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Photodegradation**

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ECETOC COLLOQUIUM

PHOTODEGRADATION

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A. INTRODUCTION

The Chairman in his introduction referred to the work of the ECETOC Task Force Photodegradation-1 published as ECETOC Technical Report no.3 (1). The TF had concluded that for photodegradation screening at the MPD (OECD) or Base-set (EEC 6th Amendment) level, none of the methods proposed to the OECD met the criteria necessary for scientific adequacy and environmental relevance. It was also concluded that at the Base-set or MPD level no photodegradation testing is necessary. Tests are justified only at higher levels (e.g. level 2, EEC). In section C of the Report the bases for developing adequate test methods for photodegradation in air and water were outlined, and recommendation for future work were made.

On the basis of the Report, the ECETOC Scientific Committee has established a TF Photodegradation-2 with the following Terms of Reference :

"To recommend fundamental and/or development studies needed to develop practical tests valid for the requirements of level 2 of the 6th Amendment covering the photodegradation of chemicals in air and water, in that order of priority and importance".

Before starting work, however, it was decided that a Colloquium should be organised to promote technical discussion with outside experts, so as to inform the Task Force of new developments in the scientific community, and so avoid any possible duplication of work in the future.

The Chairman emphasised that the principal aim of the Colloquium was to discuss photodegradation in air, which presents the most difficult problems. Nevertheless, the other aspects of photodegradation in the environment were also briefly discussed.

B. DISCUSSION AND CONCLUSIONS

1. Soil Photodegradation

Dr. Guth gave a short exposé of soil photodegradation testing. It

was the general opinion that, for soil, this type of testing is of minor importance. The distribution coefficients

$\frac{C_{\text{air}}}{C_{\text{water}}}$ and $\frac{C_{\text{air}}}{C_{\text{soil}}}$ permit an estimation of when a chemical is most

likely to be present in soil. There are more complex calculations, which include data on use patterns, but they do not permit anymore accurate estimate of distribution.

2. Photodegradation in the Aqueous Phase

Dr. Philp explained the principles of the protocol for testing photodegradation in water which will be used in a collaborative exercise by 15 industry laboratories (See Technical Report no.3; direct photolysis measurements in the aqueous phase, (1)). The compounds selected for preliminary assessment of the method have been chosen to check the reproducibility and accuracy over the spectral range 295 nm to 400 nm.

Tests will be performed with standard water and with conventional well-specified light sources. An estimation of the mean lifetime for this elimination process can be made from the measured quantum yield for decomposition. Possible interfering factors were discussed, such as the nature of the water (e.g. distilled water, river water, sea water), the exceptionally high reactivity of the thin surface layer (Lovelock 1980), the possible presence of impurities in the chemical tested and its physical state. Physical state arising when compounds with low solubility are dissolved in organic solvents before mixing with water may cause serious experimental difficulties. As the experiments are to be performed at an environmentally relevant pH, the buffers used could also interfere, although it was assumed that this factor can be neglected.

It was concluded that the proposed protocol will give results which are relevant for the prediction of the lifetime of a chemical in the aqueous phase. For comparative purposes a single standard

test using standard distilled water is desirable. If no photodegradation occurs and microbial degradation is also very slow, then further testing in a more environmentally relevant type of water (e.g. sea water, pond water) may be undertaken.

3. Photodegradation in Air

Dr. Philp on behalf of the Task Force, and after him the invited experts, introduced some test procedures currently under investigation by various research teams throughout the world. All methods had been extensively discussed at an International Workshop on "Test Methods and Assessment Procedures for the Determination of the Photochemical Degradation Behaviour of Chemical Substances" - Berlin, December 1980.

In summary the following methods can be mentioned :

- Measurements are made in PTFE bags (Pitts (2), Cox (3)) or in glass chambers (Becker (4)). The test chemical, together with a reference substance, is dispersed homogeneously in the reaction chamber. Afterwards the reactants are added, ozone by direct injection and OH^\bullet in the form of a precursor which is photolysed or decomposed in situ to form OH^\bullet radicals. The disappearance of the test and reference substances is measured using conventional analytical techniques. The ratio of the reaction constants of the test and the reference substance is obtained.
- The methods described by Drs. Zetzsch and Zellner (5) (6) involve a direct OH^\bullet reactivity measurement in a small reaction volume, by Flash Photolysis Resonance Fluorescence or by an Excimer Laser Photolysis System. Both are absolute measurement methods, based on the determination of OH^\bullet consumption.

ECETOC (1) favoured the experimental verification of the primary photochemical reactions with chemicals in the gas phase.

The generally accepted sequence of importance for homogeneous reactions is i) OH^\bullet reactions, ii) O_3 reactions, and iii) direct photolysis. At the Fraunhofer-Institute for Toxicology and Aerosol

Research in Germany heterogeneous photoreactions of chemicals in an aerosol form are to be studied (7).

3.1. Homogeneous reactions in the air

From the discussions it appeared that the sequence of importance $\text{OH}^\bullet > \text{O}_3 > \text{direct photolysis}$ is not so well established as generally thought. HO_2 radical reactions might in some cases be as important as O_3 reactions, and for directly-absorbing chemicals (in daylight) direct photolysis should not be underestimated. For the purposes of further discussion the original sequence: OH^\bullet reactions, O_3 reactions (HO_2^\bullet) and direct photolysis was, however, assumed to be still correct.

3.1.1. OH^\bullet radical reactions

The following conclusions were derived from the discussions :

- a) the two series of experimental methods to determine OH^\bullet reactivity (Becker, Cox, Pitts and Zellner, Zetzsch) give comparable k_{OH^\bullet} values for compounds so far tested.
- b) Both type of methods have their specific limitations, advantages and disadvantages which are schematically summarised in appendix B.
- c) No further developments are necessary concerning the fundamental principles of the existing test methods. The Cox, Becker, Pitts methods could be extended to measurements of k_{OH^\bullet} for chemicals of lower vapour pressure by improving the analytical technique. One limiting factor may be the adsorption of the compound on the walls which would influence the measured decay in the chamber. This can be important if the partial pressure in the system is close to the saturation pressure. The reactivity of cresols, having a vapour pressure of 0,3 mbar at room temperature, has been studied by this technique.

The Zetzsch-Zellner method can be extended to compounds

with low volatility by raising the temperature of the whole system. Wall effects are negligible but the measured rate constants have to be extrapolated down to atmospheric temperatures. Nevertheless, the difficulties anticipated in the course of this development seem easier to overcome than those associated with the technique employing large reaction chambers. Zetzsch has determined rate constants for reactants having a saturation pressure of 10^{-2} mbar with his current apparatus. The fate of chemical compounds of low volatility is however uncertain. There are some observations indicating that removal by OH radicals may be important for these substances.

- d) The reactivity, k_{OH} , permits the calculation of an upper limit for the lifetime of a chemical in the atmosphere.

3.1.2. O₃ reactions

From the discussions the following conclusions can be derived :

- a) No fundamental difficulties exist in measuring O₃ reactivities. Chemiluminescence (8) (9) and absorption spectrometry (10) permit measurement of the disappearance of the ozone (9) (10), while the disappearance of the test material is measured by GLC.
- b) Although the O₃ concentration in the atmosphere is higher than the OH[•] concentration, the study of O₃ reactivity is important only when the lifetime calculated from OH[•] reactions is very long, ie. when the substance does not degrade adequately by photoreaction with OH[•].
- c) The literature suggests that O₃ reactions are fast with hydrocarbons if an adduct can be formed with the O₃ molecule. Olefinic compounds are typical examples, but it is not well established that these are the only chemicals which react with O₃. Thus it cannot be ruled out that O₃ testing may be valuable even for non-olefins, when OH[•] reactions are slow.

3.1.3. HO₂[·] reactions

Prof. Becker, while studying OH[·] radical reactions by the "dark" source $\text{HO}_2\text{NO}_2 \rightleftharpoons \text{NO}_2 + \text{HO}_2^{\cdot}$ has shown that in some cases HO₂[·] reactions may be as important, or more important, than O₃ reactions (e.g. glyoxal $k_{\text{HO}_2} \approx 1.10^{-14}$, formaldehyde $k_{\text{HO}_2} \approx 1.10^{-13}$ in nitrogen)

Studies to date have never given higher reaction rates for HO₂[·] than for k_{OH}. Fundamental studies may be justifiable since concentrations of HO₂[·] are high in the atmosphere ([HO₂[·]] > 100 [OH[·]]). But, as for ozone reactions, consideration of HO₂[·] reactivity is only justifiable when OH[·] photoreactions are too slow.

3.1.4. Direct photolysis

Direct photolysis encompasses all disappearance pathways of the directly photo-excited molecule in the absence or presence of oxygen. These disappearance pathways may consist of e.g. direct photolysis, photoconversion or photo-oxidation. It was concluded that :

- a) It is not certain that direct photolysis can be neglected for chemicals which absorb in the spectrum of light reaching the ground and for which there is an experimental proof of their disappearance in the atmosphere (e.g. aldehydes).
- b) There is no well-established method which permits the measurement of the absorption spectrum and the quantum yield in the same device.
- c) In the development of an experimental method, problems may arise when the quantum yield is pressure- and wavelength-dependent. Gas actinometry is not so well developed, and only a few actinometers are available.

3.2. Photoreactions in an Heterogeneous Phase (Aerosols)

Only a limited time was devoted to this problem yielding several questions and no conclusions.

- a) What is the importance of aerosol studies for chemicals which are released in the atmosphere ? The mean lifetime of an aerosol is about 10 days (11) during which period it is eliminated from the air by precipitation, scavenging or sedimentation. This means that molecules ~~adsorbed~~ or absorbed in an aerosol have to undergo decomposition within this on lifetime.
- b) The mechanism of photodegradation of a chemical in an aerosol or on its surface is not the same as for the chemical in pure air, since the physico-chemical properties of the solid substrate will influence the possible photoreactions (cf. critique of GSF test in ECETOC Technical Report no.3 (1), p.13).
- c) Our knowledge about aerosol **chemistry** is very limited. A research programme investigating this topic has just been started in Germany (7).

APPENDIX 1

ATTENDANCE LIST

Chairman : Prof. Dr. J. Lemaire - Univ. of Clermont-Ferrand

Secretary : Dr. W.J. Bontinck - ECETOC - Brussels

ECETOC :

Dr. J. Leahey	ICI - Plant Prot. Div. Bracknell (GB)
Dr. I. Campbell	ICI - Mond. Div. - Cheshire (GB)
Dr. J.A. Guth	CIBA GEIGY - Basel (CH)
Dr. R. Wilmes	BAYER - Wuppertal (D)
Dr. J. Neu	BASF - Ludwigshafen (D)
Dr. J. Philp	UNILEVER - Bedford (GB)
Dr. O. Klais	HOECHST - Frankfurt (D)
Dr. J.P.C.M. van Dongen	SHELL - Amsterdam (NL)

INVITED EXPERTS :

Prof. Dr. K.H. Becker - Universität - Gesamthochschule , Wuppertal (D)
Dr. R.A. Cox - Atomic Energy Res. Est., Harwell (UK)
Priv. Doz. Dr. R. Zellner - Universität Göttingen (D)
Priv. Doz. Dr. C. Zetzsch - Universität Bochum (D)
Dr. J. König - Fraunhofer Inst. für Toxikologie und Aerosolforschung,
Münster (D)
Dr. R. Schubert - Univ. Brussels - ULB - Consultant to the European
Commission DG XI (B)

APPENDIX 2

OH· RADICAL REACTIONS : METHODOLOGIES

Methodology	Present limitations of use for both type of methodologies	Advantages	Disadvantages
<p><u>Large Chamber Experiments</u></p> <p><u>Glass-vessels :</u> Becker (4)</p> <p><u>PTFE-bags :</u> Cox (3) Pitts (2)</p>	<p>$P_{\text{saturation of chemical}} \geq 10^{-2}$ mbar</p> <p>$k_{\text{OH}\cdot} \geq 3.10^{-13}$ cm³.mol⁻¹.s⁻¹</p> <p>lifetime \leq 1/3 year</p>	<p>- low cost equipment PTFE bag (without NO_x analyser not necessary) + 450.000 BF</p> <p>glass-vessel : < 700.000 BF</p> <p>- glass vessel method permits work at higher temperatures and at different pressures with negligible wall effects</p>	<p>-cost of manpower (1-2 experiments per day - complete study 1-2 weeks)</p> <p>-wall effects with PTFE bag method, possibility of secondary reactions</p> <p>-PTFE bag method limits experiments to atmospheric pressure and room temperature</p> <p>-difficulties to measure slower reacting compounds</p>
<p><u>Laser Flash or Light Flash</u></p> <p><u>Photolysis combined with Resonance Fluorescence :</u></p> <p>Zellner (6) Zetzsch (5)</p>	<p>$k_{\text{OH}\cdot} \cdot P_{\text{sat.chem}} \geq 4.10^{-16}$ cm³.mol⁻¹.s⁻¹.mbar</p> <p>(substances with benzene reactivity can be measured if $p_{\text{sat}} > 4.10^{-4}$ mbar)</p>	<p>- permits study of lower volatile chemicals</p> <p>- possibility to measure a wider range of reaction rates</p> <p>- possibility to work at higher temperatures (Zellner (6))</p> <p>- lower cost of operation</p> <p>- no wall effects</p> <p>- absolute measurements</p>	<p>-cost equipment Zetzsch: 2.10⁶ BF Zellner: 4.10⁶ BF</p> <p>-for compounds with low rate constants possible influence of impurities</p> <p>-analysis of photo-products is difficult</p> <p>-measurement in air at 1 mbar is impossible.</p>

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