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Project Summary

Hydroxyl Radical Rate Constant Intercomparison Study

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An intercomparison study was conducted to evaluate the OH rate constant measurement protocol developed by researchers at the University of California at Riverside. Researchers at the University of North Carolina at Chapel Hill (UNC), Research Triangle Institute (RTI), and Northrop Services, Inc.—Environmental Sciences (NSI) used the protocol to measure the room temperature OH rate constants for ethane, benzene, chlorobenzene, and *sec*-butanol. At least three measurements were made for each compound, and each experiment was analyzed using the time-included and time-excluded methods described in the protocol. The full report of this research project provides the data collected for each compound.

The room temperature OH rate constants determined by NSI-ES and UNC were in good agreement and also, with the exception of the previously unreported rate constant for *sec*-butanol, agreed with the literature values. Agreement was found using both methods of analysis. The rate constants for ethane, benzene, and chlorobenzene obtained by RTI using the time-excluded method also agreed with the literature values; however, when the same data were analyzed using the time-included method, no such agreement was found. The OH rate constant for *sec*-butanol determined by RTI was approximately one-third the value obtained by NSI and UNC. It was not possible to identify the source of this discrepancy.

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

The reactions of hydroxyl radicals (OH) with organic compounds play an important role in atmospheric chemistry. Reaction with OH is the dominant homogeneous gas phase removal mechanism for many volatile organic compounds. Rate constants for reaction with OH must be established to assess the role of organic compounds in ozone production and also to determine their atmospheric persistence, which is of primary importance when the organic compounds are toxic chemicals.

Recently, researchers at the Statewide Air Pollution Research Center at the University of California at Riverside (UCR) developed for the U.S. Environmental Protection Agency (EPA) a protocol for measuring the OH reaction rate constants of organic compounds. To validate the protocol, EPA contracted with Northrop Services, Inc.—Environmental Sciences (NSI) to conduct a series of OH rate constant determinations using the UCR protocol. The results of this study have recently been published. To further validate the protocol, EPA requested NSI to conduct an intercomparison study. This report summarizes the results of the study.

Researchers at the University of North Carolina at Chapel Hill (UNC) and Research Triangle Institute (RTI), as well as NSI, participated in the study. Each group independently measured the

room temperature OH rate constants for ethane, benzene, chlorobenzene, and *sec*-butanol. At least three rate constant measurements were made for each compound, and each experiment was analyzed using the two methods of calculation described in the UCR protocol. The full report compares the values for the OH rate constants obtained by each group. Where possible, the results are compared with literature values. Details concerning the exact experimental procedures employed by each group and recommendations for improving the protocol are referenced in the full report.

Experimental Approach

The experimental approach employed was that described in the UCR protocol (1). 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 (CH_3ONO), 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.

If it is assumed that the loss mechanisms for the test compound are reaction with OH and a first-order reaction, and that the only loss mechanism for the reference compound is reaction with OH, the rates of removal for the test and reference compounds can be described by the following equations:

$$\frac{d}{dt}[Test] = -k_T\,[Test][OH] - k\,[Test] \quad (I)$$

$$\frac{d}{dt}[Ref] = -k_R\,[Ref][OH] \quad (II)$$

where $[Test]$ and $[Ref]$ are the concentrations of the test and reference compounds, respectively, k is a first-order rate constant for the test compound, and the k_R and k_T values are the OH rate constants for reaction with the reference and test compounds, respectively.

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

$$\frac{1}{t}\,ln\,\frac{[Test]_{t_o}}{[Test]_t} = \frac{k_T}{k_R}\,\frac{1}{t}\,ln\,\frac{[Ref]_{t_o}}{[Ref]_t} + k, \quad (III)$$

where $[Test]_{t_o}$ and $[Ref]_{t_o}$ are the concentrations of the test compound and the reference compound at time t_o, respectively, and $[Test]_t$ and $[Ref]_t$ are the respective concentrations at time t. If $1/t\ ln([Test]_{t_o}/[Test]_t)$ is plotted against $1/t\ ln([Ref]_{t_o}/[Ref]_t)$, a straight line should be obtained with slope equal to k_T/k_R and intercept equal to k. The value for the test compound OH rate constant is immediately obtained from the slope because the reference compound OH rate constant is known.

Equation III can be reduced further if it is assumed that the only removal mechanism for the test compound is reaction with OH, i.e., $k = 0$. Under these circumstances Equation III can be simplified, and the following result is obtained:

$$ln\,\frac{[Test]_{t_o}}{[Test]_t} = \frac{k_T}{k_R}\,ln\,\frac{[Ref]_{t_o}}{[Ref]_t}. \quad (IV)$$

Equation IV differs from Equation III in that the former is not explicitly time dependent. If $ln([Test]_{t_o}/[Test]_t)$ is plotted against $ln([Ref]_{t_o}/[Ref]_t)$, a straight line should be obtained with slope equal to k_T/k_R, the same result found using Equation III, but here, a value of zero is found for the intercept. If the compound under investigation satisfies the assumptions stipulated for the application of Equation IV, the rate constants obtained using Equations III or IV should be equal. Each rate constant measurement made during this study was analyzed using both Equations III and IV, and analyses based on Equations III and IV are denoted as the TI method (time-included method) and the TE method (time-excluded method), respectively.

Both Equations III and IV are in the form of the straight line equation, $y = mx + b$. Least squares linear regression analyses were conducted to obtain values for the slope (m), intercept (b), and the correlation coefficient squared (r^2) for each experiment. In addition, standard deviations for the slope (σ_m) and intercept (σ_b) were calculated.

Experimental Method

All irradiations were conducted in pillow-shaped 2-mil FEP Teflon bags that were constructed by heat-sealing three sides of two 4-ft × 8-ft sheets of FEP Teflon. Swagelok fittings were mounted in the wall of each bag and served as reaction bag ports for filling and evacuating the bag, as well as for sampling its contents.

The NSI reaction chamber consisted of a wooden cylindrical frame split lengthwise with two light banks that contained five lamps each mounted on the inner side of the frame. Each light bank contained a mixture of sun lamps and black lamps. A 180-cfm blower was mounted at the top of the frame and was used to remove heat from the chamber. The reaction chambers used by RTI and UNC were designed and constructed by NSI. The chamber was a 2-ft × 2-ft × 4-ft aluminum box. Light banks were mounted on two of the inner sides of the chamber and contained a mixture of sun lamps and black lamps. Each bank contained positions for six lamps. A 1/80-hp ventilation blower was mounted on the top of the chamber. Thermometers were mounted inside both types of reaction chambers.

The detection systems and the methods for sampling were selected by the individual research groups. UNC used a combination of three automated Carle Model 211 packed column FID gas chromatographs to monitor the concentrations of test and reference compounds. Automatic gas sample loop injections were used to sample the bag contents. RTI used Perkin Elmer 3920B and Sigma 300 FID gas chromatographs to monitor the contents of the reaction bag. The gas chromatographs were connected in series with the reaction bag, and sampling was accomplished by pumping a gas sample through a connected Teflon tube and manually injecting the sample into the gas chromatographs. NSI used Perkin Elmer Model 900 and GOW-MAC Model 750 gas chromatographs. Gas sampling valves were used to sample the contents of the bag during the ethane, benzene, and chlorobenzene experiments. *sec*-Butanol was sampled by bubbling a 5-L volume through an impinger containing 2 mL of CH_3OH. A 10-μL aliquot of the solution was injected onto the gas chromatograph. Additional experimental details, which include the GC columns and conditions employed by each group, are referenced in the full report.

NO_x concentrations were determined by both NSI and UNC using a Bendix Model 8101-B $NO/NO_2/NO_x$ analyzer. In addition, UNC used a Bendix Model 8002 analyzer for monitoring O_3. RTI did not monitor NO_x and O_3 during the irradiations and relied on a high NO concentration (~15 ppm) to prevent O_3 formation. O_3 concentrations were not monitored by NSI because the NO concentrations measured during the irradiations prevented its formation.

The CH_3ONO was prepared by dropwise addition of 50% sulfuric acid (H_2SO_4) to a stirred, saturated solution of sodium nitrite ($NaNO_2$) in methanol (CH_3OH). A nitrogen (N_2) stream was used to transfer the CH_3ONO from the reaction system to a liquid N_2 cold trap, where it was collected. The transfer line consisted of two bubblers in series in

front of the cold trap to remove H_2SO_4 nd H_2O. The first bubbler contained a saturated solution of sodium hydroxide (NaOH), and the second contained Drierite desiccant.

A typical OH rate constant determination was begun by filling the bag with clean air, mixing its contents, and evacuating it a number of times. The bag was then filled with clean air to its final volume (~100 L). During the filling process, NO, CH_3ONO, and the test and reference hydrocarbons were introduced into the bag. All chemicals used during the study had purities greater than 99% and were not purified further. 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%. During the irradiation, GC samples were taken as frequently as possible. Typical irradiation times ranged from 30 min to 60 min. The temperature was recorded each time a GC sample was taken.

Results and Discussion

OH rate constant data for ethane, benzene, chlorobenzene, and *sec*-butanol are provided in the appendix of the full report. The appendix contains for each experiment the average temperature, the reference compound employed, the initial concentrations of the test and reference compounds, the slopes and intercepts and their standard deviations, and the square of the correlation coefficient obtained using both the TI and TE methods. The results for each compound and the reference rate constants used to convert the slopes into OH rate constants are also summarized in the full report. The reference OH rate constants employed, with the exception of the benzene rate constant employed by UNC, are those recommended in the literature. The OH rate constant for benzene used by UNC is the value the investigators determined during the study.

The full report also provides, in tabular form, final summaries for the rate constants determined by using the two methods of calculation. In these tables, the temperatures are the averages of the individual temperatures shown for each experiment in the appendix. N is the number of experiments performed by each group for each compound. The values for the rate constants and the square of the correlation coefficients are averages obtained from the individual experiments. The standard deviations in the rate constants are based on the deviations of the rate constants from the above-mentioned average rate constants.

Ethane

The TI method OH rate constants were as follows.

(Northrop) $0.264 \pm 0.019 \times 10^{-12}$ cm^3/molecule-s, $r^2 = 0.9501$

(UNC) $0.273 \pm 0.059 \times 10^{-12}$ cm^3/molecule-s, $r^2 = 0.9783$

(RTI) $0.188 \pm 0.495 \times 10^{-12}$ cm^3/molecule-s, $r^2 = 0.4851$

The r^2 values obtained by Northrop and UNC indicate that the data can be adequately described by a straight line; however, the r^2 value found by RTI is low. The poor fit obtained by RTI is also reflected in the large deviation (263%) in the rate constant obtained. Even though the value of the rate constant is at the lower limit for which the protocol can be employed, good results are expected because ethane concentrations can be measured accurately and it is unlikely that ethane undergoes reactions other than that with OH. However, RTI reported substantial problems with increases in the ethane concentrations at the start of the irradiation. RTI attributed the increases to mixing problems.

The values obtained for the OH rate constant using the TE methods were as follows.

(Northrop) $0.273 \pm 0.010 \times 10^{-12}$ cm^3/molecules-s, $r^2 = 0.9904$

(UNC) $0.302 \pm 0.050 \times 10^{-12}$ cm^3/molecule-s, $r^2 = 0.9522$

(RTI) $0.255 \pm 0.026 \times 10^{-12}$ cm^3/molecule-s, $r^2 = 0.8305$

The results obtained by Northrop and UNC are in reasonable agreement with those found using the TI method. The RTI value for r^2 is still relatively low, but far better than that obtained using the TI method.

That the r^2 obtained using the TE method is substantially greater than that found with the TI method may be, at first, somewhat surprising since the TI calculation method appears more complete because it takes into account first-order processes for ethane. However, this distinction may be misleading. The slopes obtained using each method are based on a least squares regression analysis of the data. An examination of this analytical method shows that the magnitude of the calculated slopes and intercepts and the values for r^2 are strongly influenced by the large data points in the set.

The relative importance of a given data point in the two calculation methods differs. The independent variable used in the TE method, $ln([Test]_{t_o}/[Test]_t)$, monotonically increases during the irradiation because the test compound concentration decreases throughout the experiment. However, the situation is reversed if one uses the TI method, in which the independent variable is $1/t\ ln([Test]_{t_o}/[Test]_t)$. In the absence of reactions of the test compound other than that with OH, it can be shown that $1/t\ ln([Test]_{t_o}/[Test]_t)$ is equal to the average OH concentration times the OH rate constant during the time interval from 0 to t. The dominant source of OH in this system is the photolysis of CH_3ONO, and because the CH_3ONO concentration decreases during the irradiation and the sinks for OH (in particular, the concentration of NO_2) increase, it is reasonable to expect that the average OH concentration should decrease as a function of time. If this is the case, the slope obtained using the TI method depends most strongly on the short-time irradiation points, as opposed to the TE method, where the long-time irradiation points influence the calculation of the slope, intercept, and r^2, and hence the rate constant.

The discrepancy in the RTI results is consistent with this argument. The good agreement found between the two methods used by Northrop and UNC suggests that during these experiments the dominant removal mechanism for ethane and the reference compound was reaction with OH. However, in the past, Northrop has encountered problems similar to those experienced by RTI.

Reports in the literature recommend a value of 0.275×10^{-12} cm^3/molecule-s for the room temperature (25°C) OH rate constant, with an uncertainty of ±20%. With the exception of the RTI value obtained using the TI method, the experimentally determined values found in this study are in agreement with the literature values, as well as with each other.

Benzene

The OH rate constants and the associated values determined for r^2 using the TI method are as follows:

(Northrop) $0.876 \pm 0.276 \times 10^{-12}$ cm^3/molecule-s, $r^2 = 0.9731$

(UNC) $1.041 \pm 0.071 \times 10^{-12}$ cm^3/molecule-s, $r^2 = 0.9657$

(RTI) $0.544 \pm 0.043 \times 10^{-12}$ cm^3/molecule-s, $r^2 = 0.6646$

The values obtained using the TE method were as follows.

(Northrop) $0.949 \pm 0.183 \times 10^{-12}$ cm^3/molecule-s, $r^2 = 0.9921$

(UNC) $1.070 \pm 0.075 \times 10^{-12}$ cm^3/molecule-s, $r^2 = 0.988$

(RTI) $1.054 \pm 0.047 \times 10^{-12}$ cm^3/molecule-s, $r^2 = 0.9642$

All of the values overlap except for the RTI value found using the TI method; however, the standard deviation of this determination is misleading. The RTI results displayed in the full report show that although the TI method deviations for experiments RTI-1 and RTI-2 are relatively small (11% and 7%, respectively), the value obtained in RTI-3 is large (86%). The small (8%) deviation in the average for the three experiments may be fortuitous. The improvement in the precision of the results using the TE method over that of the TI method may be associated with factors cited in the discussion of the RTI ethane results.

The recommended value for the room temperature (25°C) OH rate constant for benzene is 1.28 ± 10^{-12} cm^3/molecule-s, with an estimated uncertainty of ±30%. The results obtained here are slightly below this value, but with the exception of the RTI TI method result, there is overlap when the error bars are included. A comparison between the RTI results and those obtained by Northrop and UNC is further complicated because of the elevated temperature (33.8°C) at which RTI investigators conducted their experiments.

Chlorobenzene

The following OH rate constants were found for chlorobenzene using the TI method.

(Northrop) $0.789 \pm 0.190 \times 10^{-12}$ cm^3/molecule-s, $r^2 = 0.9169$

(UNC) $0.784 \pm 0.129 \times 10^{-12}$ cm^3/molecule-s, $r^2 = 0.9692$

(RTI) $0.707 \pm 0.306 \times 10^{-12}$ cm^3/molcule-s, $r^2 = 0.6116$

The RTI experiments were again conducted at an elevated temperature (35.8°C). The corresponding values found by the TE method were as follows.

(Northrop) $0.593 \pm 0.116 \times 10^{-12}$ cm^3/molecule-s, $r^2 = 0.9777$

(UNC) $0.756 \pm 0.101 \times 10^{-12}$ cm^3/molecule-s, $r^2 = 0.9662$

(RTI) $0.696 \pm 0.129 \times 10^{-12}$ cm^3/molecule-s, $r^2 = 0.9754$

All of the results overlap; however, there are large uncertainties in the RTI (43%) and NSI (27%) TI method values. As was postulated for the RTI TI method determinations for ethane and benzene, the uncertainty may be due to a heterogeneous reaction that occurs early in the irradiation and that cannot be described by the parameterization of the TI method.

The values of the rate constant are in reasonable agreement with two reported measurements that are referenced in the full report. One group obtained a value of $0.88 \pm 0.11 \times 10^{-12}$ cm^3/molecule-s at 26 ± 2°C using the UCR protocol, and another reported a value of $0.67 \pm 0.05 \times 10^{-12}$ cm^3/molecule-s at 23°C using the flash photolysis resonance fluorescence method.

sec-Butanol

The TI method OH rate constants determined were as follows.

(Northrop) $10.30 \pm 2.48 \times 10^{-12}$ cm^3/molecule-s, $r^2 = 0.9692$

(UNC) $11.55 \pm 1.77 \times 10^{-12}$ cm^3/molecule-s, $r^2 = 0.9854$

(RTI) $4.01 \pm 1.38 \times 10^{-12}$ cm^3/molecule-s, $r^2 = 0.7581$

The corresponding TE method rate constants were as follows.

(Northrop) $9.40 \pm 0.87 \times 10^{-12}$ cm^3/molecule-s, $r^2 = 0.9894$

(UNC) $7.37 \pm 1.65 \times 10^{-12}$ cm^3/molecule-s, $r^2 = 0.9917$

(RTI) $2.71 \pm 0.20 \times 10^{-12}$ cm^3/molecule-s, $r^2 = 0.9681$

The UNC and Northrop values overlap, but they are approximately a factor of three larger than the values found by RTI. Although this rate constant has not been previously measured, it can be estimated using the predictive methods developed recently by Atkinson. A value of 8×10^{-12} cm^3/molecule-s is found using the technique. This result is in reasonable agreement with the Northrop and UNC measurements. There are no obvious reasons for the low RTI values. The major difference between the experimental approaches used by NSI and UNC and that used by RTI is that the Northrop and UNC experiments were conducted at 24°C, whereas the RTI experiments were conducted at an average temperature of 34°C. Because it is expected that the OH rate constant increases as a function of increasing temperature, the difference in temperature makes the discrepancy more difficult to explain.

Conclusions and Recommendations

The room temperature OH rate constants determined with the UCR protocol for ethane, benzene, chlorobenzene, and *sec*-butanol by NSI and UNC were in good agreement and also, with the exception of the previously unreported rate constant for *sec*-butanol, agreed with the values recommended in the literature. The agreement was found using both the TE and TI methods. The rate constants for ethane, benzene, and chlorobenzene obtained by RTI using the TE method also agreed with the literature values; however, when the same data were analyzed using the TI method, no such agreement was found. The OH rate constant for *sec*-butanol determined by RTI was approximately one-third the value obtained by Northrop and UNC. It was not possible to identify the source of this discrepancy.

The results of this intercomparison study suggest that additional studies should be conducted to expand the data base and thus assess accurately the validity of the protocol. Special emphasis should be placed on determining which of the two calculation methods should be employed.

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***J. J. Bufalini** is the EPA Project Officer, see below.*
The complete report, entitled "Hydroxyl Radical Rate Constant Intercomparsion Study," (Order No. PB 87-111 142/AS; Cost: $11.95, subject to change) will be available only from:
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