



## Project Summary

# Reactions of Dissolved Pollutants with Ozone in Aqueous Solutions

C. H. Kuo

The kinetics of aqueous-phase oxidation of selected hydrocarbons by ozone at 5 to 35°C were investigated. The experiments were conducted in aqueous solutions with pH values ranging from 2 to 7 using a stopped-flow spectrophotometer interfaced to a data-acquisition system.

Ozonation reactions of olefinic compounds, including cyclohexene, cyclopentene, and 1-pentene were much faster in the aqueous solutions than in the vapor phase. The average rate constants of the bimolecular reactions were  $4 \times 10^6 \text{ L gmol}^{-1} \text{ s}^{-1}$  or larger, and were nearly independent of the pH value and temperature. Experimental results indicated that saturated hydrocarbons such as cyclohexane, cyclopentane, hexane, and pentane were not reactive with dissolved ozone. Benzene and toluene reacted with ozone at moderate rates in acidic solutions, but the ozonation of benzene was very rapid in neutral solutions. Orders of the ozonation reactions of aromatic compounds changed with acidity, indicating a possible shift in the mechanisms of the reactions.

Preliminary tests by chromatography showed that acids and aldehydes were formed in ozonation of the olefins and that oxidation of benzene produced benzoquinone and hydroquinone. The detection of high-molecular-weight compounds in the solutions indicated the polymerization of some species in the reactions.

*This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle*

*Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back.)*

### Introduction

Hydrocarbons are among the major pollutants emitted into the atmosphere from mobile and stationary sources such as automobiles, petroleum refineries, and chemical manufacturing facilities. Although atmospheric hydrocarbons vary considerably in structure, many species are reactive and may be oxidized to form secondary and tertiary pollutants. One of the most important oxidizing agents in the atmosphere is ozone ( $\text{O}_3$ ) produced by photochemical reactions in the stratosphere. A fraction of the  $\text{O}_3$  diffuses into the troposphere and contributes to the background  $\text{O}_3$  concentration in all atmospheres. Oxidation of the atmospheric hydrocarbons by  $\text{O}_3$  in the vapor and liquid phases can produce chemical species that are hazardous to public health and the environment. Under overcast, high-humidity conditions, dissolved pollutants may be oxidized to secondary and tertiary aerosols in the liquid phase. Rates and mechanisms of the conversion, however, are not well known.

The present research was undertaken to investigate the kinetics of the oxidation of some saturated hydrocarbons, olefins, and aromatic compounds by  $\text{O}_3$  in the aqueous phase. The compounds chosen for this study include benzene, cyclohexane, cyclohexene, cyclopentane, cyclopentene, hexane, pentane, 1-pentene, and toluene. Although the oxidation rates

of some of these pollutants in organic solvents are reported in the literature, little information is available concerning the kinetics of reactions in the aqueous phase.

A stopped-flow spectrophotometer (Durrum Model D-110) was applied to conduct the kinetic experiments in solutions of various pH values and temperatures. Absorbance data were collected through an automatic data acquisition system interfaced to the spectrophotometer. The effects of acidity and temperature on the rates of the reactions were investigated. Identifications of products of the oxidation reactions were also attempted using a gas chromatograph (Hewlett-Packard Model 5840A).

## Procedure

The kinetic experiments were conducted at temperatures varying from 5 to 35°C in aqueous solutions with pH values ranging from 2 to 7. A buffer solution was prepared by adding appropriate amounts of chemicals such as HCl, Na<sub>2</sub>HPO<sub>4</sub>, NaH<sub>2</sub>PO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, or NaOH in distilled water for control of the pH value and ionic strength. Ozone gas was produced from a Welsbach Model T-408 ozonator using extra dry, pure oxygen. Any possible impurities in the buffer solution were oxidized by bubbling O<sub>3</sub> gas in the solution for several hours. Unreacted O<sub>3</sub> was displaced by bubbling off nitrogen gas. The aqueous solution of a pollutant was prepared by adding a known quantity of the pollutant reactant (less than the solubility limit) to the buffer solution and agitating with a magnetic stirrer for several hours to a few days until homogeneity was achieved. Also, a portion of the buffer solution was used to prepare the O<sub>3</sub> solution.

The spectrophotometer system was calibrated in accordance with procedures specified by the manufacturer. By circulating coolant water, the temperature in the spectrophotometer system was maintained at the desired value during an experiment. The aqueous solutions of the pollutant reactant and O<sub>3</sub> were kept at the same temperature in an isothermal bath. Before an experimental run, a portion of the O<sub>3</sub> solution was removed and stored in a reservoir syringe in the spectrophotometer. Another reservoir syringe was used to store the aqueous solution of the pollutant reactant. The two drive syringes were then filled from the two storage syringes containing the two reactants in the separate solutions with an identical pH value and at the same temperature. After data from the reaction system and

sampling specifications were entered onto a computer terminal, a flow actuator was triggered. This resulted in simultaneous activations of both the stopped-flow spectrophotometer and data-acquisition systems. Absorbances of the mixed reacting solution were recorded as a function of reaction time and stored in the computer memory. After the termination of sampling of a run or a series of experiments, the absorbance data were recalled from data files in the data-acquisition system and analyzed by appropriate methods.

Analyses of the reaction products were performed using the gas chromatograph. Injection samples were prepared by mixing two reactant solutions or by bubbling of O<sub>3</sub> in a solution containing a pollutant. After complete depletion of O<sub>3</sub>, aqueous samples were injected directly into columns with packings such as 5% FFAP to obtain chromatograms of the reaction products. To use other columns in which aqueous samples were not acceptable, the reaction products had to be extracted from the aqueous solution by ether and concentrated before injection. The range of column temperature and rate of temperature increase were programmed to achieve best results in separation of the reaction products. Retention times of the reaction products were compared with those of standard reagents to identify the products of reaction. Also, blank tests were performed to detect any contaminants in the buffer solution.

## Results

Oxidation of several saturated hydrocarbons including cyclohexane, cyclopentane, hexane, and pentane by O<sub>3</sub> in aqueous solutions was investigated. Absorbance data for these systems were best fitted by three-halves-order kinetics with respect to O<sub>3</sub> concentration. These kinetics of reaction were identical to those of self decomposition of O<sub>3</sub> in the absence of any contaminant. Also, the apparent rate constants calculated for these systems are nearly identical to the rate constants for decomposition reactions at the same conditions as the experiments. These results suggest that the ozonation reactions were insignificant compared with the decomposition reaction of ozone in the solutions.

Olefinic compounds such as cyclohexene, cyclopentene, and 1-pentene were very reactive with O<sub>3</sub> at rates of ozonation much faster than the corresponding rates of O<sub>3</sub> decomposition. The kinetics of ozonation of cyclohexene were

second order with first order each in concentration of both reactants. The ozonation rate was not significantly affected by temperature variation, and the half-life of reaction of cyclohexene was less than one millisecond. At 25°C, the second-order rate constant increase slightly with acidity in the pH range of 2 to 7, and an average rate constant of 3.9 × 10<sup>6</sup> L gmol<sup>-1</sup> s<sup>-1</sup> was calculated. The second-order rate constants for cyclopentene-O<sub>3</sub> and 1-pentene-O<sub>3</sub> reactions were estimated to be on the order of 1 × 10<sup>7</sup> gmol<sup>-1</sup> s<sup>-1</sup> though accurate determinations were not possible because of limitations of the stopped-flow apparatus. Since the rate constants for the ozonation reactions of these compounds in the vapor phase varied from 3 × 10<sup>3</sup> to 4 × 10<sup>4</sup> L gmol<sup>-1</sup> s<sup>-1</sup>, the above results suggest that O<sub>3</sub> can react with the olefinic compounds much faster in the aqueous phase than in the vapor phase. By using a 5% FFAP and a Chromosorb 101 glass column in the gas chromatograph, acetic acid, acetaldehyde, and butyraldehyde were detected as products of ozonation of cyclopentene and pentene in the solutions. In addition, several compounds with molecular weights ranging from 82 to 249 were traced, but the identities of the individual compounds have not been established. Although the formation of high-molecular-weight compounds has not been reported in the ozonation reactions in the vapor phase, the acids and aldehydes have been detected. Experimental results also indicated that the stoichiometric ratio was unity for the reaction between cyclohexene and O<sub>3</sub>.

The stoichiometric ratio of benzene to O<sub>3</sub> in the ozonation reaction varied from 0.97 to 1.26. Thus, it may be reasonable to consider the ratio as unity for the reaction in aqueous solutions. The kinetics of oxidation of benzene were one-half order each in concentrations of benzene and O<sub>3</sub>, and the rate constant increased with pH value and temperature. For example, for the reactions in aqueous solutions with a pH value of 3, the rate constants increased from 5.5 × 10<sup>-4</sup> to 0.012 L/s as the temperature changed from 5 to 35°C. In neutral solutions, the fast reaction was first order with respect to O<sub>3</sub> concentration and independent of benzene concentration. Again, the rate constants increased from 7.8 to 12.2 L/s in the temperature range of 5 to 25°C. An OV-17 glass column was used in the gas chromatograph to detect products of benzene ozonation. Following the separation, a mass spectrometer was used to obtain mass spectra of the individual

species. Benzoquinone (p-quinone) was identified in all samples. In addition, hydroquinone (1, 4-dihydroxy benzene) was also detected in the neutral solutions. Several spectra with molecular weights above 108 were detected, but definite identification of these products has not been possible. The results of the kinetic experiments and product analyses seem to suggest that there might be a shift in the mechanism of ozonation depending upon the acidity

The reaction between toluene and O<sub>3</sub> was faster in acidic and slower in neutral solutions than the benzene-O<sub>3</sub> reaction. In the acidic solutions, the ozonation reaction of toluene was first order with respect to both concentrations of toluene and O<sub>3</sub>. In the neutral solutions, the reaction was first order in O<sub>3</sub> only with a rate constant of 0.19 L/s at 25°C. Similar to the ozonation of benzene, mechanisms of the ozonation of toluene might be different at various acidities as suggested by the results of the kinetic studies.

## Conclusions

Saturated hydrocarbons including cyclohexane, cyclopentane, hexane, and pentane studied in this research were not very reactive with O<sub>3</sub> in the aqueous phase. The three-halves-order rate constants for these systems are nearly identical to the corresponding rate constants for self decomposition of O<sub>3</sub> in the solutions at similar conditions.

Cyclohexene can react rapidly with O<sub>3</sub> in an aqueous solution at a half-life of less than one millisecond. The kinetics of ozonation were first order with respect to both concentrations of O<sub>3</sub> and cyclohexene. The reaction was influenced very little by the pH value and temperature of the solutions. Although reliable information on very rapid kinetics of ozonation of cyclopentene and 1-pentene could not be obtained because of equipment limitations, the reaction rate constants are estimated to be of the order of  $1 \times 10^7$  L gmol<sup>-1</sup> s<sup>-1</sup>. These reactions were many times faster than the rates of ozonation of the olefinic compounds in the vapor phase. Preliminary tests by the method of gas chromatography indicated that in addition to acids and aldehydes, some high-molecular-weight compounds were formed in the ozonation reactions in the solutions

The rate of ozonation of benzene was much faster than that of toluene in neutral solutions, though the two reactions proceeded only at moderate rates in acidic solutions. The kinetics of ozonation

were first order with respect to O<sub>3</sub> but independent of benzene or toluene concentration in a neutral solution. In acidic solutions, however, the ozonation kinetics were influenced by concentrations of all reactants. In the reaction between benzene and ozone, benzoquinone was formed in the acidic solutions, and further reaction to hydroquinone was detected in the neutral solutions. Contrary to common belief, benzene was found to be reactive with O<sub>3</sub> in the aqueous phase. The

mechanisms of ozonation might be different depending upon the pH values of the solutions.

The stoichiometric ratio of near unity was determined in this research for the reactions of benzene and cyclohexene with O<sub>3</sub>, suggesting that the ozonation reactions are bimolecular in nature. Possible shift in mechanisms of the ozonation reactions with acidity was indicated by changes in orders of reactions of the aromatic compounds at various pH values.

*C. H. Kuo is with Mississippi State University, Mississippi State, MS 39762.*

*J. L. Durham is the EPA Project Officer (see below).*

*The complete report, entitled "Reactions of Dissolved Pollutants with Ozone in Aqueous Solutions," (Order No. PB 84-211 218; Cost: \$10.00, subject to change) will be available only from:*

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