



## Project Summary

# Reactions of Ozone with Organics in Aqueous Solutions

C. H. Kuo and H. M. Barnes

**Rates of ozonation of some aromatic pollutants in the aqueous phase were studied by the stopped-flow technique. The kinetic experiments were conducted in distilled water and in aqueous solutions of pH range from 2 to 7 at 5 to 35°C.**

**Aromatic amines including aniline and  $\alpha$ -naphthylamine-ozone reaction was enhanced by temperature, but the faster reaction between aniline and ozone remained at a nearly constant rate for all temperatures.**

**The order of reaction between toluene and ozone varied with acidity though the rate of reaction was moderate. Polycyclic aromatic hydrocarbons including naphthalene, phenanthrene, and anthracene were reactive with ozone according to second order kinetics. Rate constants of the reactions increased as the temperature increased and acidity of the solutions decreased.**

***This Project Summary was developed by EPA's Atmospheric 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

Aromatic compounds are among the major pollutants emitted into the atmosphere from mobile and stationary sources such as automobiles, petroleum refineries, and chemical manufacturing and fuel combustion facilities. Although atmospheric organics 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 atmo-

sphere is ozone produced in photochemical reaction in the stratosphere. A fraction of the ozone diffuses into the troposphere and contributes to the background ozone concentration in all atmospheres. Oxidation of the organic compounds by ozone in vapor and liquid phases can result in formation of hazardous and/or toxic products. Under overcast, high-humidity conditions, dissolved pollutants may be oxidized in the liquid phase to produce secondary and tertiary aerosols. Rates and mechanisms of the conversion, however, are not well known. The present research, therefore, was undertaken to investigate kinetics of oxidation of toluene, naphthalene, phenanthrene, anthracene, aniline, and  $\alpha$ -naphthylamine by ozone in the aqueous phase.

A stopped-flow spectrophotometer (Durrum Model D-110) was applied to conduct the kinetic experiments in distilled water and in aqueous solutions of various pH values and temperatures. Absorbance data were collected through an automatic data acquisition system interfaced to the spectrophotometer. Effects of the temperature and acidity on the oxidation rate were investigated.

### Procedure

The kinetic experiments were conducted at temperatures varying from 5 to 35°C in distilled water and 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,  $\text{Na}_2\text{HPO}_4$ ,  $\text{NaH}_2\text{PO}_4$ , or  $\text{Na}_2\text{SO}_4$  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 ozone

gas in the solution for several hours, and unreacted ozone was displaced by bubbling of nitrogen gas. An 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 agitated by a magnetic stirrer for several hours to a few days to achieve homogeneity. Also, a portion of the buffer solution was utilized to prepare the ozone 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 two aqueous solutions of the pollutant reactant and ozone were kept at the same temperature in an isothermal bath before an experimental run. A portion of the ozone solution was then removed and stored in a reservoir syringe in the spectrophotometer. Another reservoir syringe was filled with the aqueous solution of the pollutant reactant. Two separate drive syringes in the stopped-flow apparatus then were filled from the two storage syringes containing the two reactants in the separate solutions of an identical pH value at the same temperature. Following the entry of data of the reaction system and sampling specifications through 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 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 correlated and analyzed using appropriate rate equations.

## Results

Aniline and  $\alpha$ -naphthylamine were very reactive with ozone and constituents of buffer solutions. To avoid errors in measurements, therefore, the kinetic experiments were carried out only in distilled water. The overall kinetics of ozonation of both aniline and  $\alpha$ -naphthylamine were second order with first order each in ozone and the organic reactants. For the aniline-ozone reaction, the rate was nearly independent of temperature with an average second order rate constant of  $2.4 \times 10^5$  l/M-s. The ozonation rate of  $\alpha$ -naphthylamine was slightly lower with the second order rate constant

changing from  $5.3 \times 10^4$  to  $1.3 \times 10^5$  l/M-s as the temperature increased from 5 to 35°C. Tests also were made to determine the reactivity of these compounds with hydrogen peroxide in the aqueous phase. No significant change in the absorbance of a mixed solution of the hydrogen peroxide and the organic species was detected. The result seemed to suggest that neither aniline nor  $\alpha$ -naphthylamine was reactive with hydrogen peroxide in the absence of a catalyst in the solutions.

As expected, toluene reacted with ozone at a moderate rate in the aqueous phase. The ozonation reaction was second order in acidic solutions, and the rate constant varied from 10.5 to 53.3 l/M-s in the temperature range of 10 to 35°C. In neutral buffer solutions, the reaction was first order with respect to the ozone concentration but was nearly independent of the concentration of toluene. As the temperature increased from 10 to 35°C, the first order rate constant increased from 0.02 to 1.6 l/s. Although the rate of the toluene-ozone reaction was slightly higher than that of the benzene-ozone reaction investigated in an earlier work, the phenomenon of dependence of the reaction order on the acidity was observed in both systems. This might be indicative of a shift in reaction mechanisms with pH value of a buffer solution for both the toluene-ozone and benzene-ozone reactions.

The simplest molecule of polynuclear aromatic hydrocarbons, naphthalene was much more reactive than the simple aromatic hydrocarbons such as benzene and toluene with ozone in aqueous solutions. The kinetics of ozonation of naphthalene was first order with respect to concentrations of both ozone and naphthalene. The reaction rate was enhanced by temperature, and at 25°C, the second order rate constant increased from 850 to 3,750 l/M-s as the pH value of aqueous solutions increased from 3 to 7.

The ozonation of phenanthrene seemed to be controlled by initial attachment of ozone molecules at the 9,10 bond of phenanthrene because of its double-bond character. The overall kinetics can be treated as second order, the reaction rate was promoted by both temperature and pH value of an aqueous solution. At 25°C, the reaction rate constant increased from  $1.94 \times 10^4$  l/M-s in strongly acid solutions to  $4.75 \times 10^4$  l/M-s in neutral solutions. Activation energies of the reaction were estimated to be 7 kcal/mole at the pH value of 3 and 23 kcal/mole in other acidic and neutral solutions.

Experiments also were carried out to study the rate of reaction between anthracene and ozone in the aqueous phase. The reaction was extremely fast with half reaction life of less than a few milliseconds. Analyses of the absorbance data indicated that the second order rate constant is about  $2 \times 10^7$  l/M-s in acidic solutions at temperatures varying from 10 to 35°C.

The results of this research project indicate quantitatively the order of decreasing reactivity of aromatic hydrocarbons with ozone as follows: anthracene > phenanthrene > naphthalene > toluene. Although this reactivity trend has been suggested by several earlier investigators, very little information is available in the literature regarding the kinetics and rates of the ozonation reactions. The research also shows that aniline and  $\alpha$ -naphthylamine are very reactive with ozone according to the second order kinetics. The rate data were obtained to assist EPA's Risk Assessment unit investigation of the organic pollutants.

## Conclusions

Aromatic amines can be very reactive with ozone, as well as reagents of buffer solutions. In distilled water, aniline reacted with ozone according to second order kinetics, and the reaction rate constant is nearly independent of temperature between 10 to 35°C at  $2.4 \times 10^5$  l/M-s. The reaction between  $\alpha$ -naphthylamine and ozone was slightly slower, the second order rate constant is enhanced by temperature, increasing from  $0.53 \times 10^5$  l/M-s in the temperature range of 10 to 35°C.

The present research confirmed that polycyclic aromatic hydrocarbons in general are more reactive than simple aromatic hydrocarbons with ozone in the aqueous phase oxidation. Of the aromatic compounds investigated, the reaction between anthracene and ozone was the fastest with the second order rate constant of  $2 \times 10^7$  l/M-s in acidic solutions. The ozonation of phenanthrene also was fast and the rate constant increased with pH value and temperature. At 25°C, the second order rate constant increased from  $1.94 \times 10^4$  to  $4.75 \times 10^4$  l/M-s as the pH value varied from 2.2 to 7.0. The second order reaction between naphthalene and ozone was moderate with the rate constant varying from 850 to 3750 l/M-s as the pH value increased from 3 to 7 at 25°C. As expected, the rate of ozonation of toluene was lowest among the system of oxidation reactions of aromatic hydrocarbons.

carbons investigated. Similar to the ozonation of benzene, the order of reaction of toluene changed with acidity, indicating a possible shift in the mechanism of reaction.

*C. H. Kuo is with Mississippi State University, Mississippi State, MS 59762.*

*H. M. Barnes is the EPA Project Officer (see below).*

*The complete report, entitled "Reactions of Ozone with Organics in Aqueous Solutions," (Order No. PB 85-191 171/AS; Cost: \$10.00, subject to change) will be available only from:*

*National Technical Information Service*

*5285 Port Royal Road*

*Springfield, VA 22161*

*Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:*

*Atmospheric Sciences Research Laboratory*

*U.S. Environmental Protection Agency*

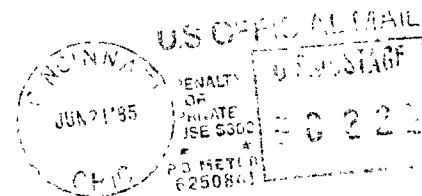
*Research Triangle Park, NC 27711*

PC

United States  
Environmental Protection  
Agency

Center for Environmental Research  
Information  
Cincinnati OH 45268

Official Business  
Penalty for Private Use \$300



0000329 PS

U S ENVIR PROTECTION AGENCY  
REGION 5 LIBRARY  
230 S DEARBORN STREET  
CHICAGO IL 60604