



Project Summary

Experimental Protocol for Determining Absorption Cross Sections of Organic Compounds

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An experimental protocol for the determination of gas phase absorption cross sections and the calculation of maximum photolysis rates is described in detail. Utilization of this protocol will provide a basis for evaluating the possible relative importance of one atmospheric reaction pathway (photolysis) for organic substances emitted into the environment.

The experimental technique involves measuring the absorption spectrum over the wavelength region 285-825 nm at various known gas phase concentrations of the test compound in one atmosphere of ultra-pure air. From the measured absorbances (averaged over 10 nm wavelength regions), absorption cross sections (again averaged over 10 nm wavelength increments) can be calculated. These absorption cross sections, together with solar flux data from the literature, permit calculation of the photolysis rates under atmospheric conditions. Since a photolysis quantum yield of unity is assumed in these calculations, the resulting photolysis rates are upper limits.

Calculating the maximum photolysis rate permits an assessment of the importance of photolysis (in comparison to reaction with ozone and with the hydroxyl radical) as an atmospheric

reaction pathway. If the photolysis rate is shown to be of importance, further experimental data on the quantum yield for photolysis under atmospheric conditions are required to precisely determine the actual photolysis rate.

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 at the University of California, Riverside, is developing and validating 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 hydroxyl radical, and
- for aromatic compounds containing an -OH substituent group, reaction with the nitrate (NO₃) radical.

In order to assess (a) a given compound's atmospheric lifetime with respect to these gas phase removal processes, and (b) the relative importance for that compound of each of these reaction pathways, rate constants for photolysis and/or chemical reaction must be experimentally determined. The protocol described here permits the determination, at room temperature of absorption cross sections of organics. These absorption cross sections can be used, in conjunction with available solar flux data, to calculate maximum photolysis rates.

Rationale

For a chemical to be removed from the atmosphere by photolysis, it must (a) absorb light in the wavelength region applicable to the troposphere ($\lambda \geq 290$ nm), and (b) having absorbed light, undergo isomerization or decomposition.

For tropospheric purposes, the wavelength region of interest is that between ~290 and 800 nm. The short-wavelength cutoff is determined by the transmission properties of the atmosphere. The long-wavelength limit is determined by thermochemistry, since light of wavelength ≥ 800 nm has insufficient energy to break chemical bonds of ground state molecules.

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

compound + $h\nu \rightarrow$ products
is given by

$$k_p = \int_{\lambda=290}^{800} \sigma_{\Delta\lambda} \phi_{\Delta\lambda} J_{\Delta\lambda} d\lambda \quad (\text{Eq. 1})$$

where σ_{λ} is the absorption cross section at wavelength, λ , ϕ_{λ} is the corresponding quantum yield (the fraction of the molecules that absorb light and subse-

quently isomerize or decompose; always ≤ 1.00 for atmospheric conditions), and J_{λ} is the solar flux at wavelength λ . Since the solar flux is conveniently tabulated as average values of $J_{\Delta\lambda}$ over 10 nm intervals the integral in Equation 1 can be replaced by a summation to yield

$$k_p = \sum_{\lambda=290}^{800} \sigma_{\Delta\lambda} \phi_{\Delta\lambda} J_{\Delta\lambda} \quad (\text{Eq. 2})$$

where $\sigma_{\Delta\lambda}$ and $\phi_{\Delta\lambda}$ also represent the absorption cross section and quantum yield averaged over 10 nm intervals.

Since $\phi_{\lambda} \leq 1.00$, an upper limit to the atmospheric photolysis rate is given by

$$k_p^{\text{max}} = \sum_{\lambda=290}^{800} \sigma_{\Delta\lambda} J_{\Delta\lambda} \quad (\text{Eq. 3})$$

and, since values of $J_{\Delta\lambda}$ are readily available (Peterson 1976), an upper limit to k_p can be calculated from a knowledge of the absorption cross section, σ_{λ} , which can be averaged over 10 nm intervals to yield $\sigma_{\Delta\lambda}$. Should the compound fail to exhibit a sufficient absorption cross section or should it have a vapor pressure too low to yield an accurately determinable absorbance, an order of magnitude approximation to its vapor phase spectrum may be acquired from solution phase data.

The actinic flux, J_{λ} , is also a function of elevation and zenith angle, which are, in turn, functions of the time of day, season, and various light attenuating factors (cloud cover, dust, etc.). A compilation of $J_{\Delta\lambda}$ values, averaged over the entire day for the summer and winter solstices and the spring and fall equinoxes at 10°, 30°, and 50°N latitude, is included in the complete report. From these data and values of $\sigma_{\Delta\lambda}$ determined using the protocol, upper limits to k_p (i.e., k_p^{max}) may be derived, yielding lower limits to the photolysis lifetime, τ_p , since

$$\tau_p = 1/k_p \quad (\text{Eq. 4})$$

Comparison of this calculated photolysis lifetime with the lifetimes calculated for reaction with ozone (Pitts et al. 1981a) and with the hydroxyl radical (Pitts et al. 1981b) allows an assessment of the possible importance of photolysis as an atmospheric removal process. If photolysis is of possible importance, further experimental testing is necessary to determine the actual photolysis rate under atmospheric conditions.

Description of the Protocol

Obtaining Absorption Cross Section

The gas phase absorption spectra are obtained using a cylindrical Pyrex cell 10 cm in length fitted with quartz end windows and a commercially available spectrophotometer with an absorbance sensitivity of 0.001 at a signal-to-noise ratio of unity.

The test compound, if a liquid, is degassed using a greaseless, high-vacuum gas-handling rack. Known pressures of the compound are introduced into the gas absorption cell, which is then filled to atmospheric pressure with dried ultra high purity air.

The ultraviolet (UV)-visible spectrum is measured relative to a matched cell filled with dried ultra high purity air from the same cylinder. The spectrum is measured from 285 to 825 nm using minimum slit openings. This procedure is repeated with at least two other pressures of differing factors of between 2 and 10 (e.g., 1, 5, and 20 torr), depending on the strength of the absorption and the sensitivity and stability of the spectrophotometer. Since many compounds do not absorb at the longer wavelengths, it is acceptable to begin the scan at ~50 nm above the onset of the lowest energy absorption.

Immediately prior to and after each set of runs, a blank spectrum is obtained. The UV cell is evacuated to 10^{-5} torr and filled with dried ultra high purity air. The cell is then placed in the spectrophotometer and a spectrum obtained relative to the reference cell, using the same sources, scale, and slit widths that will be used for sample spectra.

If the properties of the compound (e.g., width of absorption cross sections, vapor pressure) are such that the maximum absorbance obtainable is one-tenth of the most sensitive spectrophotometer scale or less (i.e., ≤ 0.001 absorbance), a solution phase study should be undertaken. While not capable of yielding an accurate value for σ_{λ} , solution phase results are reproducible and yield an order-of-magnitude approximation.

Calculating the Maximum Photolysis Rate Constant

The blank spectrum, with both the reference and sample cells filled with

either dried ultra high purity air or solvent, is used to correct the sample spectra for absorbance due to small spectral differences between the cells. A matched pair of cells should require minimal correction.

The average absorbances over each of the 10 nm intervals for which $J_{\Delta\lambda}$ values are listed (e.g., 285-295, 295-305 nm, etc.) are tabulated. Photochemical cross sections are determined from the Beer-Lambert Law

$$\sigma_{\Delta\lambda} = A_{\Delta\lambda}/1C$$

where $\sigma_{\Delta\lambda}$ is the wavelength-averaged cross section (in $\text{cm}^2 \text{molecule}^{-1}$), l is the cell pathlength (in cm), C is the concentration of absorbing species (in molecules cm^{-3}), and $A_{\Delta\lambda}$ is the wavelength-averaged absorbance (in logarithm to the base e units). An absorbance given in base 10 units must be multiplied by 2.3026 to convert to base e units.

The cross sections, $\sigma_{\Delta\lambda}$, are combined with the solar intensities for 10° , 30° , and 50°N latitude. These day-averaged $J_{\Delta\lambda}$ values will yield a day-averaged maximum photolysis rate constant, k_p^{max} , of

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

Since the quantum efficiency for many photochemical processes is less than unity, k_p^{max} will most often represent an upper limit to the true photolysis rate constant.

References

- Petersen, J. T. 1976. *Calculated Actinic Fluxes (290-700 nm) for Air Pollution Photochemistry Applications*. EPA-600/4-76-025, U.S. Environmental Protection Agency, RTP, NC.
- Pitts, J. N., Jr., A. M. Winer, D. R. Fitz, S. M. Aschmann, and R. Atkinson. 1981a. *Experimental Protocol for Determining Ozone Reaction Rate Constants*. EPA-600/S3-81-024, U.S. Environmental Protection Agency, RTP, NC.
- Pitts, J. N., Jr., A. M. Winer, S. M. Aschmann, W. P. L. Carter, and R. Atkinson. 1981b. *Experimental Protocol for Determining Hydroxyl Radical Reaction Rate Constants*. Report to EPA Grant No. R806661-01, Statewide Air Pollution Research Center, University of California-Riverside, Riverside, CA (in preparation).

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The complete report, entitled "Experimental Protocol for Determining Absorption Cross Sections of Organic Compounds," (Order No. PB 82-121 161; Cost: \$7.50, subject to change) will be available only from:

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