

Photochemical Induced Oxidation of Refractory Organics with Hydrogen Peroxide

A method of oxidizing certain refractory organics utilizing photochemical activated hydrogen peroxide is discussed. Emphasis is placed on the removal of acetate ion found in effluents resulting from wet-oxidation of organic wastes. The kinetics and mechanism of the process are discussed along with the possible advantages of the method over metal ion catalyzed hydrogen peroxide oxidation.

Introduction

During the course of an investigation into the application of wet air oxidation technology for treatment of ship board wastes, it became apparent that one of the problems inherent in this method is the refractory nature of the acetate ion. Since acetate ion represents the last organic in a series of oxidation steps, effluents resulting from wet-oxidation are too high in COD to be discharged.

A similar problem has also been reported by Hurwitz, (1965). Recycling the effluent at normal operating temperatures does not lead to significant reduction in COD. Consequently we have investigated an effluent "polishing" process utilizing photochemical activated hydrogen peroxide. We have found that, although this procedure may not be suited for larger scale treatment due to economic factors, it may find limited application in situations involving certain hard-to-oxidize organics, such as acetates and phenols.

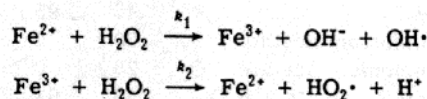
Experimental Section

All hydrogen peroxide-metal ion catalyzed reactions were carried out in evacuated, sealed glass tubes. After reaction, the gaseous products were collected and analyzed with a mass spectrometer. Acetic acid or phenols remaining in the reaction mixtures were analyzed with a gas chromatograph using Porapak columns. Hydrogen peroxide concentrations were determined iodometrically. TotalCOD was determined by a standard acid dichromate method. Quantitative determinations of carbon dioxide were made by absorption in barium hydroxide solution. Photochemical reactions were carried out in either a Vycor reaction vessel surrounded by a quartz coil or in a thermostated Pyrex glass vessel equipped with an immersion lamp. Both light sources utilized a low-pressure mercury arc and were obtained from Ultra-violet Products, Inc., San Gabriel, CA.

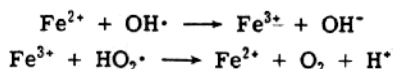
All reacting solutions were simultaneously stirred and degassed with prepurified nitrogen. Light intensity measurements were made with a standard uranyl oxalate actinometer.

Results and Discussion

The problem of specialized treatment of refractory organics with hydrogen peroxide has been investigated by Bishop, et al. (1968). However, this work was not directed toward any particular type of organic compounds. They utilized the ferrous/ferric ion-hydrogen peroxide reaction, a well-known system for the production of hydroxyl radicals. They found that, although hydrogen peroxide and iron salts separately are not effective oxidants, together they oxidized most of the complex organics present in municipal wastewaters. When hydrogen peroxide and iron salts are combined, hydroxyl radicals are produced (Barb, et al., 1959)



Although this sequence is desirable from the point of view of OH production, it is consuming H₂O₂, especially when other possible reactions are considered.



Thus a problem arises in that a substantial portion of the theoretical oxidation equivalent of the hydrogen peroxide is unavailable for oxidation. In the case of acetate removal our results confirm this as shown in Table 1. These results were obtained on model solutions prepared by mixing 10 ml of 0.25 M acetic acid with 10 ml of 1.0 M hydrogen peroxide, followed by 5.0 ml of 5.0 X 10⁻³ M metal ion solution. These solutions were heated for 1 hr at 130°C in evacuated, sealed glass tubes. After reacting, they were cooled to room temperature and both gas and liquid phases were analyzed. As expected, the greatest amount of acetic acid removal corresponded to the lowest O₂/CO₂ ratios. Further experiments with slightly different ferrous or ferric ion concentrations and temperatures did not significantly improve the performance of this method. Therefore it was decided to investigate the behavior of photochemical produced OH radicals. For this series of experiments solutions of similar concentrations were used except no metal ions were present. The results obtained are presented in Table 11.

Table I. Effect of Catalysts on the Oxidation of Acetic Acid by Hydrogen Peroxide

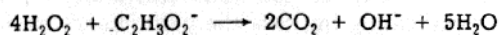
Catalyst	% Reduction of acetic ^a acid	Ratio O ₂ /CO ₂ ^b
Fe ²⁺	32	2.6
Co ²⁺	2	>10
Cu ²⁺	29	4.1
Cr ₂ O ₇ ²⁻	4	>10
CrO ₄ ²⁻ + NH ₄ Ac	66	2.1
MoO ₄ ⁻	2	>10
Blank	2	>10

^a In all runs, including the blank, all of the hydrogen peroxide was gone at the end of 1 hr. ^b It should be noted that the larger this ratio the greater the loss of theoretical oxidation equivalents of H₂O₂. The amount of CO₂ used includes a small quantity of CO which is also produced.

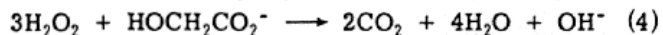
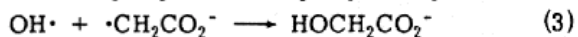
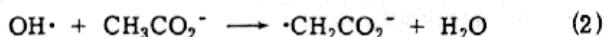
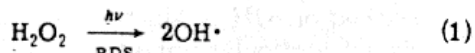
These results clearly illustrate the advantage of this method of -OH production compared to metal-ion catalysis. Of particular importance is the low O₂/CO₂ ratios for the acetate solutions.

As a result of these preliminary experiments, we decided to investigate the system further in order to determine the kinetics and mechanism of the oxidation process. Kinetic measurements were carried out in a thermostated reaction flask maintained at a temperature of 45°C. The results of typical kinetic runs are given in Figure 1. As illustrated, the rate of removal of hydrogen peroxide is first order and is a function of the light intensity.

The rate of removal of hydrogen peroxide is also four times the rate of acetate removal which is in agreement with the stoichiometry



and the low O₂/CO₂ ratios. As expected, varying the initial concentration of acetate had no effect on the reaction rate. Thus the mechanism of reaction in the case of acetate oxidation appears to be



Step 2 is consistent with the fact that small quantities of succinic acid are detected in the reaction mixture when excessive amounts of acetate are initially present. Step 4 is consistent with the fact that the rate of total CO₂ (CO₂ plus HCO₃⁻) production corresponds very nearly to the rate of removal of acetate. Also hydrogen peroxide is observed to react rapidly with glycolate ion. Final analysis of solutions show that this method can lead to as much as 97% COD removal; thus no stable intermediates are suggested.

Table II. H₂O₂-Acetic Acid/Acetate Reaction Initiated by Uv Light. Temperature 25°C

Reactants	Reac- time	% Re- mov- al of acetic acid/ main- ing	% Re- main- ing	Ratio O ₂ /CO ₂
Acetic acid + H ₂ O ₂	20	35	45%	0.87
Ammonium acetate + H ₂ O ₂	45	>95	4%	0.12
Ammonium acetate	20	0
Ammonium acetate + O ₂ ^a	20	0
Sodium acetate + H ₂ O ₂	30	93	8%	0.14
Sodium monochloroacetate + H ₂ O ₂ ^b	20	84	7%	0.07
Sodium trichloroacetate + H ₂ O ₂	45	60	0	2.4

^a O₂ bubbled in at 1 atm. ^b No Cl₂ or chlorine containing products found other than Cl⁻. Data presented is average of at least two experiments.

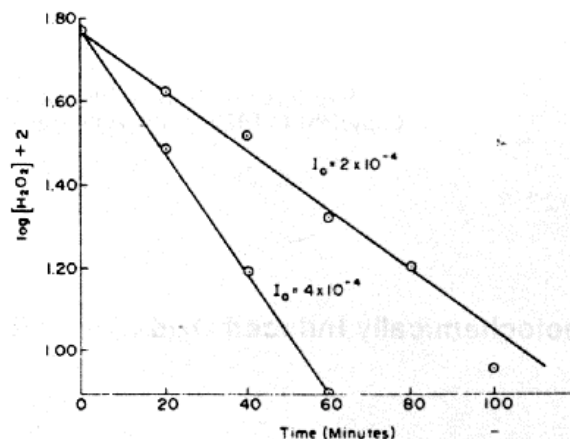
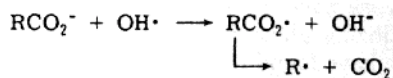


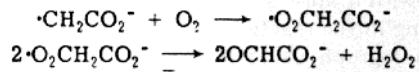
Figure 1. Photolysis of 0.5 M hydrogen peroxide in the presence of sodium acetate. Light intensities in units of einsteins/l. min; temp 45°C.

A step leading to carboxylate radical formation, CH₃CO₂⁻, is not included since no CH₄ or C₂H₆ products were detected. However, that CC₁₃CO₂⁻ does undergo some reaction, suggests that:



is a possibility (Anbar, et al., 1966).

As expected, temperature had little effect in the rate of reaction (Hunt and Taube, 1952). Reactions carried out in solutions saturated with oxygen show a slight decrease in the rate of hydrogen peroxide removal compared to those carried out with nitrogen. Presumably oxygen enters into the reaction according to the sequence



This process may be of greater importance at higher oxygen pressures.

Although this work deals mainly with acetate ion oxidation, preliminary experiments suggest that this method is equally suited for treatment of a large variety of phenolic wastes.

Conclusions

Our results lead us to believe the uv-hydrogen peroxide system has several advantages over a metal ion-hydrogen peroxide system (Bishop, et al., 1968) which may eventually lead to its utilization. Among them are: (1) the reaction need not be limited to pH ranges compatible with metal ion solubility and (2) no hydrogen peroxide is lost due to metal-ion oxidation and reduction. The use of uv light may also prove to have beneficial side effects when treating wastes which contain certain hard-to-dispose of viruses. Thus this process may eventually be used in conjunction with other methods of wastewater treatment employing hydrogen peroxide such as bio-oxygen stabilization (Chin, et al., 1973).