

**HYDROPHOBIC ORGANIC COMPOUNDS REACTION RATES WITH  
PEROXY-ACID TREATMENT IN ENGINEERED SYSTEMS: PREDICTION OF  
REACTIVITY USING MOLECULAR MODELING AND PEST**

by

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## ABSTRACT

Persistent organic contaminants in the environment pose an environmental risk due to widespread occurrence and toxic properties. Research of remediation techniques to degrade environmental contaminants has been an area of heightened interest. Advanced oxidation processes (AOPs) are a group of methods that have been used to successfully degrade organic contaminants in water, soil, sediments, and sludges. AOPs typically utilize the oxidative potential of the hydroxyl radical ( $\text{HO}^\bullet$ ) to degrade contaminants. The peroxy-acid process is an AOP that combines acetic acid ( $\text{CH}_3\text{COOH}$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and has been found to be effective method for the degradation of polycyclic aromatic hydrocarbons (PAHs). The combination of  $\text{CH}_3\text{COOH}$  and  $\text{H}_2\text{O}_2$  will produce peracetic acid (PAA) which is also a strong oxidizer. Therefore, the peroxy-acid process can potentially utilize both  $\text{HO}^\bullet$  and PAA as oxidative species for the degradation of organic contaminants.

The formation of PAA is catalyzed by strong acids, such as sulfuric acid ( $\text{H}_2\text{SO}_4$ ). Previous studies evaluating the degradability of a PAH, benzo[a]pyrene, by the peroxy-acid process, have found a positive correlation between PAA concentration and the rate of reaction. Experiments were conducted to determine the effect of catalyst volume on the production of PAA over time, using  $\text{H}_2\text{SO}_4$  as the catalyst in peroxy-acid solutions containing 3 mL of  $\text{CH}_3\text{COOH}$  and 3 mL of  $\text{H}_2\text{O}_2$ . It was found that the production of PAA increased significantly with all volumes of  $\text{H}_2\text{SO}_4$  in 24 hours in comparison to un-catalyzed solutions. Studies were also conducted using aniline to determine how PAA concentration would affect the degradation rate of an organic compound smaller and more soluble than benzo[a]pyrene. The rate of aniline degradation was significantly higher with an increase in PAA concentration, indicating the oxidative potential of PAA for the degradation of organic contaminants like aromatic amines and PAHs.

Computational calculations have been found to be a successful method in predicting reactivity. Several of these methods were evaluated to determine if properties calculated by *ab-initio* methods or descriptors calculated by the Property-Encoded Surface Translator (PEST) program could be used as a model to predict reactivity using

the peroxy-acid process. Reaction rate constants ( $k$ ) in  $\text{hr}^{-1}$  for nine PAHs (*e.g.*, acenaphthene, anthracene, benzo[a]pyrene, benzo[k]fluoranthene, fluoranthene, fluorene, naphthalene, phenanthrene, and pyrene) were determined by a peroxy-acid treatment method that utilized  $\text{CH}_3\text{COOH}$ ,  $\text{H}_2\text{O}_2$ , and a  $\text{H}_2\text{SO}_4$  catalyst to degrade the polyaromatic structures. Molecular properties of the selected nine PAHs were derived from molecular structures optimized at B3LYP/6-31G\* and HF/6-31G\* levels of theory. The PEST descriptor properties were derived at the 0.002 electrons/Bohr<sup>3</sup> isosurface of each molecule, roughly corresponding to the van der Waals radius. Properties of molecular energy, adiabatic and vertical ionization potential (IP), highest occupied molecular orbitals (HOMO), HOMO/lowest unoccupied molecular orbital (LUMO) gap energies and HOMO/singly occupied molecular orbital (SOMO) gap energies were not correlated with rates of peroxy-acid reaction. PEST descriptors were calculated from B3LYP/6-31G\* optimized structures and were found to have significant levels of correlation with  $k$ .

The investigation of the use PEST descriptors to predict reactivity by the peroxy-acid process was continued with ten substituted naphthalene compounds, including 1-bromonaphthalene, 1-fluoronaphthalene, 2-ethylnaphthalene, 2-methylnaphthalene, 1-methylnaphthalene, 2-bromonaphthalene, 2-chloronaphthalene, 2-ethoxynaphthalene, 2-methoxynaphthalene and naphthalene. PEST descriptors were calculated from B3LYP/6-31G\* optimized structures of these ten selected substituted naphthalene compounds. Rate constants were derived for these ten compounds and found to have higher levels of correlation with PEST descriptors than had been encountered from the previous study of PAH compounds. Models using minimum local ionization potential (PIP.MIN) and a histogram of the gradient of the K electronic kinetic energy normal to the isosurface (DKN.H7) were evaluated and found to agree within 10 % of experimentally derived values of  $k$  in most instances. There appear to be multiple PEST descriptors that could be used to predict reactivity by the peroxy-acid process. The application of using PEST descriptors to predict degradation reaction rates at sites with multiple contaminants and could prove to be a valuable asset for effective remediation design by identifying probable rates of degradation for PAHs, substituted naphthalene compounds, and other organic contaminants in the environment.