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Supplementary Information

for

# Structure-Reactivity Relationships and Substituent Effect Additivity in the Aqueous Oxidation of Chlorophenols by Cerium(IV)

Adrienn Simon, Csaba Ballai, Gábor Lente, István Fábián

Department of Inorganic and Analytical Chemistry, University of Debrecen, Debrecen, Hungary. Fax: 36-52-489-667; Tel: 36-52-512-900 Ext.: 2373; E-mail: lenteg@delfin.klte.hu

**Acid Dissociation Constants (Linear Algebraic Method).** The combined pH-metric and spectrophotometric data were evaluated based on the following equation:

$$\frac{A_{\lambda,pH}}{c_{tot}\ell} = \frac{\varepsilon_{\lambda,HA}10^{-pH} + \varepsilon_{\lambda,A}10^{-pK}}{10^{-pH} + 10^{-pK}} \tag{1}$$

The results were arranged in a data matrix of dimensions $n \times m$, where $n$ is the number of individual spectra measured at different pH values (typically 10-20) and $m$ is the number of wavelengths used (typically about 100-150 with a interval of 1 nm in the UV range of the spectrum). The data matrix $A$ has the following form:

$$A = \begin{pmatrix} A_{\lambda 1,\mathrm{pH1}} & A_{\lambda 1,\mathrm{pH2}} & \cdots & A_{\lambda 1,\mathrm{pHn}} \\ A_{\lambda 2,\mathrm{pH1}} & A_{\lambda 2,\mathrm{pH2}} & \cdots & A_{\lambda 2,\mathrm{pHn}} \\ \vdots & \vdots & \ddots & \vdots \\ A_{\lambda m,\mathrm{pH1}} & A_{\lambda m,\mathrm{pH2}} & \cdots & A_{\lambda m,\mathrm{pHn}} \end{pmatrix} \tag{S1}$$

The molar fraction matrix X is defined as follows.

$$X = \begin{pmatrix} \frac{10^{-pH1}}{10^{-pH1} + 10^{-pK}} & \frac{10^{-pK}}{10^{-pH1} + 10^{-pK}} \\ \frac{10^{-pH2}}{10^{-pH2} + 10^{-pK}} & \frac{10^{-pK}}{10^{-pH2} + 10^{-pK}} \\ \vdots & \vdots \\ \frac{10^{-pHn}}{10^{-pHn} + 10^{-pK}} & \frac{10^{-pK}}{10^{-pHn} + 10^{-pK}} \end{pmatrix} \tag{S2}$$

Using an initial estimate for the p$K$, the residual matrix, which gives the difference of measured data and the best fit to Equation 1 can be calculated as follows:

$$res = A - XX^{+}A \tag{S3}$$

where $X^{+}$ Moore-Penrose generalized matrix inverse of $X$. The sum of the residuals is then obtained as:

$$R^2(\mathrm{p}K) = \mathrm{Tr}(res^{\mathrm{T}}\mathrm{r}es) \tag{S4}$$

where $res^{\mathrm{T}}$ is the transpose of matrix $res$ and Tr means the trace of a square matrix. The $\mathrm{R}^2(\mathrm{p}K)$ function was minimized with a one-dimensional Simplex method to obtain the estimate of the p$K$.

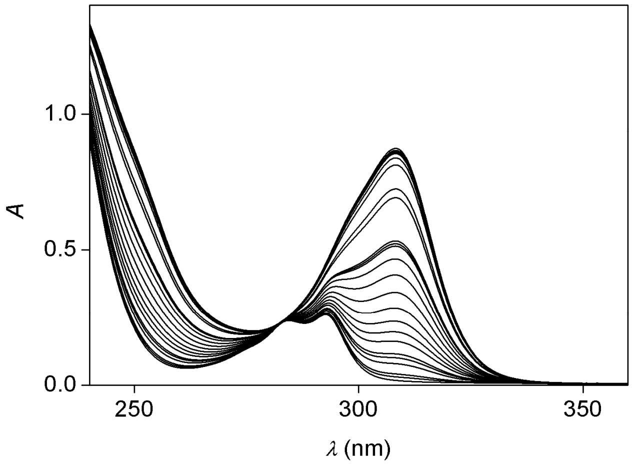

**Fig. S1.** UV-vis spectrum of 2,3,5,6-tetrachlorophenol as a function of pH. Concentration: 0.10 mM, optical path length: 1.000 cm, *T* = 25.0 ºC, pH values: 10.05, 9.44, 7.84, 7.17, 7.12, 7.10 7.08, 7.00, 6.91, 6.64, 6.37, 5.96, 5.87, 5.51, 5.48, 5.45, 5.37, 5.26, 5.13, 5.01, 4.90, 4.78, 4.69, 4.50, 4.43, 4.31, 3.92, 3.72, 3.05.

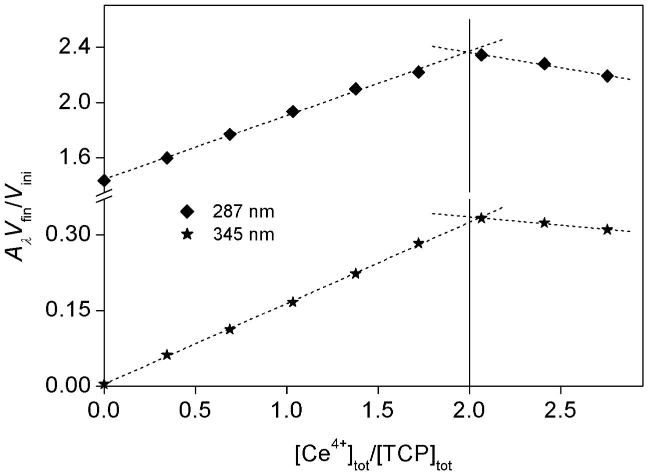

**Fig. S2.** Spectrophotometric titration of an aqueous solution of 2,4,6-trichlorophenol with cerium(IV) sulfate. Initial solution: *V* = 2.00 cm$^3$, [246] = 0.690 mM. Titrant: [Ce(IV)] = 4.75 mM. Increments: 0.100 cm$^3$. Optical path length: 1.000 cm, *T* = 25.0 ºC.

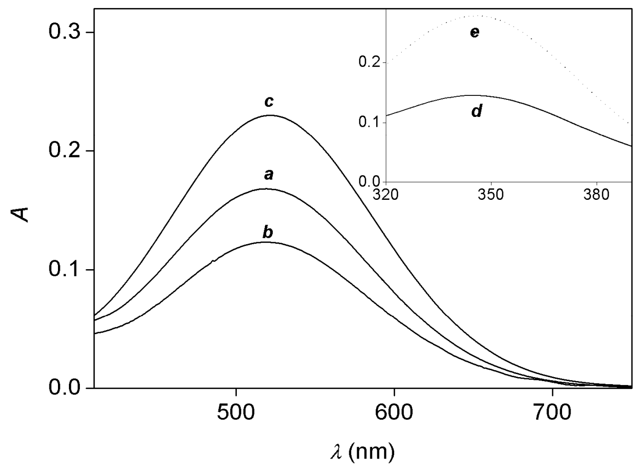

**Fig. S3.** Identification 2,6-dichloro-1,4-benzoquinone as a product in the reaction of 2,4,6-trichlorophenol with cerium(IV) sulfate. Experiment: 246 (0.431 mM) was mixed with Ce(IV) (0,648 mM), then EDTA was added (0,778). The pH was set to 4 by addition of aqueous NaOH, and the resulting solution was reacted with a 35% solution of $H_2O_2$ (**a**) or illuminated (**b**). A deep purple color developed, the spectrum of which is identical to the independently know spectrum of 2,6-dichloro-3-hydroxy-1,4-benzoquinone (**c**).[37] Inset: spectrum of the product from Fig. 1 (***d***), the independently known spectrum of 2,6-dichloro-1-4-benzoquinone (***e***).[37]

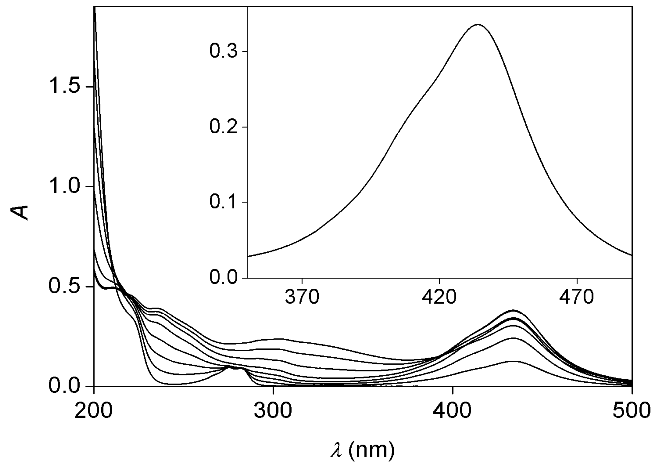

**Fig. S4.** Spectra recorded during the spectrophotometric titration of an aqueous solution of 2,6-dichlorophenol with cerium(IV) sulfate. $V = 2.00$ cm$^3$, [26] = 48.5 μM. Titrant: [Ce(IV)] = 396 μM. Increments: 0.100 cm$^3$. Optical path length: 1.000 cm, $T = 25.0$ ºC. Inset: spectrum at 1.23 ratio magnified.

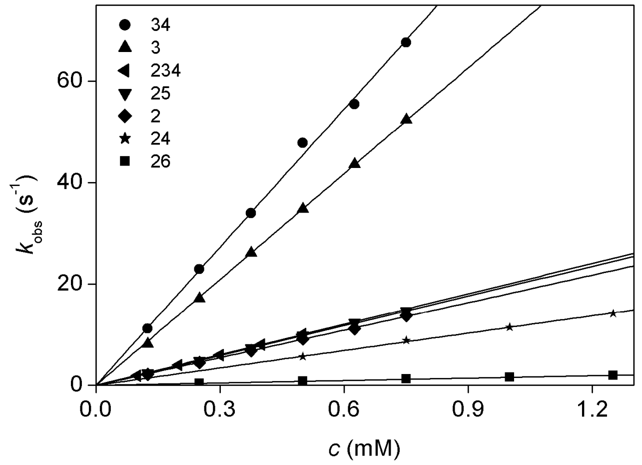

**Fig. S5.** Pseudo first-order rate constants as a function of chlorophenol concentration in the oxidation of various chlorophenols by cerium(IV) ion. Medium: 0.10 M $H_2SO_4$. $T$ = 25.0 ºC.

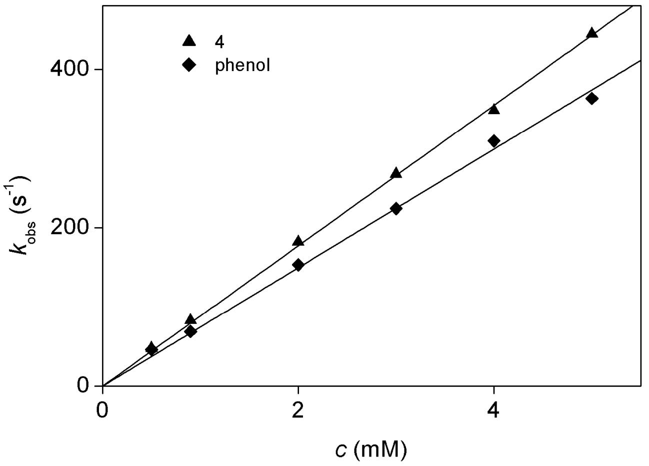

**Fig. S6.** Pseudo first-order rate constants as a function of chlorophenol concentration in the oxidation of various chlorophenols by cerium(IV) ion. Medium: 0.10 M $H_2SO_4$. $T$ = 25.0 ºC.

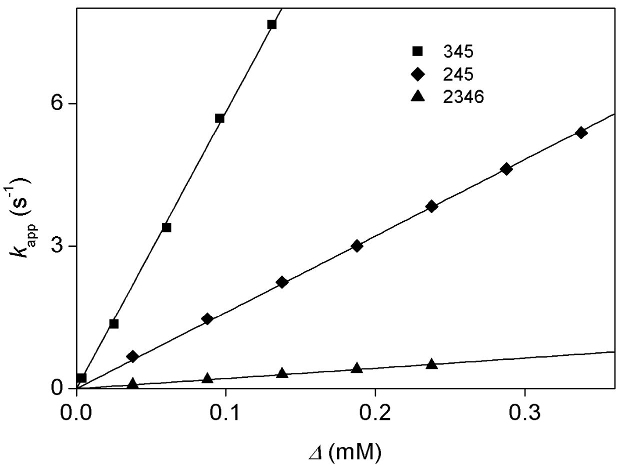

**Fig. S7.** Apparent rate constants from second-order fits as a function of chlorophenol concentration in the oxidation of various chlorophenols by cerium(IV) ion. Medium: 0.10 M $H_2SO_4$. $T$ = 25.0 ºC.

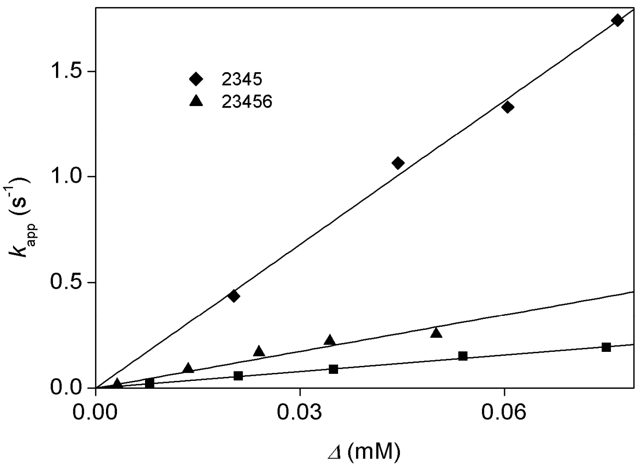

**Fig. S8.** Apparent rate constants from second-order fits as a function of chlorophenol concentration in the oxidation of various chlorophenols by cerium(IV) ion. Medium: 0.10 M $H_2SO_4$. $T$ = 25.0 ºC.

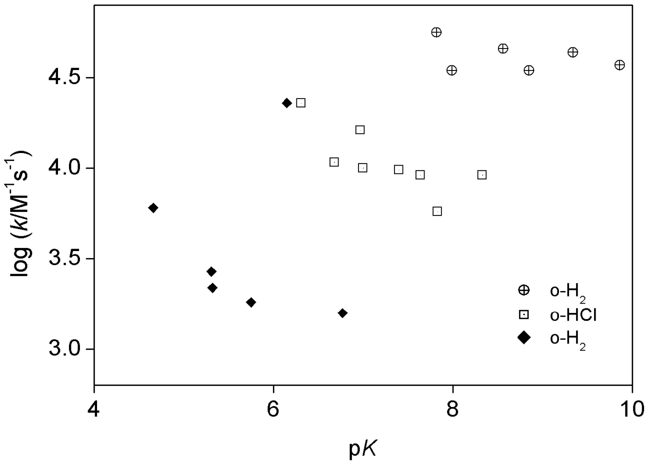

**Fig. S9.** Rate constants of the oxidation by cerium(IV) as a function of the p$K$ value for the studied chlorphenols.

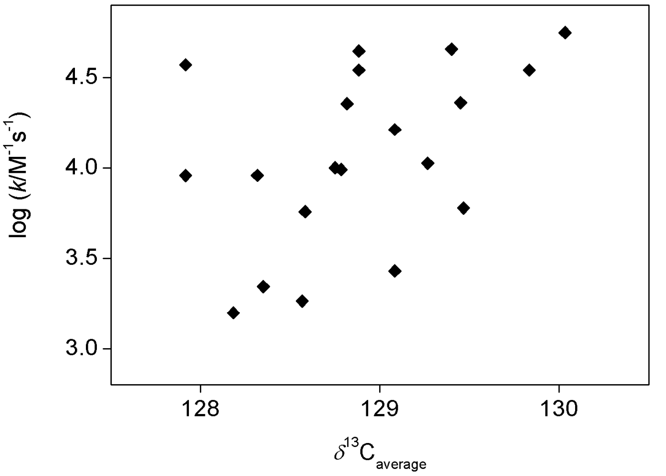

**Fig. S10.** Rate constants of the oxidation by cerium(IV) as a function of the average $^{13}C$ NMR chemical shifts for the studied chlorphenols.

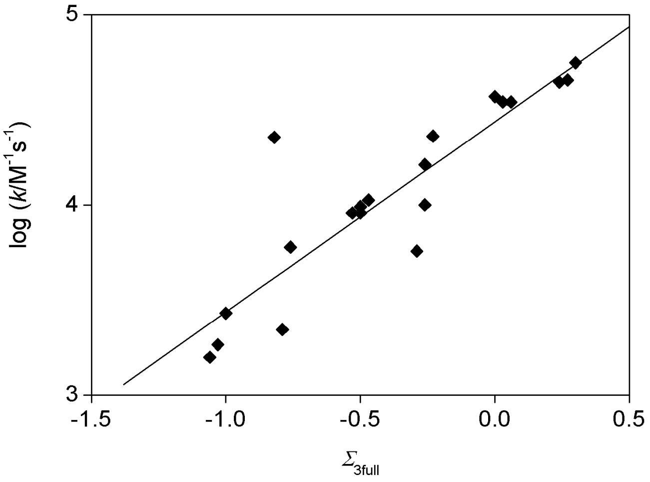

**Fig. S11.** Rate constant measured in the oxidation of studied chlorophenols by cerium(IV) as a function of the sum of substituent constants.

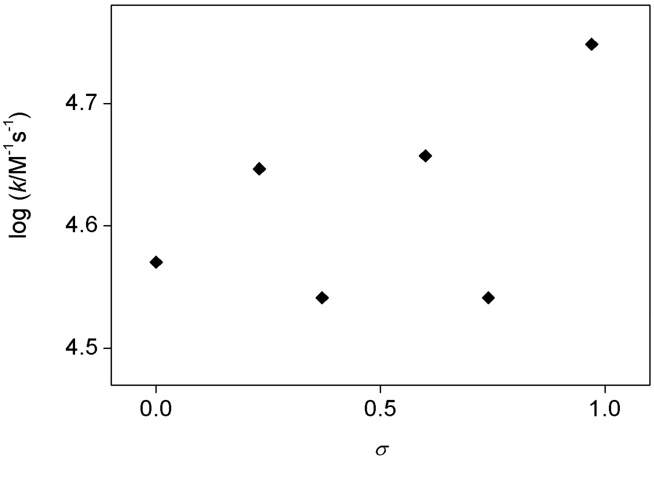

**Fig. S12.** Attempted conventional Hammet plot for chlorophenols without ortho substituents.

**Table S1** Detailed p*K*, NMR chemical shift and rate constant data (also including deuterated compounds only used in reference 10).

| | pK | α-H | β-H | γ-H | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $k$ ($M^{-1}s^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| phenol | 9.86 | 6.91 | 7.30 | 7.01 | 155.3 | 115.6 | 129.9 | 121.2 | $(3.72 \pm 0.03)\times10^{4}$ |
| 2-chlorophenol | 8.33 | 7.05 | 7.34<br>7.20 | 6.89 | 151.5 | 120.1<br>116.5 | 129.2<br>128.6 | 121.6 | $(9.07 \pm 0.05)\times10^{3}$ |
| 3-chlorophenol | 8.85 | 6.89<br>6.76 | 7.18 | 6.97 | 155.9 | 116.1<br>113.8 | 135.1<br>130.8 | 121.6 | $(3.48 \pm 0.01)\times10^{4}$ |
| 4-chlorophenol | 9.34 | 6.78 | 7.20 | - | 153.8 | 116.9 | 129.8 | 126.1 | $(4.43 \pm 0.02)\times10^{4}$ |
| 2,3-dichlorophenol | 7.64 | 6.94 | 7.10 | 7.03 | 152.8 | 119.2<br>114.6 | 132.8<br>128.2 | 122.3 | $(9.08 \pm 0.11)\times10^{3}$ |
| 2,4-dichlorophenol | 7.83 | 6.96 | 7.32<br>7.15 | - | 150.3 | 120.6<br>117.3 | 128.8<br>128.7 | 125.8 | $(5.72 \pm 0.05)\times10^{3}$ |
| 2,5-dichlorophenol | 7.40 | 7.05 | 7.22 | 6.86 | 152.0 | 118.5<br>116.8 | 133.9<br>129.7 | 121.8 | $(9.79 \pm 0.03)\times10^{3}$ |
| 2,6-dichlorophenol | 6.77 | - | 7.27 | 6.83 | 148.1 | 121.3 | 128.5 | 121.4 | $(1.58 \pm 0.01)\times10^{3}$ |
| 3,4-dichlorophenol | 8.56 | 6.97<br>6.70 | 7.29 | - | 154.6 | 117.7<br>115.4 | 133.1<br>131.1 | 124.5 | $(4.54 \pm 0.05)\times10^{4}$ |
| 3,5-dichlorophenol | 7.99 | 6.76 | - | 6.97 | 156.5 | 114.7 | 135.7 | 121.7 | $(3.48 \pm 0.04)\times10^{4}$ |
| 2,3,4-trichlorophenol | 7.00 | 6.93 | 7.30 | - | 151.4 | 120.5<br>115.0 | 131.3<br>129.0 | 125.3 | $(1.00 \pm 0.05)\times10^{4}$ |
| 2,3,5-trichlorophenol | 6.68 | 6.98 | - | 7.07 | 153.0 | 118.0<br>115.2 | 133.7<br>133.3 | 122.4 | $(1.06 \pm 0.06)\times10^{4}$ |
| 2,3,6-trichlorophenol | 5.75 | - | 7.20 | 7.07 | 149.2 | 120.5<br>119.5 | 132.1<br>128.0 | 122.1 | $(1.84 \pm 0.01)\times10^{3}$ |
| 2,4,5-trichlorophenol | 6.97 | 7.14 | 7.42 | - | 150.8 | 119.1<br>118.0 | 132.3<br>129.9 | 124.4 | $(1.63 \pm 0.03)\times10^{4}$ |
| 2,4,6-trichlorophenol | 6.15 | - | 7.28 | - | 147.1 | 121.8 | 128.3 | 125.6 | $(2.27 \pm 0.08)\times10^{4}$ |
| 3,4,5-trichlorophenol | 7.82 | 6.92 | | | 154.2 | 116.6 | 134.6 | 123.6 | $(5.6 \pm 0.3) \times 10^{4}$ |
| 2,3,4,5-tetrachlorophenol | 6.31 | 7.15 | | | 151.0 | 119.3<br>116.1 | 133.1<br>132.7 | 124.5 | $(2.3 \pm 0.2) \times 10^{4}$ |
| 2,3,4,6-tetrachlorophenol | 5.32 | - | 7.43 | - | 147.9 | 121.6<br>119.6 | 130.9<br>128.5 | 121.6 | $(2.21 \pm 0.08) \times 10^{3}$ |
| 2,3,5,6-tetrachlorophenol | 5.31 | | | 7.23 | 150.1 | 119.0 | 131.9 | 122.6 | $(2.7 \pm 0.1) \times 10^{3}$ |
| pentachlorophenol | 4.66 | - | - | - | 148.3 | 119.9 | 131.7 | 125.3 | $(6.0 \pm 0.9) \times 10^{3}$ |
| phenol-$d_6$ | 9.80 | - | - | - | 155.5 | 115.1 | 129.4 | 120.5 | |
| 2,4,6-trichlorphenol-$d_2$ | 6.10 | - | - | - | 147.1 | 121.7 | 128.0 | 125.4 | |