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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 ($\text{OH}^\bullet$), ozone (O_3), singlet oxygen (O_2^1 g), hydroperoxy radical (HO_2) or nitrate radical (NO_3) react with the chemical. Current knowledge indicates that of these reactive species it is mainly $\text{OH}^\bullet$ 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 $\text{OH}^\bullet$ 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 = 10^5 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 ($\text{OH}^\bullet$), ozone (O_3), hydroperoxyl radical ($\text{HO}_2^\bullet$), singlet oxygen ($\text{O}_2 \Delta_g$) and nitrate radical ($\text{NO}_3^\bullet$). 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 $\text{OH}^\bullet$ is the dominant photo-induced reaction of hydrocarbons in the atmosphere. The only class of compounds known not to react with $\text{OH}^\bullet$ 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 $\text{OH}^\bullet$, O_3 and $\text{HO}_2^\bullet$. Reactions with $\text{OH}^\bullet$ are generally the fastest. Only for some alkenes, alkadienes or terpenes does the rate of removal by O_3 exceed that by $\text{OH}^\bullet$, and in these cases the lifetime derived from $k_{\text{OH}^\bullet}$ is, in any case, very short, i.e. a fraction of a day. The similarity between the reaction of $\text{OH}^\bullet$ 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 $\text{OH}^\bullet$ 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 $\text{HO}_2^\bullet$ are of secondary importance (cf. Table 1). Some evidence has been obtained that alkenes, phenols and cresols react with $\text{NO}_3^\bullet$ 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 $\text{NO}_3^\bullet$ 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 $\text{OH}^{\cdot}$ and O_3 , and direct photolysis. It found that the experimental principles for measuring $\text{OH}^{\cdot}$ 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	$10^{12} \cdot k_{OH^{\bullet}}$	$t_{1/2}^{OH^{\bullet}} (1)$	$10^{18} \cdot k_{O_3}$	$t_{1/2}^{O_3} (2)$	Direct photolysis $t_{1/2} (3)$	$10^{18} \cdot k_{HO_2^{\bullet}}$	$t_{1/2}^{HO_2^{\bullet}} (4)$
Alkanes							
methane	0.0077	1,000	1.4×10^{-6}	6.0×10^6			
ethane	0.27	30	1.2×10^{-6}	7.0×10^6			
propane	1.1	7.3	6.8×10^{-6}	1.0×10^6			
iso-butane	2.2	3.6	2.0×10^{-6}	4.0×10^6			
n-butane	2.7	3.0	9.8×10^{-6}	8.0×10^5		<3.0	< 1.3×10^4
Haloalkane bromomethane	0.038	210			1.5×10^5		
Aldehydes formaldehyde acetaldehyde	10 16	0.8 0.5	3.4×10^{-2}	235	0.23 1.1	6.0×10^4	0.6

TABLE 1 (contd.)

Compound	$10^{12} \cdot k_{OH^\bullet}$	$t_{OH^\bullet}^{(1)}$ 1/2	$10^{18} \cdot k_{O_3}$	$t_{O_3}^{(2)}$ 1/2	Direct photolysis $t_{1/2}^{(3)}$	$10^{18} \cdot k_{HO_2^\bullet}$	$t_{HO_2^\bullet}^{(4)}$ 1/2
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	$10^{12} \cdot k_{OH^\bullet}$	$t_{1/2}^{OH^\bullet} (1)$	$10^{18} \cdot k_{O_3}$	$t_{1/2}^{O_3} (2)$	Direct photolysis $t_{1/2} (3)$	$10^{18} \cdot k_{HO^\bullet_2}$	$t_{1/2}^{HO^\bullet_2} (4)$
<u>Haloalkenes</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 $\text{OH}^\bullet$ is :

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

Assuming an average tropospheric $\text{OH}^\bullet$ concentration over the year of 10^6 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 O_3 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 1×10^{12} 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 $\text{HO}_2^\bullet$ 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 $[\text{HO}_2^\bullet]$ of 2×10^8 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 $\text{OH}^\bullet$ and O_3 , 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 $\text{OH}^\bullet$ and O_3 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 $k_{\text{OH}^\bullet}$ and k_{O_3} 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 $k_{\text{OH}^\bullet}$ for mono- and poly-substituted benzenes. For those reactions where the addition of $\text{OH}^\bullet$ to the benzene ring is the first step, $k_{\text{OH}^\bullet}$ 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 $\text{OH}^{\bullet}$ (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 $\text{OH}^{\bullet}$ with chemicals, based on flash or laser photolysis combined with resonance fluorescence determination of the $\text{OH}^{\bullet}$ 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 $\text{OH}^{\bullet}$ 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 (H_2O or HNO_3), yielding OH radicals which react with the test compound (time < 1 s). The disappearance of the radicals is monitored by resonance fluorescence. An $\text{OH}^{\bullet}$ 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

concentration, leading to unacceptable errors in the calculated rate constant. This situation does not arise where the experimental design includes some means of monitoring the individual reactant concentrations.

In a large-chamber experiment where the time-dependent concentration of test compound is determined analytically, no presumption is made about the exclusive interaction of the OH radicals. Variations in the latter are taken into account by the inclusion of the reference compound and its simultaneous analytical determination. In this way the reactive impurities will compete for OH radicals with both the test and reference compounds.

- e) Wall and side reactions. In the large-chamber technique, loss of test compound by adsorption on the walls has to be minimised by maintaining the partial pressure of the reactants well below their saturation pressure. This limits the technique to compounds with saturation pressures far above 10 Pa. In addition, continuous oxidation of the materials present may produce high concentrations of other radicals and/or O_3 , leading to a faster loss of reactants. Therefore in the Cox (1981) and Pitts (1981-b) techniques the duration of the experiment is limited to less than 1 hour so that the measured disappearance of the test chemical is controlled only by the reaction with OH $\cdot$. This, in fact, determines the lower limit of detectable removal rates as : $k_{OH\cdot} > 3 \times 10^{-13} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$. (Atkinson et al., 1982-c,d).

In the FPRF and LPRF techniques, direct photolysis of the reactant may yield products which consume OH $\cdot$ in competitive reactions. In those cases where side reactions are expected, additional experimentation will be necessary to find the optimal conditions for eliminating or minimizing these.

- f) Temperature dependence. The abstraction of an H atom by OH $\cdot$ has a positive activation energy which means that $k_{OH\cdot}$ increases with temperature. On the other hand the rate constants of the addition reactions of OH $\cdot$ decrease as temperature increases. The temperature-dependence of $k_{OH\cdot}$ for aromatic compounds is more

complex since they can react with OH[•] by both addition and H[•] abstraction.

Temperature dependence will, in general, be of secondary importance in estimating atmospheric lifetime. Although the temperature in the troposphere decreases with altitude, uncertainties in the distribution of OH[•] concentration will far outweigh errors due to measuring reaction rates at room, rather than tropospheric, temperature. The $k_{OH^{\bullet}}$ of reactions (e.g. of methane, halogenated methanes) with relatively high activation energies corresponding to long lifetimes, can be corrected for temperature dependence (Handwerk and Zellner, 1978) :

$$k_{OH^{\bullet}}^T = k_{OH^{\bullet}}^{T_0} \left[1 - \exp\left(-\frac{E_i}{R} \cdot \alpha \cdot Z\right) \right] \cdot \left(\frac{E_i}{R} \cdot \alpha \cdot Z\right)^{-1}$$

$k_{OH^{\bullet}}^T$ = rate constant at temperature T (K)

$k_{OH^{\bullet}}^{T_0}$ = experimental rate constant at T_0 (290K)

E_i = activation energy in Joule.mole⁻¹

R = gas constant (8.31 Joule.K⁻¹.mole⁻¹)

α = $(\Delta T / \Delta Z) \cdot T_0^{-2}$

$\Delta T / \Delta Z$ = temperature gradient (-6.5 K.km⁻¹)

Z = average height of troposphere (12 km)

The use of elevated temperature can be useful to circumvent the adsorption or condensation of chemicals of low volatility, but in this case the temperature-dependence has to be known in order to extrapolate the results to ambient temperature. For measurements at above room temperature the FPRF or LPRF methods are very suitable since the apparatus is easy to thermostat. A procedure for such measurements is described by Atkinson et al.,(1979) and Zellner, (1982).

- g) Reaction products. One potential advantage of large-chamber experiments is that they allow the accumulation of the oxidation

products for analysis. Only a few compounds have been so studied, e.g. $\text{CS}_2 + \text{OH}^\cdot$ (Barnes et al., 1983-b); hydrocarbons, especially CH_4 (Atkinson et al., 1979; Heicklen, 1976); and chloroethylenes (Voigt, 1982). Little is known about the photo-transformation products of aromatics.

2.1.5. Comparison of techniques. Each technique for investigating $\text{OH}^\cdot$ reactions has its advantages and limitations, summarised in Table 2. Within the limits of accuracy of the methods, the relative and absolute measurement techniques yield comparable values for the rate constants. This is demonstrated in Table 3 in which relative values from large-chamber experiments are compared with absolute values obtained mostly by FPRF. The LPRF and FPRF techniques have a higher sensitivity and a larger range of application. They also allow the measurement of $k_{\text{OH}^\cdot}$ for reactants having a rather low saturation pressure

$$(k_{\text{OH}^\cdot} \times p_{\text{sat}} > 4.10^{-18} \text{ Pa. cm}^3 \cdot \text{molecule}^{-1} \text{ s}^{-1}).$$

However, the large-chamber technique has the advantage that with minor modification it can also be used to measure O_3 reactions and can operate at higher pressure. (see 2.2 below). The latest relative measurements have shown excellent agreement with those from absolute techniques (Atkinson et al., 1982-d; 1983).

Degradation by photochemically-produced radicals has been studied for a long time, and a large number of research groups have been involved. Nevertheless the determination of a rate constant is difficult and possible side reactions have to be taken into account for each study. Accurate data can be expected only if the work is carried out by an experienced photochemist.

2.1.6. Conclusions. The large-chamber and flash or laser photolysis techniques described above are adequate for determining the rate constant of reaction of a chemical with $\text{HO}^\cdot$ in the atmosphere, provided that this is carried out by an experienced photochemist.

TABLE 2
COMPARISON OF METHODS FOR DETERMINING $k_{OH\cdot}$

	Flash or laser photolysis with resonance fluorescence	Large chamber technique
Type of measurement	Absolute value of $k_{OH\cdot}$	Relative value of $k_{OH\cdot}$
Species monitored	$OH\cdot$ disappearance at constant reactant concentration	Disappearance of reactant and reference compound compared at undefined $OH\cdot$ concentration
Total pressure in system	Normally, 10^3 - 10^5 Pa	Atmospheric
Diluent gas	Normally Helium, Argon, Nitrogen. Oxygen concentration limited.	Air
Main equipment	Reaction vessel (ca. 1 litre) Flash-light or laser resonance lamp Gas handling system Photon-counting device plus signal averager	PTFE bag or glass reaction vessel (40 - 500 l.) Fluorescence lamps Gas handling system Analytical equipment and NO_x analyser
Sensitivity	$k_{OH\cdot} > 10^{-15} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ if $k_{OH\cdot} \times P_{\text{sat}}$ is $> 4 \times 10^{-18} \text{ Pa} \cdot \text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$	$k_{OH\cdot} > 3 \times 10^{-13} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$
Saturation pressure (P_{sat}) of test chemical	Vessel can be heated, therefore P_{sat} limited only by temperature attainable	P_{sat} must be well above 10 Pa
Interfering factors	Impurities in chemical compete in $OH\cdot$ consumption. No wall reactions	Impurities generally do not interfere. Wall reactions interfere
Product analysis	Difficult because of low concentration	Feasible because of larger reaction volume and conversion

TABLE 3
COMPARISON OF k_{OH} RATE CONSTANTS ($10^{12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) MEASURED BY RELATIVE (LARGE-CHAMBER)
AND ABSOLUTE (FPRF or LPRF) METHODS

Compound	Relative Measurements, Large Chamber		Absolute Measurements	
	Cox et al. (1980-a) Cox (1980-b)	Atkinson et al. (1979) Atkinson et al. (1982-b) Atkinson et al. (1982-d) Becker and Fink (1982) 40 l = B1; 420 l = B2 Klopffer (1982-a,b) (K)	LPRF Zellner (1983)	FPRF Atkinson et al. (1979) (1982-d) (A); DeMore et al. (1982) (M)
Alkanes ethane propane n-butane iso-butane n-pentane neo-pentane iso-pentane 2-methyl-pentane 2,3-dimethyl butane n-hexane cyclohexane	1.9 5.0 3.5 5.0 3.8	0.29 1.6-2.2 2.6-2.9 1.9 4.1 0.77 3.1 5.0 6.3-4.3-5.4 5.7 6.2-6.7-7.5-7.6	0.25 1.3 2.5 2.3 3.9 6.8	1.1 (M) 2.4-2.7 (A) 2.5 (A) 0.82-0.91 (A) 7.4 (A) 8.0 (A)
Alkenes ethene propene iso-butene 1-butene cis-2-butene trans-2-butene 2-methyl-2- butene cyclohexene 2,3-dimethyl-2- butene	8.0 24.0 63	8.5 25 27 48 62-59 68 86 62-73 108	8.8 - 9.7 30 50 38 67	8.0 (M) - 7.9 (A) 25 (A) 35 (A) 52 (A) 54 (A) 70 (A) 78 (A) - 87 (A) 110 (A) - 122 (A)

TABLE 3 (continued)

Compound	Relative Measurements, Large Chamber			Absolute Measurements	
	Cox et al.(1980-a) Cox (1980-b)	Atkinson et al.(1979) Atkinson et al.(1982-b) Atkinson et al.(1982-d)	Becker and Fink(1982) 40 I = B1; 420 I = B2 Klöpffer (1982-a,b) (K)	LPRF Zellner (1983)	FPRF Atkinson et al.(1979) (1982-d)(A); DeMore et al.(1982) (M)
Conjugated alkenes 1,3-butadiene isoprene	79	73 96	69(B1), 62(B2)	65	69 (A) 93 (A)
Halogenated alkene trichloro-ethene		2.1	3.0 (K)		2.4 (A) 2.2 (M)
Aldehydes formaldehyde acetaldehyde		6.5-14 15		14	10 (M) 16 (A)
Alcohols methanol ethanol iso-propanol		1.1 3.3 6.7	1.0 (B2) 3.2 (B1), 3.7(B2) 6.9 (B2)	0.80 2.9 4.1	1.0 (A) 2.5 (A) 5.5 (A)
Ether tetrahydro- furan		14			16 (A)

TABLE 3 (continued)

Compound	Relative Measurements, Large Chamber		Absolute Measurements	
	Cox et al. (1980-a) Cox (1980-b)	Atkinson et al. (1979) Atkinson et al. (1982-b) Atkinson et al. (1982-d)	Becker and Fink (1982) 40 I = B1; 420 I = B2 Klöpper (1982-a,b) (K)	LPRF Zellner (1983) FPRF Atkinson et al. (1979) (1982-d) (A); DeMore et al. (1982) (M); Zetsch (1982) (Z)
Aromatic hydrocarbons benzene : methyl- ethyl- n-propyl- 1,2-dimethyl- 1,3-dimethyl- 1,4-dimethyl- 1,2,3-trimethyl- 1,2,4-trimethyl- 1,3,5-trimethyl- diphenyl naphthalene	0.8 7.2 13 19	<2.8 3.9 7.5 5.8 12 21 12 25 33 49	1.2 (B1), 1.1 (B2); 1.1 (K) 6.1 (B1) 13 (K) 7.4 (K) 20 (K)	1.1 1.2 (A); 1.1 (Z) 6.4 (M); 5.5 (A) 8.0 (A) 5.9 (A) 13 (A); 14 (Z) 24 (A); 24 (Z) 13 (A) 27 (A) 35 (A) 52 (A) 5.8 (Z) 19 (A)
Phenol o-cresol		4.7		34-4.7 (A)
Halogenated aromatics p-dichloro- benzene 1,2,4-trichloro- benzene			0.48 (K) 0.6 (K)	0.33 (Z) 0.52 (Z)

2.2. O_3 Phototransformations

2.2.1. Review of methods. Most of the techniques developed for studying the reactions of O_3 with organic chemicals have been directed to evaluating the fate of chemicals in smogs (Herron et al., 1979). The most comprehensively-described methods for measuring the rate of reaction of O_3 with (small) organic molecules in the atmosphere are those of Mill et al. (1981) and Pitts et al. (1981-c). They involve measuring the rate of loss of O_3 from a mixture of O_3 with the chemical and pure air in a Teflon bag. Loss of O_3 results from reaction at the wall of the chamber (rate constant k_w) or with the chemical (rate constant k_{O_3}), where

$$-\frac{d[O_3]}{dt} = k_w + k_{O_3} \cdot [\text{chemical}] [O_3]$$

An excess of the chemical at least ten-fold relative to O_3 is used, and the concentration of the test compound is assumed to be constant throughout the reaction, so that

$$-\frac{d \ln [O_3]}{dt} = k_w + k_{O_3} \cdot [\text{chemical}]$$

The equipment is similar to that used for k_{OH} determination (cf. C, 2.1.1) and consists of:

- a Teflon bag or other reaction vessel, with ports for the introduction of O_3 and the test chemical, and for taking samples for analysis;
- a generator yielding between 1 and 5% O_3 in air;
- a chemiluminescence O_3 analyser;
- a gas handling system;
- analytical equipment for monitoring the test and reference compound.

k_w is first measured by monitoring the rate of loss of O_3 from a mixture of O_3 in air at the concentration as used in the

experiment, and in the absence of the chemical. Then, from the experiment with excess of the chemical $-\frac{d \ln [O_3]}{dt}$ is plotted

against the concentration of the chemical to yield a straight line of slope k_{O_3} and intercept k_w .

The partial pressure of the test chemical should be far below its saturation pressure (cf. 2.1.3.e). Because the reaction is monitored by following $[O_3]$, the method is sensitive to reactive impurities in the test compound and the build-up of reaction products.

2.2.2. Conclusions. The Pitt's technique allows ozone rate constants of above $10^{-20} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ to be adequately measured for compounds at concentrations of up to 10 ppm in the gas phase, which encompasses the reactivities of interest from an atmospheric point of view.

2.3. Direct phototransformation of molecules irradiated with polychromatic light in the gas phase.

Although much literature is available on photochemical and photo-physical primary processes in the gas phase, very little work has been published on the prediction of the environmental degradation rate by direct photolysis (Mill et al, 1981). It has therefore been decided, in this report, to concentrate on defining the experimental criteria necessary for such measurements.

2.3.1. Background. The quantum yield of phototransformation of a molecule in the gas phase depends essentially on the excitation wavelength. When a polyatomic molecule absorbs quasi-monochromatic radiation, a vibrational excited level of an electronically excited state, for example the lowest excited singlet state $S_1^{v'}$, is populated (in most studies the influence of the rotational fine structure is not analysed). From this specific level, $S_1^{v'}$, many events can occur :

- i) a very fast monomolecular phototransformation into fragments, radicals or an isomer;
- ii) a fast radiative process such as resonance-fluorescence;
- iii) a radiationless transition to an upper vibrational level of another excited state (for example $S_1^{v'} \rightarrow T_1^{v'}$) or to an upper level of the ground state ($S_1^{v'} \rightarrow S_0^{v''}$);
- iv) a vibrational intramolecular relaxation. The vibrational energy is distributed among other vibrational levels of the excited state;
- v) a vibrational intermolecular relaxation with loss of energy through many collision processes with either the same molecules in the ground state or with foreign gases. The relaxed molecule is deactivated on the lowest vibrational level of the excited state (S_1^0);
- vi) a bimolecular quenching process which deactivates the molecule back to the ground state;
- vii) a bimolecular process with a reactive molecule like oxygen (photooxidation) or with the primary photoproducts.

All these processes, when fast enough, compete on each vibrational level of the excited state. The main precursor is often the lowest vibrational level of the excited state, since its lifetime is orders of magnitude longer than the lifetime of $S_1^{v'}$. This, however, is not always the case and thus the quantum yield of phototransformation, related to the possible processes i) to vii), is a function of :

- the wavelength of the excitation light,
- the total pressure of the gas phase,
- the temperature,
- the nature of the inert gas,
- the presence of reactive molecules such as oxygen.

In the environment the molecule under investigation is at a very low partial pressure in the presence of air. Thus, the quantum yield should be measured at low partial pressure and it should be checked that it is independent of the partial pressure. The total gas phase pressure can be made close to real atmospheric pressures.

2.3.2. Determination of the rate of direct phototransformation. The ultimate technique for predicting the rate of direct phototransformation of a molecule in daylight, in the gas phase, would be to determine the corresponding quantum yields in monochromatic light over the whole range of the absorption spectrum of the chemical. This is lengthy, complex and very expensive, and a sequential approach is therefore recommended :

- i) First, the rate of direct phototransformation is estimated from the absorption spectrum of the compound in the gas phase with the assumption that the quantum yield of transformation is one (Appendix 2). This gives an upper limit for the rate. If this rate is negligible compared to the rates of disappearance by reaction with $\text{OH}^\cdot$ or O_3 (cf. section C.1.), no further investigation is needed.

In order to measure a rate of phototransformation by direct absorption of light, the absorption spectrum of the chemical in the gaseous state should be measured. A simpler, but obviously more approximate, technique is to determine the absorption spectrum of the molecule dissolved in an inert organic solvent. In such a condensed phase the spectrum is strongly perturbed by collisions and only a residual vibrational structure can be observed. Nevertheless, as an approximation, the absorption spectrum in the condensed phase can be assumed to be an envelope of that in the gas phase.

The range over which the absorption spectrum should be measured is complicated by the problem of the anticipated airborne distribution. If we consider the case where the distribution is only below the ozone layer, the cut-off for the spectral emission of daylight is at approximately 295 nm, and this is the lower limit for phototransformation. When airborne distribution extends above the ozone layer, exceeding approximately 15 km, the spectral distribution of available radiation extends to 200 nm. Thus the design of any laboratory experiment to determine the direct phototransformation of airborne molecules must be preceded by an assumption about the extent of the vertical distribution. Although this is a complex problem it is likely that only the most persistent airborne chemicals e.g. some haloalkanes, will be subject to this complication.

It is stressed again that this rough approach is useful only for deciding whether direct phototransformation can be neglected or further measurements are necessary.

- ii) The second stage is the direct determination of the rate of phototransformation of the molecule in the gas phase with polychromatic light. The light source should very closely approximate the spectral distribution of daylight for this test to be useful for estimating lifetimes in the atmosphere. Because quantum yields of vapour phase phototransformations may be wavelength-dependent, the intensity and spectral distribution of the light source should be fully characterised. Such a technique does not raise any fundamental questions, although wall effects and indirect phototransformation (through an uncontrolled formation of e.g. $\text{OH}^{\bullet}$) must be taken into account. The relative importance of indirect phototransformation can be evaluated by scavenging techniques. Possible wall effects might be controlled by adequate surface treatment.

The use of daylight is also possible but it requires a continuous characterization of the incident light intensity and spectral distribution throughout the duration of the experiment (cf. ECETOC, Technical Report no.3, 1981).

- iii) The ultimate step is to determine the quantum yields of phototransformation with monochromatic light in the wavelength ranges defined as the overlap of the daylight and of the light absorbed by the chemical. Such an approach is necessary only if there is a suspicion that the phototransformation quantum yield is strongly dependent on the exciting wavelength. If several overlapping absorption bands contribute to the overall phototransformation rate such behaviour is not unlikely. For chemicals which absorb weakly and/or have small quantum yields, monochromators of high light-intensity output are necessary. High-intensity tunable laser systems may also be used.

With monochromatic light the quantum yield of phototransformation is measured as:

ϕ = fraction of molecule phototransformed per absorbed photon.

The lifetime τ of the chemical can be calculated (ECETOC, 1981, p.51) from :

$$\tau = \left[\int_{\lambda_1}^{\lambda_2} \phi(\lambda) \cdot I(\lambda) \cdot \sigma(\lambda) \cdot d\lambda \right]^{-1} = \frac{1}{k_p}$$

where

$\phi(\lambda)$ = quantum yield of phototransformation at wavelength λ

$I(\lambda)$ = photon flux at wavelength λ , in photons. $\text{cm}^{-2} \cdot \text{s}^{-1}$

$\sigma(\lambda)$ = absorption cross section of a single molecule, in cm^2 .

λ_1, λ_2 = wavelength range over which the compound absorbs in the solar region.

k_p = rate of direct photolysis

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

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

The experimental set-up shown below (Pitts and Calvert, 1966; Horowitz et al., 1982 a-b) incorporates the principle features necessary :

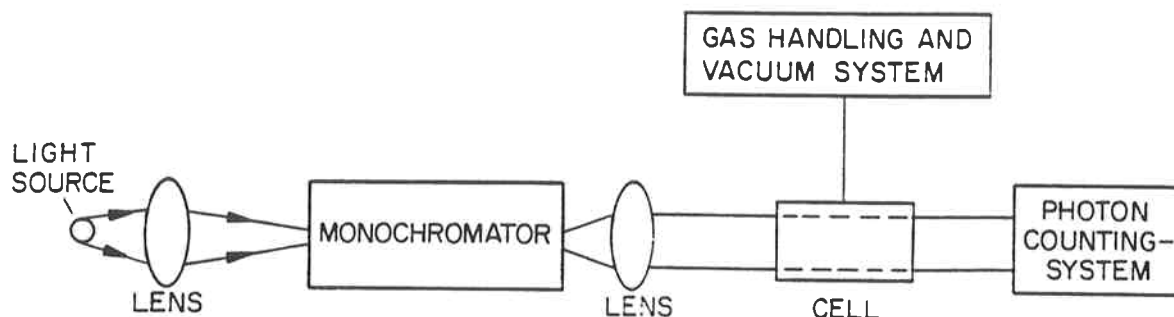


FIG. 1: SCHEMATIC SET-UP OF AN APPARATUS FOR DIRECT PHOTOLYSIS MEASUREMENTS

The following precautions are recommended :

- i) The absorbed intensity $I_a(\lambda)$ should be measured under the same experimental conditions as is the rate of disappearance especially under the same spectral width of the excitation light, and preferably under the same total pressure. It should not be computed from an absorption spectrum recorded in an independent spectrophotometer. Actinometry in the gas phase, and measurements of the absorbed intensity and disappearance rate, must therefore be carried out in the same experimental device.
- ii) The absorbance of the molecule should usually be kept low enough to ensure a homogeneous absorption rate throughout the whole cell (absorbance lower than 0.1 for the total optical path length).
- iii) Wall effects might be important, but not as much as in OH $\cdot$ reactions. Care should be taken to illuminate a minimum wall surface area. The effect of surface treatment of the wall could be investigated.
- iv) If secondary chemical reactions occur, implying radical formation in the first photodissociative step, scavenging of radicals might be attempted.

The quantum yield can alternatively be measured with high accuracy with a high intensity laser system (e.g. C.W. dye laser) over a range of several wavelengths. If only one absorption band contributes to the photolysis, the quantum yield obtained is representative for the whole spectral range. This may be especially true if only the long-wavelength tail of the absorption spectrum of the compound extends above 300 nm. The apparatus is expensive but its use does save time.

2.3.3. Conclusions

Data on the direct phototransformation of chemicals in the atmosphere are very scarce. A sequential approach for determining the rates of such reactions is recommended.

D. GENERAL CONCLUSIONS

The most significant phototransformations for the removal of chemicals in the atmosphere are, in order of importance, reaction with $\text{OH}^\cdot$ and O_3 . Some recently-developed techniques for measuring the corresponding rate constants, and hence atmospheric lifetimes, of chemicals undergoing these reactions are considered to be adequate for the purpose, provided that their limitations are borne in mind.

No adequate experimental protocols are available at present for determining the rate of direct phototransformation. The Task Force has laid down the principles for determining this, and made recommendations for the further development of experimental methods.

In assessing the rate of phototransformation of a chemical in the atmosphere, a preliminary estimate of the relative importance of $\text{OH}^\cdot$ and O_3 reactions and direct phototransformation should first be made. The second step is the experimental determination of the rate constant of the process or processes estimated to be dominant. It is emphasised that the experimental techniques require that the operator has a fundamental knowledge of photochemistry and experience in doing such work.

E. AREAS DESERVING FURTHER INVESTIGATION

1. The present experimental methods for measuring $\text{OH}^\cdot$ reactivity should be adapted so as to permit measurements on compounds of lower volatility. Work has already started in this field.
2. More experimental work is needed to develop a satisfactory method for assessing direct phototransformation.
3. Further research is needed to assess the importance of the photochemical reactions of chemicals adsorbed or absorbed in liquid or solid aerosols.
4. The predictive calculation and correlation methods for estimating $k_{\text{OH}^\cdot}$ and k_{O_3} should be further developed.

F. APPENDICES

APPENDIX 1

A. ESTIMATION OF OH[•] REACTION RATE CONSTANTS (Mill et al., 1981)

The rate constant for the reaction of a substance with hydroxyl radicals is computed as an additive property. It is assumed that the rate constant of the reaction of the total molecule with OH[•] is the sum of the rate constants for the reactivities of each portion of the molecule :

$$k_{OH^{\bullet}} = \sum_{i=1}^i n_i \cdot \alpha_{H_i} \cdot \beta_{H_i} \cdot k_{H_i} + \sum_{j=1}^j n_j \cdot \alpha_{E_j} \cdot k_{E_j} + \sum_{\lambda=1}^{\lambda} n_{\lambda} \cdot \alpha_{A_{\lambda}} \cdot k_{A_{\lambda}}$$

The first term corresponds to the abstraction of hydrogen atoms : k_{H_i} is the reactivity of i^{th} hydrogen atom which depends on the degree of substitution on the adjacent atom; α_{H_i} and β_{H_i} account for the effects of substitution respectively in the α and β positions; n_i is the number of equivalent hydrogen atoms.

The second term corresponds to addition to a double bond : k_{E_j} is the reactivity of the j^{th} carbon atom double bond, and α_{E_j} is taken as unity except when a hydrogen atom is attached to the double bond; n_j accounts for the repetition of each unique double bond.

The third term corresponds to addition to aromatic rings : $k_{A_{\lambda}}$ is the reactivity of the λ^{th} aromatic group; $\alpha_{A_{\lambda}}$ accounts for the effects of halogen atom on the ring.

The various rate constants k_{H_i} , k_{E_j} , $k_{A_{\lambda}}$ and the corrective factors have been

determined in preliminary experiments on typical compounds (methane, ethane, ethene, benzene...).

For substituted alkanes the above approach has been further developed by Heicklen (1981-b) in order to include the temperature dependence of $k_{OH^{\bullet}}$. In this scheme, $k_{OH^{\bullet}}$ is calculated according to the following equation :

$$k(T) = (8\pi kT/\mu)^{1/2} (\sigma_R^O)^2 \sum_i \gamma_i \exp \left\{ -a(D_i - D_O) T/RT \right\}$$

provided that $D_i \geq D_O(T)$, where

- $k(T)$ = reaction rate coefficient at absolute temperature T
 κ = Boltzmann's constant
 μ = reduced mass of reacting species
 σ_R^O = intrinsic reaction radius for an OH $\cdot$ radical reaction with a C-H bond, of bond length 1.5×10^{-8} cm
 γ_i = number of equivalent C-H bonds of each type in the molecule
 D_i = bond dissociation enthalpy for each type of C-H bond
 $D(T)_O$ = a temperature-dependent energy parameter
 R = ideal gas constant

If D_i is taken as the C-H bond dissociation enthalpy at 298° K, then
 $\alpha = 0.323$ and D_O is obtained from the empirical formula

$$D_O^{-1} = 1.062 \times 10^{-2} + 3.52 \times 10^{-6} \times T$$

where D_O is in kcal/mole and T is in K. This relationship is valid for T between 200 and 400 K. The bond dissociation enthalpy is estimated with the aid of an empirical relationship.

B. ESTIMATION OF O_3 REACTION RATE CONSTANTS (Mill et al., 1981).

As for the rate constant for HO $\cdot$ reactions, k_{O_3} is computed as the sum of rate constants for the reactivities of the various³ reactive groups (aliphatic or aromatic C=C, etc.). The k_{O_3} values of the individual groups are tabled in the cited paper.

APPENDIX 2

CALCULATION OF MAXIMUM PHOTOLYSIS RATES (Pitts et al., 1981-a)

Under atmospheric conditions the photolysis rate constant k_p in day^{-1} is given by

$$k_p = \int_{290}^{800} \sigma(\lambda) \cdot \phi(\lambda) \cdot j(\lambda) \cdot d\lambda$$

with $\sigma(\lambda)$ = absorption cross-section at wavelength λ
in $\text{cm}^2 \cdot \text{molecule}^{-1}$

$\phi(\lambda)$ = quantum yield at wavelength λ , assumed as unity
in these calculations.

$j(\lambda)$ = solar flux at wavelength λ , in $\text{photons} \cdot \text{cm}^{-2} \cdot \text{day}^{-1}$

The solar flux is conveniently tabulated as average values of $\langle \Delta \lambda \rangle$ over 10 nm intervals, so that the above equation becomes

$$k_p = \sum_{290}^{800} \sigma(\Delta \lambda) \cdot j(\Delta \lambda)$$

From the absorption spectrum, the absorption cross-section can be determined according to the Beer-Lambert law

$$\sigma_\lambda = \ell^{-1} \cdot [P]_0^{-1} \cdot \ln \frac{I_0}{I}$$

where ℓ = cell pathlength in cm

I_0 and I = intensities of incident and final light in $\text{photons} \cdot \text{cm}^{-2}$

$[P]_0$ = concentration of the test compound in $\text{molecules} \cdot \text{cm}^{-3}$
= $p \times 2.654 \times 10^{14} \cdot T^{-1}$

p = partial pressure of test compound in Pa

T = test temperature in K

Possible deviations from the Beer-Lambert law should be checked from the consistency of the data on cross-sections at three different pressures. In cases where there is a pressure dependence, the low-pressure values are preferred.

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