



Project Summary

Experimental Protocol for Determining Hydroxyl Radical Reaction Rate Constants

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and Roger Atkinson

An experimental protocol has been developed to determine the gas-phase rate constants for the reactions of the hydroxyl (OH) radical with chemicals at room temperature. This protocol provides a basis for evaluating the relative importance of one atmospheric reaction pathway (i.e., attack by the OH radical) for organic substances that may be emitted into the environment.

The experimental technique is based on monitoring the disappearance rates of the test compound and a reference organic in irradiated methyl nitrite-NO-organic-air mixtures. (The reference is an organic species whose OH radical reaction rate constant is accurately known.) Irradiations, employing blacklamps emitting in the actinic region, are carried out in ~ 75-liter cylindrical Teflon bags. The concentrations of the reactants are: methyl nitrite (CH_3ONO), 0 to ~ 15 ppm; NO, ~ 5 ppm; test compound, ~1 ppm; and reference organic, ~ 1 ppm. The test compound and reference organic are monitored by gas chromatography, NO, NO_2 , NO_3 by chemiluminescence, and ozone (O_3) by chemiluminescence. Using this technique, OH radical rate constants $\geq 3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ (the range of primary interest from an atmospheric point of view) can be measured.

This Project Summary was developed by EPA's Environmental Science 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

Under the sponsorship of the U.S. Environmental Protection Agency (EPA), the Statewide Air Pollution Research Center (SAPRC) at the University of California, Riverside, has developed and validated experimental protocols to assess the atmospheric fates and lifetimes of organic compounds.

Chemical compounds emitted into the atmosphere are removed or degraded by pathways involving gas-phase reactions or wet or dry deposition. Laboratory and environmental chamber studies have shown that for the ambient atmosphere, the following homogeneous gas-phase removal routes are likely to be important:

- Photolysis, which involves absorption of light followed by decomposition or isomerization;
- Reaction with O_3 ;
- Reaction with OH radical; and
- For aromatic compounds containing an -OH substituent group, reaction with the nitrate (NO_3) radical.

To assess (a) the atmospheric lifetime of compounds with respect to these gas-phase removal processes, and (b) the relative importance of each of these reaction pathways, rate constants for photolysis and/or chemical reaction must be experimentally determined for individual compounds.

The experimental procedures detailed in this protocol are designed to determine rate constants for reactions of the OH radical with organics and certain inorganics at room temperature. Knowledge of these rate constants may allow estimation of the atmospheric lifetimes of these compounds with respect to attack by OH radicals as shown below.

In the atmosphere, where the reaction, OH + chemical → products occurs, the decay of the chemical via this reaction is given by,

$$-d[\text{chemical}]/dt = k^{\text{OH}} [\text{OH}][\text{chemical}] \quad (\text{I})$$

where [] denotes concentration and k^{OH} is the rate constant for reaction of the OH radical with the particular chemical. Equation (I) may be rearranged to yield

$$-dn[\text{chemical}]/dt = k^{\text{OH}}[\text{OH}] \quad (\text{II})$$

and, providing the OH radical concentration remains constant,

$$\ln([\text{chemical}]_{t_0}/[\text{chemical}]_t) = k^{\text{OH}}[\text{OH}] (t-t_0) \quad (\text{III})$$

where $[\text{chemical}]_{t_0}$ and $[\text{chemical}]_t$ are the concentrations of the chemical at times t_0 and t , and \ln is the logarithm to the base e .

In the ambient troposphere, OH radical concentrations vary as a function of time of day from a negligibly low level at night to a peak at around solar noon. However, for approximate lifetime calculations, an average OH radical concentration of $\sim 8 \times 10^5 \text{ molecule cm}^{-3}$ may be assumed for the northern hemisphere. The assumptions inherent in these calculations must be borne in mind, especially for organics whose lifetime is one day or less. The $1/e$ lifetime, τ^{OH} , of any chemical with respect to reaction with the OH radical (i.e., the time for the concentration of the chemical to decrease by a factor of $e = 2.7$ due to reaction with the OH radical) is given by,

$$\tau^{\text{OH}} = (k^{\text{OH}}[\text{OH}])^{-1} \quad (\text{IV})$$

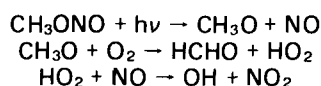
where $[\text{OH}]$ is the ambient atmospheric OH radical concentrations.

For a typical troposphere OH radical concentration of $8 \times 10^5 \text{ molecule cm}^{-3}$, the rate constants which yield $1/e$ lifetimes of one hour, one day, one week, one month, and one year are given in Table 1 for the three sets of most commonly used units. For lifetimes longer than about one day, the variation of temperature with altitude must be taken into account for rigorous calculations.

Table 1. Rate Constants for Reaction with the OH Radical which Yield Selected $1/e$ Lifetimes in the Presence of $8 \times 10^5 \text{ molecule cm}^{-3}$ of OH Radicals

Lifetime	Rate Constant		
	$\text{ppm}^{-1} \text{ min}^{-1}$	$\text{liter mole}^{-1} \text{ sec}^{-1}$	$\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$
One hour	5.2×10^6	2.1×10^{11}	3.5×10^{-10}
One day	2.1×10^4	8.8×10^9	1.5×10^{-11}
One week	3.0×10^3	1.3×10^9	2.1×10^{-12}
One month	7.0×10^2	2.9×10^8	4.8×10^{-13}
One year	5.8×10^1	2.4×10^7	4.0×10^{-15}

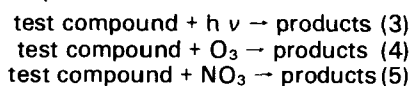
The experimental approach described below is based on measuring the relative disappearance rates of the test compound and of a reference organic in the presence of OH radicals.



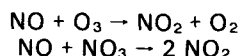
OH radicals are generated from the photolysis of varying concentrations of CH_3ONO in air. In the presence of added organics, the OH radicals react as shown below. The reactions are identified with Arabic numerals so as to facilitate interpretation with the corresponding rate constants, k_1 , k_2 , etc.



In addition, the test compound may, in some cases, also photolyze, react with O_3 , and/or react with the NO_3 radical:



Reactions (4) and (5) will be unimportant provided that excess NO is present since O_3 and NO_3 both react rapidly with NO:



If the organics are lost only by reaction with OH radical, and, for the test compound, by photolysis, then,

$$\begin{aligned} -d[\text{test compounds}]/dt &= k_1[\text{OH}][\text{test compound}] \\ &+ k_3[\text{test compound}] \quad (\text{V}) \end{aligned}$$

$$-d[\text{reference organic}]/dt = k_2[\text{OH}][\text{reference organic}] \quad (\text{VI})$$

where k_1 and k_2 are the OH radical rate constants for reaction (1) and (2), respectively, and k_3 is the photolysis rate constant. Hence,

$$d\ln[\text{test compound}]/dt = k_1[\text{OH}] + k_3, \quad (\text{VII})$$

$$\text{and} \quad d\ln[\text{reference organic}]/dt = k_2[\text{OH}]. \quad (\text{VIII})$$

Elimination of the OH radical concentration and integration leads to the following expression:

$$\begin{aligned} \frac{1}{(t-t_0)} \ln \left\{ \frac{[\text{test compound}]_{t_0}}{[\text{test compound}]_t} \right\} &= \\ k_3 + \frac{k_1}{k_2(t-t_0)} & \\ \ln \left\{ \frac{[\text{reference organic}]_{t_0}}{[\text{reference organic}]_t} \right\} &= \quad (\text{IX}) \end{aligned}$$

where $[\text{test compound}]_{t_0}$ and $[\text{reference organic}]_{t_0}$ are the concentrations of the test compound and the reference organic, respectively, at time t_0 ; $[\text{test compound}]_t$ and $[\text{reference organic}]_t$ are the corresponding concentrations at time t . Note that Equation (IX) is valid even if the OH radical concentration varies with time.

Hence, a plot of $(t-t_0)^{-1} \ln([\text{test compound}]_{t_0}/[\text{test compound}]_t)$ against $(t-t_0)^{-1} \ln([\text{reference organic}]_{t_0}/[\text{reference organic}]_t)$ should yield a straight line of slope k_1/k_2 and intercept k_3 . Knowing k_2 , the rate constant, k_1 , may then be derived. If the test compound does not photolyze (i.e., $k_3 = 0$), then Equation (IX) can be simplified to yield the following relationship:

$$\begin{aligned} \ln \left\{ \frac{[\text{test compound}]_{t_0}}{[\text{test compound}]_t} \right\} &= \\ \frac{k_1}{k_2} \ln \left\{ \frac{[\text{reference organic}]_{t_0}}{[\text{reference organic}]_t} \right\} &= \quad (\text{X}) \end{aligned}$$

A plot of $\ln([\text{test compound}]_{t_0}/[\text{test compound}]_t)$ versus $\ln([\text{reference organic}]_{t_0}/[\text{reference organic}]_t)$ should yield a straight line of slope k_1/k_2 with a zero intercept.

The concentrations of the test compound and the reference organic are monitored before and during irradiation of the $\text{CH}_3\text{ONO}/\text{NO}/\text{test compound}/\text{reference organic}/\text{air}$ mixtures by gas

chromatography. Hence, the lower limit to k_1 that can be determined is set by the precision of the gas chromatographic analyses, but is expected to be of the order of $\leq 3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ which corresponds (Table 1) to an atmospheric lifetime of greater than one month.

Experimental

Irradiations are carried out in a ~75-liter cylindrical Teflon bag which is made from FEP Teflon sheet heat-sealed around the edges and fitted with a Teflon injection and sampling port, as shown in Figure 1. Actinic radiation is provided by a fluorescent lamp assembly as shown in Figure 2. It consists of a circular array of twenty-four 15-Watt blacklights (GE F15T8-BL15) mounted in a cylindrical aluminum frame. The lamps are arranged on three electrical circuits, eight lamps per circuit, with every third lamp being on a given circuit, an arrangement which allows for three different light intensities. In the bottom of the chamber is a fan that circulates a large volume of air to minimize heating.

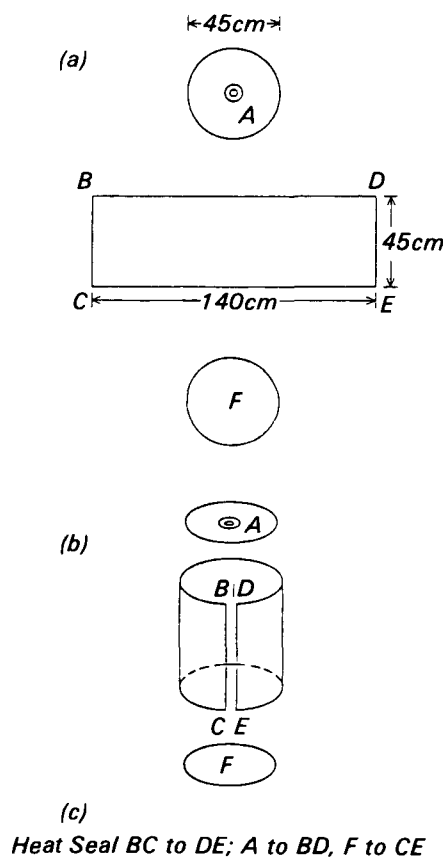


Figure 1. Construction of the Teflon reaction bag.

A cylindrical wire mesh screen inside the lamp assembly in which the Teflon bag is placed (Figure 2) prevents the reaction bag from contacting the lamps or the fan.

Methyl nitrite is prepared by the dropwise addition of 50% H_2SO_4 to methanol saturated with sodium nitrite. The CH_3ONO produced is swept out of the reaction flask by a stream of ultra-high purity nitrogen, passed through a trap containing saturated NaOH solution to remove any H_2SO_4 , dried by passage through an anhydrous CaCl_2 trap and collected in a trap at 196 K. The CH_3ONO is then degassed and vacuum distilled on a greaseless high-vacuum system and stored under vacuum at 77 K in the dark. Known amounts of the CH_3ONO , NO, and the reference and reactant organics are flushed from Pyrex bulbs by a stream of ultra-zero air into the Teflon reaction bag, which is then filled with additional ultra-zero air

Discussion

Initial concentrations of the reactants are typically: CH_3ONO , zero to ~15 ppm; NO, ~5 ppm; and test and reference organics, ~1 ppm. The NO is present to minimize O_3 formation and any reaction with the organics. The organic reactants

are monitored by gas chromatography prior to and during the irradiations. With this protocol, the irradiation should be terminated and the last gas chromatographic samples taken after ~30 min for full light intensity, ~45 min for two-thirds maximum light intensity, or ~60 to 90 min for one-third maximum light intensity. Since it is preferable to have two to four gas chromatographic analyses during the irradiation, the optimum light intensity is then determined by the gas chromatographic retention times. As an example, Figure 3 shows a typical set of gas chromatograms for an n-butane + propene system, for which sampling periods of 15 min were employed.

For organics that react with O_3 (i.e., the alkenes), care should be taken not to obtain data when the reaction with O_3 becomes important (i.e., reaction with O_3 should contribute <10% of the organic reaction rate with the OH radical).

The rate constant for the reaction of OH radicals with the test compound, relative to that for the reaction of OH radicals with the reference organic, is then obtained from the experimental data by using Equations (IX) or (X). An example of a plot of Equation (IX) is shown in Figure 4 for a series of carbonyls, with cyclohexane as the reference organic.

Conclusions

The experimental technique presented has been validated by demonstrating excellent agreement between rate constants obtained by this method and corresponding literature values. A list of recommended reference organics is provided in the detailed protocol along with their room temperature OH radical rate constants.

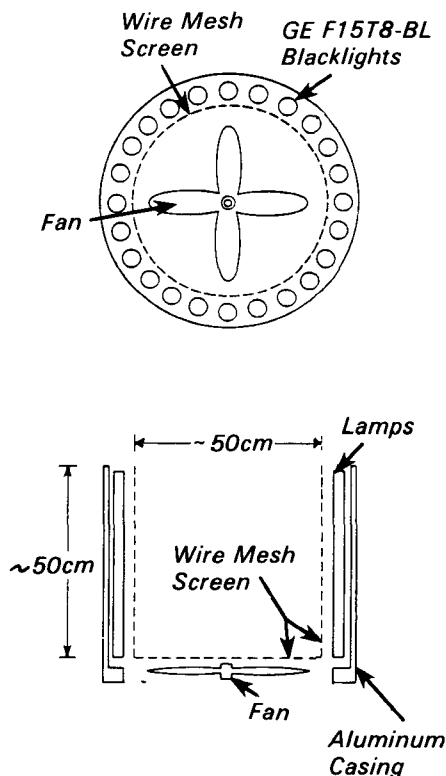


Figure 2. Fluorescent lamp assembly.

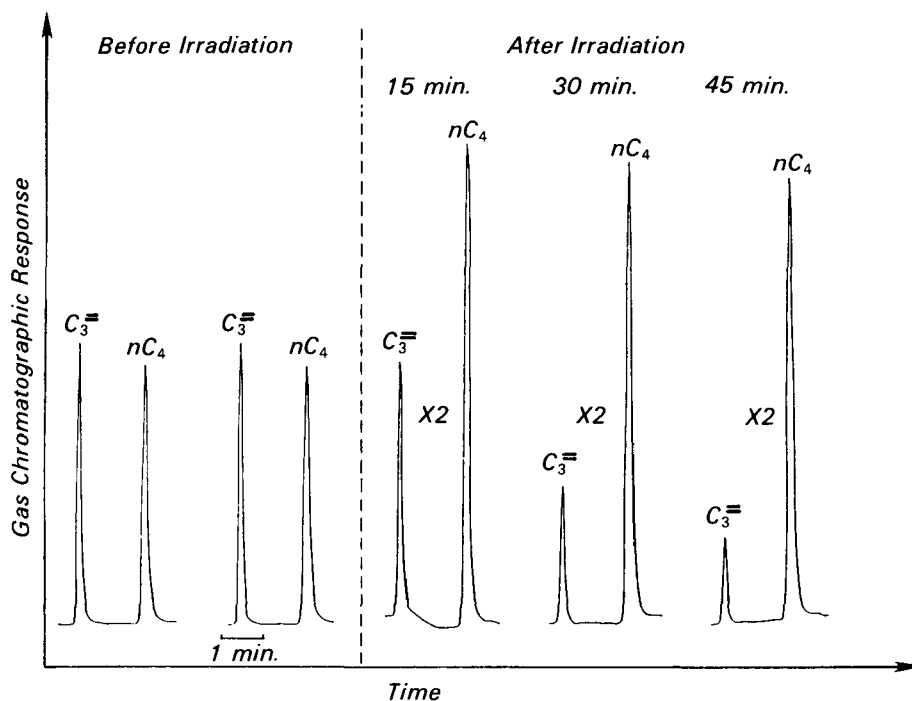


Figure 3. Example of gas chromatographic analysis of propene ($C_3=$) and n-butane (nC_4) during a CH_3ONO/NO /propene/n-butane/air irradiation.

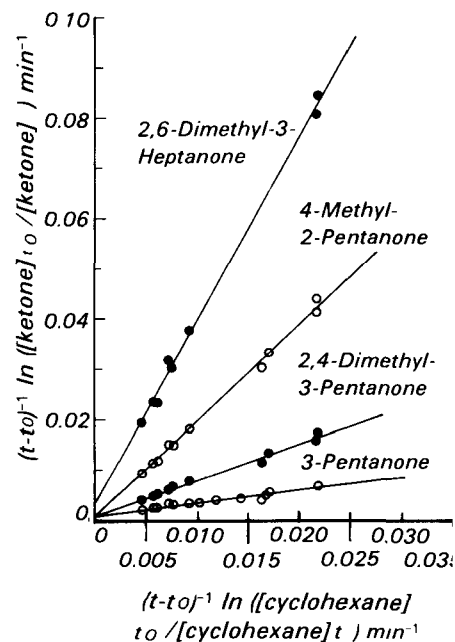


Figure 4. Plot of equation (IX) for a series of ketones, using cyclohexane as the reference organic.

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Bruce W. Gay, Jr., is the EPA Project Officer (see below).

The complete report, entitled "Experimental Protocol for Determining Hydroxyl Radical Reaction Rate Constants," (Order No. PB 82-256 066; Cost: \$7.50, subject to change) will be available only from:

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