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**The Phototransformation of Chemicals
in Water: Results of a Ring - Test**

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OF CHEMICALS IN WATER :
RESULTS OF A RING - TEST**

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SUMMARY

In its Technical Report No.3, published in 1981, ECETOC (European Chemical Industry Ecology and Toxicology Centre) discussed experimental methods for assessing the photodegradation of chemicals in the environment and set out the criteria which such methods should meet if they were to be both scientifically adequate and environmentally relevant. For assessing the photodegradability of chemicals present in the aquatic environment it was recommended that a technique developed by the Laboratoire de Photochimie at the University of Clermont-Ferrand, France, be examined in a ring-test.

The results of such a ring-test are presented and discussed in detail in this report. The ring-test was performed in 1982-3 by 12 industrial laboratories and one University laboratory, using a common experimental procedure and slightly different forms of apparatus for determining quantum yields in the phototransformation of 4 reference chemicals in water. Variations in the experimental set-up proved to be less important than adherence to the protocol in producing adequately consistent values of the quantum yield. The report includes a detailed description of the experimental method used.

From the quantum yield the environmental half-life of a chemical can be calculated, and full details of such calculations are given.

A. INTRODUCTION

It is important for providing information on photodegradation for legislative requirements that adequate experimental methods are available. In a previous report ECETOC (1981) has discussed the criteria for scientifically adequate and environmentally relevant methods for assessing the photodegradation of chemicals, and made proposals for developing suitable methods. This work has been continued by a Task Force which was set up "to recommend fundamental and/or development studies needed to develop practical methods valid for the requirements of level 2 of the 6th Amendment to the 1967 Directive on the Classification, Labelling and Packaging of Dangerous Substances (European Communities) covering the photodegradation of chemicals in air and water, in that order of priority and importance". That part of the Task Force's work on phototransformation in water is described in this Technical Report.

B. BACKGROUND

Biodegradation is considered the most likely pathway of elimination of organic chemicals from the aquatic environment. Phototransformation, which occurs mainly near the water surface (to depths of 0.1 m for turbid rivers or about 30 m for the oceans), and hydrolysis, may also be important. An assessment of phototransformation in water is relevant for regulatory purposes only when biodegradation is unlikely to occur.

In water, primary (direct) phototransformations are the main reactions occurring, while secondary reactions involving free radicals (alkoxy radicals, HO^\cdot , HO_2^\cdot) and singlet oxygen are generally less important. For direct phototransformation the environmental lifetime, which is the ultimate parameter for assessing the fate of a chemical, can be derived from the experimentally-determined quantum yield, (ϕ), i.e. the number of molecules phototransformed per number of photons absorbed (ECETOC, 1981; Appendix 1). For reactions in water this is an unequivocal parameter, independent of the type and characteristics of the light source used in its determination and considered to be constant in each absorption band.

Quantum yields can be determined in experiments with mono- or poly-chromatic light sources. With monochromatic light the experimental procedure and subsequent calculations are relatively simple but the equipment is rather expensive. With polychromatic light the equipment costs less but the

calculations are more complex. Experiments with polychromatic light also permit an easier determination of quantum yields of substances with low photoreactivity. When the 1981 ECETOC report was written there existed no well-validated method for measuring quantum yields of a chemical in water with polychromatic light, but the Task Force had recommended that for this purpose the experimental technique developed by the Laboratoire de Photochimie of the University of Clermont-Ferrand be assessed in a ring-test. This has now been done, and is described in this report.

The lifetime of a chemical undergoing direct phototransformation in the aqueous environment depends not only on the quantum yield and absorption spectrum of the compound but also on the light intensity and spectral distribution of daylight. Data on these are available for various geographical regions. For any one region the absolute number of incident photons in each spectral range can thus be calculated. From this number, and a knowledge of the quantum yield and light absorption spectrum of the chemical, a theoretical lifetime of this chemical in the top layer of the aqueous system can be calculated (see ECETOC, 1981, p.51). However, the real lifetime of a chemical in an aqueous system also depends on the penetration of light into the water, which in turn depends on a variety of system-related variables. A computer programme, SOLAR (Zepp and Cline, 1977), is available for calculating the lifetime in a particular aquatic system as a function of these system-related variables. Appendix I.D gives examples of the theoretically-calculated lifetimes of the chemicals whose investigation is described in this report, and an example of the calculation of an environmentally more relevant lifetime using the SOLAR programme. Although the use of this programme is necessary for obtaining information on a real, local situation, calculation of the theoretical lifetime is very useful in giving a preliminary estimate of the persistence of a chemical in water.

C. EXPERIMENTAL TECHNIQUE USED IN THE RING-TEST

Thirteen laboratories (cf. section I) using the same experimental protocol participated in the ring-test in 1982 and early 1983. The final protocol presented in this report (Appendices 1,2,3) arose from a consideration of the results from, and comments by, the participants.

1. Chemicals Tested

The following chemicals were used in the study :

- i) pentachlorophenol at $\text{pH} > 6$,
- ii) 2,4-dichlorophenol at $\text{pH} > 6$,
- iii) 3,4-dichloroaniline at $\text{pH} > 6$,
- iv) 4-nitrophenol at $\text{pHs} < 2$ and ≥ 9 .

They were chosen to represent simple molecules whose main absorption bands covered the relevant part of the range of daylight wavelengths, and which had a wide range of quantum yields (ϕ). Neutral 3,4-dichloroaniline absorbs mainly at 310 nm, near the lower limit (295 nm) of the daylight range. Anionic 4-nitrophenol absorbs mainly at around 400 nm - chemicals absorbing at higher wavelengths are coloured and their photodegradation would be observable simply by the disappearance of colour. The selected chemicals had values of ϕ covering the range 10^{-1} to 10^{-7} .

Chemicals of high purity were used, but were not always from a common batch - see section D.2.2.2. iii) in which the effect of impurities is discussed.

Other details were specified as follows :

- a) concentration in water : 10^{-4} to 10^{-5} mole.litre $^{-1}$;
- b) temperature: 20° - 40°C ; preferably controlled to $\pm 2^{\circ}\text{C}$, and recorded;
- c) analytical determinations : UV or high performance liquid chromatography (HPLC);
- d) inorganic buffer : optional. The type used should be recorded.

2. Apparatus

Different types of instruments, the majority of which corresponded to the principles laid down in the former report (ECETOC, 1981), were used in the ring-test (cf. Appendix 2 and Table 1 in Appendix 4). The light sources were mercury or xenon arc lamps with suitable optical filters incorporated to eliminate radiation below 295 nm, the ultraviolet radiation cut-off in terrestrial daylight. Some laboratories also performed parallel measurements with monochromatic light.

3. Determination of the Incident Light Energy

The spectral intensity distribution from the lamp/filter combination was determined in two ways: by calculation from the spectral output data supplied by the lamp manufacturer and the measured absorbance of the filter, or by measurement using calibrated spectroradiometers. In one case

a comparison of the data was made, and revealed an acceptable compatibility of results for the two methods, except for the shortest wavelength region where there was some discrepancy.

Absolute incident light intensity was evaluated actinometrically over the wavelength range 300 to 490 nm at the same time as irradiation of the test samples, generally in standard quartz cuvettes of 1 cm pathlength.

4. Determination of the Disappearance Quantum Yield

All participants were asked to follow strictly the indications laid down in the protocol for the final calculation of the quantum yield. (Appendices 1,3)

5. Reporting

Reports were written according to the example given in the protocol (see Appendix 1.C of this report). The layout of tables and figures should be as in tables 10, 11, 12, and 13 (Appendix 4) and figures 1,2,3,4, and 5 (Appendix 5) of the protocol. Any special observations and remarks were added separately.

D. RESULTS OF RING-TEST AND DISCUSSION

1. Results

The results are summarised in Tables 2 to 6 (Appendix 4). The following critical experimental parameters which could have influenced the results are indicated : initial concentration, temperature during the measurement, pH and type of buffer used, analytical method for measuring the concentration of the chemical, and type of light filter. When the disappearance quantum yield was also determined with a monochromatic light source, this was noted. On collating the data it was found that there were slight inconsistencies in the concentration used, the pH of the aqueous buffered solution (acid and alkaline conditions chosen to give neutral molecules and anions respectively) and the temperature during the irradiation.

2. Discussion

2.1. Sources of errors in the ring-test

Two major types of errors are considered : errors which relate to the precision of the method (reproducibility) and systematic errors which relate to the accuracy of the method.

2.1.1. Reproducibility. Results are normally expressed as $x \pm \Delta x$, where Δx is a measure of the reproducibility. The attainment of reproducibility is not in itself proof that an accurate series of measurements has been made, since systematic errors may enter into all the measurements in the series. The following factors influence the reproducibility of the results.

Determination of the rate of disappearance. This rate is calculated from the variation in concentration of the test chemical as a function of time (at least two measurements). The precision of the HPLC determinations ($\pm 5\%$) or UV-analytical procedure (up to $\pm 10\%$ when extraction is needed) mainly determines the spread of individual results obtained in any one laboratory.

Determination of the concentration of unreacted actinometer. As this is based on well-established analytical methods, spreads of less than $\pm 5\%$ are expected.

Measurement of the absorption spectra of the test chemical solution and actinometer solution. With adequate equipment, errors in absorbance of less than $\pm 5\%$ are expected.

Because of the limited number of results it was impossible to perform a complete statistical analysis. It was nevertheless possible to see from the results that reproducibility was acceptable, regardless of the type of light (poly- or mono-chromatic) and apparatus used (Table 7, Appendix 4), although it might have been expected that, in most cases, a better reproducibility would have been achieved with monochromatic light for which the incident light can be better controlled (cf. Appendix 2).

2.2.2. Accuracy - Systematic errors. Systematic errors giving rise to the observed spread in inter-laboratory results may originate as follows.

- i) Errors may result from the assumption that the actual light intensity parameters of the polychromatic lamp conform to the specifications of the manufacturer. This could especially be true for an aged lamp and will have its maximum effect on compounds absorbing only in the 295-330 nm region. These errors may be largely eliminated by determining the emitted light intensity by photometry, which, however, requires rather expensive equipment and adequate practical experience.

An inter-laboratory comparison of quantum yields obtained with polychromatic light was made according to the type of apparatus used (ECETOC, optical bench, and other types; Table 8, Appendix 4). The calculated coefficients of variation are an indication of the accuracy. Tables 8-1 to 8-3 (Appendix 4) give similar coefficients for the results obtained with monochromatic light. It is concluded that the accuracy of the determination is similar for the different types of apparatus and light, despite the limited number of results. The optical bench, however, gave systematically higher quantum yields for those chemicals with a higher ϕ (pentachlorophenol, 2,4-dichlorophenol and 3,4-dichloroaniline).

- ii) Errors resulting from a change in the absorption characteristics of the borosilicate filter as a result of further solarisation. It was found during the ring-test that further solarisation changed the spectral light intensity distribution and shifted the cut-off wavelength towards the visible light region (cf. fig. 4, Appendix 5). It was considered that if the absorption band of the solution of the chemical coincided with the cut-off region of the filter, difficulties would be expected in the measurement of the quantum yield. The results obtained (Tables 8, Appendix 4) supported this expectation but the effect was not as significant as expected (e.g. 3,4-dichloroaniline, $\lambda_{\max} = 297$ nm; nitrophenol pH=2, $\lambda_{\max} = 262$ nm).

Such errors may be eliminated by the use of non-ageing filters (e.g. 305 Schott or Corning long-pass filters) placed before the cuvettes.

- iii) Errors may also result from the presence of impurities which may

differ from one sample of test compound to another. This influence was tested by five laboratories who first determined the quantum yield on samples of dichloroaniline obtained from different sources, and afterwards on a sample of identical origin (Koch Light). Mean values for the quantum yield of 0.049 and 0.073 were found, respectively. Considering the normal variation between individual measurements in one laboratory, this indicates that, for this compound at least, impurities had no significant effect.

- iv) Errors may also vary according to the absolute value of the quantum yield. The chemicals tested have quantum yields ranging from 0.20×10^0 to 1×10^{-6} . The results (Tables 8, Appendix 4) indicate that the accuracy of the measurements is about the same over the whole range.

2.2. Advantages and disadvantages of different types of apparatus and light sources.

The most important advantages and disadvantages are summarised in Table 9 (Appendix 4).

E. CONCLUSIONS

Seven types of apparatus (Table 1, Appendix 4) have been used to measure the photolysis quantum yields of 4 chemicals under polychromatic (12 laboratories) and monochromatic (3 laboratories) light, according to a common test protocol. The main absorption bands of the chemicals covered the practically-relevant part of the daylight-wavelength range, and the quantum yields varied between about 10^{-1} and 10^{-6} . The results with both types of light were in good agreement.

The quantum yield is a characteristic property of a chemical when the light distribution is well characterised during its measurement. However, where the light absorbed is near the short-wavelength cut-off a decrease in accuracy of the measured quantum yield is possible, but nevertheless the overall accuracy of such measured quantum yields is sufficient to permit an adequate calculation of the lifetime of a chemical in aqueous solution under specified environmental conditions. As shown in Appendix 1-D the calculated lifetime also depends on the penetration of light into the water and many other factors

which are likely to give larger variations in lifetime than does the inaccuracy in determining quantum yield.

The reproducibility and accuracy of quantum yields obtained with the ECETOC/University of Clermont-Ferrand apparatus with polychromatic light (6 laboratories) were similar to or better than those obtained with monochromatic light (3 laboratories). The accuracy was improved by the use of non-solarising, long-pass filters placed before the cuvettes.

Two apparatuses (laboratories L and M), in principle similar to the ECETOC apparatus, gave results with similar reproducibility and accuracy. One apparatus (laboratory K) did not fully conform to the criteria laid down for the ring-test, although it gave acceptable quantum yields. In such apparatuses in which the light geometry is not well-defined, the measurements on compounds with more than one main absorption band will present problems. The conventional optical bench apparatus with polychromatic light gave quantum yields of similar reproducibility but of somewhat higher values for those chemicals with a higher ϕ . The disadvantage of this apparatus is that the experiments take longer to perform.

A disadvantage of the methods with polychromatic light is that the calculation is more complicated, but this can be overcome by the use of a desk-top computer. Calculation is easier for the method with monochromatic light, but the higher cost of the equipment will limit its use to those laboratories which specialise in photochemistry. For chemicals which absorb weakly or have small quantum yields, the light intensity available from the monochromator needs to be especially high. The principal advantages of the use of the ECETOC and similar apparatuses with polychromatic light are : the relatively low cost, the shorter duration of the experiments and the possibility to determine the quantum yield of substances with low photoreactivity.

The protocol presented in this report is recommended for determining the quantum yield of direct phototransformation, and hence the calculated environmental lifetime, of a chemical in water under specified environmental conditions, when such data are required for the legislative notification of a chemical.

F. APPENDICES

APPENDIX 1 : EXPERIMENTAL PROTOCOL FOR AQUEOUS PHOTOLYSIS STUDY

A. PRINCIPLE OF METHOD

B. DEFINITIONS AND UNITS

1. Photolytic Lifetime
2. Quantum Yield
3. Einstein
4. Molar Extinction Coefficient
5. Light Absorption and Light Transmission Intensities

C. MEASUREMENT OF QUANTUM YIELD

1. Equipment
2. Procedure
 - 2.1. Preparation of materials
 - 2.2. Determination of the quantum yield
 - 2.2.1. With polychromatic light
 - 2.2.2. With monochromatic light
 - 2.3. Reporting

D. CALCULATION OF THE LIFETIME OF A CHEMICAL

1. Theoretical lifetime
2. Environmental lifetime

A. PRINCIPLE OF METHOD

The method is designed to measure the quantum yield ϕ of direct photolysis of a chemical in aqueous solution. The quantum yield can then be used to estimate the lifetime of the chemical in the aquatic environment.

B. DEFINITIONS AND UNITS

1. Photolytic Lifetime

The lifetime (τ) of a photodegradable compound under sunlight, and in a solution of low absorbance (where the absorbed light intensity is proportional to the concentration) can be calculated from the formula :

$$\tau = \frac{1}{k} = \frac{1}{2300 \int_{\lambda_1}^{\lambda_2} \phi \cdot I_0(\lambda) \cdot \epsilon(\lambda) \cdot d\lambda} \quad (I)$$

Many authors use the term half-life ($t_{1/2}$) which is defined by

$$t_{1/2} = \ln 2 \cdot \tau = 0.7 \times \tau.$$

- k is the pseudo-first-order rate constant of direct photolysis in s^{-1}
- ϕ is the quantum yield of disappearance under excitation extending from λ_1 to λ_2 nm in $\text{mole.einstein}^{-1}$
- $I_0(\lambda)$ is the intensity of incident light of wavelength λ expressed in $\text{einstein.cm}^{-2} \cdot \text{s}^{-1} \cdot \text{nm}^{-1}$
- $\epsilon(\lambda)$ is the molar extinction coefficient at wavelength λ expressed in $\text{litre.mole}^{-1} \cdot \text{cm}^{-1}$
- τ is the lifetime in seconds.
- 2300 takes into account the conversion of litres into cm^3 and of decadic molar extinctions into a Napierian basis.

The lifetime of a chemical in water can therefore be calculated from its quantum yield, its molar extinction coefficient and the known intensities of natural daylight. It depends, additionally, on several other environmental variables which are described in section D.

2. Quantum Yield (ϕ)

The quantum yield of disappearance is defined as the number of moles reacting per number of einsteins absorbed (i.e. number of molecules reacting per number of photons absorbed). It is calculated from an experimentally-determined rate of disappearance of the irradiated compound and from the total amount of light energy absorbed during the irradiation.

$$\phi = \frac{R}{10^3 \int_{\lambda_1}^{\lambda_2} \overline{I_a(\lambda)} \cdot d\lambda} \quad (\text{II})$$

where R = rate of disappearance of the irradiated compound
in mole.litre⁻¹. s⁻¹

$\overline{I_a(\lambda)}$ = the mean value of the absorbed light intensity
at a wavelength λ (nm) in einstein.cm⁻³.s⁻¹.nm⁻¹

10⁻³ = constant for converting mole.litre⁻¹.s⁻¹ to mole.cm⁻³.s⁻¹

3. Einstein

This is a unit of energy equal to the energy of N photons (N = Avogadro's number). It is not a constant, as are the classical energy units, but is wavelength-dependent.

$$1 \text{ einstein} = \frac{N \cdot h \cdot c}{\lambda (\text{cm})} = \frac{119.7 \times 10^6}{\lambda (\text{nm})} \cdot \text{Watt} \cdot \text{s} \quad (\text{III})$$

where N = number of molecules per mole =
6.022 x 10²³ (Avogadro's number)

$\frac{hc}{\lambda}$ = the energy of one photon with wavelength λ in cm.

h (Planck constant) = 6.626 x 10⁻³⁴ Joule.s

c (light velocity) = 3 x 10¹⁰ cm.s⁻¹

λ (cm) = 10⁻⁷ x λ (nm)

1 Watt = 1 Joule.s⁻¹

4. Molar Extinction Coefficient, $\epsilon(\lambda)$.

According to the Beer-Lambert law :

$$\epsilon(\lambda) = OD(\lambda) \cdot \ell^{-1} \cdot C^{-1} \quad (IV)$$

expressed in litre.mole⁻¹.cm⁻¹ where

OD (λ) = absorbance or optical density at wavelength λ

ℓ = optical path, identical to cell pathlength in cm

C = concentration of the chemical in mole.litre⁻¹

5. Light Absorption and Light Transmission Intensities

When incident light of intensity $I_i(\lambda)$ at a wavelength λ (nm) passes through a filter or other light-absorbing medium with absorbance OD(λ) at a wavelength λ , the transmitted light intensity per unit surface $I_t(\lambda)$ is calculated from

$$I_t(\lambda) = I_i(\lambda) \cdot 10^{-OD(\lambda)} \quad (V)$$

and is expressed in photons.cm⁻².s⁻¹.

The absorbance OD(λ) is measured with a spectrophotometer.

The absorbed light intensity per unit volume $I_a(\lambda)$ is calculated from

$$I_a(\lambda) = \frac{1}{\ell} \left[I_i(\lambda) - I_t(\lambda) \right] = \frac{I_i(\lambda)}{\ell} \left[1 - 10^{-OD(\lambda)} \right] \quad (VI)$$

and is expressed in photons.cm⁻³.s⁻¹, with ℓ the optical path expressed in cm.

The absorption of a solution is then defined as $\frac{I_a(\lambda) \cdot \ell}{I_i(\lambda)}$

The transmittance is defined as $T = 1 - \frac{I_a(\lambda) \cdot \ell}{I_i(\lambda)} = \frac{I_t(\lambda)}{I_i(\lambda)}$