



## Project Summary

# Validation of OH Radical Reaction Rate Constant Test Protocol

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A study was conducted to evaluate the OH rate constant measurement protocol developed by researchers at the University of California at Riverside. The protocol, which is a relative rate method, was used to measure room temperature OH rate constants for a series of low molecular weight, high volatility alkanes, alkenes, aromatics, oxygen-containing compounds, and chlorinated compounds. The full report of this research project provides OH rate constants for 21 compounds and a comparison of each value with those reported in the literature.

The OH rate constants obtained were in good agreement with literature values for all classes of compounds except for chlorinated compounds, for which rate constants had not been previously determined for most of the compounds studied. The protocol can be used to determine OH rate constants as low as  $0.5 \times 10^{-12}$  cm<sup>3</sup>/molecule-sec. The results obtained for chlorinated compounds suggest that Cl reactions can interfere with the OH rate constant determination; however, if the chlorinated compound is irradiated under conditions of high reference to test compound concentration ratios, the effect can be reduced. Further research is required to establish the validity of the protocol for determining OH rate constants of chlorinated compounds.

*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

Recently, increased attention has been given to the possible adverse health effects associated with exposure to industrial chemicals emitted into the atmosphere. To address this issue, the Environmental Protection Agency (EPA) Office of Pesticides and Toxic Substances was established in 1977 to gather the information necessary to determine the health risks associated with exposure to present or future airborne chemicals. To evaluate the risks, the distribution, toxicity, and environmental fate and lifetime of industrial chemicals must be established.

The first step in establishing atmospheric lifetimes is to identify the major removal processes. Gas phase homogeneous removal processes have been investigated extensively in the laboratory and the results suggest that there are four major removal pathways. The suggested pathways are: (1) reaction with hydroxyl radicals (OH); (2) reaction with ozone (O<sub>3</sub>); (3) photodissociation; and (4) reaction with nitrate radicals (NO<sub>3</sub>). To investigate these processes, a series of protocols that determine the atmospheric lifetimes associated with OH and O<sub>3</sub> reactions, as well as photolysis have been developed for EPA by researchers at the Statewide Air Pollution Research Center at the University of California at Riverside (UCR).

To validate the protocols, EPA contracted with Northrop Services, Inc.-Environmental Sciences to conduct a series of OH and O<sub>3</sub> rate constant determinations, using the UCR methods. The results of the OH rate constant validation

study, where room temperature rate constants for 21 compounds were determined, are presented in the full project report. Rate constants were determined for five classes of hydrocarbons: alkanes, alkenes, aromatics, oxygen-containing compounds, and chlorinated compounds. The values obtained were compared, where possible, with literature values. A lower limit for which the rate constants can be evaluated with the protocol was also estimated. Special emphasis was placed on the determination of OH rate constants for chlorinated compounds where the possibility existed that Cl reactions could occur.

## Experimental Approach

The experimental approach employed was that developed by the UCR. Rate constants for OH were determined by using a relative rate method, in which the test compound was irradiated in air in the presence of methyl nitrite ( $\text{CH}_3\text{ONO}$ ), nitric oxide (NO), and a reference compound whose OH rate constant was well known. The theoretical chemical reaction sequence is described in the full report.

The rates of reaction with OH are assumed to satisfy the following equations:

$$\frac{d}{dt}[\text{Test}] = -k_{10}[\text{Test}][\text{OH}] \quad (\text{I})$$

$$\frac{d}{dt}[\text{Ref}] = -k_{11}[\text{Ref}][\text{OH}] \quad (\text{II})$$

where [Test] and [Ref] are the concentrations of the test and reference compounds, respectively, and the  $k_i$  values are the associated OH rate constants. Equations I and II operate under the assumption that the compounds react only with OH and are invalid if other reactive species such as chlorine radicals (Cl) are present during the irradiation.

Equations I and II can be combined and integrated. The result is

$$\ln \frac{[\text{Test}]_{t_0}}{[\text{Test}]_t} = \frac{k_{10}}{k_{11}} \ln \frac{[\text{Ref}]_{t_0}}{[\text{Ref}]_t} \quad (\text{III})$$

where  $[\text{Test}]_{t_0}$  and  $[\text{Ref}]_{t_0}$  are the concentrations of the test compound and the reference compound at time  $t_0$ , respectively, and  $[\text{Test}]_t$  and  $[\text{Ref}]_t$  are the respective concentrations at time  $t$ .

If  $\ln([\text{Test}]_{t_0}/[\text{Test}]_t)$  is plotted against  $\ln([\text{Ref}]_{t_0}/[\text{Ref}]_t)$ , a straight line should be obtained with slope equal to  $k_{10}/k_{11}$  and intercept equal to zero. The value for the

test compound OH rate constant is immediately obtained from the slope since the reference compound OH rate constant is known.

## Experimental Method

All irradiations were conducted in pillow-shaped 2-mil Teflon bags. Bags were constructed by heat-sealing three sides of a 4- x 8-ft sheet of Teflon. A Teflon Swagelok O-Seal straight-thread connector was mounted on the bag and was used for filling and evacuating the bag, as well as sampling its contents. The volumes of the bags employed ranged from 50 to 60 L. The irradiation chamber consisted of a wood cylindrical frame, split lengthwise with two light banks mounted on the inner side of the frame. Each light bank contained five black lamps (General Electric F40 BLB). A 180 cfm blower was mounted at the top of the frame and was used to remove heat from the chamber. To further minimize temperature increases during the irradiation, the frame was left open approximately 15 cm during the experiments. A thermometer was mounted inside the frame and the maximum temperature increase found during all the experiments was 2 °C. The initial bag temperature was controlled by the laboratory temperature and the temperatures measured during all the experiments ranged from 21° to 26 °C.

A typical OH rate constant determination consisted of first filling the bag with approximately 30 L of clean air (Zero 1.0 Grade from MG Scientific), mixing its contents, and then evacuating it. The bag was then filled with clean air to a final volume of approximately 55 L. The flow rate was 10L/min and was measured with a calibrated rotometer. During the filling process, NO,  $\text{CH}_3\text{ONO}$ , and the test and reference hydrocarbons were introduced into the bag by injecting the compounds into a glass tee that was mounted in the clean air fill line. All glass syringes were used for the liquid and gas injections. The purity of all hydrocarbons employed was greater than 99%, and they were not further purified. Laboratory lights were turned off and the reaction chamber was covered during the time the bag was being filled, and these conditions were maintained until the irradiation began. After the bag was filled and required amounts of gases added, it was kneaded to ensure good mixing.

The initial concentrations of  $\text{CH}_3\text{ONO}$  and NO were approximately 25 ppm and 20 ppm, respectively. The initial test compound concentration ranged from 0.5

ppm to 4.0 ppm, whereas the reference compound concentration ranged from 0.5 ppm to 64 ppm. The initial test and reference compound concentrations were determined by gas chromatography (GC). The chromatographic conditions employed to detect the compounds are listed in the full report. The initial  $\text{CH}_3\text{ONO}$  and NO concentrations were based on the amount of compound injected.

A series of GC samples were taken before the irradiation began in order to determine the stability of the test and reference compounds in the dark. In general, the sampling continued until successive peak heights of the compounds differed by less than 2%. Once the irradiation began, the NO was monitored continuously and GC samples were taken every 5 or 10 min, depending on the retention times of the compounds. Typical irradiation times ranged from 30 min to 60 min.

The hydrocarbon analyses were conducted using two gas chromatographs (Perkin Elmer Model 900 and a GOW-MAC Model 750). Both gas chromatographs contained flame ionization detectors. Nitric oxide concentrations were determined with a Bendix Model 8101-B NO/NO<sub>2</sub>/NO<sub>x</sub> analyzer.

The  $\text{CH}_3\text{ONO}$  was prepared by dropwise addition of 50% sulfuric acid ( $\text{H}_2\text{SO}_4$ ) to a stirred saturated solution of sodium nitrite ( $\text{NaNO}_2$ ) in methanol ( $\text{CH}_3\text{OH}$ ). A 50 ml/min  $\text{N}_2$  stream was used to transfer the  $\text{CH}_3\text{ONO}$  from the reaction system to a liquid  $\text{N}_2$  cold trap, where it was collected. The transfer line consisted of two bubblers in series in front of a collection trap used to remove  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$ . The first bubbler contained a saturated solution of sodium hydroxide (NaOH) and the second contained Drierite dessicant.

Multiple irradiations were conducted for each compound in order to generate a data base. Different reference compounds and initial reference to test compound concentration ratios were employed. A special protocol was developed to investigate the OH rate constants of chlorinated compounds. In this case, the initial concentration of test compound was held fixed at 4.0 ppm and the initial reference compound concentration was varied from 1.0 ppm to 64 ppm. The initial  $\text{CH}_3\text{ONO}$  concentration was also held constant during the set of experiments. In addition to using this protocol to investigate chlorinated compounds, it was also employed to determine rate constants for propane and isobutane.

## Results and Discussion

Data for each OH rate constant determination are provided in the appendix of the full report. The data include the identity of the reference compound, the initial concentrations of the test and reference compounds, the average temperature and percent deviation, the slope, intercept, and correlation coefficient obtained from Equation III, and the experimentally determined value for  $k_{OH}$ . The results are further summarized in the report; the average OH rate constants are listed, as well as the average temperatures and percent deviations associated with the rate constants. The report also provides, for comparison, rate constants reported by other researchers.

The OH rate constants obtained for the alkane class consisting of ethane, propane, isobutane and cyclohexane were in agreement with those in the literature. The ethane results suggested that the method can be used to measure rate constants as small as  $3 \times 10^{-13}$  cm<sup>3</sup>/molecule-sec. However, this may not be the appropriate lower limit for compounds that are more difficult to detect than ethane. Results of this study support the fact that the rate constants obtained for propane and isobutane were independent of the reference to test compound ratio and were consistent with the model in that the only reactive species in the irradiated mixture was OH.

The results for the two alkenes studied (*trans*-2-butene and isoprene), the five aromatic compounds (benzene, toluene, ortho-xylene, meta-xylene, and para-xylene) and the oxygen-containing compounds (acrolein, methacrolein, and methylethyl ketone) were also in good agreement with the literature. The rate constant found for propylene oxide ( $1.11 \times 10^{-12}$  cm<sup>3</sup>/molecule-sec) agreed with a value obtained by another researcher using the relative rate method. However, it was a factor of two larger than a value obtained by another researcher who used a flash photolysis resonance fluorescence method. The percent deviation for propylene oxide results reported in the full report was 68%. Much of the deviation was probably due to the difficulty in measuring propylene oxide.

A large number of experiments were conducted in this study to evaluate the OH rate constants of chlorinated compounds. Many potentially hazardous compounds contain chlorine, and the potential for reactions of the test and reference compound with Cl (if it is produced) is great. A value of  $1.86 \times 10^{-12}$  cm<sup>3</sup>/molecule-sec was

found for the OH rate constant for trichloroethylene. The relatively large value for the percent deviation ( $\pm 36\%$ ) from the recommended literature value was surprising since the magnitude of the rate constant found was well above the lower limit for the protocol, and there were no inherent difficulties in measuring trichloroethylene. Results for this study suggested the possibility of reactions other than OH attack since the measured effective rate constant was shown to be a function of the initial n-butane to trichloroethylene concentration. Recent evidence shows that reactive atomic chlorine is produced in irradiated trichloroethylene/nitrous acid (HONO)/NO/air mixtures. Once produced, Cl readily reacts with trichloroethylene to produce trichloroacetyl chloride, which releases Cl and thereby propagates a Cl chain reaction.

It is reasonable to expect that Cl is produced in this system, and in addition it is likely that the production rate of Cl is proportional to the trichloroethylene concentration. At low [Ref]/[Test] ratios there exists the possibility that Cl reactions will be important, and therefore the relative decreases in the test and reference concentrations as a function of time will reflect the tendency of the two compounds to react with both OH and Cl. The results, therefore, cannot be used to obtain the OH rate constant. However, at high [Ref]/[Test] ratios the system will tend to be dominated by OH reactions since the source of Cl compared to OH is reduced, and a major sink for Cl, hydrogen abstraction from n-butane, will have been enhanced. Results of this study indicated that for [Ref]/[Test] > 10, the effective rate constant was essentially independent of the concentration ratio. The OH rate constant obtained in this region was  $2.85 \times 10^{-12}$  cm<sup>3</sup>/molecule-sec.

Analyses similar to that employed for trichloroethylene were used to evaluate the rate constants for vinylidene chloride, allyl chloride, benzyl chloride, and chlorobenzene. The results for vinylidene chloride, allyl chloride, and benzyl chloride also suggested similar evidence for Cl reactions. The OH rate constants derived for vinylidene chloride, allyl chloride, and benzyl chloride using high [Ref]/[Test] ratios were  $14.5 \times 10^{-12}$ ,  $17.2 \times 10^{-12}$ , and  $2.82 \times 10^{-12}$  cm<sup>3</sup>/molecule-sec, respectively. Rate constants for these compounds have not been reported previously.

The average value found for the OH rate constant for chlorobenzene was  $0.55 \times$

$10^{-12}$  cm<sup>3</sup>/molecule-sec with a percent deviation of 37%. The data were too scattered to determine whether there were any Cl reactions occurring in the system. The value obtained for the rate constant was close to that cited as the lower limit for the UCR protocol ( $0.3 \times 10^{-12}$  cm<sup>3</sup>/molecule-sec) and therefore the scatter was not surprising. The value for the rate constant was in reasonable agreement with two recent measurements.

The average OH rate constant found for epichlorohydrin was  $0.55 \times 10^{-12}$  cm<sup>3</sup>/molecule-sec and the percent deviation was 22%. This result agrees with a literature value obtained by the flash photolysis resonance fluorescence technique. However, data were not taken at enough reference points during this study to test concentration ratios in order to detect the presence of Cl reactions. It is unlikely that a difference would be detected with such a low value for the OH rate constant.

Experiments were also conducted to determine the OH rate constants with three slowly reacting compounds. The experiments were unsuccessful because the decreases in the test compound concentrations during the irradiations were within the experimental uncertainty of the measurements. These results further substantiate the validity of the lower limit of  $3 \times 10^{-13}$  cm<sup>3</sup>/molecule-sec for OH rate constants obtained with the UCR protocol.

## Conclusions and Recommendations

The OH rate constants determined with the UCR protocol for compounds in the alkane, alkene, and aromatic classes were in good agreement with literature values, as were those for oxygen-containing compounds. It was found that there was a potential for Cl reactions to interfere with the determination of OH rate constants of chlorinated compounds. However, it was found that the interference could be decreased by measuring the effective rate constant as a function of the initial reference to test hydrocarbon ratio and by obtaining the OH rate constant from the asymptotic region (large values for the reference to test compound ratio), where the effective rate constant is independent of the concentration ratio. Verification of this method is required and could be obtained by comparing the results of this study with those obtained with the flash photolysis resonance fluorescence method. In the flash photolysis method, the OH rate constant is determined from

the decay of the OH concentration and therefore should not be influenced by CI reactions.

Rate constants as small as  $3 \times 10^{-13}$  cm<sup>3</sup>/molecule-sec (ethane) were obtained using the UCR method. For compounds that are more difficult to measure, it is likely that the lower limit is  $5 \times 10^{-13}$  cm<sup>3</sup>/molecule-sec.

All compounds investigated in this study were low molecular weight species (molecular weight <200) with substantial vapor pressures at room temperature. If the UCR method is to be used for the determination of high molecular weight, low volatility compounds, for which wall loss may be substantial and quantitative detection difficult, additional studies will have to be conducted to validate the protocol.

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*The complete report, entitled "Validation of OH Radical Reaction Rate Constant Test Protocol," (Order No. PB 86-166 758/AS; Cost: \$9.95, 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:*

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