



Project Summary

Experimental Protocol for Determining Photolysis Reaction Rate Constants

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An experimental protocol for the determination of photolysis rates of chemicals which photolyze relatively rapidly in the gas phase at room temperature has been developed, and is described in detail. This procedure provides a basis for evaluating the relative importance of one atmospheric reaction pathway (i.e., photolysis) for organic substances which may be emitted into the environment and which strongly absorb actinic radiation and photodecompose with high efficiencies. This technique is based upon monitoring the disappearance rates of the test compound and of a reference organic, both of whose OH radical reaction rate constants are accurately known, in irradiated NO-organic-air mixtures.

Irradiations employing blacklamps emitting in the actinic region are carried out in ~75-l volume cylindrical Teflon bags. The concentrations of the reactants are: NO, ~5 ppm; test compound, ~1 ppm; reference organic, ~1 ppm. The test compound and reference organic are monitored by gas chromatography; NO, NO_x and O₃ are monitored by chemiluminescence. The light intensity in the experimental system is monitored by NO₂ actinometry, and corrections for the differences in light intensity between the experimental system and the atmosphere are made by multiplying the measured photolysis rate of the test compound by the ratio of the calculated atmospheric photolysis rate to the measured laboratory NO₂ photolysis rate.

Ideally, the light source in the chamber should have the same spectral

distribution and intensity as solar radiation at the earth's surface at the appropriate latitude. Unfortunately, practical limitations (i.e., cost and complexity) dictate the use of blacklamps, the type typically used in environmental chamber studies of the photooxidations of organics. The fact that the spectral distribution provided by these lamps is different from the solar spectral distribution leads to uncertainties when extrapolating the chamber results to ambient conditions.

Depending on the reproducibility of the analysis technique, it is anticipated that photolysis rates $\geq 1 \times 10^{-5} \text{ sec}^{-1}$ in the chamber can be determined using the technique. This limits the procedure to these organics which photolyze relatively rapidly, such as nitrites, α -dicarbonyls and nitrosamines. However, while the technique cannot be used for simple aldehydes and ketones and other relatively weakly absorbing organics, for most species this may not be a serious limitation because their atmospheric lifetimes are determined mainly by reaction with OH radicals.

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

Under the sponsorship of the U.S. Environmental Protection Agency, 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 ozone.
- Reaction with the hydroxyl radical.
- For aromatic compounds containing an -OH substituent group, reaction with the nitrate (NO_3) radical.

In order 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 enable rate constants for photolysis of organics and certain inorganics to be determined at room temperature. With a knowledge of these rate constants, the atmospheric lifetimes of these compounds may be estimated with respect to photolysis as shown below. Due to experimental limitations, this protocol is applicable only for organics which photolyze relatively rapidly (lifetimes of ≤ 30 hrs). These include strongly absorbing species which photodissociate rapidly, such as nitrites, α -dicarbonyls and nitrosamines. Fortunately, most organics which photolyze also react rapidly with the hydroxyl radical, so for these compounds this shortcoming is not overly serious in terms of estimating atmospheric lifetimes. However, there are a few organics (e.g., acetone, methyl ethyl ketone and diethyl ketone) which react only slowly with OH radicals and do not react with O_3 , and which photolyze at rates lower than the range for which this protocol is useful; for these compounds alternate techniques for determining photolytic lifetimes are required.

Under atmospheric conditions, the photolysis rate constant, k_p , for the reaction



is given by

$$k_p = \int_{290 \text{ nm}}^{800} \sigma_{\lambda} \Phi_{\lambda} J_{\lambda} d\lambda \quad (I)$$

where σ_{λ} is the absorption cross-section at the wavelength λ , Φ_{λ} is the corresponding quantum yield (the fraction of molecules absorbing light which subsequently isomerize or decompose; always ≤ 1.00 for elementary reactions), and J_{λ} is the solar flux at the wavelength λ .

The short wavelength cut-off of $\lambda \approx 290$ nm is determined by the transmission properties of the atmosphere, while the long wavelength limit is set by thermochemistry, since light of wavelength > 800 nm is not of sufficient energy to break chemical bonds of ground state, thermally stable molecules. The solar flux is conveniently tabulated as average values of $J_{\Delta\lambda}$ over 10 nm intervals, so the integral in equation (I) can be replaced by a summation to yield

$$k_p = \sum_{\lambda=290 \text{ nm}}^{800} \sigma_{\Delta\lambda} J_{\Delta\lambda} \Phi_{\Delta\lambda} \quad (II)$$

where $\sigma_{\Delta\lambda}$ and $\Phi_{\Delta\lambda}$ also represent the absorption cross-section and quantum yield values averaged over 10 nm intervals. Tabulated values of $J_{\Delta\lambda}$ for various latitudes and various times are given elsewhere (Peterson 1976, Hendry and Kenley 1979, Pitts et al. 1981).

Thus from a knowledge of the absorption coefficients $\sigma_{\Delta\lambda}$ of the organic of interest, the quantum yields $\Phi_{\Delta\lambda}$ for photolysis reactions which lead to its removal, and with the tabulated values of $J_{\Delta\lambda}$, the photolysis rate constant k_p can in principle be calculated for any latitude, season, and time of day without the necessity for experimental rate measures. However, the accurate determination of quantum yields for organic compounds in air as a function of wavelength is a highly complex and time-consuming proposition, and the routine determination of absolute quantum yields is not practical at the present time.

On the other hand, a relatively straightforward experimental protocol is available for the measurement of absorption coefficients of organics (Pitts et al. 1981). Since quantum yields for elementary photochemical reactions cannot exceed unity, then upper limits to the atmospheric photolysis rate constants can be estimated, on the assumption that $\Phi_{\lambda} = 1.00$

$$k_p^{\text{max}} = \sum_{\lambda=290}^{800} \sigma_{\Delta\lambda} J_{\Delta\lambda} \quad (III)$$

This approach, which is described in

detail elsewhere (Pitts et al. 1981), is useful for determining the organics for which atmospheric removal by photolysis is not important. However, for those organics whose maximum photolysis rate is significant, a more quantitative indication of the actual tropospheric photolysis rates must also be obtained experimentally.

General Approach Employed

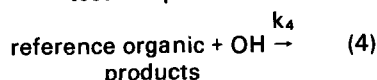
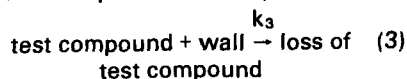
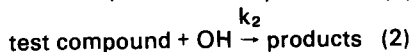
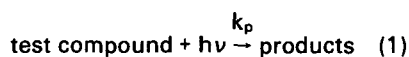
The approach described in this document for obtaining estimates for atmospheric photolysis rates for organics consists of (1) experimentally measuring in the laboratory the photolysis rate (or its upper limit) of the organic in air, employing a light source whose intensity and spectral distribution approximates as closely as practical that of the troposphere; (2) measuring the rate of NO_2 photolysis upon irradiation with the same light source and the same intensity as used in the organic photolysis rate measurements; and (3) estimating the photolysis rate of the organic in the troposphere from the known tropospheric NO_2 photolysis rates based on the assumption that the NO_2 /organic photolysis rate ratios is the same in the experimental system as in the troposphere. This approach involves a number of assumptions which may not always be valid, and the uncertainties and limitations involved are discussed in detail in the report.

Laboratory Measurement of Photolysis Rates

The experimental approach for the laboratory measurement of the photolysis rate of the organic test compound is based on measuring the disappearance rates of that compound and of a reference organic in irradiated NO-test compound-reference organic-air mixtures, where conditions are such that the major loss processes for the test compound should only be photolysis and perhaps reaction with the hydroxyl radical. The reference organic is chosen to be a compound which does not photolyze and whose major loss process in such systems is reaction with the hydroxyl radical, preferably with a rate constant similar to that of the test compound. The NO levels employed are sufficiently high that the concentrations of O_3 and NO_3 are suppressed, so that reaction of the organics with these species is minimized.

Thus the reactions which must be considered in the NO-organic-air system used to determine photolysis rates are

those listed below:



Note that in practice, for a test compound whose behavior in the gas phase may not be well characterized, the possibility of heterogeneous removal (reaction 3) must be considered. Based on the above reactions, we can derive:

$$-d \ln [\text{test compound}] / dt = k_2 [\text{OH}] + k_p + k_3 \quad (IV)$$

and

$$-d \ln [\text{reference organic}] / dt = k_4 [\text{OH}] \quad (V)$$

and hence,

$$\frac{1}{(t-t_0)} \ln \left\{ \frac{[\text{test compound}]_{t_0}}{[\text{test compound}]_t} \right\} = \frac{1}{(t-t_0)} \frac{k_2}{k_4} \ln \left\{ \frac{[\text{reference organic}]_{t_0}}{[\text{reference organic}]_t} \right\} + (k_p + k_3) \quad (VI)$$

where t_0 is the time of the beginning of the irradiation and t is any time during the irradiation when both the test and reference compounds were measured. Thus a plot of $\ln([\text{test compound}]_{t_0}/[\text{test compound}]_t)$ against $\ln([\text{reference organic}]_{t_0}/[\text{reference organic}]_t)$ should yield a straight line plot with an intercept of $k_p + k_3$ or, alternatively, since the rate constant ratio k_2/k_4 will be known, values of $(k_p + k_3)$ can be calculated from the experimental data and equation (IV). If reaction (3) is assumed to be primarily dark decay, k_3 can be measured by monitoring the rate of decay of the test compound in the dark, allowing k_p in principle to be calculated.

Laboratory Measurement of the NO_2 Photolysis Rate

The experimental approach for measuring the rate of photolysis of NO_2 in the

laboratory system ($k_{\text{NO}_2}^{\text{lab}}$) is based on measuring the amount of NO_2 converted to NO when an NO_2 in N_2 mixture is irradiated while passing through a quartz tube at a known flow rate (Zafonte et al. 1977). The experimental NO_2 photolysis rate, $k_{\text{NO}_2}^{\text{lab}}$, is given by

$$k_{\text{NO}_2}^{\text{lab}} = \frac{\Delta[\text{NO}]}{[\text{NO}_2]} \cdot \frac{F}{V} \cdot \frac{1}{\phi} \quad (VII)$$

where $\Delta[\text{NO}]$ is the measured increase in the NO concentration resulting from photolysis, $[\text{NO}_2]$ is the NO_2 concentration in the tube, F is the total flow rate through the tube (generally $\sim 3 \text{ liter min}^{-1}$), V is the volume of the portion of the tube exposed to the photolyzing light, and ϕ is the effective quantum yield for the net production of nitric oxide upon photolysis. This effective quantum yield was calculated by Zafonte et al. (1977) to be 1.61 ± 0.07 under the range of reactant concentrations generally employed ($[\text{NO}_2] \approx 1-4 \text{ ppm}$; $[\text{NO}]_0 \approx 0-0.3 \text{ ppm}$). Zafonte et al. (1977) also calculated that no correction for refraction of light through quartz is necessary when a tubular reactor is employed.

Estimation of the Tropospheric Photolysis Rate of the Test Compound

The tropospheric photolysis rate of NO_2 ($k_{\text{NO}_2}^{\text{trop}}$) can be calculated as a function of the solar zenith angle, Z , from tabulated solar fluxes, $J_{\lambda}^{\text{trop}}(Z)$ and the known NO_2 absorption coefficients, $\sigma_{\lambda}^{\text{NO}_2}$ and photo-decomposition quantum yields, $\phi_{\lambda}^{\text{NO}_2}$ using the equation

$$k_{\text{NO}_2}^{\text{trop}}(Z) = \int_{\lambda=290}^{430} J_{\lambda}^{\text{trop}}(Z) \sigma_{\lambda}^{\text{NO}_2} \phi_{\lambda}^{\text{NO}_2} d\lambda \quad (VIII)$$

The solar zenith angle depends on the time of day, the latitude, and the time of the year, and can be calculated as shown below:

$$Z = \arccos[\sin(L) \cdot \sin(D) \cdot \cos(H)] \quad (IX)$$

$$\text{where } H = \left(\frac{\text{hours from midnight}}{24} \right) \times 360 \text{ degrees}$$

L = the latitude, and D = the solar declination angle at the time of year of interest (which can be obtained, for example, from a nautical almanac).

The ratio of the tropospheric to the laboratory measured NO_2 photolysis rates

can then be used to obtain an approximate estimate of the tropospheric photolysis rate, k_p^{trop} , of the organic test compound from the photolysis rate measured in the laboratory:

$$k_p^{\text{trop}} \approx k_p^{\text{lab}} \frac{k_{\text{NO}_2}^{\text{trop}}}{k_{\text{NO}_2}^{\text{lab}}} \quad (X)$$

The validity of equation (X) critically depends on how closely the spectral distribution of the photolyzing light in the laboratory system approximates that of the troposphere; this is discussed in the following section.

Limitations and Uncertainties

The minimum photolysis rate constant which can be measured using the technique described here depends on the precision and reproducibility of the gas chromatographic analysis of the test compound and the reference organic. Based on our experience with the proposed experimental system, it is anticipated that the photolysis rate constants must be at least $\sim 1 \times 10^{-5} \text{ sec}^{-1}$ in order to be measurable. Thus this technique is only useful for organics which are highly photoreactive (much more so than, for example, simple aldehydes and ketones), and should not be attempted for organics whose value of k_p^{max} , calculated from the measured absorption coefficients (Pitts et al. 1981) using equation (III), is less than 10^{-5} sec^{-1} . A more detailed discussion is given in the full report.

Experimental

Irradiations are carried out in a ~ 75 -l volume cylindrical Teflon bag which is constructed out of 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 24 15-W blacklights (GE F15T8-BL15) mounted in a cylindrical frame constructed out of aluminum. The lamps are arranged on three electrical circuits, eight lamps per circuit, with every third lamp being on a given circuit. This allows the use of three different light intensities. In the bottom of the chamber is a fan which circulates a large volume of air to minimize the amount of heating. A cylindrical wire mesh screen inside the lamp assembly in which the Teflon bag is placed (Figure 2) keeps the reaction bag from contact with the lamps or the fan.

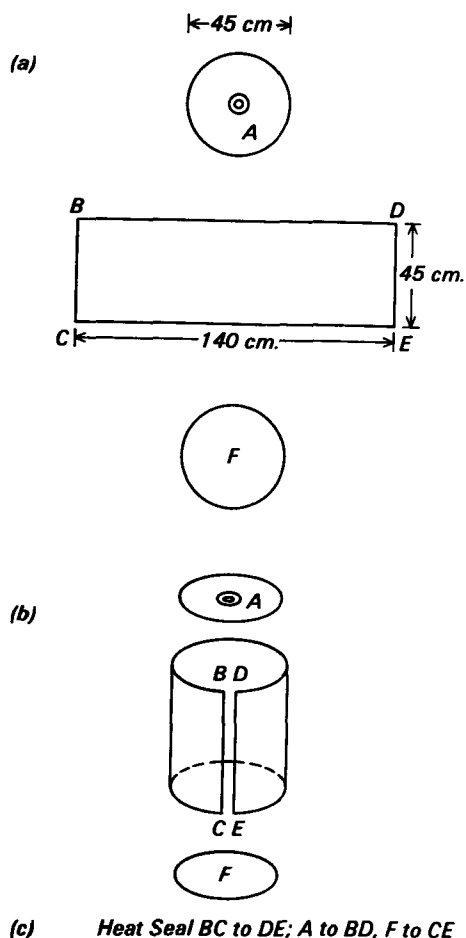


Figure 1. Construction of the Teflon reaction bag.

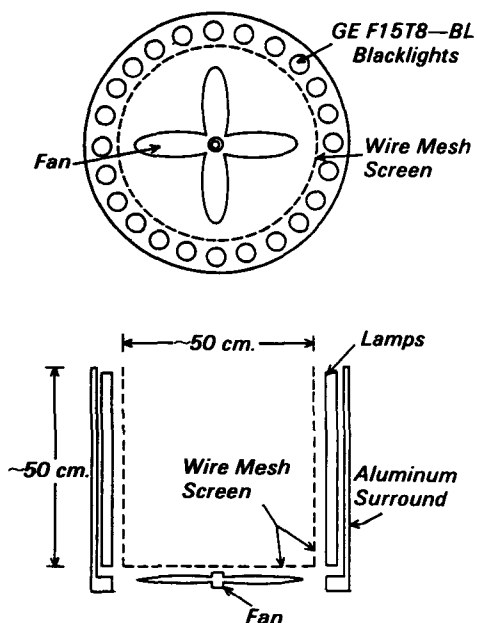


Figure 2. Fluorescent lamp assembly.

Initial concentrations of the reactants are typically: NO, ~5 ppm; test and reference organics, ~1 ppm. The NO is present to minimize O₃ formation and any reaction with the organics. The organic reactants are monitored by gas chromatography prior to and during the irradiations. With the protocol developed here, the irradiation should be carried out for at least one hour at full light intensity.

For organics which react with ozone (i.e., the alkenes) care should be taken not to obtain data when the reaction with O₃ becomes important (i.e., reaction with O₃ should contribute <10% of the organic reaction rate with the OH radical).

Conclusion

The results are analyzed using equation (VI). The detailed protocol provides a list of recommended reference organics together with a detailed discussion of potential problems associated with this technique.

References

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- Peterson, J. T., 1976. Calculated Actinic Fluxes (290-700 nm) for Air Pollution Photochemistry Applications. EPA-600/4-76-025, June.
- Pitts, J. N., Jr., A. M. Winer, D. R. Fitz, A. K. Knudsen and R. Atkinson, 1981. Experimental Protocol for Determining Absorption Cross Sections of Organic Compounds. EPA-600/3-81-051, December.
- Zafonte, L., R. L. Rieger and J. R. Holmes, 1977. Nitrogen Dioxide Photolysis in the Los Angeles Atmosphere. Environ. Sci. Technol., 11, 483.

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

The complete report, entitled "Experimental Protocol for Determining Photolysis Reaction Rate Constants," (Order No. PB 84-110 139; Cost: \$8.50, subject to change) will be available only from:

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