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**Relevance to Model Experiments to
Photodegradation in the Environment**

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RELEVANCE OF MODEL EXPERIMENTS TO
PHOTODEGRADATION IN THE ENVIRONMENT

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SUMMARY :

An ECETOC Task Force has reviewed the state of the art in photodegradation and is defining what work needs to be done to improve the methodology for assessing the photodegradation of chemicals in the environment.

A definition of criteria for model experiments relevant to photodegradation in the environment, using artificial light, is proposed. Conditions of testing for water, soil and air photodegradations have been assessed and will be presented. The formerly proposed OECD test methods have been criticised in the light of these criteria and are considered unsuitable as official test methods. A derived methodology for aqueous photolysis is proposed in annex.

I. INTRODUCTION

According to legislation expected to be enforced in most Western European countries, any new chemical must be characterised by its degradability when it is released into the environment. Up to now, no well-defined methods for testing the photodegradability of chemicals in air, soil or water have been accepted for legislative purposes. This situation looks reasonable if the final OECD Chemical Testing Program report is considered. In February 1980, this report concluded :

"that none of the methods examined, fully met its objective ; that in no case were test variables sufficiently controlled to ensure reproducibility ; and that there was no significant relationship with degradation in the environment".

The OECD Committee recommended :

"that additional work is needed on each test before it could be regarded as a validated test procedure from which prediction of environmental degradation could be made".

The European Chemical Industry Ecology and Toxicology Center (ECETOC), an organisation of 41 Western European chemical companies formed, in response to the market increase in the need to test and evaluate the potential hazard to man and/or the environment from the industry's products, set up a Task Force with the following terms of reference :

"To review the state of the art in photodegradation, to assess and make a constructive critique of existing test methods ; and to define what work needs to be done to improve the methodology for assessment the photodegradation of chemicals in the environment".

The work of this Task Force began in October 1979 and up to now, general principles for the relevance of model experiments have been put forward ; a methodology for aqueous photodegradation is defined and testing for photodegradability in soil and air is still under discussion.

Photodegradation is one of the possible routes for elimination of man-made chemicals from the environment. This may occur in any medium (air, water, or soil) depending i.a. on the physical and/or chemical properties of the substance. The importance of photo-chemical degradation processes will be different according to the media where they take place. In the atmosphere, photochemically-induced processes will predominate for those chemicals which by volatilization may be present in considerable amounts. In water and soil, biodegradation will always be the most important pathway for elimination of biodegradable man-made chemicals from the environment. It is however possible that environmentally significant concentrations may occur in water for chemicals whose biodegradation is very slow. In those case photodegradation may become important.

When considering photo-reactions in the environment, it is necessary to make a distinction between primary photo-degradation and secondary, chemical degradation. Whereas, in the case of primary photochemistry, light interacts with the test substance directly by absorption, or indirectly by energy transfer from an excited photosensitizer, secondary chemistry involves the reaction of photolytically-generated reactive species with the test material.

These reactive species could be :

- Radicals formed in dissociative processes of photolabile inducers like OH.
- Excited forms of molecules oxygen such as singlet oxygen O_2^* ($^1\Delta g$) formed through excitation of photosensitizers or as O_3 .
- Any reactive species formed in photocatalytic oxidation such as observed with photoconductive metal oxides (TiO_2 , ZnO , MgO , ...).
- Any catalyst generated through a photochemical step, such as a base which catalyses the hydrolysis of the compound in question.

The secondary chemistry involving the reaction of photolytically-generated radicals is of particular importance in air photodegradation. The relative importance of the two classes of photodegradation mechanisms, i.e. primary photochemistry versus secondary can only be estimated experimentally.

2. CRITERIA FOR MODEL EXPERIMENTS

Any experimental method for testing the photo degradation has to cover the following points, if it is to be relevant to photodegradation in the environment.

2.1. The light source ; cells: -----

Although experiments made with natural light are the most relevant for photolysis, existing meteorological conditions in many countries do not permit reproducible experiments. Even in those countries where such experiments are possible, an exact description of test procedures is necessary for comparison of the data observed.

The use of artificial light sources eliminates the above-mentioned difficulties and has the additional advantage that it permits accelerated tests. A prerequisite for the environmental relevance of an irradiation experiment is the practical limitation of the wavelengths in the incident light to values longer than 295 nm. (1, 2, 3, 4, 5, 6)

If this condition is fulfilled any artificial light source is acceptable when the spectral distribution and the intensity of the emitted light is known. The relevance of model experiments does not depend on the spectral distribution of the incident light.

If the choice of the source is not of primary importance for scientific reasons, the type of source used, the filters and the walls of the cells must be precisely defined (nature of the source, nature and age of filters, nature of the walls and geometry of cells, geometry of the incident light). Two technical solutions are possible : either standardizing the whole irradiation device or determining the absolute values of the photons absorbed in every spectral range (i.e. measuring quantum yields).

2.2- Irradiation in solution (7, 8, 9, 10, 11)

- For solution photodegradation, water is recommended as the solvent of choice and the only one of environmental relevance.

- If it is experimentally shown that the photolysis mechanism is not concentration dependent, the concentration to be used is only determined by practical reasons. If the photolysis mechanism is shown to be concentration dependent, the concentration of the solution of the test substance should be as close as possible to the Predicted Environmental Concentration.

- The isolation and identification of the photodegradation product require the use of rather more concentrated solutions. In most cases a material balance is impossible.

- When there is a need to characterize the photodegradation products, it may be necessary to add a co-solvent, to solubilize both the test substance and its degradation products. Up to now, acetonitrile is the recommended co-solvent.

- The question of the environmental relevance of photodegradation experiments with a sensitizer is very controversial. But it is very difficult to propose in a testing method the use of a specific sensitizer, as these are different according to the chemical nature of the product being tested. It is preferable that photolysis tests should be performed in "standardised" water (of relevant pH).

2.3- Irradiation on soil

As said before, model experiments for photodegradation on soil have only been briefly discussed by the ECETOC Task Force. The trends in this field are simply noted below.

The irradiation of materials on silica gel, soil, leaf surfaces or glass plates is described in the literature (12, 13, 14, 15). Modifications of adsorption, emission spectra and photochemical properties have been reported for adsorbed molecules, especially on

silica gel (16). Moreover, silica gel may act as a photocatalyst for hydrolysis. A procedure which is more truly representative of the environmental situation, but which is more tedious and has greater analytical difficulties, is the illumination of material which has been incorporated into soil at concentrations approximating to actual practice, or has been coated onto leaf surfaces in thin films of material.

2.4. Irradiation in air.

Photodegradation in the atmosphere involves at least three major competitive mechanisms which should be taken into account in any experimental method.

- Primary photolysis, if the test substance is absorbing in the spectral range above 295 nm. and decomposes.
- Secondary reactions with OH radicals (a "typical" global background level of OH radical would be 10^5 to 10^7 radicals. mol. l^{-1})
- Secondary reactions with O_3 .

To date, scientific studies rather than test development have been carried out on air photodegradation and only few research groups are working in this field (17) (18)

a) primary photolysis can be examined in a suitable experimental device. It should be noted that wall reactions can play a very large part, but this should not rule out the possibility of environmentally relevant experiments. The wall effects must be investigated by comparing results from vessels with and without surface treatment.

b) secondary photochemistry involving OH and O_3 or any other radicals can also be studied but two further criteria are imposed.

- a known stationary concentration of radicals higher or equal to the typical global background level.
- in the case of smaller vessels the eventual wall effect should be studied by comparing results with or without surface treatment.

2.5. Critique of test methods discussed by OECD

Three methods were particularly discussed in the OECD Chemicals Testing Programme - Degradation/Accumulation Group - Photodegradation.

1. The Fujiki Test - Laboratory Gas Phase Photodegradation Test
2. The EPA Test - Laboratory Water Phase Photodegradation Test
3. The GSF Test - Laboratory Surface Photomineralisation Test

When we consider the above mentioned criteria, we must confirm the conclusions of the final OECD Chemical Testing Programme report that none of the formerly proposed test-methods are relevant to photodegradation in the environment, and are not suitable as official test-methods for photodegradation experiments on chemicals.

The following specific remarks support this conclusion.

2.5.1. Fujiki-Test (18)

To shorten the test duration, no cut-off edge of wavelength at 295 nm is proposed. This allows photoreactions with chemicals at wavelength which cannot be absorbed in the environment.

The test in itself has some intrinsic deficiencies :

- it is only usable for very volatile substances;
- the measured degradation rates are concentration-dependent;
- as a result of the small reactor-volume, wall-effects will be very important;
- the continuous circulation of the irradiated gases with a tube pump provokes absorption and adsorption;
- the purity of the carrier gas is not defined.

2.5.2. EPA-Test (7)

- a) The light source is sunlight using reference compounds as chemical actinometers. The use of sunlight introduces many difficulties, e.g. unsatisfactory reproducibility and long exposure.
- b) There is a problem associated with sample purity and the recommended lowest molar extinction coefficient of any sample to be tested. Chemical purity is not in itself sufficient and must be supplemented by an optical purity.

- c) The quality of the water should be standardised (e.g. pH)
- d) The reaction tubes recommended by E.P.A. are of glasses which are not satisfactory because of the UV cut-off and its tendency to solarize.

2.5.3. - GSF-Test (15)

- a) As already mentioned above, the investigation of photo-reactions in an adsorbed state represent only a special case of degradation processes occurring in the environment.
- b) A more theoretical objection is that we do not know the photomineralisation mechanism.
- c) The test description is in its present state insufficient.

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