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CORRELATING OXIDATION KINETICS FOR ORGANIC SOLUTES: A COMPARISON OF  
QSARS FOR THE MAJOR AQUEOUS OXIDANTS

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Correlation analysis of rate constants is an important part of most studies on aqueous oxidation kinetics because it provides (i) validation of experimental results, (ii) mechanistic insight, and (iii) quantitative structure-activity relationships (QSARs) that are the basis for predicting oxidation rates for substrates that have not been investigated previously. Prof. Hoigné's investigations over that last 20 years have produced an abundance of reliable rate data, which in turn have provided numerous illustrations of the power of correlation analysis. These correlation analyses include the kinetics of substituted phenols reacting with a host of aqueous oxidants (OH,  $^1\text{O}_2$ ,  $\text{O}_3$ , and  $\text{ClO}_2$ ), under otherwise comparable conditions. As a class, substituted phenols are among the most ubiquitous in the environment (as natural products and as contaminants) and are among the most suitable for correlation analysis. The oxidants that have been studied in this context exhibit a range of oxidation mechanisms and include many of the major oxidizing species in both sunlit natural waters and engineered water-treatment systems.

Taken together, the available correlation analyses of phenol oxidation by the various aqueous oxidants comprise a set of data sets, suitable for systematic comparison. Such a treatment—suggested by Prof. Hoigné to me in 1991—amounts to a “second-order” or “meta” analysis of QSARs. This paper will explore the notion of meta-QSAR analysis, its validity and utility, and what it might reveal about relationships between the major aqueous oxidants of organic substances.

Graphically, the various correlations between  $k$ 's for reaction with one environmental oxidant and  $k$ 's for reaction with another can be represented by the scatter plot matrix shown in Figure 1. Several combinations give satisfactory correlations, particularly the values of  $k_{\text{ArO}^-}$  for  $^1\text{O}_2$  and  $\text{ClO}_2$ . Linear regression on these data gives

$$\log k(^1\text{O}_2) = 5.5 (\pm 0.2) + 0.36 (\pm 0.03) \log k(\text{ClO}_2) \quad (1)$$

with  $s = 0.16$  and  $r = 0.9075$  for  $n = 10$ . There are no outliers, and all of the phenoxides for which both rate constants are available were included in the correlation. Such correlations may have predictive value: e.g.,  $k_{\text{ArO}^-}$  for initial oxidation of the pesticide 4,6-dinitro-*o*-cresol (DNOC) with  $\text{ClO}_2$  may be estimated from data available for  $^1\text{O}_2$ . The result ( $k_{\text{ArO}^-} \approx 8 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ ) indicates reaction of the contaminant will be insignificant under water-treatment conditions.

However, the main benefit of this type of analysis is likely to be in evaluating the quality and mechanistic implications of previously reported data. For example, the agreement reflected in Equation 1 implies that substituent effects are parallel for phenoxide oxidation by  $\text{ClO}_2$  and

$^1\text{O}_2$ , even though only the rate of reaction with  $\text{ClO}_2$  is likely to be controlled by outer-sphere electron transfer [4, 6]. This result is consistent with the possibility that the rate of oxidation by  $^1\text{O}_2$  is limited at the precursor formation step [5].

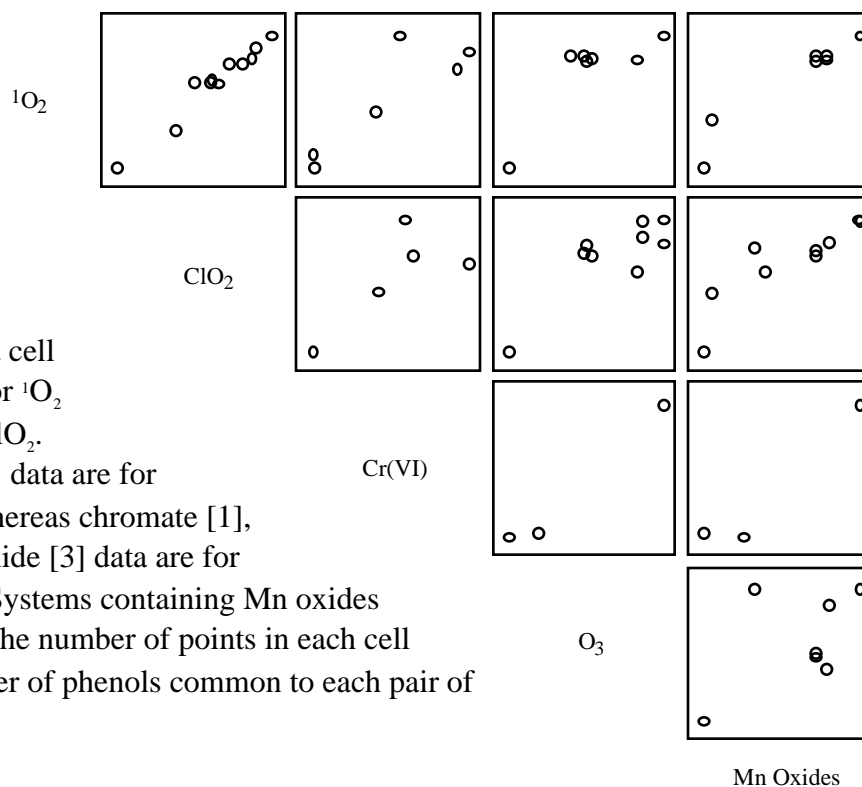
**Figure 1.**

Scatter plot correlation matrix

of log second-order rate constants for phenol oxidation.

For example, the first cell represents  $\log k_{\text{ArO}}^-$  for  $^1\text{O}_2$  versus  $\log k_{\text{ArO}}^-$  for  $\text{ClO}_2$ .

$^1\text{O}_2$  [5,6] and  $\text{ClO}_2$  [4] data are for phenoxide anions, whereas chromate [1], ozone [2], and Mn oxide [3] data are for protonated phenols. Systems containing Mn oxides were heterogeneous. The number of points in each cell varies with the number of phenols common to each pair of data sets.



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