

Calculating photolysis rates and estimating photolysis lifetimes

Many chemical species in the environmental sciences undergo direct photolysis. This *ECG Environmental Brief* explains how the rate and typical photolysis lifetime for simple photolytic reaction can be calculated and highlights some common issues. Often the calculation of the photolytic lifetime is enough to decide if a photolytic process should be further studied or can be considered unimportant and ignored.

Chemicals and pollutants in the atmosphere, water and even snowpack may be directly photolysed by solar radiation. It is useful to know how fast this process may be or to calculate a photolysis lifetime (time to decay to $1/e$ of an initial concentration).

Consider a pollutant chemical, A, released to the environment that is photolabile. The pollutant, A, may absorb a photon of solar radiation, $h\nu$



The rate of loss of concentration of chemical A, [A] is

$$d[A]/dt = -J[A] \quad (2)$$

The coefficient, J is dependent on the intensity of solar radiation and the photo-physical properties of chemical A and may be calculated as

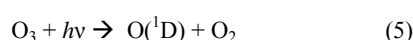
$$J = \int \Phi(\lambda, T) \sigma(\lambda, T) F(\theta, \lambda) d\lambda \quad (3)$$

where Φ is the quantum yield for photolysis of chemical A and σ is the absorption cross-section, both as a function of wavelength, λ and temperature, T . The solar spherical or point irradiance is $F(\theta, \lambda)$. The quantity $F(\theta, \lambda)$ is often termed as the "actinic flux" but this term is often wrong and misleading (1), θ is the solar zenith angle. For well-studied pollutants, values of the quantum yield and absorption cross-section data can be found in the scientific literature or publications such as (2). The calculation or measurement of spherical or point irradiance can be tricky, however, radiative transfer codes [e.g. (3)] and tables [e.g. (4)] can be used to calculate point irradiances. The quantity, J , is a first-order reaction decay constant, thus the reciprocal of J is a characteristic lifetime (i.e. time τ for the concentration of A, [A] to decay to $1/J$ or $\sim 37\%$ of its initial concentration).

$$\tau = 1/J \quad (4)$$

Calculation of a value of J

As an example of how to calculate a photolysis rate coefficient, J , consider the photolysis of gas-phase ozone in the atmosphere at a temperature of 273K, i.e.



Reaction (5) is an important step in the production of atmospheric hydroxyl radicals responsible for removal of atmospheric volatile organic compounds. The top panel of **Figure 1** plots the absorption cross-section and quantum yield for reaction (5), along with solar point irradiance (for a solar zenith angle of 60° with no cloud, aerosol and an ozone column of 300 Dobsons), as a function of wavelength. The product of the absorption cross section, quantum yield and solar point irradiance (i.e. $\Phi(\lambda, T)\sigma(\lambda, T)F(\theta, \lambda)$) is displayed in the middle panel of **Figure 1**. The shaded area in this panel is equal to the photolysis rate coefficient in equation (3) and be calculated using Simpson's rule or similar. For the example in the figure, the photolysis rate coefficient is $12.1 \times 10^{-6} \text{ s}^{-1}$ and corresponds to a photolysis lifetime with respect to $\text{O}({}^1\text{D})$ formation of ~ 23 hours.

Cautionary points in calculating J

The calculation of values of J should always consider issues with convolution, whether the calculation is an underestimate, the applicability of the quantum yield, the logarithmic base of the absorption cross-section and the differences between photochemistry and photolysis.

The absorption cross-section, quantum yield and spherical irradiance are all functions of wavelength. These quantities change rapidly with wavelength and for the absorption spectra (especially for gaseous species, such as BrO) may be very structured on the scale of less than 0.1 nm, yet calculations of the photolysis rate coefficients are often performed at 1 to 10 nm resolution. To calculate accurate photolysis rate coefficients, the cross-section must be convoluted to be the same resolution as the point irradiance and quantum yield.

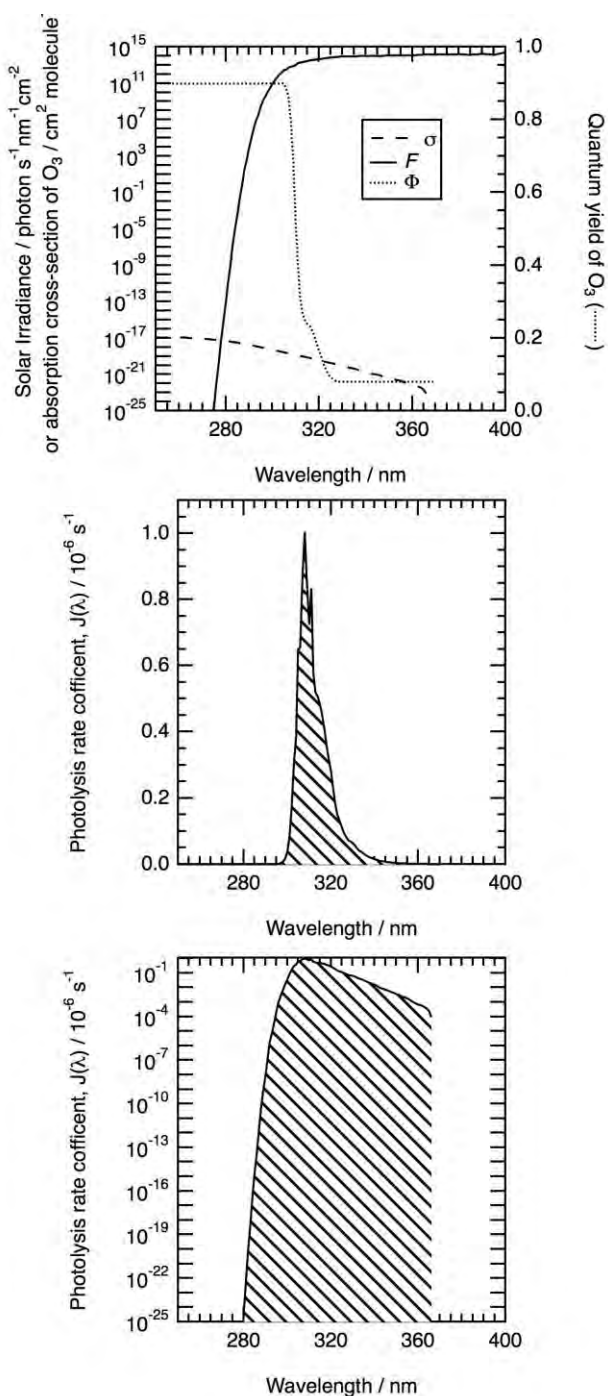


Figure 1. Calculation of J for photolysis of gas-phase ozone to produce $O(^1D)$. No data are available at wavelengths above ~ 360 nm.

Many calculations of photolysis rate coefficients are an underestimate. The solar irradiance increases rapidly with wavelength in the UV part of the spectrum, whilst the cross-section and quantum yield often decrease rapidly with wavelength in the same wavelength range (see top panel of **Figure 1**). The increase in solar irradiance is over many orders of magnitude, whilst the absorption cross-section is rarely measured over two or three orders of magnitude. Thus a long wavelength tail of equation (3) is often missing. The effect is obvious in the bottom panel of **Figure 1**, which is the middle panel plotted on a logarithmic scale.

Careful reading of the quantum yield in the literature is needed. The quantum yield can be determined for the number of molecules photolysed (i.e. loss of a pollutant) or as the number of reactive molecules generated. If there is more than one possible product then there will be a quantum yield for each reaction channel. (For example, for the photolysis of nitrate in water there is one quantum yield for formation of nitrite anion and one quantum yield for the formation of nitrogen dioxide.) To calculate the rate of total loss of starting material, photolysis rate coefficients must be calculated for each channel.

For calculation of photolysis rate coefficients, the absorption cross-section should be recorded or converted to the value derived from the Beer-Lambert law using base e as opposed to base 10. Most spectrometers record absorption cross-section as base 10.

Photolysis tends to generate more reactive species as products than the initial reactant and there is often subsequent chemistry between reactant and product that may further remove the initial reactant. Thus it is important to realise that equation (4) is the photolysis lifetime, i.e. respect to photolysis, and not a photochemical lifetime that may be different owing to chemical reaction following the photolysis.

Conclusions

The calculation of an estimate of J and its use in the calculation of the rate of photolysis of a chemical or a photolytic lifetime in the environment is reasonably straightforward, but care should also be taken to make sure an accurate calculation is being performed. Further information is available in the references; this document is merely an overview to demonstrate that the calculation is facile.

References

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