table S1. The DFT calculation results of 2,6-DCBQ.



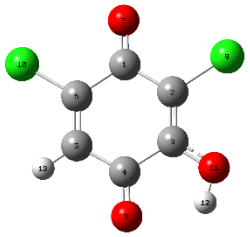
Label	Site	f^+	f^-	f^0	ω_k	N_k
1	C	0.0859	0.0103	0.0481	0.19161	0.01452
2	C	0.056	0.0631	0.0595	0.12479	0.08917
3	C	0.0668	0.1051	0.0859	0.14888	0.1486
4	C	0.0776	0.0199	0.0487	0.17294	0.02815
5	C	0.0668	0.1051	0.0859	0.14888	0.1486
6	C	0.056	0.0631	0.0595	0.12479	0.08917
7	O	0.1416	0.06	0.1008	0.31564	0.08476
8	O	0.1414	0.0771	0.1092	0.31534	0.10892
9	Cl	0.1133	0.2064	0.1598	0.25257	0.29179
10	Cl	0.1133	0.2064	0.1598	0.25257	0.29179
11	H	0.0408	0.0418	0.0413	0.09094	0.05906
12	H	0.0408	0.0418	0.0413	0.09094	0.05906

Table S2. The DFT calculation results of 2,6-DCBQ*.



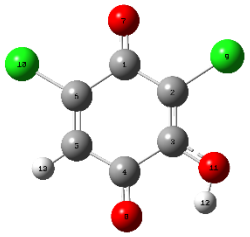
Label	Site	f^+	f^-	f^0	ω_k	N_k
1	C	0.0861	0.0086	0.0473	0.22698	0.00988
2	C	0.0509	0.058	0.0544	0.13418	0.0663
3	C	0.0651	0.0992	0.0821	0.17174	0.11337
4	C	0.0794	0.0189	0.0492	0.20953	0.02164
5	C	0.0651	0.0992	0.0821	0.17174	0.11337
6	C	0.0509	0.058	0.0544	0.13418	0.0663
7	O	0.1485	0.0612	0.1048	0.39164	0.06995
8	O	0.1487	0.0813	0.115	0.39213	0.09293
9	Cl	0.1132	0.2178	0.1655	0.29869	0.24899
10	Cl	0.1132	0.2178	0.1655	0.29869	0.24899
11	H	0.0394	0.04	0.0397	0.10405	0.04567
12	H	0.0394	0.04	0.0397	0.10405	0.04567

Table S3. The DFT calculation results of OH-DCBQ.



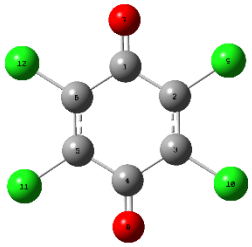
Label	Site	f^+	f^-	f^0	ω_k	N_k
1	C	0.0733	0.0181	0.0457	0.14544	0.0359
2	C	0.0385	0.1009	0.0697	0.07633	0.19971
3	C	0.0428	0.0868	0.0648	0.08499	0.1719
4	C	0.095	0.0142	0.0546	0.18848	0.02816
5	C	0.0661	0.0592	0.0627	0.13116	0.11721
6	C	0.0721	0.031	0.0516	0.1431	0.06135
7	O	0.1297	0.0686	0.0991	0.25731	0.13572
8	O	0.1379	0.0628	0.1003	0.2735	0.12429
9	Cl	0.1009	0.2346	0.1678	0.20015	0.46444
10	Cl	0.1242	0.1386	0.1314	0.2464	0.27436
11	O	0.0535	0.1134	0.0835	0.10613	0.22452
12	H	0.0257	0.0383	0.032	0.05105	0.07582
13	H	0.0402	0.0333	0.0368	0.0797	0.06596

Table S4. The DFT calculation results of OH-DCBQ*.



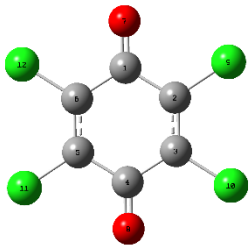
Label	Site	f^+	f^-	f^0	ω_k	N_k
1	C	0.0711	0.0214	0.0463	0.18878	0.05109
2	C	0.0517	0.1021	0.0769	0.13725	0.24364
3	C	0.045	0.1015	0.0733	0.1196	0.2421
4	C	0.0872	0.0177	0.0524	0.23155	0.04211
5	C	0.0527	0.0516	0.0522	0.13994	0.12312
6	C	0.0563	0.033	0.0446	0.14937	0.07872
7	O	0.1419	0.0816	0.1118	0.37677	0.19461
8	O	0.1416	0.0843	0.1129	0.37582	0.20096
9	Cl	0.1139	0.2	0.157	0.30241	0.47717
10	Cl	0.1167	0.1313	0.124	0.30975	0.31317
11	O	0.0561	0.1027	0.0794	0.14903	0.24505
12	H	0.0291	0.0399	0.0345	0.07724	0.09525
13	H	0.0366	0.0328	0.0347	0.09728	0.07826

Table S5. The DFT calculation results of TCBQ.



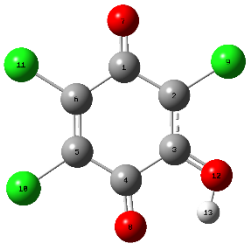
Label	Site	f^+	f^-	f^0	ω_k	N_k
1	C	0.0754	0.01	0.0427	0.185	0.01648
2	C	0.0462	0.0591	0.0527	0.11343	0.09699
3	C	0.0462	0.0591	0.0527	0.11343	0.09699
4	C	0.0754	0.01	0.0427	0.185	0.01648
5	C	0.0462	0.0591	0.0527	0.11343	0.09699
6	C	0.0462	0.0591	0.0527	0.11343	0.09699
7	O	0.1269	0.0538	0.0903	0.31134	0.08833
8	O	0.1269	0.0538	0.0903	0.31134	0.08833
9	Cl	0.1027	0.159	0.1308	0.25198	0.26098
10	Cl	0.1027	0.159	0.1308	0.25198	0.26098
11	Cl	0.1027	0.159	0.1308	0.25198	0.26098
12	Cl	0.1027	0.159	0.1308	0.25198	0.26098

Table S6. The DFT calculation results of TCBQ*.



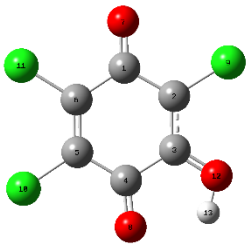
Label	Site	f^+	f^-	f^0	ω_k	N_k
1	C	0.0772	0.0095	0.0433	0.19261	0.01303
2	C	0.0453	0.0561	0.0507	0.11306	0.07685
3	C	0.0453	0.0561	0.0507	0.11306	0.07685
4	C	0.0772	0.0095	0.0433	0.19261	0.01303
5	C	0.0453	0.0561	0.0507	0.11306	0.07685
6	C	0.0453	0.0561	0.0507	0.11306	0.07685
7	O	0.1287	0.0527	0.0907	0.32121	0.0723
8	O	0.1287	0.0527	0.0907	0.32121	0.0723
9	Cl	0.1018	0.1628	0.1323	0.2541	0.22324
10	Cl	0.1018	0.1628	0.1323	0.2541	0.22324
11	Cl	0.1018	0.1628	0.1323	0.2541	0.22324
12	Cl	0.1018	0.1628	0.1323	0.2541	0.22324

Table S7.The DFT calculation results of OH-TCBQ.



Label	Site	f^+	f^-	f^0	ω_k	N_k
1	C	0.0663	0.0168	0.0416	0.14994	0.03822
2	C	0.0389	0.0999	0.0694	0.088	0.22683
3	C	0.0368	0.0842	0.0605	0.08317	0.19117
4	C	0.0916	0.012	0.0518	0.20717	0.02734
5	C	0.049	0.04	0.0445	0.11078	0.09084
6	C	0.0654	0.0343	0.0498	0.14799	0.07779
7	O	0.1236	0.0646	0.0941	0.27957	0.14671
8	O	0.1304	0.0577	0.094	0.29483	0.13101
9	Cl	0.0976	0.2093	0.1535	0.22067	0.47535
10	Cl	0.1051	0.1249	0.115	0.23781	0.28353
11	Cl	0.1196	0.1229	0.1212	0.27041	0.27903
12	O	0.05	0.0975	0.0738	0.11316	0.22142
13	H	0.0257	0.0359	0.0308	0.05813	0.08152

Table S8.The DFT calculation results of OH-TCBQ*.



Label	Site	f^+	f^-	f^0	ω_k	N_k
1	C	0.0686	0.0143	0.0414	0.16048	0.02666
2	C	0.0384	0.0879	0.0632	0.08991	0.16373
3	C	0.0392	0.0729	0.0561	0.09163	0.13589
4	C	0.0933	0.0104	0.0519	0.21842	0.01944
5	C	0.0454	0.045	0.0452	0.10632	0.08382
6	C	0.0618	0.0394	0.0506	0.14469	0.07343
7	O	0.1256	0.0619	0.0937	0.29384	0.11532
8	O	0.1318	0.056	0.0939	0.30843	0.10427
9	Cl	0.0991	0.2064	0.1527	0.23188	0.38447
10	Cl	0.1028	0.1377	0.1202	0.24045	0.2566
11	Cl	0.1161	0.1355	0.1258	0.27177	0.25242
12	O	0.0536	0.0992	0.0764	0.12538	0.18478
13	H	0.0243	0.0333	0.0288	0.05698	0.06211

References

Chamorro, E., Chattaraj, P.K. and Fuentealba, P. (2003) Variation of the electrophilicity index along the reaction path. The Journal of Physical Chemistry A 107(36), 7068-7072.

De Vleeschouwer, F., Van Speybroeck, V., Waroquier, M., Geerlings, P. and De Proft, F. (2007) Electrophilicity and nucleophilicity index for radicals. Organic Letters 9(14), 2721-2724.

Chattaraj, P. K., Giri S., Duley S. (2011) Update 2 of: Electrophilicity Index. Chemical Reviews 111(2), PR43- PR75

Lu, T., Chen F. (2012) Multiwfn: A multifunctional wavefunction analyzer. Journal of Computational Chemistry 33, 580-592

Olah, J., Van Alsenoy, C. and Sannigrahi, A.B. (2002) Condensed fukui functions derived from stockholder charges: Assessment of their performance as local reactivity descriptors. Journal of Physical Chemistry A 106(15), 3885-3890.

Parr, R. G.; Yang, W. T. (1984) Density Functional-Approach to the Frontier-Electron Theory of Chemical-Reactivity. Journal of the American Chemical Society 106(14), 4049-4050.

Pérez, P., Toro-Labbé, A., Aizman, A. and Contreras, R. (2002) Comparison between experimental and theoretical scales of electrophilicity in benzhydryl cations. The Journal of Organic Chemistry 67(14), 4747-4752.

Qian, Y., Wang, W., Boyd, J. M., Wu, M., Hrudey, S. E. and Li, X-F. (2013) UV-Induced Transformation of Four Halobenzoquinones in Drinking Water. Environmental Science & Technology 47(9), 4426-4433

Roy, R.K., Usha, V., Paulovič, J. and Hirao, K. (2005) Are the local electrophilicity descriptors reliable indicators of global electrophilicity trends? The Journal of Physical Chemistry A 109(20), 4601-4606