Journal of Hazardous Materials, 34 (1993) 245–260
Elsevier Science Publishers B.V., Amsterdam

Destruction of cresols by chemical oxidation

Y. Zheng, D.O. Hill and C.H. Kuo*

Department of Chemical Engineering, Mississippi State University, Mississippi State, MS 39762 (USA)

(Received June 6, 1992; accepted in revised form October 21, 1992)

Abstract

This work investigates the reaction rates and kinetics of the oxidative destruction of cresol isomers in water by ozone and hydrogen peroxide. Cresols are oxidized slowly by hydrogen peroxide though the reaction rates are enhanced in the presence of Fenton's reagent and other catalysts. Rapid oxidation takes place between ozone and a cresol isomer for complete conversion to intermediates in less than 0.1 second. Further reactions or decomposition of the intermediates result in rupture of the aromatic ring and production of carbon oxide, acetic and other acids. Three moles of ozone are required for the destruction of a cresol isomer, and the overall kinetics is first order with respect to the concentrations of ozone and cresol isomer. At 25 °C, the reaction rate constants are 32 240, 60 870 and 45 460 $M^{-1}s^{-1}$ respectively, for the ozonation of *o*-, *m*- and *p*-cresol. In the temperature range of 10 to 40 °C, *m*-cresol is the most reactive species of the three isomers with ozone in the aqueous phase.

1. Introduction

The present work concerns the reaction of three cresol isomers with hydrogen peroxide and ozone in water at various temperatures. Cresols, also known as methylphenols or hydroxytoluenes, are toxic compounds used in the manufacture of wood preservation agents, pesticides, phenolic resins and other industrial compounds. Like many phenolic compounds, these chemicals are found in drinking water and industrial waste streams, and treatment for removal or destruction of these compounds is required. Cresols also are present in the atmosphere, and according to a recent NATICH report [1], the total emission rate in the United States is about 75 tons/year. These compounds are classified as hazardous air pollutants in Title III of the 1990 Clean Air Act Amendments; and the US Environmental Protection Agency is required to promulgate emission limitations for these compounds based on maximum achievable control technology. The present research, therefore, was undertaken to study the reactivity and kinetics of the chemical oxidation of the

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*To whom correspondence should be addressed.

cresol isomers in water. Results obtained from this investigation might be useful to both air and water pollution abatement.

There is little information in the literature regarding the oxidation of cresols by hydrogen peroxide. None the less, the favorable treatment of water containing *o*- and *m*-cresols by ozone was reported as early as 1953 by Niegowski [2]. The rupture of the aromatic rings of *o*- and *p*-cresols following ozone treatment was reported by Dore et al. [3], and products of the ozonation were identified by Bauch et al. [4]. Hoigne [5] indicated that the ozonation rate of cresols is very fast with large rate constants. The reaction of ozone with cresols in gas–liquid contactors was investigated by Gould [6], Gurol and Nekouinaini [7], Beltran et al. [8], and others. Although some phenolic compounds are not amendable to biological treatment, Wang [9] reported that anaerobic biological treatment of *o*-cresol and other compounds is attainable if sufficient oxidation is induced by ozone.

In the gas–liquid systems used by earlier investigators to study the ozonation of cresols, the mass transfer rates were controlled by both diffusion of the ozone in the liquids as well as chemical reactions. Thus, reliable data may not be available for accurate assessment of the reaction kinetics of the oxidation process. In this work, the stopped-flow technique was applied to study the ozonation reactions in a homogeneous, liquid phase reactor. Absorbance data were obtained and analyzed to determine reaction rates and orders of the oxidation reactions. In addition, an agitated reactor was used to study some slow reactions between cresols and hydrogen peroxide with or without catalysts.

2. Experimental details

Ozone gas was produced from a Welsbach Model T-408 ozonator using pure, extra dry oxygen. The ozone gas was then bubbled into distilled water for 10 to 30 minutes depending upon the desired concentrations. The initial concentrations of the dissolved ozone were determined by both iodiometric titration and spectrophotometric technique, as discussed in some earlier publications [10, 11]. An aqueous solution of hydrogen peroxide was prepared by dilution of the concentrated solution (30 wt%, ACS reagent).

The ozone gas also was introduced into distilled water to oxidize any contaminants before the water was used to prepare the reactant solution of a cresol isomer. All cresol isomers were ACS grade reagents purchased from the Aldrich Chemical Company.

A stopped-flow spectrophotometer system (High-Tech Scientific Model SF-51) was used to conduct the kinetic experiments. Prior to an experimental run, two reactant solutions (dissolved ozone or hydrogen peroxide in one and cresol isomer in another) were kept in two driving syringes at a specified temperature maintained through a thermostat flow circuit around a spectrometer unit in the system. By actuating a pneumatic flow circuit, the two solutions were mixed rapidly in a mixing jet and allowed to flow into an observation cell (0.04 cm^3 in volume) where the mixed solution was stopped abruptly. Simultaneously, a monochromatic light was allowed to pass through the solution during the reaction in the mixing cell, and its resultant intensity was projected on to a photomultiplier tube. This output, proportional to the light intensity transmitted by the reacting solution, was processed and stored in an automatic data acquisition system for further analysis. The stopped-flow apparatus is advantageous in allowing complete mixing of the two reactants in less than one millisecond, and therefore, the absorbance changes in the mixed solution during a rapid reaction can be traced. The system is designed for continuous measurement of the transmittance or absorbance of the solution at a fixed wavelength between 200 to 800 nm.

A gas chromatograph (Hewlett-Packard Model 5840A) was utilized to measure concentrations of cresols in some reactions. It was also applied to determine the stoichiometry and products of the ozonation reactions using several packed columns.

3. Analysis of kinetic data

The oxidation reactions studied in this work are irreversible, and the kinetic data can be analyzed by assuming an overall reaction of the following type:

$$aA + bB \rightarrow pP + qQ + \cdots \tag{1}$$

According to the above reaction, the rate of depletion of the reactants, A and B, can be written as,

$$\frac{1}{a}\frac{dC_A}{dt} = \frac{1}{b}\frac{dC_B}{dt} = -kC_A^m C_B^n \tag{2}$$

If A is a limiting reactant by conducting an experiment with B in large excess, then eq. (2) can be simplified to:

$$\frac{dC_A}{dt} = -k'C_A^m \tag{3}$$

where,

$$k' = akC_B(t)^n \approx akC_B(0)^n \tag{4}$$

By assuming a reaction order, m, with respect to the concentration of A, eq. (3) can be integrated to yield:

$$\frac{C_A(t)}{C_A(0)} = \exp(-k't) \quad \text{for} \quad m = 1 \tag{5}$$

and,

$$\left\{\frac{C_A(t)}{C_A(0)}\right\}^{1-m} = 1+(m-1)C_A(0)^{m-1}k't \qquad \text{for} \quad m \neq 1 \tag{6}$$

In the stopped-flow reactor, the total absorbance of a reacting solution is measured continuously as a function of the reaction time. Preliminary tests showed that in dilute solutions, the absorbance of an individual component increases linearly with its concentration, as dictated by Beer's law. Under this condition, the following relationship between the absorbance and the concentration of the limiting reactant A can be derived [11]:

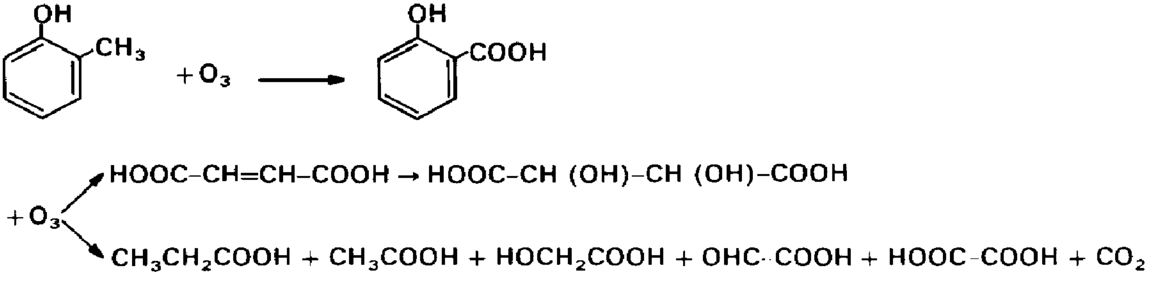
$$\frac{C_A(t)}{C_A(0)} = \frac{S(t)-S(\infty)}{S(0)-S(\infty)} \tag{7}$$

where $S(0)$ represents the initial absorbance of the mixed solution and $S(\infty)$ is the asymptotic absorbance measured at the end of a reaction period.

Equations (5), (6) and (7) imply that the concentration or absorbance data obtained in an experiment can be plotted against the reaction time, t, in a certain manner to verify the reaction order (m) assumed. If the reaction is first order with respect to A, then a linear plot can be obtained on a semi-logarithmic scale for the dimensionless concentration or absorbance versus time. For other values of m, a plot of the dimensionless concentration or absorbance of exponent $(1-m)$ versus time yields a straight line. The apparent rate constant, k', can be calculated from the slope of the straight line. According to eq. (4), a straight line can be drawn from a logarithmic plot of k' versus $C_B(0)$ for various experiments conducted at the same condition of temperature and acidity. Therefore, the reaction order (n) with respect to B and the overall rate constant, k, can be determined from such a plot.

4. Mechanism and stoichiometry of ozonation

As mentioned earlier, the ozonation products were identified by Bauch et al. [4]. They reported that the decomposition of 80% for cresols was achieved with 2 moles of ozone per mole of the cresol isomer, and that at least 3 moles of ozone were required for complete destruction. According to these investigators, the methyl group of each cresol is oxidized to the corresponding carboxylic acid in the initial ozonation. Continued ozonation results in rupture of the aromatic ring and produces maleic acid which is oxidized further to mesotartaric acid. Several acids including propionic, acetic, glycolic, glyoxylic and oxalic acids, and carbon dioxide are also formed. For example, the ozonation of *o*-cresol produces salicylic acid initially, and the other acids as the final products:

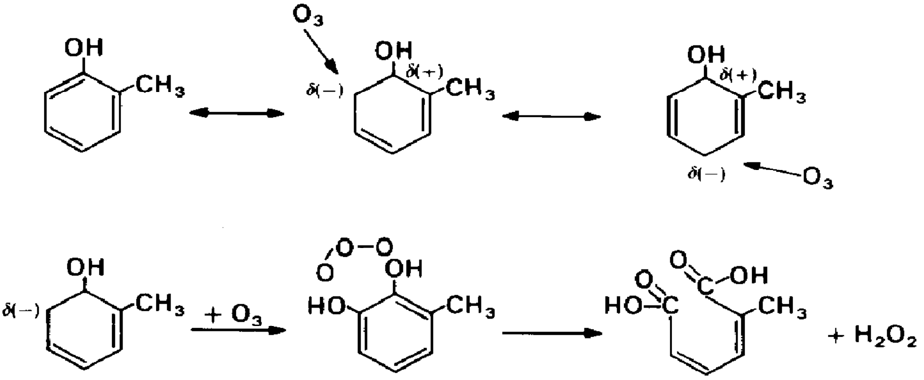


$$+O_3 \rightarrow \begin{cases} HOOC\text{-}CH{=}CH\text{-}COOH \rightarrow HOOC\text{-}CH(OH)\text{-}CH(OH)\text{-}COOH \\ CH_3CH_2COOH + CH_3COOH + HOCH_2COOH + OHC\text{-}COOH + HOOC\text{-}COOH + CO_2 \end{cases}$$

(8)

Several of the above acids are also produced in the ozonation of phenol [11, 12].

Beltran et al. [8] reported that two moles of ozone were consumed per mole of *o*-cresol in the gas–liquid system. This is in agreement with the two strongest nucleophilic positions in the *o*-cresol to activate the *ortho* and *para* positions of the hydroxyl group, as suggested by the authors. Similar to the earlier conclusion of Dore et al. [3], the authors suggested that methylcatechol is produced in the attack of the first ozone molecule, and the 1,3-dipolar addition of the second ozone molecule breaks the aromatic ring as follows:



(9)

It is likely that the dicarboxylic acid can be oxidized further, though no identification of the final products was reported by Beltran et al. [8].

Another possible mechanism can be postulated on the basis of the hexagon formula of Kekule (proposed in 1865), as discussed by Haijman and Wibaut [13]. From the result of the ozonation of benzene to form a triozonide, it was confirmed that benzene behaves as a compound with three double bonds and that the six carbon–carbon bonds in the benzene nucleus are equivalent. In the ozonation of *o*-xylene and 1,2,4-trimethyl benzene to form aldehydes and ketones, the ozone addition was not affected by steric hindrance of the methyl groups as concluded by Haijman and Wibaut [13]. If this same conclusion holds for the methyl and hydroxyl groups of cresols, then three ozone molecules would be required to attack one molecule of a cresol isomer to form a triozonide in the initial step. Further decomposition and reaction of the triozonide may produce the acids identified by Bauch et al. [12].

The stoichiometries of the ozonation of the three cresol isomers were determined in this work. In each experiment, two reactant solutions with different concentrations of the cresol isomer and dissolved ozone were mixed, and two solution samples withdrawn at 5 or 20 minutes. One sample was utilized to determine the residual amount of the cresol by the chromatographic method using a carbowax 20M column. Another sample was titrated to determine the concentration of residual ozone in the solution. The ratio of moles of ozone consumed per mole of cresol reacted is calculated to be about three for all measurements. Results of the various measurements are plotted in Fig. 1 indicating that the cresol was consumed completely if the initial ratio was 3 moles of ozone or more per mole of cresol. If the initial ratio was less than three, then the dissolved ozone was completely consumed but a fraction of the cresol was not reacted. Some tests were also performed in the stopped-flow system by continued measurement of the absorbance of a mixed solution. The total absorbance increased very rapidly and then declined indicating the formation and further decomposition of products of high absorbance. If the dissolved ozone was in large excess in an experiment, then the rate of decrease of the absorbance was very slow after a short period (less than one second). By assuming that the slow rate of the absorbance decrease was due to self-decomposition of the excessive ozone, the amount of ozone consumed was again estimated to be about 3 moles per mole of cresol. Thus both the chromatographic and spectrophotometric methods confirmed that three moles of ozone

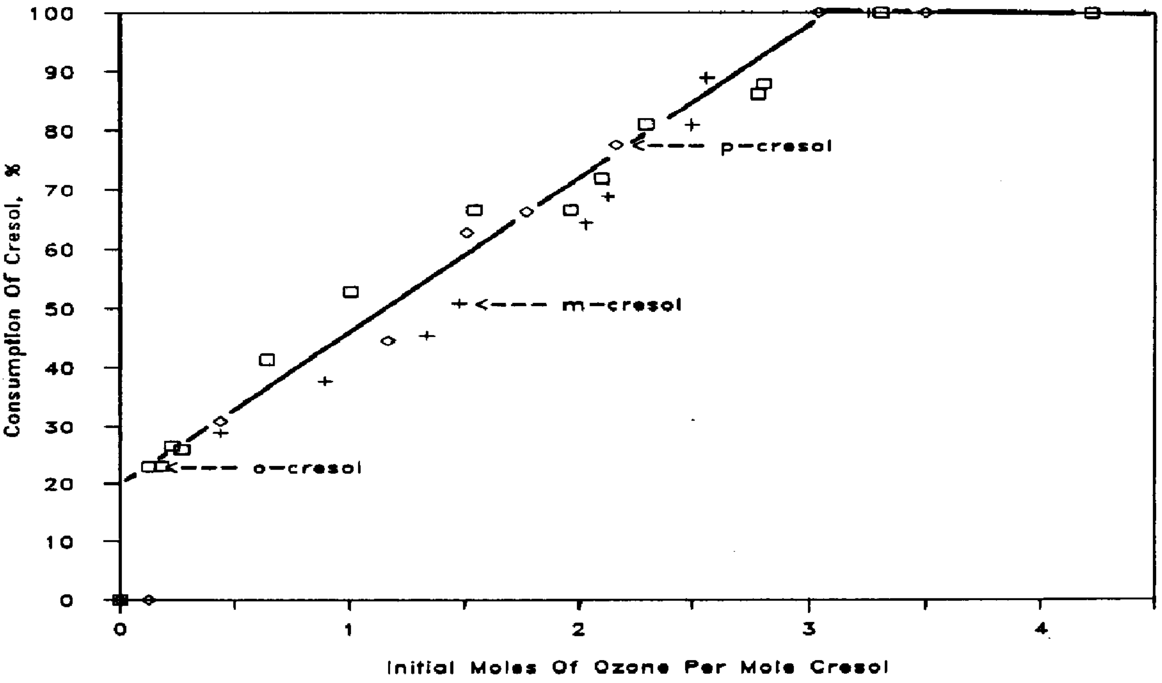


Fig. 1. Cresol–ozone reaction in water. Effect of initial mole ratio.

are needed for complete conversion of each mole of cresol in the ozonation reaction. This result is in general agreement with that concluded by Bauch et al. [4].

Attempts were made to identify the final products of the ozonation. In such a test, ozone gas was introduced continuously into an aqueous solution containing the cresols, and a small sample withdrawn and injected into the gas chromatograph every 20 min for a total of 2 h. Acetic acid was detected but several other peaks in the chromatograms could not be identified. In each experiment, the concentration of the acetic acid increased as the concentration of the cresol decreased with time, suggesting that the acetic acid is a stable product in the ozonation.

From the foregoing discussion, it can be concluded that 3 moles of ozone are required for complete consumption of each mole of cresol. This result does not agree well with the stoichiometric ratio of two determined in some gas–liquid contactors [8]. It should be cautioned that for complete destruction to carbon dioxide and water, 5.67 moles of ozone per mole of cresol are required from the stoichiometric calculation. In actual applications of the ozonation process, the ratio could be higher than 5.67 because of possible side reactions [4]. Several mechanisms of the ozone attack might be possible as discussed earlier. However, it is not known which path is predominant in the ozonation of cresols.

5. Kinetics of ozonation of cresols

Preliminary tests were conducted to determine the absorbance behavior of cresols and ozone in aqueous solutions in the wavelength range of 200–300 nm. For all cresol isomers, the absorbance of a solution increases to a maximum at about 220 nm and then declines to a minimum at 250 nm before approaching another maximum value at 280 nm. For a solution with dissolved ozone, the absorbance increases gradually to a maximum value at 254 nm and then declines, as discussed in some earlier papers [10, 11]. Since the solubilities of cresols are much higher than that of ozone, it is desirable to carry out a kinetic experiment with cresols in large excess. Based on this consideration, the absorbances were measured at the fixed wavelength of 250 nm in the kinetic runs to minimize the contribution of the excessive reactants (cresols). This allows significant variation in the absorbance during a reaction to reflect the concentration change of the limiting reactant, ozone, in the solution. This, in turn, enhances the accuracy of results obtained in analyses of the kinetic data.

The kinetic experiments were carried out in distilled water at temperatures ranging from 10 to 40 °C. The initial pH value of a mixed solution was about 5.2 but varied slightly depending upon the initial concentrations of the reactants. The pH value decreased slightly during reaction, and could be as much as 0.5 less than the initial value at the end of the experiment. The initial concentration of dissolved ozone in the solutions varied from 0.000 025 to 0.0004 *M*. For the cresol isomers, the initial concentration ranged from 0.000 25 to 0.0125 *M* in the experiments.

As indicated earlier, the absorbance of a mixed solution increases rapidly to a maximum (within 0.1 s for all cases) in the early period and then declines in the latter life of the reaction. This phenomenon is demonstrated in Fig. 2 for several runs with different initial concentrations of *o*-cresol and dissolved ozone in water. For analyses of the kinetic data, it is only necessary to utilize the absorbance data obtained during the early period, as discussed by Li et al. [11].

Regression analyses were performed on the absorbance data by assuming different values for *m*, the order of reaction with respect to the concentration of ozone. The absorbance data from the three experimental runs given in Fig. 2 are utilized in Fig. 3. As shown in this figure, straight lines can be drawn for these runs by plotting the dimensionless concentration or absorbance against the reaction time on a semi-logarithmic scale. As dictated by eqs. (5) and (7), these results illustrate that the kinetic data can be best fitted by assuming first order with respect to the concentration of ozone. The result of the regression analyses confirmed this finding. The apparent rate constants then can be calculated from the slopes of the straight lines (or from the regression analyses).

The apparent rate constant can be plotted against the initial concentration of cresol on a logarithmic scale to determine the order with respect to *o*-cresol,

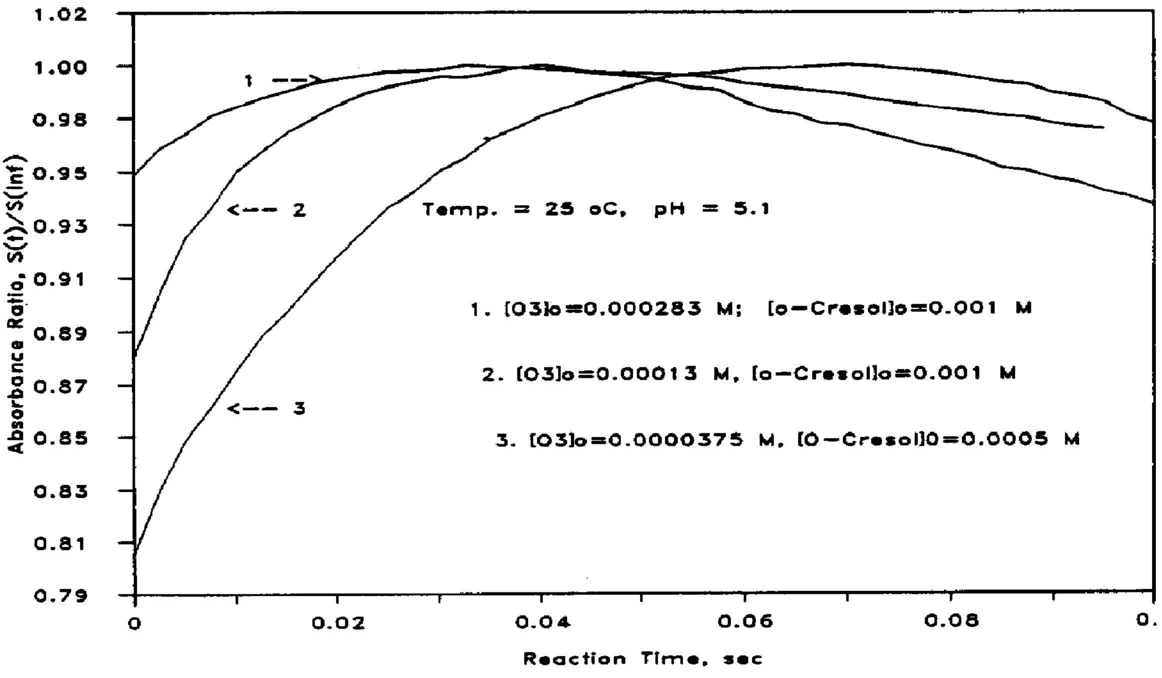


Fig. 2. Absorbance during reaction. Ozonation of *o*-cresol in water at 25 °C.

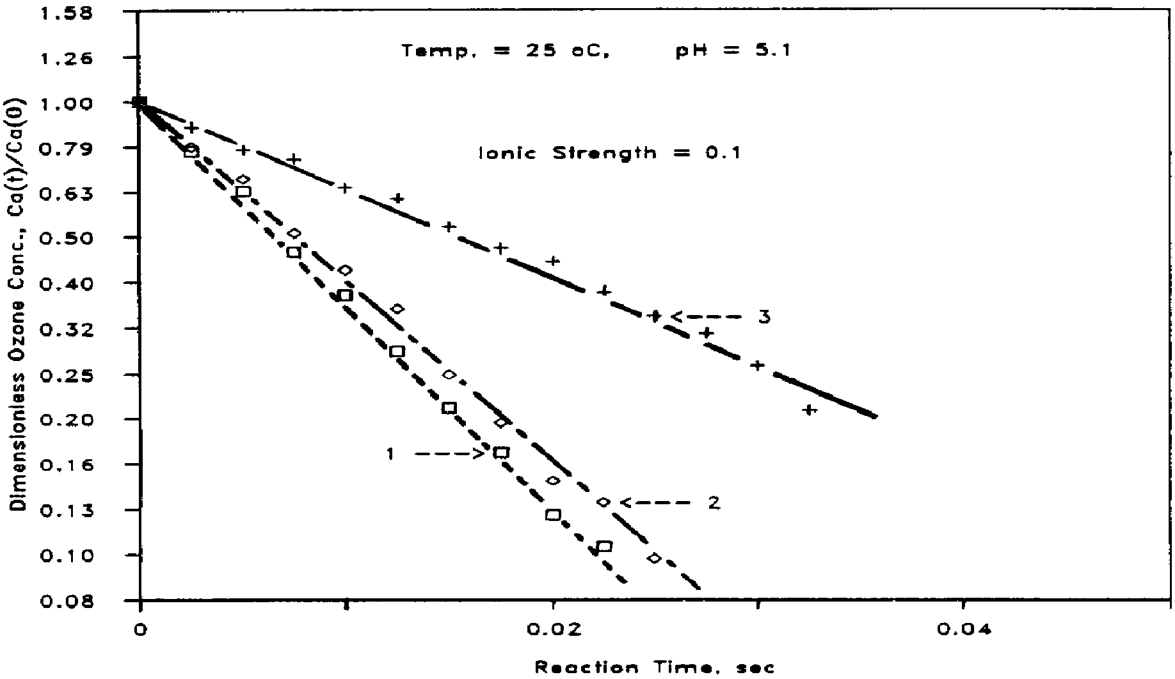


Fig. 3. Ozone concentration in reactions. Ozonation of *o*-cresol in water at 25 °C.

n, as indicated by eq. (4). Figure 4 shows the apparent rate constants obtained for all experiments conducted at three different temperatures for the ozonation of *o*-cresol in water. The apparent rate constants obtained for the ozonation of *m*- and *p*-cresol are given in Figs. 5 and 6. As illustrated in these figures, the slopes are nearly unity for all systems though best correlations are drawn from the experiments conducted at 10 °C. At higher temperatures, appreciable fractions of the reactants were consumed before complete mixing (in one millisecond or less) causing large errors in the data analyses. The slope of unity in these figures indicates that the ozonation reaction can be treated as first order with respect to the concentration of a cresol. Using the stoichiometry of 3 moles of ozone to react with each mole of cresol ($a=3$, $b=1$) determined in this work, the overall rate constant, k, for each experimental run can be calculated from eq. (4) by substituting $n=1$. The average rate constants for the overall reactions at different temperatures and the standard deviations are tabulated in Table 1.

The average second order rate constants for the ozonation of *o*-cresol are 13 460, 32 240 and 58 600 1/*M*s at 10, 25 and 40 °C respectively. For the ozonation of *m*-cresol, the overall rate constants are 25 990, 60 870 and 120 870 1/*M*s respectively, at 10, 25 and 40 °C. The rate constants are 20 900, 45 460 and 96 640 1/*M*s at the three respective temperatures for the *p*-cresol–ozone reaction. The standard deviations vary from 8 to 30% for the three isomers at different temperatures. For the total of 58 experiments conducted in this research, the

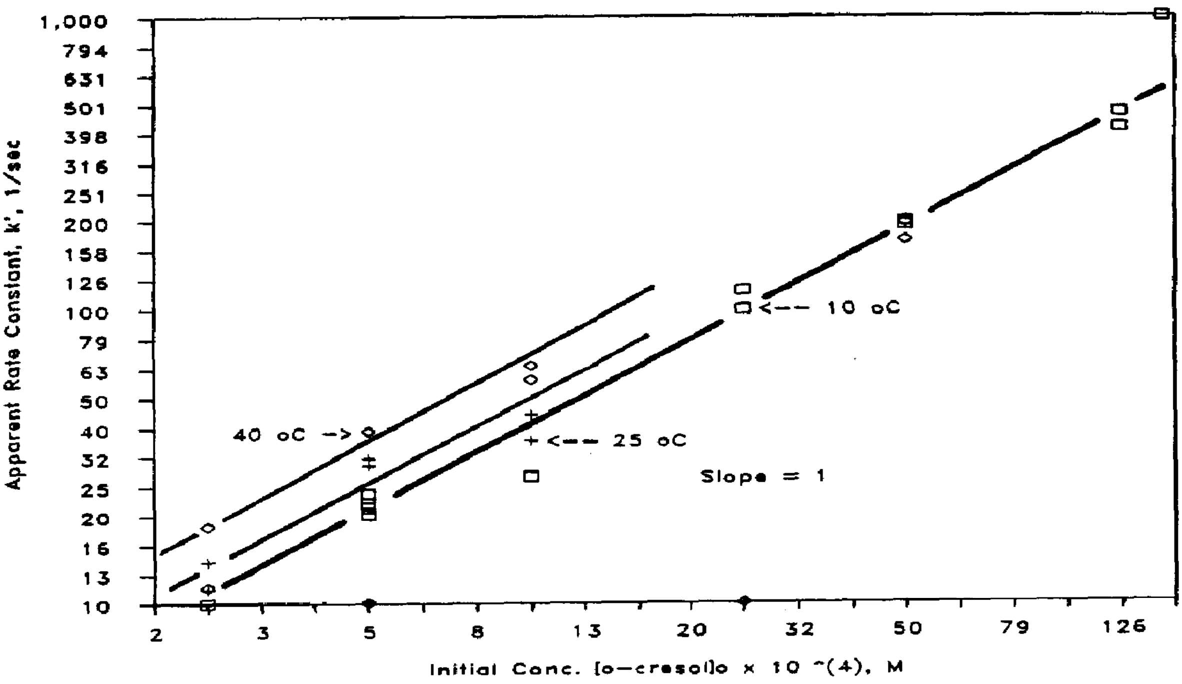


Fig. 4. Apparent rate constant. Ozonation of *o*-cresol in water.

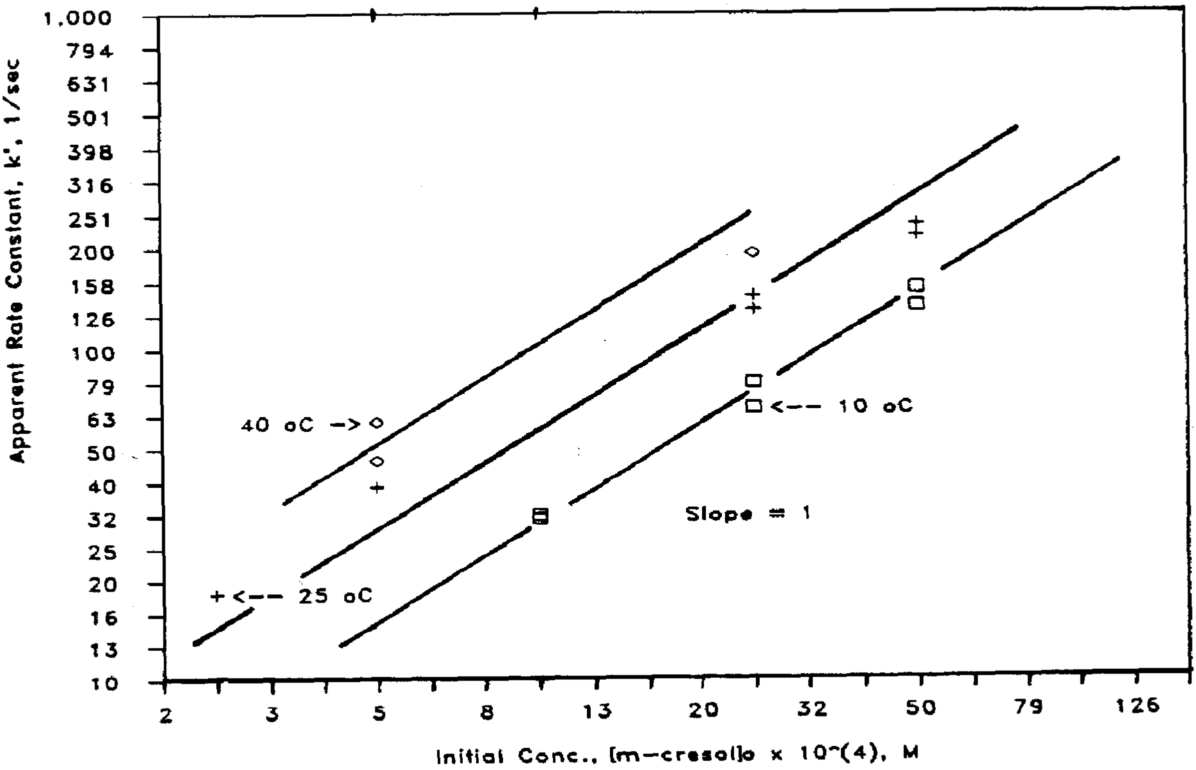


Fig. 5. Apparent rate constant. Ozonation of *m*-cresol in water.

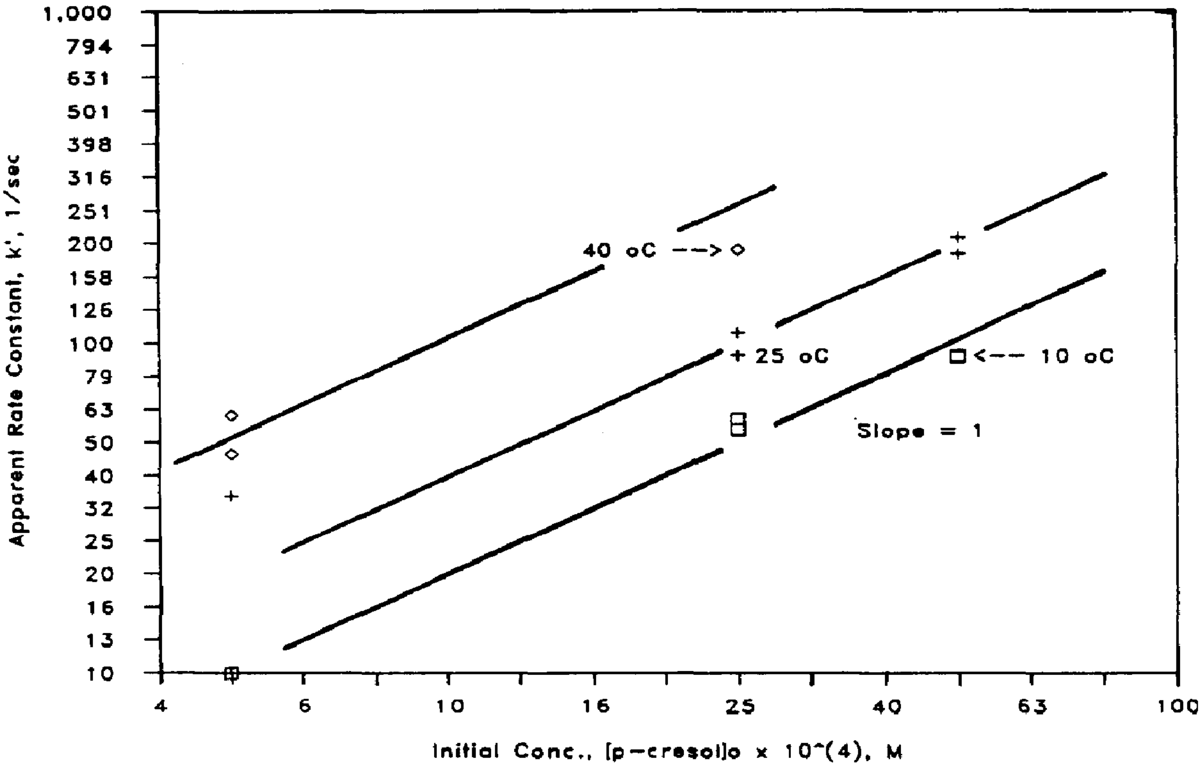


Fig. 6. Apparent rate constant. Ozonation of *p*-cresol in water.

TABLE 1

Overall rate constants for ozonation of cresols in water

Pollutant	Temperature (°C)	Average rate constant (1/*M* s)	Standard deviation (1/*M* s)	Deviation (%)
o-Cresol	10	13 460	2 965	22.0
	25	32 240	5 582	17.3
	40	58 600	17 300	29.5
m-Cresol	10	25 990	4 603	17.7
	25	60 870	14 204	24.1
	40	120 870	10 204	8.4
p-Cresol	10	20 900	2 408	11.5
	25	45 460	13 505	29.7
	40	96 640	22 666	23.5

individual rate constants deviated less than 30% from the average values except for two runs. The deviations were 41 and 52% for these two runs, probably due to the depletion of large fractions of the reactants prior to the dead time, yielding large errors in the absorbance measurements. The average

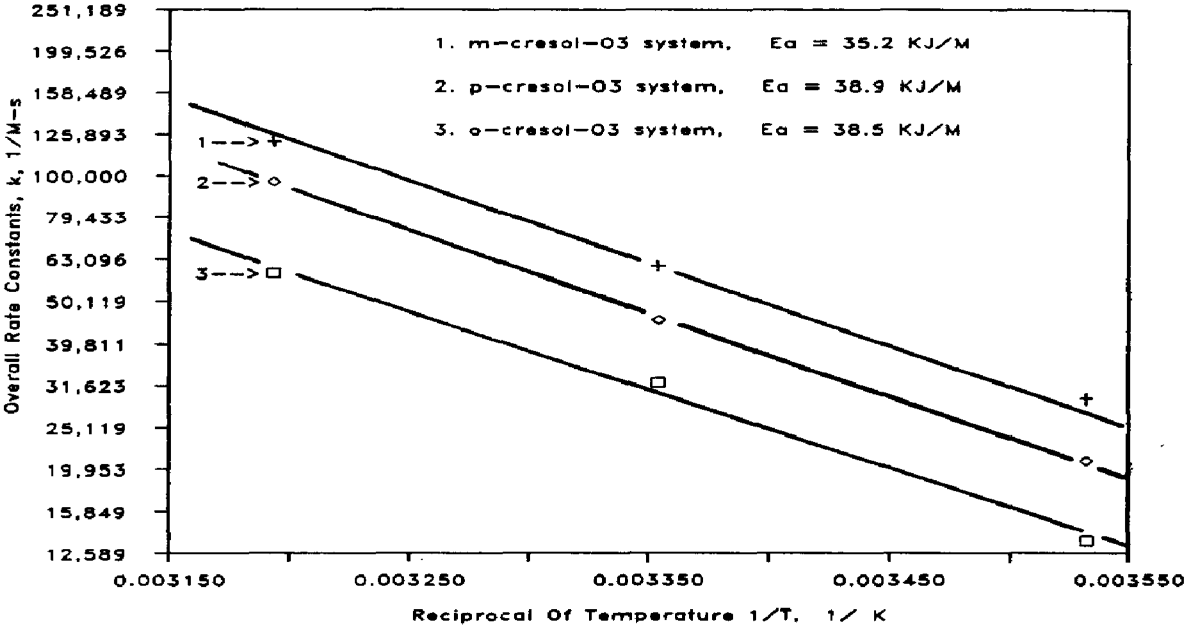


Fig. 7. Overall rate constant. Ozonation of cresols at 10 to 40 °C.

rate constants are plotted in Fig. 7 in accordance with the Arrhenius equation to observe the temperature effect. The calculated activation energies are 38.5, 35.2 and 38.9 kJ/*M* respectively, for the ozonation of *o*-, *m*- and *p*-cresol. The differences in the activation energies are small though the reaction rates are different; the ozonation rate of *o*-cresol is the slowest and that of *m*-cresol, the fastest, at a fixed temperature.

6. Oxidation with hydrogen peroxide

Preliminary tests indicated the rates of oxidation between the cresols and hydrogen peroxide are very slow with or without the presence of a catalyst. The absorbance of a mixed solution changed little in the stopped-flow reactor even after several hours of reaction. Since analysis of the absorbance data may not yield accurate results under this circumstance, there are no advantages in using the stopped-flow system. Therefore, the kinetic experiments were conduced in the agitated reactor with hydrogen peroxide in large excess to observe the reactivity of cresols. For each experiment, samples were drawn every hour for about 10 h, and the cresol concentrations determined by the gas chromatographic method using a carbowax 20M column.

The concentration profiles of *o*-cresol are illustrated in Fig. 8 for two experimental runs with or without a catalyst (Fe_2O_3, 0.5 wt%). Although the oxidation speed was enhanced in the presence of Fenton's reagent, the reaction was

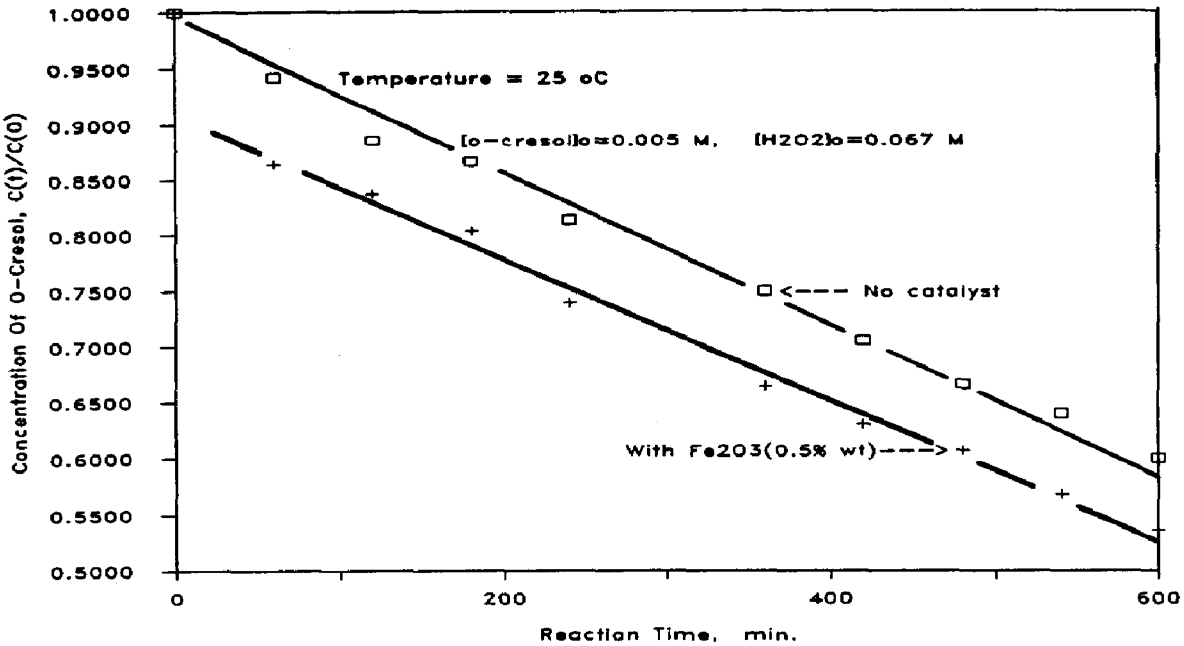


Fig. 8. Hydrogen peroxide–cresol system. Oxidation in water at 25°C.

very slow at 25 °C. As can be seen from the figure, less than 50% of the *o*-cresol was consumed after the reaction time of 10 h.

Regression analyses of the kinetic data were performed. For the hydrogen peroxide–cresol experiments, the cresol is the limiting reactant with hydrogen peroxide in large excess. With this exception, the concentration data can be analyzed in the same manner as those for the ozonation reactions. The reaction is found to be first order with respect to the concentration of *o*-cresol, and one-half order with respect to the concentration of hydrogen peroxide. The overall reaction between the cresol and hydrogen peroxide is one and one-half order for the reactions of all cresol isomers.

The overall rate constants are 0.000055 and 0.000069 $M^{-0.5}s^{-1}$ for the reaction between *o*-cresol and hydrogen peroxide with and without Fenton's reagent at 25 °C, respectively. The rate constants for *m*- and *p*-cresol oxidation are slightly lower, though the reactions were enhanced in the presence of ferric oxide.

7. Discussion

The experimental results indicate that the cresols are not very reactive with hydrogen peroxide. In addition to the data reported, several other catalysts (both soluble and insoluble) were tested in this work yielding similar results. However, this does not rule out the oxidation potential of hydrogen peroxide under other circumstances (for example, enhancement by ultraviolet light irradiation). Hydrogen peroxide of high concentration (50% or more) is available for commercial applications, and it may be suitable for treatment of some liquid wastes containing cresols.

In the ozonation of the cresols, the absorbance of a mixed solution increased very rapidly to a maximum value in less than 0.1 s and then declined, as demonstrated in Fig. 2. This absorbance behavior suggests the possible formation of ozonides with high absorptivity in the early period, and further reaction or decomposition of the ozonides in the latter life of a reaction. None the less, the reaction mechanism is not determined in this work, though there are several possible reaction paths, as discussed in an earlier section. The only conclusion arrived at in this research is that 3 moles of ozone are required to react with each mole of a cresol isomer to produce acetic acid and other products.

The overall kinetics of the ozonation of cresols is second order with first order in each reactant. The reaction is very rapid with the second order rate constants of 32 240, 60 870 and 45 460 $1/M$s at 25 °C for the ozonation of *o*-, *m*- and *p*-cresol respectively. This implies that *m*-cresol is the most reactive species of the three isomers at room temperatures. These phenolic compounds are more reactive than simple phenol with ozone. The ozonation of phenol was studied previously in this laboratory [11]; the overall reaction is also second order with the rate constant of 29 520 $1/M$s in distilled water at 25 °C. Thus, the ozonation rates of *o*-, *m*- and *p*-cresol respectively, are 1.1, 2.1 and 1.5 times faster than that of phenol. These rate ratios are different from those reported by other investigators [7], but the discrepancy is not unexpected. Many heterogeneous systems such as gas–liquid contactors are designed for mass transfer studies [14]. Because of complex influences of chemical reactions on mass transfer rate, these reactors might not be suitable for obtaining kinetic information for homogeneous, liquid phase reactions. The stopped-flow spectrophotometer system used in this work is advantageous in enabling measurements of rapid changes in absorbance for a reaction with half-life of as short as a few milliseconds. The absorbance data obtained in the very short period can then be analyzed to yield accurate results on the kinetics of the reaction.

The influence of temperature on the ozonation rates is similar for the three cresol isomers. As the temperature increases four times from 10 to 40 °C; the rate constant increases 4.1 to 4.6 times for each species. As indicated in the Arrhenius plot in Fig. 7, the three lines for the three isomers are nearly parallel. The calculated activation energies are 38.5, 35.2 and 38.9 kJ/M, respectively, for *o*-, *m*- and *p*-cresol. The small differences in the activation energies might suggest that the mechanism governing ozonation is the same for the three isomers.

Though the initial pH value of the reactants in the distilled water was about 5.2, it dropped to as low as 4.7 at the end of some reactions. The increase in the acidity of the reacting solution might be indicative of the formation of acetic and other acids identified in this and other reports [4]. To apply the ozonation process to oxidize soils or water contaminated by cresols, further treatment for acid removal might be required.

The information obtained in this research might be useful to air pollution control as indicated earlier. Due to the high reactivities of cresols, any cresols emitted into the atmosphere might be converted in a short period to the acids as secondary pollutants in the presence of ozone and moisture.

8. Conclusions

This research studied the oxidation rates of *o*-, *m*- and *p*-cresol by hydrogen peroxide and ozone in water at a temperature range from 10 to 40 °C. Hydrogen peroxide is not very reactive with cresols, even in the presence of Fenton's reagent. The overall kinetics is first order with respect to the concentration of the cresol isomer and one-half order with respect to the concentration of hydrogen peroxide. The overall rate constants are 0.000 055 and 0.000 069 $M^{-0.5}s^{-1}$ for the oxidation in the absence and presence of Fenton's reagent. The oxidation rates of *m*- and *p*-cresol are also slow though the reactions are catalyzed by metal oxides.

Three moles of ozone are required to react with each mole of cresol. The ozonation of cresols in water is very rapid though the reaction rates are different for the three isomers. The half-life of a reaction is only a few milliseconds for most cases. The overall kinetics of the ozonation of a cresol is second order with first order in each reactant. The reaction rate increases with temperature in the range 10–40 °C investigated in this work. For the ozonation of *o*-cresol, the overall rate constants are 13 460, 32 240 and 58 600 $1/M$s, respectively, at 10, 25 and 40 °C. The ozonation rate of *m*-cresol is the fastest; the rate constant increases from 25 990 to 120 870 $1/M$s in the temperature range of 10–40 °C. For the ozonation of *p*-cresol, the rate constant varies from 20 900 to 96 640 $1/M$s as the temperature increases from 10 to 40 °C.

The ozonation rate of cresols is faster than that of simple phenol. Of the three cresol isomers investigated, *m*-cresol is the most reactive species. On the other hand, the reaction rate between *o*-cresol and ozone is slower than those of the other isomers in the temperature range of 10–40 °C. The activation energies are nearly the same for the three isomers at about 39 kJ/M.

Acknowledgments

This project has been funded with Federal Fund as part of the program of the Gulf Coast Hazardous Substance Research Center which is supported under cooperative agreement R 815197 with the United States Environmental Protection Agency. The contents do not necessarily reflect the views and policies of the US EPA nor does the mention of trade names or commercial products constitute endorsement for use.

Nomenclature

a	Stoichiometric ratio for reactant A
b	Stoichiometric ratio for reactant B
C_A	Concentration of a limiting reactant
C_B	Concentration of an excessive reactant
k'	Apparent rate constant
k	Overall reaction rate constant
m	Reaction order with respect to a limiting reactant
n	Reaction order with respect to an excessive reactant
S	Absorbance of a reacting solution
t	Reaction time

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