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NOTES

Quantum Yields for Reaction of Pollutants in Dilute Aqueous Solution

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■ Procedures are reported for determining quantum yields for direct photolysis of pollutants at low concentrations in water. Quantum yields are used to compute half-lives for direct photolysis of aquatic pollutants under sunlight.

In a recent report, Zepp and Cline (*1*) described equations and parameters required to compute direct photolysis rates of pollutants in the aquatic environment. Photolysis rates ($-dC/dt$) can be computed by Equation 1 where k_a is the specific rate of light absorption, ϕ is the quantum yield for reaction, and C is the pollutant concentration.

$$-\frac{dC}{dt} = k_a \phi C \tag{1}$$

Usually, the quantum yield for a reaction is determined under conditions in which all the incident light or a directly measurable fraction is absorbed by the system (*2*). The concentrations of substrate employed in these experiments typically range from 10^{-3} to greater than 0.1 M. The extremely low solubilities of most organic pollutants in water preclude measurement of quantum yields under conditions of complete light absorption. In this communication a technique that can be used to determine quantum yields in very dilute solution is described. An explicit description of the use of quantum yields to compute sunlight photolysis half-lives is also included.

The general rate expression for photolysis in a cell containing volume V of solution and having exposed area A is:

$$\text{Rate} = -\left(\frac{dC}{dt}\right)_{\lambda} = \phi I_{o\lambda}\left(\frac{A}{V}\right) F_{s\lambda} F_{c\lambda} \tag{2}$$

where $I_{o\lambda}$ is the incident light intensity at wavelength, λ; $F_{s\lambda}$ is the fraction of light absorbed by the system; and $F_{c\lambda}$ is the fraction of absorbed light that is absorbed by the photoreactive substance (*3*). The terms $F_{s\lambda}$ and $F_{c\lambda}$ are expressed by:

$$F_{s\lambda} = 1 - 10^{-(\alpha_\lambda + \epsilon_\lambda C)l} \tag{3}$$

$$F_{c\lambda} = \frac{\epsilon_\lambda C}{\alpha_\lambda + \epsilon_\lambda C} \tag{4}$$

where α_λ is the absorption coefficient of the solvent, ϵ_λ is the molar extinction coefficient of the photoreactive substance, and l is the light pathlength. When light is weakly absorbed by the system ($F_{s\lambda} < 0.1$), $F_{s\lambda}$ very nearly equals $2.303\,(\alpha_\lambda + \epsilon_\lambda C)l$, and Equation 2 simplifies to a first-order rate expression:

$$\text{Rate} = 2.303\, I_{o\lambda}\left(\frac{A}{V}\right) \epsilon_\lambda l \phi C \tag{5}$$

Thus, when the light intensity, extinction coefficient, and pathlength are known, the quantum yield may be computed from the slope of a first-order plot of ln C vs. exposure time:

$$\phi = \frac{-\text{Slope}}{2.303\, I_{o\lambda}(A/V)\epsilon_\lambda l} \tag{6}$$

Procedures that can be used to determine these parameters are outlined below. Monochromatic light isolated by filters (*2*) is usually employed in these experiments.

The intensity term, $I_{o\lambda}(A/V)$, can be directly determined by exposing a solution of an appropriate reference compound, i.e., a chemical actinometer, to light in exactly the same fashion as the pollutant. The same or an identical reaction cell should be used, and the cell should be filled with the same volume. The chemical actinometer should photoreact with a well-defined quantum yield at wavelength λ. When all of the incident light is absorbed by the actinometer, i.e., $F_{s\lambda}$ is unity, the intensity term, $I_{o\lambda}(A/V)$, equals the rate of photoreaction of the actinometer divided by its quantum yield. The potassium ferrioxalate actinometer is reliable and easy to analyze (*4*).

The average pathlength of the photolysis cell can be determined experimentally by the following procedure. If the concentration of the light absorbing substance, C, in a photoreactive system is sufficiently high that $F_{c\lambda}$ (Equation 4) is close to unity, then Equation 2 reduces to:

$$(\text{Rate})_C = \phi I_{o\lambda}\left(\frac{A}{V}\right)(1 - 10^{-\epsilon_\lambda l C}) \tag{7}$$

In the special case in which $\epsilon_\lambda l C$ exceeds 2, essentially all of the light is absorbed, and Equation 7 further simplifies to Equation 8.

$$(\text{Rate})_{\max} = \phi I_{o\lambda}\left(\frac{A}{V}\right) \tag{8}$$

The ratio, X, of the rate at concentration C to the maximum rate is then given by:

$$\frac{(\mathrm{Rate})_C}{(\mathrm{Rate})_{\max}} = X = 1 - 10^{-\epsilon_\lambda l C} \tag{9}$$

Thus, a plot of $-\log(1 - X)$ vs. $\epsilon_\lambda C$ gives a straight line with a slope equal to the pathlength, l. Such a plot is shown in Figure 1 for the benzophenone-sensitized *cis-* to *trans-*isomerization of 1,3-pentadiene (*5*) in our photochemical apparatus. In Figure 1, X is the ratio of *trans*-isomer formed at benzophenone concentration C to *trans*-isomer formed at a benzophenone concentration in which all the light was absorbed (0.050 M); ϵ is the extinction coefficient of benzophenone at 313 nm, the wavelength employed in the cell pathlength determination.

If possible, the molar extinction coefficient of the pollutant (ϵ_λ, Equation 3) should be determined in water. This task is sometimes difficult, if not impossible, because the solubility limits of DDT, benzo(a)pyrene, and some other pollutants are lower than 10^{-8} M. As an alternative, we have determined extinction coefficients in mixtures of water and acetonitrile or methanol (*6*), two polar organic solvents whose refractive indices are very close to that of water (*7*). Our choice of organic solvents was dictated mainly by the theoretical prediction that, at least for strong absorption bands of nonpolar compounds, absorption coefficients should be the same for solvents with the same refractive indices (*8*).

In agreement with theory, Schwarz and Wasik (*9*) reported that the absorption spectra of several polycyclic aromatic hydrocarbons are the same in water and ethanol, another organic solvent whose refractive index is nearly the same as that of water. Polar substances are very sensitive to changes in solvent, especially if the substance forms hydrogen bonds with solvent. Because of hydrogen-bonding effects, for example, the spectra of ketones like acetone and of nitrosamines such as N-nitrosodimethylamine differ significantly in water and ethanol (*10*). Fortunately, polar substances are usually sufficiently water-soluble that their spectra can be obtained in pure water or in water mixed with only a small amount of organic solvent.

Pure chemicals, not technical grade substances, should be used in the measurement of extinction coefficients. Overestimates of extinction coefficients usually occur when technical substances are employed, because the impurities frequently absorb in the same spectral region as the pure chemical.

Quantum yields may also be determined by comparing the photolysis rates of the pollutant with a reference compound under conditions in which the light is weakly absorbed by both compounds. Such comparisons are conveniently made in the "merry-go-round" photochemical apparatus originally designed by Moses et al. (*11*). The quantum yield for reaction of the pollutant, ϕ, can be calculated:

$$\phi = \frac{(SLOPE)_P}{(SLOPE)_R} \cdot \frac{\epsilon_R \phi_R}{\epsilon_P} \tag{10}$$

where $(SLOPE)_P$ and $(SLOPE)_R$ are the slopes of log plots of concentration vs. exposure time for pollutant and reference compound, respectively; ϵ_R and ϵ_P are molar extinction coefficients of reference compound and pollutant; and ϕ_R is the quantum yield for reaction of the reference compound. Values of $\epsilon_R \phi_R$ at 313 nm for a few pesticides are: DDE in water, 12 (*6, 12*); DDE in hexane, 15 (*6, 12*); DMDE in water, 120 (*6, 12*); DMDE in hexane, 72 (*6, 12*); carbaryl in water (pH 5.5), 2.3 (*13*); parathion in water, 0.39 (*14*); methyl parathion in water, 0.43 (*15*). Unfortunately, most well-established chemical actinometers cannot be analyzed at the low concentrations required for this technique.

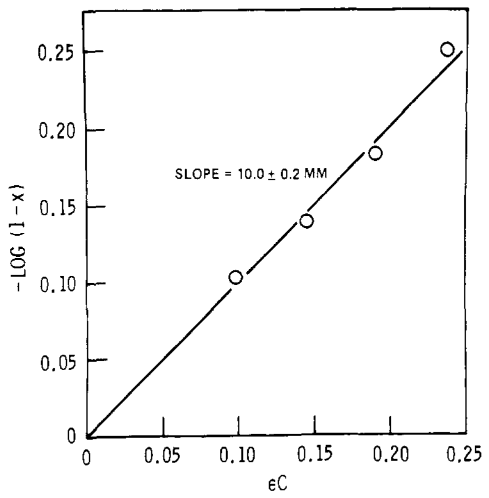

Figure 1. Determination of average cell pathlength for quantum yield studies by use of benzophenone-sensitized photoisomerization of *cis*-1,3-pentadiene

Once determined, the quantum yield for reaction can be used to compute the half-life for photolysis of the pollutant under a variety of environmental conditions (*1*). The photolysis half-life is independent of the optical properties of a water body near its surface (*1*). Estimates of the effects of light attenuation in water bodies appear elsewhere (*1*). Near surface half-lives can be computed by Equation 11 where Z_λ is underwater solar irradiance (*1*) at a wavelength interval centered at λ, and $\bar{\epsilon}_\lambda$ is the average extinction coefficient at this wavelength interval. The value of j is 6.02×10^{20} photon mole^{-1}.

$$t_{1/2} = \frac{0.693}{k_a \phi} = \frac{0.693\, j}{2.303\, \phi \sum \bar{\epsilon}_\lambda Z_\lambda} \tag{11}$$

A sample computation of the half-life of the pesticide carbaryl is presented in Table I. In computing sunlight half-lives, we have generally assumed that the quantum yield is wavelength independent in the region of sunlight absorption (*1*). This assumption is valid for most complex molecules in solution because photoreaction from second or higher electronic states usually cannot compete with the rapid radiationless decay of excited molecules to their first excited state. If photoreaction often occurred from higher excited states, excitation spectroscopy would not have general applicability (*16*). Exceptions to the general rule include certain coordination compounds. For example, the photolysis of iron (II) cyanide complexes is clearly wavelength dependent (*3*). For such cases, sunlight half-lives equal $0.693\ (\Sigma \phi_\lambda \epsilon_\lambda Z_\lambda)^{-1}$ where ϕ_λ is the average quantum yield in the wavelength interval centered at λ.

Finally, it should be emphasized that direct photolysis is but one of several potential mechanisms for photochemical transformation of pollutants. Natural substances in the aquatic environment are known to sometimes accelerate photolysis by mechanisms that are presently not defined (*6, 17*). Nonetheless, several studies (*6, 13, 15*) indicate that photolysis half-lives determined in natural waters are often nearly the same as half-lives computed by the procedures described above.

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Table I. Sample Calculations of Direct Photolysis Half-Life of Carbaryl in Water Midday, Midsummer, Latitude 40°N

Wavelength, nm	ϵ_λ	$Z_\lambda \times 10^{-14}$	$\epsilon_\lambda Z_\lambda \times 10^{-15}$
297.5	1480	0.00716	1.06
300	918	0.0240	2.20
302.5	741	0.0723	5.36
305	532	0.181	9.63
307.5	427	0.305	13.0
310	356	0.495	17.6
312.5	388	0.717	27.8
315	261	0.933	24.3
317.5	235	1.15	27.0
320	101	1.35	13.6
323	45	2.52	11.3
330	11	8.46	9.31

$\sum \bar{\epsilon}_\lambda Z_\lambda = 162$

$$k_a = \frac{2.303}{6.02 \times 10^{20}} \times 1.62 \times 10^{17} = 6.20 \times 10^{-4}\ \mathrm{s}^{-1}$$

$$\phi_{313} = 0.0060$$

$$t_{1/2} = \frac{0.693}{(0.0060 \times 6.20 \times 10^{-4})} = 1.86 \times 10^{5}\ \mathrm{s} = 51.7\ \mathrm{h}$$

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Simple Apparatus for Monitoring Land Disposal Systems by Sampling Percolating Soil Waters

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■ The treatment efficiency achieved by land disposal of effluents may conveniently be assessed by collection and analysis of waters percolating through unsaturated soil zones underlying treatment plots. A simple and inexpensive suction sampler constructed from "Swinnex"-type filter holders, membrane filters, and glass fiber filter discs is described. Air entry and vacuum loss occur only at high soil-moisture tensions; therefore, the system will sample soil waters over relatively long periods after a single evacuation. Loss of sample under high soil-moisture tensions is avoided by collecting the sample in a container separate from the sampling probe. The sampler materials cause minimal (if any) changes in sample composition.

The efficiency of conventional treatment processes is usually assessed by comparing the composition of wastewater before and after passing through the treatment process. Use of this approach for irrigation or infiltration/percolation modes of land disposal treatment requires the collection of a "treated" sample that may be compared directly with the applied effluent. This can usually be achieved by collecting waters percolating through unsaturated soil zones underlying the treatment plot, where predominantly vertical water movement can be assumed.

Collection of samples from the saturated zone (e.g., by wells) is often unsuitable for assessing treatment efficiencies, because this zone will usually contain water originating both from the applied effluent and from rain or irrigation waters infiltrating in other areas and moving laterally under the treatment plot. The proportions of mixing of waters from the different possible sources are seldom known. Installation of drains for the purpose of monitoring a land disposal site is not recommended, because "short circuiting" of relatively poor quality effluent into the drains is likely (*1, 2*).

Porous ceramic cups have been used to sample waters percolating through unsaturated soil zones for a variety of investigations including assessment of the effectiveness of systems for land application of effluents (*3*) and movement of nitrates through soils (*4, 5*). In a typical application the sampler is inserted into a tightly fitting hole bored in the soil profile and then evacuated to a pressure that will withdraw water present in the soil profile under soil-moisture tensions in the range of interest. The water sample collects in the ceramic cup and is withdrawn after removing the bung sealing the tube to which the porous cup is connected.

Porous ceramic cup samplers are often unsuitable for determination of phosphorus concentrations in soil solution because of adsorption/desorption reactions that can cause significant changes in concentrations of this element in sampled solutions. For example, one ceramic cup examined at this laboratory released phosphorus to distilled water passed through it, giving concentrations of ca. 0.025 g/m^3 P. A similar but smaller problem may exist for ammonium ion and other cations.

A further disadvantage of some porous cup samplers is associated with the storage of sample in the porous cup, in that

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