Supplementary Materials for

Degradation of sulpiride in water by UV/Cl process: Kinetics, reaction mechanism and transformation pathways

Heng Zhang[a, b, c], Miao Chen[a, b, c], Changsheng Guo[a, b, c], Jingpu Fan[a, b, c], Jian Xu[a, b, c, *]

[a] State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing, 100012, China

[b] State Environmental Protection Key Laboratory of Ecological Effect and Risk Assessment of Chemicals, Chinese Research Academy of Environmental Sciences, Beijing, 100012, China

[c] Center for Environmental Health Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing, 100012, China

[*]: all correspondence should be addressed. Tel: 86-10-84916028; Fax: 86-10-84916028; E-mail: xujian@craes.org.cn

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Reactions involved in the reactive radicals in UV/chlorine process. (S1-S15)

$$ClO^{-} \xrightarrow{hv} O^{\cdot -} + Cl\cdot \quad (S1)$$

$$HClO \xrightarrow{hv} \cdot OH + Cl\cdot \quad (S2)$$

$$\cdot OH \rightleftharpoons O^{\cdot -} + H^{+} \qquad pK_a=11.9 \quad (S3)$$

$$\cdot OH + HClO \longrightarrow ClO\cdot + H_2O \qquad 2.0\times10^{9}\ M^{-1}s^{-1} \quad (S4)$$

$$\cdot OH + ClO^{-} \longrightarrow ClO\cdot + OH^{-} \qquad 8.8\times10^{9}\ M^{-1}s^{-1} \quad (S5)$$

$$\cdot OH + Cl^{-} \rightleftharpoons ClOH^{\cdot -} \qquad k_{+}=4.3\times10^{9}\ M^{-1}s^{-1}$$

$$k_{-}=6.1\times10^{9}\ M^{-1}s^{-1} \quad (S6)$$

$$\cdot OH + OH^{-} \rightleftharpoons O^{\cdot -} + H_2O \qquad k_{+}=1.3\times10^{10}\ M^{-1}s^{-1}$$

$$k_{-}=1.8\times10^{6}\ M^{-1}s^{-1} \quad (S7)$$

$$Cl\cdot + HClO \longrightarrow ClO\cdot + H_20 \qquad 3.0\times10^{9}\ M^{-1}s^{-1} \quad (S8)$$

$$Cl\cdot + ClO^{-} \longrightarrow ClO\cdot + Cl^{-} \qquad 8.2\times10^{9}\ M^{-1}s^{-1} \quad (S9)$$

$$Cl\cdot + Cl^{-} \rightleftharpoons Cl_2^{\cdot -} \qquad k_{eq}=5.9\times10^{4}\ M^{-1} \quad (S10)$$

$$Cl\cdot + OH^{-} \longrightarrow ClOH^{\cdot -} \qquad 1.8\times10^{10}\ M^{-1}s^{-1} \quad (S11)$$

$$ClOH^{\cdot -} + H^{+} \rightleftharpoons Cl\cdot + H_2O \qquad k_{+}=2.1\times10^{10}\ M^{-1}s^{-1}$$

$$k_{-}=1.3\times10^{3}\ M^{-1}s^{-1} \quad (S12)$$

$$Cl_2^{\cdot -} + \cdot OH \longrightarrow HClO + Cl^{-} \qquad 1.0\times10^{9}\ M^{-1}s^{-1} \quad (S13)$$

$$Cl_2^{\cdot -} + Cl_2^{\cdot -} \longrightarrow Cl_2 + 2Cl^{-} \qquad 9.0\times10^{8}\ M^{-1}s^{-1} \quad (S14)$$

$$Cl_2^{\cdot -} + Cl\cdot \longrightarrow Cl_2 + Cl^{-} \qquad 2.1\times10^{9}\ M^{-1}s^{-1} \quad (S15)$$

$$HClO \leftrightarrows ClO^{-} + H^{+} \qquad k_{a(HClO)} \quad (S16)$$

HClO: $$\delta_{HClO} = \frac{[H^{+}]}{[H^{+}] + k_{a(HClO)}} \quad (S17)$$

ClO^-: $$\delta_{ClO^{-}} = \frac{k_{a(HClO)}}{[H^{+}] + k_{a(HClO)}} \quad (S18)$$

$$\mathrm{SLP^{+} \rightleftarrows SLP + H^{+}} \qquad k_{a1} \tag{S19}$$

$$\mathrm{SLP \rightleftarrows SLP^{-} + H^{+}} \qquad k_{a2} \tag{S20}$$

$$\mathrm{SLP^{+}}: \delta_{cat} = \frac{[\mathrm{H^{+}}]^2}{[\mathrm{H^{+}}]^2 + k_{a1(SLP)}[\mathrm{H^{+}}] + k_{a1(\mathrm{SLP})}k_{a2(\mathrm{SLP})}} \tag{S21}$$

$$\mathrm{SLP}: \delta_{neu} = \frac{k_{a1(SLP)}[\mathrm{H^{+}}]}{[\mathrm{H^{+}}]^2 + k_{a1(\mathrm{SLP})}[\mathrm{H^{+}}] + k_{a1(\mathrm{SLP})}k_{a2(\mathrm{SLP})}} \tag{S22}$$

$$\mathrm{SLP^{-}}: \delta_{ani} = \frac{k_{a1(SLP)}k_{a2(\mathrm{SLP})}}{[\mathrm{H^{+}}]^2 + k_{a1(\mathrm{SLP})}[\mathrm{H^{+}}] + k_{a1(\mathrm{SLP})}k_{a2(\mathrm{SLP})}} \tag{S23}$$

$$SLP^{+} + \mathrm{HClO} \rightarrow products \qquad k_{\mathrm{SLP^{+}\cdot HClO}} \tag{S24}$$

$$SLP^{+} + \mathrm{ClO^{-}} \rightarrow products \qquad k_{\mathrm{SLP^{+}\cdot ClO^{-}}} \tag{S25}$$

$$SLP + \mathrm{HClO} \rightarrow products \qquad k_{\mathrm{SLP\cdot HClO}} \tag{S26}$$

$$SLP + \mathrm{ClO^{-}} \rightarrow products \qquad k_{\mathrm{SLP\cdot ClO^{-}}} \tag{S27}$$

$$\mathrm{SLP^{-}} + \mathrm{HClO} \rightarrow products \qquad k_{\mathrm{SLP^{-}\cdot HClO}} \tag{S28}$$

$$SLP^{-} + \mathrm{ClO^{-}} \rightarrow products \qquad k_{\mathrm{SLP^{-}\cdot ClO^{-}}} \tag{S29}$$

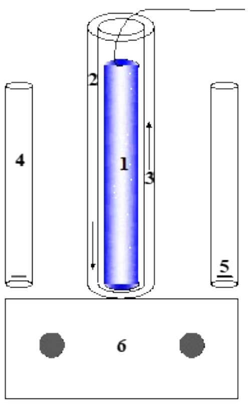


Figure S1. The schematic diagram of the experimental setup: (1) Low-pressure Hg UV lamp, (2) quartz tube, (3) cooling water, (4) photoreactor, (5) magnetic stirrer, (6) magnetic stirrer apparatus.

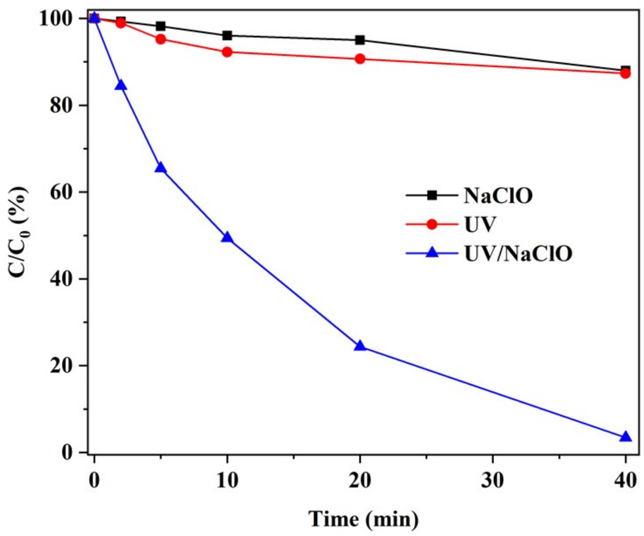


Figure S2. Removal of SLP under different oxidation treatment. Experimental conditions: $[SLP]_0$ = 2 μmol/L, $[NaClO]_0$ = 100 μmol/L, UV intensity = 0.12 mW·cm^{-2}, pH 7.0, T = 25 ± 1^{o}C.

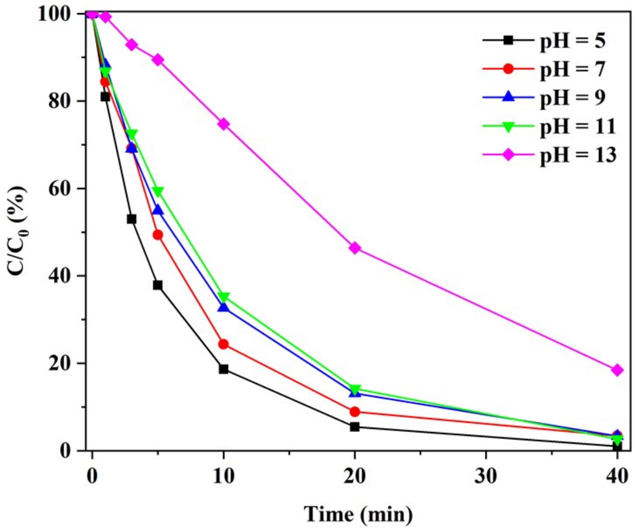


Figure S3. Effect of initial pH on SLP degradation by NaClO. Experimental conditions: $[SLP]_0$ = 2 μmol/L, $[NaClO]_0$ = 100 μmol/L, UV intensity = 0.12 mW·cm^{-2}, pH 7.0, T= 25 ± 1^{o}C.

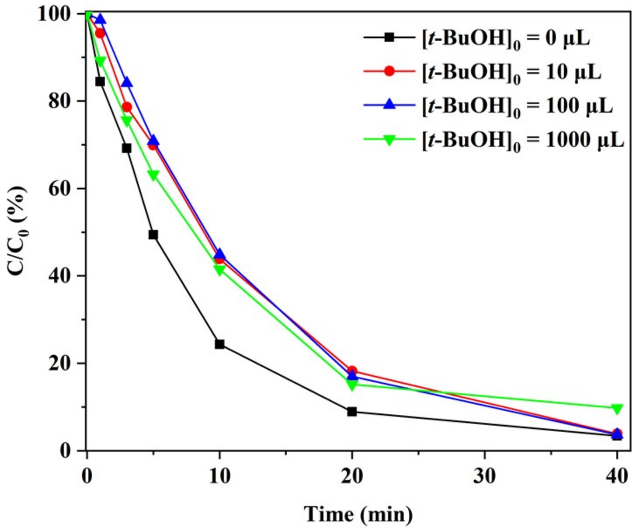


Figure S4. Effect of *t*-BuOH on SLP degradation by NaClO. Experimental conditions: $[SLP]_0$ = 2 μmol/L, $[NaClO]_0$ = 100 μmol/L, UV intensity = 0.12 mW·cm^{-2}, pH 7.0, T = 25 ± 1^{o}C.

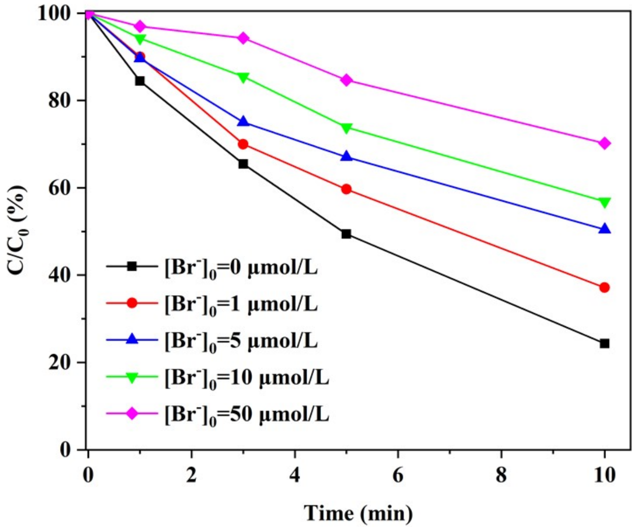


Figure S5. Effect of Br^- on SLP degradation by NaClO. Experimental conditions: $[SLP]_0$ = 2 μmol/L, $[NaClO]_0$ = 100 μmol/L, UV intensity = 0.12 mW·cm^{-2}, pH 7.0, T = 25 ± 1^{o}C.

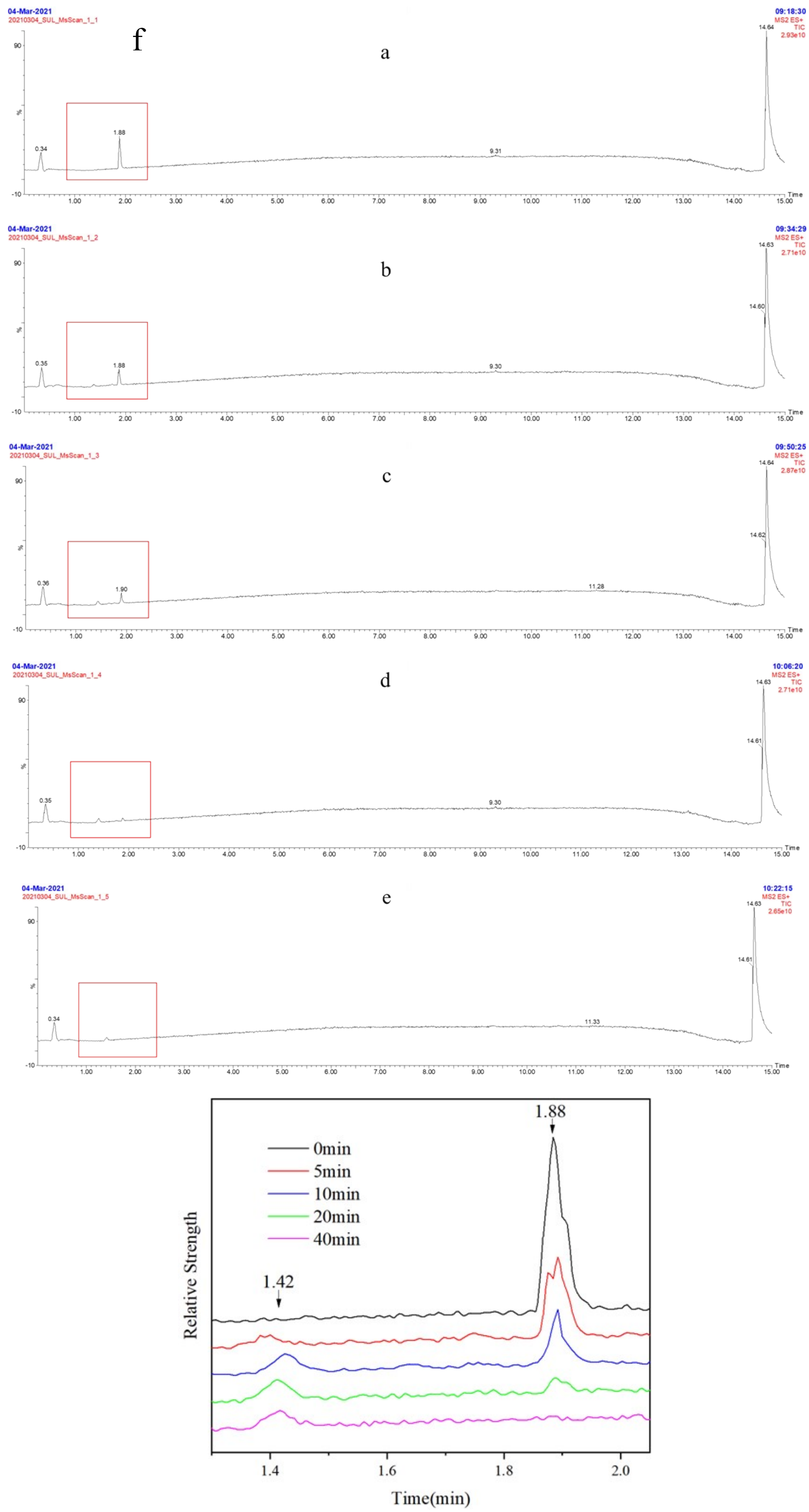


Figure S6. UPLC-MS/MS total ion chromatograms of SLP degradation at different time. (a) 0 min; (b) 5 min; (c) 10 min; (d) 20 min; (e) 40 min; (f) All times. Experimental conditions: $[SLP]_0$ = 10 μmol/L, $[NaClO]_0$ = 100 μmol/L, UV intensity = 0.12 $mW \cdot cm^{-2}$, pH 7.0, T = 25 ± 1°C.

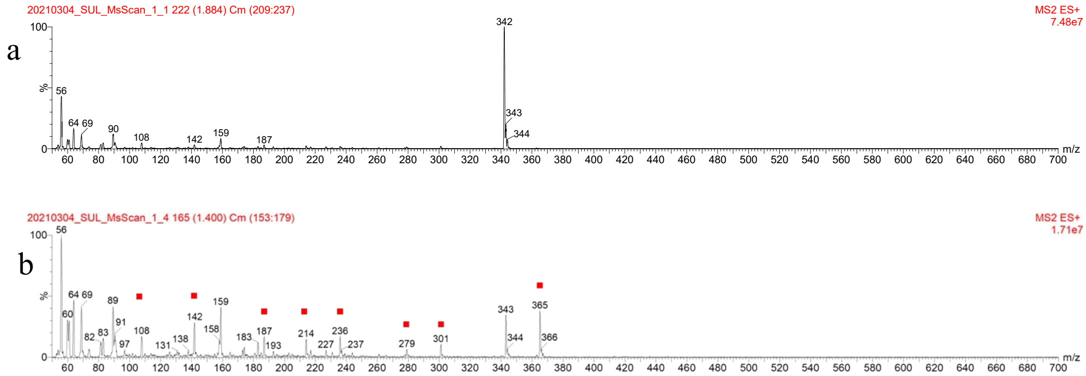


Figure S7. Mass spectra of the intermediate products.

Table S1. Chemical structures and properties of sulpiride.

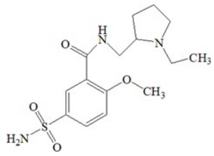
Compound	Proposed formula	Structure	CAS Number	LogP	pK_{a1}	pK_{a2}
Sulpiride	$C_{15}H_{23}N_3O_4S$		15676-16-1	2.66660	9.0	10.19

Table S2. The gradient elution condition of sulpiride.

Time（min）	Flow rate（mL/min）	Mobile phase A（%）	Mobile phase B（%）
0.00	0.400	5.0	95.0
0.50	0.400	5.0	95.0
1.50	0.400	50.0	50.0
3.50	0.400	95.0	5.0
4.50	0.400	95.0	5.0
4.60	0.400	5.0	95.0
5.00	0.400	5.0	95.0

Table S3. Optimized UPLC-MS/MS parameters for the sulpiride.

Compound	Parent ion (*m/z*)	Retention time (min)	Product ion (*m/z*)	Cone voltage (V)	Collision voltage (V)
Sulpiride	342.2	1.38	156	34	44
			214	34	30

Table S4. The gradient elution condition of SLP intermediates identification.

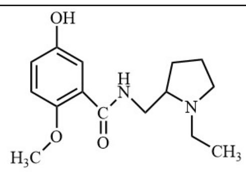
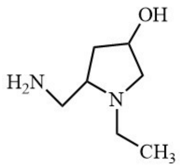
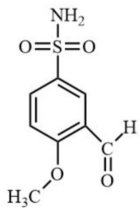
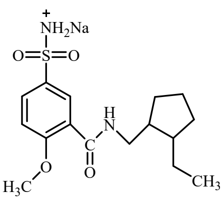
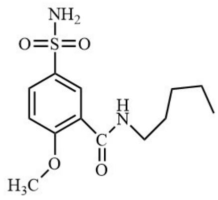
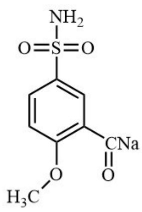
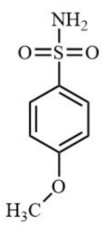
Time（min）	Flow rate（ml/min）	Mobile phase A（%）	Mobile phase B（%）
0.00	0.400	95.0	5.0
0.50	0.400	95.0	5.0
18.00	0.400	5.0	95.0
19.00	0.400	5.0	95.0
19.10	0.400	95.0	5.0
20.00	0.400	95.0	5.0

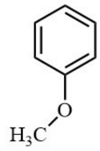
Table S5. The natural population analysis (NPA)atomic charges and Fukui functions at nuclei for SLP molecule, all units are a.u.

Labels*	NPA atomic charges	$f(\mathrm{r})^{+}$	$f(\mathrm{r})^{-}$
C1	-0.1994	0.0285	0.0299
C2	-0.2953	0.0820	0.0230
C3	-0.2703	0.0382	0.0235
C4	0.2681	0.0356	0.0208
C5	0.4909	0.0515	0.0116
C6	-0.9831	0.0357	0.0122
S7	0.2888	0.0160	0.0101
N8	-0.3619	0.0095	0.0200
O9	-0.2028	0.0258	0.0217
O10	-0.2214	0.0238	0.0250
O11	-0.2426	0.0131	0.0202
C12	-0.2928	0.0286	0.0085
C13	-0.2087	0.0391	0.0068
N14	0.0887	0.0212	0.0013
O15	-0.3010	0.0534	0.0179
C16	-0.3683	0.0081	0.0045
C17	-0.3583	0.0016	0.0174
N18	0.2584	0.0015	0.1789
C19	-0.2056	0.0070	0.0252
C20	-0.4642	0.0063	0.0253
C21	-0.1589	0.0002	0.0224
C22	-0.3091	0.0022	0.0280
C23	-0.4589	0.0079	0.0182

* The labels are presented in **Figure 6a.**

Table S6. Main fragment ions were obtained from MS analyses of sulpiride and its degradation products by NaClO.

Products	Proposed formula	Proposed structure	$[M+H]^+$
P1	$C_{15}H_{22}N_2O_3$		279
P2	$C_7H_{16}N_2O$		142
P3	$C_8H_9NO_4S$		214
P4	$C_{15}H_{23}N_3NaO_4S^+$		365
P5	$C_{13}H_{20}N_2O_4S$		300
P6	$C_8H_8NNaO_4S$		236
P7	$C_7H_9NO_3S$		187

P8	C_7H_8O		108