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No 7

**Experimental Assessment of the
Phototransformation of
Chemicals in the Atmosphere**

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**EXPERIMENTAL ASSESSMENT OF THE
PHOTOTRANSFORMATION
OF CHEMICALS IN THE ATMOSPHERE**

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Errata :

p. 6 - Table 1 - 10th line α -pinene

p. 7 - (4) - 2nd line read $k_{HO_2}^{-1}$.

p. 24 - 7th line $I(\lambda) = \dots$ in photons.cm⁻².s⁻¹.nm⁻¹.

p. 29 - 9th last line I_0 and $I \doteq \dots$ in photons.cm⁻².nm⁻¹.

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SUMMARY

As a sequel to the recommendations laid down in ECETOC Technical Report No.3, "An Assessment of Test Methods for Photodegradation of Chemicals in the Environment" (3.8.1981) an ECETOC Task Force Photodegradation-2 was set up to recommend fundamental and/or development studies needed to develop practical tests valid for the photodegradation of chemicals in air and water. In this report the Task Force presents its views on test methods covering photo-transformations of chemicals in air.

Two types of photo-induced transformation occur in the atmosphere, viz. direct and indirect. In indirect phototransformations, photochemically-formed reactive species such as hydroxyl radical (OH^\cdot), ozone (O_3), singlet oxygen (O_2^1g), hydroperoxy radical (HO_2) or nitrate radical (NO_3) react with the chemical. Current knowledge indicates that of these reactive species it is mainly OH^\cdot and probably O_3 which in general contribute significantly to the transformation of chemicals. Direct phototransformation may also be important. The contribution of the phototransformation of chemicals adsorbed or absorbed on aerosol particles is at present not sufficiently well understood to allow its relative importance to be estimated.

The Task Force recommends a tiered approach to determine the environmental lifetime of organic chemicals which are phototransformed in air. First, the rate constants of the major phototransformations should be estimated by predictive calculations to give an indication of the relative importance of the possible phototransformation pathways. Criteria are given for deciding which process (or processes) may be significant for a particular compound and which would thus need further investigation. Further development of predictive calculations is recommended.

The second step is to measure the rate constant of the selected process or processes. Various techniques for measuring the rate constant of the reaction of OH^\cdot with a chemical in air are described. The advantages and limitations of these methods are discussed and certain methods are recommended as suitable. To measure the rate constant of the reaction of O_3 with a sufficiently volatile chemical, the virtually identical methods described by Pitts et al.

and Mill et al. are recommended. The measured rate constants allow an estimation of the environmental lifetime.

No suitable experimental protocol for measuring the rate of direct phototransformation of chemicals in the atmosphere has, as yet, been developed. The theory of this process is discussed and general criteria are laid down for a relevant experimental method. The rate should first be estimated on the basis of the light absorption spectrum of the compound, and measurement of the rate constant of disappearance of the compound in the gas phase when irradiated with simulated daylight. The ultimate step is to determine the quantum yield of phototransformation at each wavelength over the range of overlap of the daylight spectrum and the light absorption spectrum of the compound. Knowledge of these quantum yields permits calculation of the environmental lifetime. Further development studies would be necessary to establish suitable test procedures for the second and third stages.

A. INTRODUCTION

In a previous report (ECETOC Technical Report No.3, 3 Aug.1981, "An Assessment of Test Methods for Photodegradation of Chemicals in the Environment"), criteria for the scientific adequacy and environmental relevance of methods for assessing the photodegradation of chemicals were laid down, and proposals for developing suitable methods were made. It is especially important that adequate and relevant methods are available for the provision of information under legislative requirements for the control of chemicals. A second ECETOC Task Force (Photodegradation-2) was therefore set up "to recommend fundamental and/or development studies needed to develop practical tests 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 air is described in this report.

B. BACKGROUND

Phototransformations have to be taken into account for gases and compounds which occur in the gas phase in environmentally significant quantities. The probability that a compound occurs in the gas phase depends not only on its vapour pressure but also on its water solubility and adsorption/desorption behaviour. Therefore even substances having a relatively low vapour pressure, e.g. down to 10^{-3} Pa*, can be found in the atmosphere in measurable quantities (Giam et al., 1980; Eisenreich et al., 1981). Whether abiotic degradation in the atmosphere can contribute significantly to the overall degradation of such compounds is still under discussion.

* 1 Pa (Pa = Pascal) = 1 Newton.m⁻²; 1 bar = 10⁵ Pa; 1 Torr = 133 Pa.

The main transformations leading to the removal of chemicals from the atmosphere involve reactions with photochemically-generated species such as the hydroxyl radical (OH^\bullet), ozone (O_3), hydroperoxyl radical (HO_2^\bullet), singlet oxygen ($\text{O}_2 \Delta_g$) and nitrate radical (NO_3^\bullet). Direct phototransformation, i.e. all transformations resulting from direct photo-excitation of the molecule, may also be important. These reactions were discussed at an ECETOC Colloquium in 1981 from which much of the following picture emerged.

It is broadly agreed that reaction with OH^\bullet is the dominant photo-induced reaction of hydrocarbons in the atmosphere. The only class of compounds known not to react with OH^\bullet are the fully-halogenated alkanes (see e.g. Atkinson et al., 1979; Mill et al., 1981; Wuebbles and Cornell, 1981), as can be seen from Table 1 in which quantitative data are given for reactions of a number and variety of compounds with OH^\bullet , O_3 and HO_2^\bullet . Reactions with OH^\bullet are generally the fastest. Only for some alkenes, alkadienes or terpenes does the rate of removal by O_3 exceed that by OH^\bullet , and in these cases the lifetime derived from k_{OH^\bullet} is, in any case, very short, i.e. a fraction of a day. The similarity between the reaction of OH^\bullet and O_3 molecules with these unsaturated hydrocarbons explains these observations in that both add to the double bond forming an addition complex which afterwards disintegrates to the reaction products. In those cases where abstraction of an H atom by OH^\bullet is the dominant pathway the competitive reaction with O_3 is expected to be very much slower. It follows from the above that reaction with O_3 is usually of secondary importance in considering the fate of organic chemicals in the atmosphere. Reaction with O_3 is, however, of interest when atmospheric processes related to smog formation (where higher levels of O_3 occur) are involved. From the limited number of results it seems that reactions with HO_2^\bullet are of secondary importance (cf. Table 1). Some evidence has been obtained that alkenes, phenols and cresols react with NO_3^\bullet radicals formed in photochemical smog systems (Jason and Niki, 1975 ; Carter et al., 1981), but the number of results is again small and the studies were exploratory. It is therefore concluded that these NO_3^\bullet reactions are only of limited importance and apply only to special environmental situations, e.g. at night in a moderately polluted atmosphere. The rate constants for reactions with singlet oxygen are, according to our present knowledge, very low and this reaction can be neglected as an elimination pathway for organic molecules (Heicklen, 1976).

Direct phototransformation is a possible removal pathway only for those chemicals which absorb in the region of solar radiation. There are

insufficient data to allow an assessment of its relative importance compared to the removal by photochemically-produced radicals (Table 1).

Chemicals may be sorbed onto aerosol particles from the vapour phase, and thence removed from the atmosphere with the aerosol. The mechanism of phototransformation of a chemical in an aerosol is not the same as that of the chemical in air since its adsorbed or absorbed state, and the physicochemical properties of the aerosol substrate, will influence the reactions. It is still not at all clear whether, in practice, the phototransformation of chemicals in aerosols contributes significantly to the overall removal of compounds of low volatility (Cupitt, 1980; Heicklen, 1981-a).

In view of the above, the Task Force decided to limit its considerations to test methods and current work on the reactions of OH^{\cdot} and O_3 , and direct photolysis. It found that the experimental principles for measuring OH^{\cdot} and O_3 reactivity in an environmentally-relevant way are reasonably well-established. On the other hand, direct photolysis in the vapour phase has not been studied in the same depth and therefore the Task Force concentrated on defining the criteria which are important for environmentally relevant measurements of this.

TABLE 1

RATE CONSTANTS AND ENVIRONMENTAL HALF-LIVES FOR REACTIONS WITH OH[•], O₃, HO₂[•] AND

FOR DIRECT PHOTOLYSIS

k in cm³.molecule⁻¹.s⁻¹ and t_{1/2} in days

(Mill et al., 1981; Barnes et al., 1981; De More et al., 1982)

All rate constants (k) are expressed in units of cm³.molecule⁻¹.s⁻¹, and half-lives in days.

Compound	10 ¹² .k _{OH[•]}	t _{1/2} ^{OH[•]} (1)	10 ¹⁸ .k _{O₃}	t _{1/2} ^{O₃} (2)	Direct photolysis t _{1/2} (3)	10 ¹⁸ .k _{HO₂[•]}	t _{1/2} ^{HO₂[•]} (4)
Alkanes							
methane	0.0077	1,000	1.4x10 ⁻⁶	6.0x10 ⁶			
ethane	0.27	30	1.2x10 ⁻⁶	7.0x10 ⁶			
propane	1.1	7.3	6.8x10 ⁻⁶	1.0x10 ⁶			
iso-butane	2.2	3.6	2.0x10 ⁻⁶	4.0x10 ⁶			
n-butane	2.7	3.0	9.8x10 ⁻⁶	8.0x10 ⁵		<3.0	<1.3x10 ⁴
Haloalkane bromomethane	0.038	210			1.5x10 ⁵		
Aldehydes							
formaldehyde	10	0.8			0.23	6.0x10 ⁴	0.6
acetaldehyde	16	0.5	3.4x10 ⁻²	235	1.1		

TABLE 1 (contd.)

Compound	$10^{12} \cdot k_{OH^\bullet}$	$t_{OH^\bullet}^{1/2}$ (1)	$10^{18} \cdot k_{O_3}$	$t_{O_3}^{1/2}$ (2)	Direct photolysis $t_{1/2}$ (3)	$10^{18} \cdot k_{HO_2^\bullet}$	$t_{HO_2^\bullet}^{1/2}$ (4)
Alkenes							
ethene	8	1.0	1.9	4.2		<3.0	<1.3x10 ⁴
propene	25	0.3	13	0.6		<3.0	<1.3x10 ⁴
1-butene	35	0.2	12	0.7		<3.0	<1.3x10 ⁴
2-butene							
cis-	54	0.2	160	0.05			
trans-	70	0.1	260	0.03			
2-methyl-2-butene	80	0.1	490	0.02			
2,3-dimethyl-2-butene	153	0.05	1510	0.005		<40	<10x10 ³
1-pentene	30	0.3	10.7	0.75			
cis-2-pentene	65	0.1	450	0.02			
1-hexene	32	0.25	11	0.7			
1-heptene	36	0.2	8.1	1.0			
cyclohexene	71	0.1	170	0.05			

TABLE 1 (contd.)

Compound	$10^{12} \cdot k_{OH} \cdot$	$t_{1/2}^{OH} (1)$	$10^{18} \cdot k_{O_3}$	$t_{1/2}^{O_3} (2)$	Direct photolysis $t_{1/2} (3)$	$10^{18} \cdot k_{HO_2}$	$t_{1/2}^{HO_2} (4)$
<u>Halalkenes</u> Ethene: chloro- trichloro- tetrachloro-	6.6 2.2 0.17	1.2 3.6 47	2.0 6.0×10^{-3} 1.7×10^{-3}	4.0 1.3×10^3 4.7×10^3			
<u>Alkadiene</u> 1,3-butadiene	77	0.1	8.4	0.95			
<u>Terpene</u> -pinene	26	0.3	160	0.05			
<u>Alkyne</u> Ethyne	0.73	11	7.8×10^{-2}	100			
<u>Alkanes</u> benzene: methyl- 1,2-dimethyl- 1,3-dimethyl- 1,4-dimethyl- 1,3,5-trimethyl- ethyl- 2-propyl-	1.4 5.9 13 20 10 49 7.5 7.8	5.7 1.3 0.6 0.4 0.8 0.2 1.1 1.0	4.6×10^{-5} 2.8×10^{-4} 1.6×10^{-3} 1.3×10^{-3} 1.6×10^{-3} 7.0×10^{-3} 5.6×10^{-4} 5.8×10^{-4}	1.7×10^5 2.9×10^4 5.0×10^3 6.2×10^3 5.0×10^3 1.1×10^3 1.4×10^4 1.4×10^4			

Notes on Table 1.

(1) The half-life for reaction with OH[•] is :

$$t_{1/2}^{\text{OH}^\bullet} = \ln 2 \times k_{\text{OH}^\bullet}^{-1} \times [\text{OH}^\bullet]^{-1}$$

Assuming an average tropospheric OH[•] concentration over the year of 10⁶ molecules.cm⁻³, the half-life is :

$$t_{1/2}^{\text{OH}^\bullet} = 8.0 \times 10^{-12} \times k_{\text{OH}^\bullet}^{-1}$$

(2) The half-life for reaction with O₃ is :

$$t_{1/2}^{\text{O}_3} = \ln 2 \times k_{\text{O}_3}^{-1} \times [\text{O}_3]^{-1}$$

Assuming an average tropospheric ozone concentration of 1x10¹² molecules.cm⁻³, the half-life is :

$$t_{1/2}^{\text{O}_3} = 8.0 \times 10^{-18} \times k_{\text{O}_3}^{-1}$$

(3) cf. this report section C.2.3.2.iii.

(4) The half-life for reaction with HO₂[•] is :

$$t_{1/2}^{\text{HO}_2^\bullet} = \ln 2 \times k_{\text{HO}_2^\bullet} \times [\text{HO}_2^\bullet]^{-1}$$

Assuming an average [HO₂[•]] of 2x10⁸ molecules.cm⁻³, the half-life is :

$$t_{1/2}^{\text{HO}_2^\bullet} = 4.0 \times 10^{-14} \times k_{\text{HO}_2^\bullet}^{-1}$$

A more detailed discussion of the estimation of the atmospheric lifetimes of chemicals is presented by Heicklen (1982).

C. ASSESSMENT OF CURRENT TEST METHODS

As a first step in assessing the phototransformation of a chemical, the relative importance of the reactions with OH[·] and O₃, and direct photolysis may be estimated from predictive calculations. The results from these can then be used to decide which phototransformation process, or processes, merit experimental investigation.

1. Predictive Calculations

Calculations have been described for estimating OH[·] and O₃ rate constants (Mill et al., 1981; Heicklen, 1981-b). These involve predicting the reactivities of each portion of the molecule and summing the rate constants derived for each of these. Brief descriptions of the procedures are given in Appendix 1. As the amount of data on k_{OH[·]} and k_{O₃} for different molecules increases and more information on the influence of specific substituent groups is obtained, this semi-theoretical approach for estimating rate constants will gain in accuracy (Atkinson, 1982-a; Zellner, 1982).

Zetzsch (1982) showed that a good correlation exists between the electrophilic substituent constant (Brown and Okamoto, 1958) and k_{OH[·]} for mono- and poly-substituted benzenes. For those reactions where the addition of OH[·] to the benzene ring is the first step, k_{OH[·]} rate constants were deduced which deviated from experimental values by less than a factor of two.

For direct photolysis the absorption spectrum is measured and a maximum rate is calculated, assuming a quantum yield of unity over all wavelengths where absorption occurs at above 295 nm (cf. Appendix 2), (Cupitt, 1980; Mill et al., 1981; Pitts et al., 1981-a).

Once the relative importance of the three basic reaction pathways is determined, an experimental investigation of the dominating process or processes should be performed. Any process for which the estimated environmental lifetime is one to two orders of magnitude longer than that of the dominating process should not be further investigated (Mill et al., 1981).

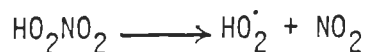
2. Experimental Determination of Rate Constants.

2.1. OH[•] Phototransformations

2.1.1. Large-chamber techniques. The chemical is introduced into a large (>40 litres) chamber together with a source of OH[•], and its concentration is periodically monitored over the duration of the experiment, normally 0.5 to 24 hours. The OH[•] is thermochemically or photochemically produced but the concentration is not monitored and therefore a reference compound of known $k_{OH^{\bullet}}$ is added. The rate constant of the chemical is computed from the decay curves of the test and reference compound, taking into account their individual concentrations. This method therefore yields a rate constant calculated from the rate of reaction relative to a standard compound (see e.g. Akimoto et al., 1979; Barnes et al., 1982-a and b; Cox et al., 1980-a; Cox, 1980-b; Cox, 1981; Klöpffer and Kohl, 1981-a; Klöpffer, 1982-a; Pitts et al., 1981-b and Wu et al., 1976).

The following equipment is necessary :

- Teflon bags or glass containers, with ports for the introduction of OH[•] precursors and the test chemical, and for taking samples for analysis;
- OH[•] source, which can be chosen from
 - i) thermal decomposition of HO₂NO₂ in the presence of NO (Barnes et al., 1982-a).



- ii) photochemical oxidation of alkene/NO_x mixtures (Klöpffer, 1982-a; Barnes et al., 1982-a).

- iii) photolysis of HONO (Cox, 1981)



- iv) photolysis of CH₃ONO/NO/O₂ mixtures (Pitts et al., 1981-b)



- gas handling system
- light sources providing the necessary photon flux for the

- photochemical generation of OH^{*} (ii to iv);
- analytical equipment for monitoring the test and reference compound.

The experiments are normally performed at atmospheric pressure and room temperature. Clean air is used as the diluent. A technique has been developed for dispersing chemicals of low volatility (Klöpffer, 1982-b).

Detailed experimental descriptions are available (Cox, 1981; Pitts et al., 1981-b; Barnes et al., 1983-a).

2.1.2. Flash or laser photolysis. Methods have been developed for determining the absolute rate constants of the reaction of OH^{*} with chemicals, based on flash or laser photolysis combined with resonance fluorescence determination of the OH^{*} radical.

In the Flash or Laser Photolysis Resonance Fluorescence (FPRF or LPRF) method (Atkinson et al., 1979; Lorenz and Zellner, 1981, 1982, 1983; Zellner, 1982; Zetsch, 1981) a gas mixture containing the reactant and an OH^{*} precursor diluted in an inert gas, are passed through the reaction vessel (total pressure $<1 \times 10^5$ Pa when Ar or He are used as a diluent gas). An intense flash, or the pulse of a laser, photolyses the precursor (H₂O or HNO₃), yielding OH radicals which react with the test compound (time <1 s). The disappearance of the radicals is monitored by resonance fluorescence. An OH^{*} resonance lamp excites a small fraction of the radicals, the fluorescence signal of which is measured by a photon-counting device. The reactant concentration exceeds that of the OH radicals so that their rate of disappearance is controlled by the reactant concentration and the rate constant. This product can be obtained from the semilog plot of the fluorescence signal versus time, but the use of a small desk computer to fit the decay curve is preferable.

The reaction chamber has, typically, a volume of about 1 litre but the reaction is monitored in a much smaller volume in the centre of the vessel where the light beams cross. Any interference by the walls is thus excluded. With a continuous gas flow the build-up of reaction products is avoided. Nevertheless, separate experiments at various

concentrations have to be performed in order to prove that apparent first-order reaction conditions apply.

2.1.3. Other Methods . Various authors (Güsten et al.,1981; Klöpffer,1981-b) have suggested that the study of OH[•] reactivity in water yields values comparable to those of the reaction in the gas phase. However, there are insufficient data to decide whether this technique is an adequate alternative to the more elaborate methods described here. If valid, it could be useful for estimating reaction rate constants of compounds of low volatility where it is difficult to maintain the compound in the vapour phase.

2.1.4. Comments on techniques. The above techniques have advantages and disadvantages, the most prominent of which are discussed below.

- a) Influence of pressure. While the rate of reaction seems to be independent of pressure for direct H-abstraction, this does not hold when an intermediate addition compound is formed. In this case the overall rate constant is pressure-dependent at low total pressures and will reach a limiting high pressure value as the total pressure increases.
- b) Presence of water vapour. In one experimental protocol (Cox,1981) it is suggested that a few percent of water vapour may be added in order to mimic normal environmental conditions, but there is no proof that water vapour has any effect on $k_{OH^{\bullet}}$.
- c) Influence of oxygen. It has been shown that oxygen can influence the $k_{OH^{\bullet}}$, especially for sulphur-containing compounds (Barnes et al.,1983-b), so that although the measured result is environmentally relevant it is not a "pure" $k_{OH^{\bullet}}$.
- d) Purity of chemical. In any direct determination of the absolute rate constant, the reagents used must be of high purity. This is particularly true in the FPRF and LPRF techniques where the concentration changes are assumed to originate exclusively from reaction with the major chemical constituent of the substance tested . As this rate constant is lower for less reactive molecules, side reactions with reactive minor constituents will contribute disproportionately to the observed fall in OH radical