

GENERAL DISTRIBUTION

OCDE/GD(92)172

ENVIRONMENT MONOGRAPH NO. 61

**THE RATE OF PHOTOCHEMICAL TRANSFORMATION
OF GASEOUS ORGANIC COMPOUNDS IN AIR UNDER TROPOSPHERIC CONDITIONS**

ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

Paris 1993

GRAPHS, TABLES AND FACSIMILES NOT AVAILABLE IN ELECTRONIC FORM

ENVIRONMENT MONOGRAPHS

This series is designed to make available to a wide readership selected technical reports prepared by the OECD Environment Policy Committee and Environment Directorate. The Environment Policy Committee recommended that this report be derestricted under the authority of the Secretary-General who subsequently agreed. Copies of Environment Monographs on a limited basis can be forwarded on request.

ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

FOREWORD BY THE SECRETARIAT

Several years ago a first draft of this report was submitted by Germany as a proposal for an OECD Guideline for Testing of Chemicals. It was the outcome of two research projects. One, sponsored by the German Ministry of Research and Technology, was conducted in several scientific institutes in Germany. It addressed laboratory methods for determining photochemical transformation of chemicals in air. The other, sponsored by the German Umweltbundesamt, was conducted at Stanford Research Institute. It addressed methods for estimating the photochemical transformation of chemicals in air.

The methods were presented and discussed at an OECD Workshop held in 1986 in Berlin. The report was redrafted in light of the discussions held at the Workshop and circulated for comments.

Due to the complexity and the specialised nature of the experimental techniques involved, it seemed not appropriate to strive for adoption of the report as an OECD Guideline. The report however contained very useful guidance on how to measure or to estimate the potential of a substance to be degraded photochemically in the air.

The text as presented in this monograph is a revision of the original report. The revision involved a great amount of cooperation and scientific contribution by the authors and those who applied the methods already, and also comprehensive editorial work. The commitment of the Umweltbundesamt, who steered the project to its present achievement, is gratefully acknowledged.

THE RATE OF PHOTOCHEMICAL TRANSFORMATION OF GASEOUS ORGANIC COMPOUNDS IN AIR UNDER TROPOSPHERIC CONDITIONS

page

SUMMARY IN FRENCH	5
1. INTRODUCTION	7
2. ESTIMATION METHODS	8
2.1 Methods to Estimate the Rate of Reaction with OH-Radicals	8
2.2 Methods to Estimate the Rate of Reaction with Ozone	22
2.3 Methods to Calculate the Maximum Rate of Direct Photo-transformation	24
3. EXPERIMENTAL METHODS	28
3.1 Absolute Methods to Determine the Rate of Reaction with OH-Radicals	28
3.2 Relative Methods to Determine the Rate of Reaction with OH-Radicals	30
3.3 Absolute Methods to Determine the Rate of Reaction with Ozone	36
3.4 Methods to Determine the Rate of Direct Phototransformation	37
4. REFERENCES	43
Appendix 1: Comparison of Estimation and Experimental Methods	45
Appendix 2: Solar Intensities at Sea Level in the Northern Hemisphere	53
Appendix 3: Method to Estimate the Rate of Reaction with OH-Radicals Sample Calculations	61
Appendix 4: Definitions and Units	93

RESUME

Lorsque des substances organiques sont émises dans la troposphère elles peuvent être transformées et dégradées suite à des réactions photochimiques. Deux types de réactions sont à l'oeuvre: les phototransformations directes et les phototransformations indirectes. Dans la phototransformation directe, la molécule, après excitation par absorption d'un photon, subit une réaction qui est généralement une oxydation par l'oxygène de l'air. Une phototransformation indirecte résulte d'une réaction de la molécule avec des radicaux hydroxyle, des molécules d'ozone ou des molécules et espèces réactives, elles-mêmes issues de réactions photochimiques. Afin d'évaluer le devenir des substances organiques dans la troposphère, ainsi que le danger potentiel dû aux produits de leur transformation photochimique, il faut impérativement connaître les vitesses des réactions photochimiques qui sont à l'oeuvre.

Parmi tous les processus de phototransformation qui peuvent avoir lieu dans la troposphère, le plus important est généralement la réaction avec les radicaux **OH**. Comparativement aux autres réactions, sa vitesse est très grande pour la majorité des molécules organiques. Les substances qui réagissent peu ou lentement avec les radicaux **OH** ne réagissent pas à un degré significatif avec les autres espèces réactives issues de réactions photochimiques.

La réaction avec l'ozone est la deuxième importante. Dans la troposphère, l'ozone est relativement abondant en comparaison avec les autres espèces photochimiques réactives. Mais toutes les molécules organiques ne réagissent pas avec l'ozone. Seuls les composés aliphatiques non saturés, les composés du soufre bivalent, les amines, les hydrocarbures aromatiques polycycliques et les phénols réagissent rapidement. Il arrive que la réaction des aliphatiques non saturés de faible poids moléculaire soit plus rapide avec l'ozone qu'avec le radical **OH**.

D'autres réactions de phototransformation indirecte interviennent également et, dans certaines conditions, celles-ci peuvent même être les plus rapides. Tel est le cas pour la réaction avec le radical nitrate pendant la nuit. S'agissant du devenir global des substances organiques gazeuses dans la troposphère, ces réactions revêtent cependant une importance mineure. Elles ne sont donc pas prises en considération dans ce document .

La phototransformation directe peut également être très rapide, mais seulement pour un nombre limité de substances organiques. Sa vitesse dépend, d'une part, du recouvrement du spectre solaire par le spectre d'absorption de la molécule, et, d'autre part, du rendement quantique qui est la fraction des molécules transformées suite à l'absorption d'un photon. Le rendement quantique peut avoir la valeur de un, mais pour la plupart des substances organiques la valeur se situe entre 0.1 et 0.001. A cause des conditions prévalant dans la troposphère, seulement les longueurs d'onde supérieures à 290 nm sont à prendre en considération.

Le présent rapport est en deux parties. La première partie traite des méthodes théoriques qui permettent de calculer une valeur d'estimation des constantes cinétiques des diverses réactions photochimiques et d'en déduire leur importance relative. La seconde partie traite des méthodes expérimentales. La plupart de ces dernières nécessitent des laboratoires spécifiques, solidement encadrés par des scientifiques et bien outillés. Ces méthodes sont surtout utilisées pour confirmer les résultats théoriques relatifs aux processus de transformation les plus importants.

Les méthodes d'estimation

Les méthodes qui sont présentées permettent de calculer les constantes de vitesse d'un grand nombre de phototransformations. A partir de ces constantes on obtient une estimation du temps de demi-vie, $t_{1/2}$, le cas échéant, en prenant en considération les concentrations des espèces réagissantes. Les méthodes ne concernent que la phase gazeuse. Dans la troposphère, les composés organiques à faible pression de vapeur sont fortement attirés vers la grande surface que présentent des aérosols et des gouttelettes d'eau. Leur adsorption sur, ou dissolution dans, ces particules créent des conditions de réactions hétérogènes ou en phase condensée. Des différences appréciables entre les vitesses de réaction réelles et celles calculées à partir des méthodes d'estimation peuvent en résulter. Un autre aspect à prendre en considération est que les constantes de vitesse calculées à l'aide des méthodes d'estimation réfèrent à la température ambiante. A des altitudes de 10 à 12 km, la température est de l'ordre de 233 à 213 K, d'où une diminution de la vitesse de réaction.

Les méthodes d'estimation de la vitesse des transformation indirectes qui ont été retenues sont basées sur des relations structure-activité. Pour chaque schéma réactionnel on part d'une constante de vitesse de base qui est caractéristique d'un groupe de substances dont la structure est analogue. Cette constante de base est établie à partir de données expérimentales. La vitesse de base se trouve modifiée par les substituants de la chaîne carbone de la molécule. Pour rendre compte de ces modifications, on multiplie la constante de base par des facteurs qui sont caractéristiques des substituants. La constante globale afférente à l'ensemble des schémas réactionnels est obtenue par sommation des constantes modifiées afférentes aux différents schémas.

Le calcul de la vitesse de phototransformation directe est basé sur une formule simple dans laquelle interviennent le coefficient d'extinction, l'intensité lumineuse et le rendement quantique. Ces trois facteurs variant en fonction de la longueur d'onde, la vitesse globale est obtenue par intégration sur la partie du spectre à prendre en compte. Généralement on prend l'unité comme valeur du rendement quantique et cela constitue une source d'erreur considérable. En effet, les rendements quantiques sont souvent très inférieurs à un. Il en résulte une sous-estimation du temps de demi-vie réel.

Les méthodes expérimentales

Pour déterminer les constantes cinétiques de phototransformations indirectes par voie expérimentale, il existe deux grands types de méthodes: les méthodes absolues et les méthodes relatives. Les méthodes relatives sont plus rapides que les méthodes absolues, mais elles impliquent qu'on dispose d'une gamme de substances étalons de réactivités parfaitement bien connues. De toute façon, les déterminations expérimentales sont onéreuses et elles doivent être réservées aux composés organiques volatils, dont la production est telle que des émissions importantes dans la troposphère puissent avoir lieu. Si tel est le cas, on n'effectuera les mesures que pour les processus qui ont préalablement été identifiés par estimation comme étant significatifs. Des méthodes absolues et relatives pour mesurer la vitesse de réaction avec les radicaux **OH** et l'ozone sont décrites dans le présent rapport.

L'évaluation par voie expérimentale de la vitesse de phototransformation directe dans la troposphère consiste à déterminer le rendement quantique de la substance étudiée à l'aide d'un actinomètre. Un actinomètre est une substance relativement volatile dont on connaît avec précision le rendement quantique et le coefficient d'extinction pour toutes les longueurs d'onde de photolyse.

1. INTRODUCTION

Organic compounds which enter the troposphere due to manufacturing processes, use patterns and their physico-chemical properties may undergo various photochemical reactions and subsequent breakdown. In order to assess the hazardous potential of these substances the various decay rates must be known.

The following photochemical processes may contribute to a chemical's reaction and breakdown or degradation in the troposphere:

direct phototransformation, i.e., excitation of a molecule through absorption of a photon followed by chemical reaction, usually oxidation through reaction with oxygen;

indirect phototransformation processes:

- reaction with OH-Radicals
- reaction with ozone
- reaction with other photochemically generated species.

In this document methods are discussed to estimate theoretically and to determine experimentally the rate of photochemically induced transformation or oxidation reactions such as reaction with OH-Radicals or ozone. These methods are developed for gaseous organic substances in the troposphere under conditions, such as temperature and solar light intensity, typically found at sea level.

The purpose of this document is to firstly enable the estimation of rate constants for photochemical processes in the troposphere. This allows the relative importance of the various processes to be determined. The laboratory based experimental methods can then be used to confirm these results for the most important processes.

Of the direct and indirect phototransformation processes possible in the troposphere, reaction with OH-Radicals is generally the most important. This is because reaction with OH-Radicals is the most rapid phototransformation process for the majority of organic chemicals. Organic chemicals that do not or only very slowly react with OH-Radicals do not react with any other photochemically formed reactive species.

Reaction with ozone is generally of secondary importance. Tropospheric ozone concentrations are relatively high compared to other photochemically formed reactive species. However only unsaturated aliphatic compounds, sulphur (II) compounds, amines, polycyclic aromatic hydrocarbons and phenolic compounds undergo ozonolysis easily. Only for low molecular weight unsaturated aliphatics may reaction with ozone in the troposphere be more rapid than reaction with OH-Radicals.

Other indirect phototransformation processes will also take place and may even be most rapid under specific conditions, such as reaction with nitrate radicals during the night. These reactions, however, are generally of minor importance considering the overall fate of gaseous organic substances in the troposphere, and are not considered further in this document.

Direct phototransformation reactions may also be very rapid but only for a limited number of organic chemicals. The rate of a direct phototransformation reaction depends (1) on the overlap between the solar light emission spectrum under tropospheric conditions and the light absorption spectrum of the compound, and (2) on the quantum yield, i.e. the fraction of the molecules of the organic chemical that is transformed after absorption of a photon. The quantum yield can be as high as 1 but for most organic compounds lies in the range of 0.1 to 0.001. Because the methods described simulate tropospheric conditions, only wavelengths greater than 290 nm are considered in emission and absorption spectra.

An estimation of an organic chemicals half-life, $t_{1/2}$, (the time period required for concentration to fall to half its initial value) may be obtained from rate constants determined according to the methods contained in this monograph, and consideration of relevant environmental factors such as $[O_3]$ (ozone concentration) and $[OH]$ (OH-Radical concentration). The methods described pertain exclusively to gaseous phase reactions. In the troposphere, organic compounds with a relatively low vapour pressure are strongly attracted towards the very large surface area of aerosols and water droplets. Adsorption onto, or solution into these particles/droplets result in heterogeneous or condensed phase conditions. These conditions may be responsible for rate lowering (via enclosure, scavengers, quenching effects) or accelerating (via catalytic effects) modifications to the phototransformation processes discussed previously.

As a final caveat, the methods described in this document generally yield kinetic data at room temperature. The upper layers of the troposphere (10 to 12 km altitude) have temperatures of 233 to 213K however. This causes a reduction in rate constants derived at room temperature which should be kept in mind.

While the estimation methods are quite simple to apply, the experimental determination of the rate of direct and indirect photochemical transformation reactions is relatively costly and requires experienced staff.

Performance of experimental determinations may only be justified for volatile organic compounds with high rates of production and/or emission to the troposphere, and then only for those photochemical transformation processes indicated to be significant by estimation methods.

2. ESTIMATION METHODS

2.1 Methods to Estimate the Rate of Reaction with OH-Radicals

2.1.1 Introduction

Depending on the structure of the organic compound involved, OH-Radicals generally react by one or more of the following pathways:

- H-Atom abstraction (eg. from alkanes, carbonyl containing and other saturated organics)
- Addition to unsaturated carbon-carbon ($C=C$ and $C\equiv C$) bonds
- Addition to aromatic rings

Each of these pathways is characterized by a bimolecular rate constant, k_{abstr} , k_{add} and k_{arom} respectively. These pathways can be considered to operate independently and therefore the overall bimolecular rate constant for reaction of OH-Radicals with gaseous organic molecules (k_{OH}) is given by the sum of the rate constants for the various individual pathways

$$k_{OH} = k_{abstr} + k_{add} + k_{arom} \quad (1)$$

One estimation method for H-Atom abstraction reactions has been proposed by Heicklen (1981) and is based upon C-H bond dissociation energies. The advantage of this approach is that the temperature dependence of k_{abstr} can be determined. Its main disadvantage is that it only applies to H-Atom abstraction reactions. A second estimation method proposed by Hendry and Kenley (1979) is based upon structure-activity relationships and is applicable to reactions involving both H-Atom abstraction and OH-Radical addition to unsaturated carbon-carbon bonds.

The estimation method described in this document has been developed by Atkinson (1985), but is analogous to that of Hendry and Kenley and has similar applicability. For H-Atom abstraction reactions this method considers the effects of substituent groups or atoms on the α -carbon, and in certain cases on the β -carbon as well. For OH-Radical addition reactions to carbon-carbon unsaturated bonds, this method involves consideration of the type of unsaturated system present (isolated, conjugated or cumulative) and the degree, orientation and identity of substitution around these systems.

For OH-Radical addition to aromatic rings Zetzch (1982) found an empirical inverse linear correlation between the logarithm of k_{arom} and the sum of the electrophilic substituent constants Σ^+ for substituted benzenes. Atkinson (1985) later developed a slightly different relationship from a modified data set. The method described in this document is that presented by Atkinson (1985).

The half-life of a compound ($t_{1/2}$) is defined as the time period required for the concentration to fall to half its initial value. The half-life with respect to reaction with OH-Radicals may therefore be expressed as

$$t_{1/2} \text{ (OH-Radical)} = \ln 2 / k_{\text{OH}} [\text{OH}]$$

2.1.2 H-Atom Abstraction

With most organic compounds capable of undergoing H-Atom abstraction, abstraction occurs from $-\text{CH}_3$, $-\text{CH}_2-$ and $-\text{CH}<$ groups. Abstraction rates are modified by substituents on these groups.

Calculation of H-Atom abstraction rate constants k_{abstr} depends then upon the estimation of $-\text{CH}_3$, $-\text{CH}_2-$ and $-\text{CH}<$ group rate constants. The magnitude of these are in turn influenced by the identity of α - and β - substituents. Thus

$$\begin{aligned} k(\text{CH}_3 -\text{X}) &= k_{\text{prim}}^{\circ} F(\text{X}) \\ k(\text{Y}-\text{CH}_2 -\text{X}) &= k_{\text{sec}}^{\circ} F(\text{X}) F(\text{Y}) \\ k(\text{X}-\underset{\text{Z}}{\overset{\text{Y}}{\text{C}}}-\text{H}) &= k_{\text{tert}}^{\circ} F(\text{X}) F(\text{Y}) F(\text{Z}), \end{aligned}$$

where k_{prim}° , k_{sec}° , k_{tert}° are H-Atom abstraction rate constants per $-\text{CH}_3$, $-\text{CH}_2-$ and $-\text{CH}<$ group for a "standard" substituent, and $F(\text{X})$, $F(\text{Y})$, $F(\text{Z})$ are the substituent factors for substituent groups. The most appropriate "standard" substituent is CH_3 , for which F is 1.00 by definition.

It should be recognized that the H-Atom of an alcohol group can also be abstracted by the OH-Radical. It is therefore necessary to introduce a group rate constant k_{OH} .

Importantly, the alcohol group also promotes the abstraction of a hydrogen atom bonded to the same carbon atom.

To determine k_{prim}° , k_{sec}° , k_{tert}° and the factors $F(-\text{CH}_2-)$, $F(-\text{CH}<)$ and $F(>\text{C}<)$ the extensive kinetic data available for the alkanes was used. A non-linear least squares fit of the available data to the general equation

$$k_{\text{abstr}} = \Sigma[k_{\text{prim}}^{\circ} F(\text{X})] + \Sigma[k_{\text{sec}}^{\circ} F(\text{X}) F(\text{Y})] + \Sigma[k_{\text{tert}}^{\circ} F(\text{X}) F(\text{Y}) F(\text{Z})] \quad (2)$$

was carried out. The data was obtained over a range of temperatures, and the temperature dependence of k° and $F(\text{X})$ was determined using an expression of the form

$$k^o = A T^2 \cdot e^{-E/RT}$$

and

$$F(X) = e^{E/RT}$$

where A is an Arrhenius pre-exponential factor, E is the activation energy (J mole⁻¹) and R the universal gas constant (8.314 J K⁻¹ mole⁻¹). From this analysis and a similar one with alcohols, the values of k_{prim}^o , k_{sec}^o , k_{tert}^o and $k_{\text{-OH}}^o$ together with relevant A and E/R values were determined, and these are compiled in Table 1. Derived values of F(X) and E/R for -CH₃, -CH₂-, -CH<, >C< and -OH substituents are found in Table 2.

Table 1: Values of k_{prim}^o , k_{sec}^o , k_{tert}^o and $k_{\text{-OH}}^o$ at 298K together with relevant values of A and E/R obtained from analysis of kinetic data for alkanes and alcohols.

Group Rate Constant	k cm ³ molecule ⁻¹ s ⁻¹	A cm ³ molecule ⁻¹ s ⁻¹ K ⁻²	E/R K
k_{prim}^o	0.144 x 10 ⁻¹²	4.47 x 10 ⁻¹⁸	303
k_{sec}^o	0.838 x 10 ⁻¹²	4.32 x 10 ⁻¹⁸	-233
k_{tert}^o	1.83 x 10 ⁻¹²	1.89 x 10 ⁻¹⁸	-711
$k_{\text{-OH}}^o$	0.036 x 10 ⁻¹²		

Comparisons of recommended experimental rate constants for the reaction of OH-Radicals with a series of alkanes, including cyclohexane which has essentially zero ring strain, are shown in Figures 1-3. The agreement is seen to be generally very good, and the experimentally observed curvature in these Arrhenius plots is also reproduced well, allowing OH-Radical reaction rate constants to be estimated for the varying temperatures encountered in the troposphere (approximately 210-300 K).

Fig. 1: Arrhenius plots of recommended experimental (\cdot) and estimated (---) rate constants for a series of n-alkanes (Atkinson, 1985).

Fig. 2: Arrhenius plots of recommended experimental (\cdot) and estimated (---) rate constants for a series of alkanes (Atkinson, 1985).

Fig. 3: Arrhenius plots of recommended experimental (·) and estimated (—) rate constants for a series of alkanes (Atkinson, 1985).

It has been observed experimentally that ring strain energies in excess of approximately 21 kJ mole⁻¹ lead to a decrease in H-Atom abstraction rate constants compared to those calculated, with the decrease being approximately exponential with increased ring strain energy. Since for polycyclic systems the overall ring strain energies are approximately the sum of the ring strain energies per ring, a correction factor per ring can be derived. For polycyclic ring systems these correction factors, F(ring), are then multiplicative. Furthermore, since the ring strain energies for rings containing O, S and N heteroatoms are similar to those for the corresponding cycloalkane rings, these ring factors can be used for heteroatom-containing rings such as oxides and cycloethers. Values for F(ring), depending only on ring size are found in Table 2.

These ring correction factors, F(ring), are applicable only to the -CH₂- and >CH- groups involved in the ring(s), with the group rate constants for non-ring -CH₃, -CH₂- and >CH- groups being calculated without the ring correction factor (See Example 3 in Appendix 3).

Based on kinetic data from haloalkanes, aldehydes, ketones, other carbonyl containing compounds, glycols, ethers, esters, nitrates and nitriles, values of F(X) and E/R for a variety of other substituents have been determined (Atkinson, 1985; Atkinson 1987; Atkinson 1988). These are found in Table 2.

The review of Atkinson (1985) gives a comparison of room temperature rate constants for H-Atom abstraction from alkanes, haloalkanes, aldehydes, ketones, other carbonyl containing compounds, alcohols, glycols, ethers, esters, nitrates and nitriles. Of 138 organic chemicals which undergo H-Atom abstraction, for only 5 do the recommended experimental and calculated room temperature rate constants disagree by more than a factor of 2.

Table 2: F(x) and E/R for substituent groups X at 298 K

Substituent Group X	Substituent Factor F(X)	E/R (K)
-CH ₃	1.00	0
-CH ₂ -	1.29	76
>CH-	1.29	76
>C<	1.29	76
-F	0.099	-689
-Cl	0.38	-288
-Br	0.30	-359
-CH ₂ Cl	0.57	-168
-CHCl ₂	0.57	-168
-CH ₂ Br	0.57	-168
-CCl ₃	0.09	-742
-CClO	0.5	
-CH ₂ F	0.85	-48
-CHF ₂	0.10	-686
-CF ₂ Cl	0.025	-1099
-CF ₃	0.075	-771
=O	8.8	648
-CHO	0.76	-82
-C(O)-	0.76	-82
-CH ₂ C(O)-	4.4	442
>CHC(O)-	4.4	442
>CC(O)-	4.4	442
-C ₆ H ₅	1.0	0
-OH	3.4	382
-O-	6.1	631
-S-	9.0	
-SS-	9.0	
-SH	9.0	
-SP-	20	
-OP-	20	
-C(O)OR	0.0	-1500
-OC(O)R	1.5	78
-CH ₂ ONO ₂	0.21	-321
>CHONO ₂	0.21	-321
>CONO ₂	0.21	-321
-ONO ₂	0.1/0.3	-893
>C=C<	< 1	
-C=C-	< 1	
-C≡N	0.14	-586
-CH ₂ CN	0.5	-207
three-membered ring	0.017	-1214
four-membered ring	0.22	-451
five-membered ring	0.80	-66
six-membered ring	1.00	0
seven-membered ring	1.00	0

As an example, the comparison between calculated and recommended experimental rate constants for H-Atom abstraction with the aldehydes formaldehyde and acetaldehyde are presented in Figure 4.

Fig. 4: Arrhenius plots of recommended experimental (---) and estimated (—) rate constants for selected aldehydes (after Atkinson, 1985).

Although amines, nitrosamines, nitramides and hydrazines were not considered in the review by Atkinson (1985), the limited data available allow approximate group rate constants $k_{\text{-NH}_2}^o$, $k_{\text{>NH}}^o$ and $k_{\text{>N-}}^o$ together with substituent factors $F(\text{-NH}_2)$, $F(\text{>NH})$, $F(\text{>N-})$ and $F(\text{>N-NO}_x)$ at 298 K to be derived:

$$k_{\text{-NH}_2}^o \approx 20 \times 10^{-12} \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{\text{>NH}}^o \approx 60 \times 10^{-12} \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{\text{>N-}}^o \approx 60 \times 10^{-12} \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{\text{NNO}_x}^o \approx 0$$

$$F(\text{-NH}_2) \approx 10 F(\text{>NH}) \approx 10$$

$$F(\text{>N-}) \approx 10 F(\text{>N-NO}_x) \approx 10$$

where $x = 1$ or 2

It should be noted that these reactions involving -NH_2 , >NH and >N- groups are not abstraction reactions, but probably occur via initial OH-Radical addition to the nitrogen atom followed by rapid decomposition of this initially energy-rich adduct to the observed products.

For the sulphur-containing organics, a similar situation exists in which OH-Radical addition to the S-atom and H-Atom abstraction from the remainder of the molecule occurs (Atkinson 1985). For thiols OH-Radical addition predominates, while for the sulphides, RSR' , H-Atom abstraction from the alkyl groups occurs in the absence of O_2 . The available room temperature data are reasonably well fit by the group rate constants $k_{\text{-SH}}^o$ and $k_{\text{-S-}}^o$ (with the value for $k_{\text{-S-}}^o$ being totally empirical for 10^5Pa total pressure of air) and the substituent factors $F(\text{-SH})$ and $F(\text{-S-})$ below:

$$k_{-SH}^{\circ} \approx 31 \times 10^{-12} \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{-S-}^{\circ} \approx 2 \times 10^{-12} \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{-SS-}^{\circ} \approx 200 \times 10^{-12} \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$F(-SH) \approx 9F(-S-) \approx 9F(-SS-) \approx 9$$

Additional substituent and group factors are given by Atkinson (1987) and Atkinson (1988):

$$k_{OH}^{\circ} \approx 0.036 \times 10^{-12} \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{p=0}^{\circ} \approx 0$$

$$k_{PS}^{\circ} \approx 55 \times 10^{-12} \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$F(-OP-) \approx 20 \quad F(-SP-) \approx 20 \quad F(-OH) \approx 3.4$$

A summary plot of calculated versus recommended experimental H-Atom abstraction rate constants at 298 K is given in Figure 5.

Fig. 5: A plot of calculated versus recommended experimental H-Atom abstraction rate constants with perfect agreement denoted by the solid line, and agreement to within a factor of 2 indicated by the area within the dashed lines.

As noted above, the agreement is good with over 90% of the calculated data being within a factor of 2 of the recommended experimental values.

2.1.3 OH-Radical Addition to Unsaturated Carbon-Carbon Bonds

The method employed is that of Atkinson (1985) which is similar to that used by Hendry and Kenley (1979). It involves recognizing the number and type of isolated, conjugated and cumulative unsaturated carbon-carbon bond systems present, and the identity and orientation of substituents around these systems. Each type of unsaturated system has a group rate constant. The room temperature (298K) group rate constants for alkenes ie. isolated or non-conjugated carbon-carbon double bond systems ($\text{CH}_2=\text{CHR}$, $\text{CH}_2=\text{CR}_2$, cis- and trans- $\text{RCH}=\text{CHR}$, $\text{RCH}=\text{CR}_2$ and $\text{R}_2\text{C}=\text{CR}_2$ where R is an alkyl substituent or hydrogen) are given in Table 3 together with the experimental data from which they are derived.

Table 3: Recommended group rate constants and experimentally observed rate constants for OH-Radical addition to alkyl substituted alkenes with varying degrees and orientation of substitution.

General Structure	Recommended Group Rate Constant ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) $\times 10^{-12}$	Alkene	Experimental Rate Constant ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) $\times 10^{-12}$
$\text{CH}_2=\text{CHR}$	26.3	Propene	26.3
		1-Butene	31.4
		1-Pentene	31.4
		3-Methyl-1-Butene	31.8
		1-Hexene	37.0
		3,3-Dimethyl-1-Butene	28.4
		1-Heptene	40.0
$\text{CH}_2=\text{CR}_2$	51.4	2-Methylpropene	51.4
		2-Methyl-2-Butene	60.7
		2-Methyl-1-Pentene	62.6
		β -Pinene	78.2
cis-RCH=CHR	56.1	cis-2-Butene	56.1
		cis-2-Pentene	65.1
		Cyclopentene	67.0
		Cycloheptene	74.1
		Bicyclo[2.2.1]-2-Heptene	49.1
		Bicyclo[2.2.2]-2-Octene	40.6

Table 3 (cont'd): Recommended group rate constants and experimentally observed rate constants for OH-Radical addition to alkyl substituted alkenes with varying degrees and orientation of substitution.

General Structure	Recommended Group Rate Constant ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) $\times 10^{-12}$	Alkene	Experimental Rate Constant ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) $\times 10^{-12}$
trans-RCH=CHR	63.7	<u>trans</u> -2-Butene	63.7
		<u>trans</u> -2-Pentene	67.0
		<u>trans</u> -4-Methyl-2-Pentene	60.8
		<u>trans</u> -4,4-Dimethyl-2-Pentene	54.8
RCH=CR ₂	86.9	2-Methyl-2-Butene	86.9
		2-Methyl-2-Pentene	88.8
		α -Pinene	53.2
		1-Methylcyclohexene	95.0
		3-Carene	87.0
		Carvomethene	127
R ₂ C=CR ₂	110	2,3-Dimethyl-2-Butene	110
		2,3-Dimethyl-2-Pentene	108

It should be emphasised that for unsubstituted or alkyl substituted alkenes, k_{add} , the bimolecular rate constant for OH-Radical addition to carbon-carbon unsaturated bonds is given by the appropriate group rate constant in Table 3. As an example, for $\text{CH}_2 = \text{CH CH}_2 \text{ CH} = \text{CH}_2$, k_{add} is given by

$$\begin{aligned}
 k_{\text{add}} &= k(\text{CH}_2 = \text{CHR}) + k(\text{CH}_2 = \text{CHR}) \\
 &= 2 \times 26.3 \times 10^{-12} \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1} \\
 &= 52.5 \times 10^{-12} \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}
 \end{aligned}$$

It should also be noted that in the above example, H-Atom abstraction from the methylene group is also possible. This process makes a relatively minor contribution to k_{OH} , but may be accounted for using the methods outlined in the previous section.

$$\text{Thus } k_{\text{OH}} = k_{\text{add}} + k_{\text{abstr}}$$

$$\begin{aligned} &= 52.6 \times 10^{-12} + k^{\circ} F(>\text{C}=\text{C}<) F(>\text{C}=\text{C}<) \\ &= 52.6 \times 10^{-12} + 0.838 \times 10^{-12} \times 1 \times 1 \\ &= 53.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \end{aligned}$$

Further similar examples of rate constant estimation are found in Appendix 3.

For conjugated double bond systems, the $\begin{array}{c} | \quad | \\ >\text{C}=\text{C} - \text{C}=\text{C}< \end{array}$ structure is considered as a single unit with the group rate constant again depending solely on the number and orientation of alkyl substituents around this structural unit. The recommended group rate constants at 298K to be used are given in Table 4 together with the relevant experimental data. Table 4 also gives the group rate constant data for OH-Radical addition to cumulative and alkyne structures, i.e., $>\text{C}=\text{C}=\text{C}<$ and $-\text{C} \equiv \text{C}-$ bonds.

Table 4: Recommended group rate constants and experimentally observed rate constants for OH-Radical addition to alkyl substituted conjugated and cumulative alkenes together with alkynes with varying degrees and orientation of substitution.

General Structure	Recommended Group Rate Constant ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ $\times 10^{-12}$)	Alkene or Alkyne	Experimental Rate Constant ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ $\times 10^{-12}$)
$\text{H}_2\text{C}=\text{CHCH}=\text{CHR}$	105	<u>cis</u> -1,3-Pentadiene	101
$\text{H}_2\text{C}=\text{CHCR}=\text{CH}_2$	105	<u>trans</u> -1,3-Butadiene	101
$\text{H}_2\text{C}=\text{CHCR}=\text{CHR}$	105	<u>cis</u> - and <u>trans</u> -2,4-Hexadiene	135
$\text{H}_2\text{C}=\text{CRCH}=\text{CHR}$	135	2-Methyl-1,3-Pentadiene	137
$\text{H}_2\text{C}=\text{CRCR}=\text{CH}_2$	135	4-Methyl-1,3-Pentadiene	137
$\text{RHC}=\text{CHCH}=\text{CHR}$	135	2,3-Dimethyl-1,3-Butadiene	122
$\text{H}_2\text{C}=\text{CHCR}=\text{CR}_2$	180	1,3-Cyclohexadiene	163
$\text{H}_2\text{C}=\text{CRCH}=\text{CR}_2$	180	1,3-Cycloheptadiene	139
$\text{RHC}=\text{CHCH}=\text{CR}_2$	180	β -Phellandrene	114
$\text{H}_2\text{C}=\text{CRCR}=\text{CHR}$	180		
$\text{RHC}=\text{CRCH}=\text{CHR}$	180	α -Phellandrene	310
$\text{R}_2\text{C}=\text{CHCH}=\text{CR}_2$	230	α -Terpinene	300
$\text{RHC}=\text{CRCH}=\text{CR}_2$	230	2,5-Dimethyl-2,4-Hexadiene	211
$\text{H}_2\text{C}=\text{CRCR}=\text{CR}_2$	230		

Table 4 (cont'd): Recommended group rate constants and experimentally observed rate constants for OH-Radical addition to alkyl substituted conjugated and cumulative alkenes together with alkynes with varying degrees and orientation of substitution.

General Structure	Recommended Group Rate Constant ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) $\times 10^{-12}$	Alkene or Alkyne	Experimental Rate Constant ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) $\times 10^{-12}$
$\text{H}_2\text{C}=\text{C}=\text{CHR}$	31	1,2-Butadiene 1,2-Pentadiene	26 35.6
$\text{H}_2\text{C}=\text{C}=\text{CR}_2$	57	3-Methyl-1,2-Butadiene	57.1
$\text{HC}\equiv\text{CR}$	7	Propyne 1-Butyne	6.1 8.1
$\text{RC}\equiv\text{CR}$	2.9		

If the alkenes or alkynes contain substituents other than alkyl, substituent factors are used. These are denoted by $C(X)$ to distinguish them from the substituent factors associated with k_{abstr} estimation. For example, for $\text{CH}_2=\text{CHX}$, k_{add} is given by

$$k_{\text{add}} = k(\text{CH}_2 = \text{CHR}) C(X)$$

and for $\text{CH}_2 = \text{CXY}$ by

$$k_{\text{add}} = k(\text{CH}_2 = \text{CR}_2) C(X) C(Y).$$

The substituent factors $C(X)$ enabling estimation of k_{add} at 298K which have been derived from available data are found in Table 5.

Table 5: Values of $C(X)$ for substituent groups X

Substituent Group X	$C(X)$
-F	0.4
-Cl	0.20
-Br	0.26
-CH ₂ Cl	0.80
-CN	0.15
-CHO	0.26
-COCH ₃	0.91
-OCH ₃	1.30
=O	1.00

A detailed comparison of the experimentally observed and calculated room temperature rate constants for OH-Radical addition to carbon-carbon unsaturated bonds has been made by Atkinson (1985). Figure 6 shows a plot of the room temperature experimental values versus the calculated rate constant. Deviation of the calculated value from the experimentally measured value by a factor of 2 is indicated by the dashed lines.

Fig. 6: A plot of calculated versus experimental OH-Radical addition rate constants, with perfect agreement denoted by the solid line, and agreement to within a factor of 2 indicated by the area within the dashed lines.

In Appendix 3, worked examples are given for rate constant estimation with substituted alkenes containing isolated, conjugated and cumulative carbon-carbon double bonds, as well as for substituted alkynes. Further examples are to be found in the review by Atkinson (1985).

2.1.4 OH-Radical Addition to Aromatic Rings

To calculate the bimolecular rate constant for OH-Radical addition to aromatic rings, k_{arom} , the relationship between k_{arom} and the sum of the electrophilic substituent constants of the aromatic ring ($\Sigma \sigma^+$) is employed. This relationship was first developed by Zetzch (1982), and later Atkinson (1985) using a modified data base presented the following equation:

$$\log k_{\text{arom}} = -1.35 \Sigma \sigma^+ - 11.69 \quad (3)$$

This expression forms the basis of the calculation method used in this document, and the plot from which it is derived is shown in Figure 7.

Fig. 7: A plot of $\log k_{\text{arom}}$ versus $\Sigma \sigma^+$ for certain substituted benzenes and biphenyl, with the solid line representing Equation (3) (Atkinson, 1985).

From Figure 7 it can be seen that for 31 out of 38 aromatic compounds involved in the correlation the calculated rate constants at 298K agree with the experimentally measured values to within a factor of 2, even though the absolute magnitude of these experimentally measured rate constants varies by a factor of approximately 700.

The values of $\Sigma \sigma^+$ for use in Equation (3) may be calculated in the following manner

- Steric hindrance is neglected and σ_o^+ is set equal to σ_p^+
- The OH-Radical adds to the position yielding the most negative value of $\Sigma \sigma^+$ (preferably a free position). This is the value of $\Sigma \sigma^+$ used in Equation (3).
- If all positions are occupied, the ipso position is treated as a meta position.

Values of σ_m^+ and σ_p^+ necessary to determine $\Sigma \sigma^+$ have been published by Brown and Okamoto (1958). These are listed in Table 6.

Table 6: Values of the electrophilic aromatic substituent constants σ_m^+ and σ_p^+ (Brown and Okamoto, 1958)

Substituent		σ_m^+	σ_p^+
Dimethylamino	-N(CH ₃) ₂	-1.7	
Trimethylammonium	-N(CH ₃) ₃	0.359	0.408
Anilino	-NHC ₆ H ₅	-1.4	
Amino	-NH ₂	-0.16	-1.3
Hydroxy	-OH	-0.92	
Acetylamino	-NHC(O)CH ₃	0.08*	-0.62*
Benzoylamino	-NHC(O)C ₆ H ₅		-0.6*
Methoxy	-OCH ₃	0.047	-0.778
Phenoxy	-OC ₆ H ₅	-0.5	
Methylthio	-SCH ₃	0.158	-0.504
Methyl	-CH ₃	-0.066	-0.311
Ethyl	-C ₂ H ₅	-0.064	-0.295
Substituent		σ_m^+	σ_p^+
Isopropyl	-CH(CH ₃) ₂	-0.060	-0.280
tert-Butyl	-C(CH ₃) ₃	-0.053	-0.256
Phenyl	-C ₆ H ₅	0.103	-0.179
beta-Naphthyl	-C ₁₀ H ₇	-0.135	
Carboethoxymethyl	-CH ₂ C(O)OC ₂ H ₅	-0.01	-0.164
Chloromethyl	-CH ₂ Cl	0.14	-0.01
Hydrogen	-H	0	0
Trimethylsilyl	-Si(CH ₃) ₃	0.011	0.021

Fluoro	-F	0.352	-0.073
Chloro	-Cl	0.399	0.114
Bromo	-Br	0.405	0.150
Iodo	-I	0.359	0.135
Carboxy	-C(O)OH	0.322	0.421
Carboxylate	-C(O)O ⁻	-0.028	-0.023
Carbomethoxy	-C(O)OCH ₃	0.368	0.489
Carboethoxy	-C(O)OC ₂ H ₅	0.366	0.482
Trifluoromethyl	-CF ₃	0.520	0.612
Cyano	-CN	0.562	0.659
Nitro	-NO ₂	0.674	0.790

* from: R. TAYLOR *Electrophilic Aromatic Substitution* Wiley & Sons, Chichester 1990

It should be noted this method is not applicable to some aromatic compounds, since they react largely by H-Atom abstraction (eg benzaldehyde). In Appendix 3 worked examples are given for estimation of k_{arom} .

2.2 Methods to Estimate the Rate of Reaction with Ozone

2.2.1 Introduction

Ozone reacts relatively rapidly only with compounds containing unsaturated carbon-carbon bonds, some polyaromatic compounds and phenols, as well as some amines and sulphides. The approach used in this document for estimating the bimolecular rate constant for reaction with ozone (k_{O_3}) in this document is a structure-activity one. In principle it is similar to the estimation methods previously described for OH-Radical abstraction and addition to unsaturated carbon-carbon bonds. The method involves selection of group rate constants for molecules containing groups capable of reaction with ozone. The reaction rate may be modified by substituents and, to account for this modification, substituent factors are employed.

The half-life for reaction of a gaseous organic compound with ozone may be calculated as follows:

$$t_{1/2 \text{ Ozone}} = \ln 2 / (k_{O_3} [O_3]) \quad (4)$$

The concentration of ozone in unpolluted air in the lower troposphere has been found to be approximately 7×10^{11} molecules cm^{-3} (Atkinson, 1984). Under such conditions then,

$$t_{1/2 \text{ Ozone}} = 9.9 \times 10^{-13} / k_{O_3} \quad (5)$$

Where $[O_3]$ is in fact higher than the value assumed, Equation (5) provides an overestimate of half-life. Analogously, where $[O_3]$ is lower, Equation (5) provides an underestimate of half-life.

2.2.2 Ozone Reaction With Unsaturated Carbon-Carbon Bonds and Aromatic Rings

In order to estimate k_{O_3} for organic compounds containing unsaturated carbon-carbon bonds or aromatic rings, using the method adopted, it is necessary to select group rate constants. For alkenes and alkynes these group rate constants vary according to the number and orientation of alkyl substituents surrounding the unsaturated carbon-carbon bond. They are tabulated in Table 7. Thus for alkyl substituted alkenes and alkynes, k_{O_3} is numerically equal to the group rate constant. As an example, for cis-2-Butene, k_{O_3} is given by

$$k_{O_3} = k(\text{cis-RCH=CHR})$$

$$= 160 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$= 1.6 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

For alkyl substituted aromatic compounds, group rate constants vary according to the number of alkyl substituents, and are also tabulated in Table 7. Again for alkyl substituted aromatics, k_{O_3} is equal to the appropriate group rate constant.

With compounds containing unsaturated carbon-carbon bonds and aromatic rings, the magnitude of k_{O_3} is also influenced by the presence of non-alkyl substituents bonded to the unsaturated carbon-carbon bond or aromatic ring. To account for this in estimation of k_{O_3} the appropriate group rate constant is multiplied by a substituent factor. Substituent factors to be used are found in Table 7, and denoted by S(X) to distinguish them from substituent factors associated with estimation of k_{OH} . As an example of the use of substituent factors, k_{O_3} for chloroethene is given by

$$\begin{aligned} k_{O_3} &= k(\text{CH}_2 = \text{CHR}) S(\text{Cl}) \\ &= 12 \times 10^{-18} \times 0.24 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \\ &= 2.88 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \end{aligned}$$

It should be noted that if a molecule contains more than one group capable of reaction with O_3 , then for estimation purposes, these groups are considered separately. Thus k_{O_3} for such a molecule is the sum of the estimated rate constants for the individual reactive groups.

Table 7: Group rate constants and substituent factors for O_3 reaction with alkenes, alkynes and aromatic compounds

General Structure	Group Rate Constant Group X $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ $\times 10^{-18}$	Substituent S(X)	S(X)
$\text{CH}_2 = \text{CH}_2$	1.9	-F	0.47
$\text{CH}_2 = \text{CHR}$	12	-Cl	0.24
<u>cis</u> - $\text{RCH} = \text{CHR}$	160	$-\text{C}_6\text{H}_5$	85
<u>trans</u> - $\text{RCH} = \text{CHR}$	260	-CHO	0.10
$\text{RCH} = \text{CR}_2$	500	-C(O)R	1.8
$\text{R}_2\text{C} = \text{CR}_2$	1500		
Cyclopentene	800		
Cyclohexene	170		
$\text{CH} \equiv \text{CR}$	0.08		
Aromatic Compounds			
Alkyl substituted	0.00005		
Dialkyl substituted	0.001-0.02		
Trialkyl substituted	0.006-0.008		
Tetraalkyl substituted	0.02		
Hexaalkyl substituted	0.04		
Phenol	3.3		

2.3 Methods to Calculate the Maximum Rate of Direct Phototransformation

2.3.1 Introduction

To undergo direct phototransformation in the troposphere, a molecule must absorb solar radiation within the wavelength range encountered in the troposphere. A measure of the strength of absorbance per molecule at a given wavelength is the absorption cross section or cross section ($\sigma(\lambda)\text{cm}^2 \text{molecule}^{-1}$). Other factors that need to be considered in determining the rate constant for direct phototransformation (k_p) are the solar radiation intensity ($J(\lambda)$ photons $\text{cm}^{-2} \text{s}^{-1}$) and the quantum yield for the process ($\phi(\lambda)$ molecule photon^{-1}). The magnitude of both solar radiation intensity and quantum yield are dependent upon wavelength (λ). For a given wavelength

$$k_p(\lambda) = \sigma(\lambda)\phi(\lambda)J(\lambda) \quad (6)$$

and an overall direct phototransformation rate constant may be obtained by summing $k_p(\lambda)$ over an appropriate wavelength range

$$k_p = \sum k_p(\lambda) = \sum \sigma(\lambda)\phi(\lambda)J(\lambda)$$

Note that k_p , in contrast to k_{OH} and k_{O_3} , is a first order rate constant, with units of s^{-1} .

An estimate of k_p may be made using published solar radiation intensity data and an assumed quantum yield of 1, in conjunction with measured values of $\sigma(\lambda)$ obtained from absorption spectroscopy. Procedures for measurement of gas phase spectra are outlined in Section 2.3.2. Where low vapour pressure or low absorption of the compound preclude an accurate measurement in the gas phase, the liquid or solution phase absorption spectrum should be measured as also outlined in Section 2.3.2. This estimation method has been previously suggested by a number of authors (Hendry and Kenley, 1979; Cupit, 1980; Mill et al. 1981 and Pitts et al., 1981).

The rate of direct photochemical transformation for compound X is given by

$$\text{Rate} = k_p [X]$$

and the half-life for direct photochemical transformation by

$$t_{1/2} (\text{Direct Phototransformation}) = \ln 2 / k_p$$

The principal source of error in this estimation method is the assumption of a quantum yield of 1. In practice quantum yields are often much lower than this. This means that the estimated value of k_p will be a maximum value or upper limit. Consequently, the estimated half-life will be a lower limit.

2.3.2 Equipment and Materials

An ultraviolet-visible spectrophotometer is necessary. Any commercial or constructed instrument is suitable if it meets the following specifications:

- (1) A sensitivity of at least 1.0×10^{-3} absorbance units.
- (2) Capable of accommodation of absorption cells with pathlengths greater than or equal to 10 cm.
- (3) Resolution must be sufficient to attain a 90% separation of two monochromatic spectral features less than 4 nm apart, peak to peak.

Gas Phase Spectra

A suitable gas handling system for charging a UV cell is schematically illustrated in Figure 8.

Fig 8: A gas handling system for charging a UV cell. The volume of region A should be minimized as much as possible in order to minimize pumping times (Mill et al., 1982).

In general, only high vacuum, greaseless, O-ring stopcocks (either Pyrex or Teflon) should be used where required. No materials other than Pyrex or Teflon should be used for any of the components of the vacuum system shown in Figure 8. Grease should be rigorously excluded from this system, as should metal and rubber. Stopcocks should be positioned to minimize sample contact with O-rings wherever possible. All joints and connections should be made so that air leaks are limited to less than 10^{-4} Pa liter s^{-1} for the whole system including the absorption cell.

The manometer or pressure gauge should be capable of measuring pressures absolutely, to below 1% of the pure component vapour pressure of the chemical under investigation. The same manometer, or another connected in parallel, should also be capable of determining atmospheric pressure to within at least $\pm 5\%$.

For all pressure measurements, mercury must be rigorously excluded from the system to avoid contamination, since it is a powerful photo-chemical sensitizer.

UV cells with a pathlength of 10 cm are commonly employed in obtaining gas phase UV-Vis spectra. The cells should be constructed of Pyrex tubing with a diameter compatible with the spectrophotometer. Parallel quartz (commercial grade or better) windows should be attached using a low pressure epoxy glue. A sidearm should be affixed to the cell as shown, consistent with the space requirements of the spectrophotometer sample chamber.

Solution phase spectra

A matched pair of quartz cells, with 1cm pathlengths or larger, may be used if high enough concentrations of the chemical under investigation can be obtained in suitable solvents. In addition, 10cm cells similar to those described above for the gas phase work can also be used for solution phase spectra. Cells with a pathlength of 10 cm are to be preferred since measurable absorbances may be expected to be ten times larger than in the 1 cm pathlength cells.

The main difference between the gas phase cells described earlier and 10cm solution phase cells is in the sidearm. A stopcock is not necessary with liquids and an O-ring seal is undesirable in the presence of some liquid solvents. A dry glass joint cap over the sidearm to prevent significant evaporation during the measurement is all that is necessary; caps of Teflon are also satisfactory. As long as no direct contact is allowed between liquid solvent and the cap used, any material may be used to reduce evaporation rate.

Standard analytical volume and mass measurement techniques should be used to prepare solutions. In particular, glassware should be washed thoroughly in appropriate nonetching cleaning solutions, then rinsed at least three times with purified water and allowed to dry at temperatures below 40 °C.

2.3.3 Procedures for Measurement of Spectra

Gas phase spectra

The following procedure is recommended for use with the apparatus shown in Figure 8. The UV cell is attached to the apparatus by a vacuum-tight joint and evacuated to less than 10^{-3} Pa, if possible, but to at least one-hundredth of the pure component vapour pressure of the compound to be introduced into the cell. Several millilitres of liquid compound are then placed in or condensed into the sample reservoir and degassed by at least 3 repeated freezing, pumping, and thawing cycles. The compound is allowed to warm to room temperature, and a vapour sample allowed to expand into the UV cell and manometer. The stopcock to the sample cell is closed, and the initial volume of test chemical is pumped away. The pump is closed off, and the stopcock to the sample cell is opened again to allow another sample of the test chemical to expand into the cell.

After the sample cell stopcock is closed, sufficient time should be allowed for the temperature and pressure to reach equilibrium. It may be necessary to wait 15-30 minutes for the pressure to equilibrate enough so that it changes less than 5 % in a time interval equal to that necessary for a spectrum to be obtained.

The equilibrium pressure is read, and the stopcocks to the cell and reservoir are closed. The vapour in the connecting tube is pumped out. Then air, dried over molecular sieves, or synthetic air from a cylinder is allowed to fill the connecting tubing first and then allowed to enter the UV cell until atmospheric pressure is obtained. The stopcock on the cell is then closed, and the cell is disconnected from the apparatus and placed in the UV spectrophotometer. The UV-Vis spectrum is measured using a matched cell (filled with air) as a reference according to the manufacturer's directions.

At least two spectra should be recorded, preferably 15 or more minutes apart, to check for any differences due to mixing. If a significant difference appears, a third spectrum must be obtained at a later time. Maximum turbulence at the time the air component is added will minimize this problem. If mixing times are too long to be practical, premixing of air and sample in a large-volume cell may be a solution to the problem, providing the gaseous mixture can be left to mix for more than 12 hours (for a 20-litre mixture).

The above procedure should be repeated at two other pressures of the test compound if possible. The pressures should differ by at least a factor of two and preferably five to ten, providing the absorption is strong enough at the lower pressure to be determined with reasonable precision using the spectrophotometer available.

Solution phase spectra

Any solvent that does not absorb significantly in the wavelength region above 290nm, that dissolves the compound under investigation sufficiently, and that does not react or associate with the test compound can be used. Examples of nonassociating solvents are hexane, cyclohexane, carbon tetrachloride, and methylene chloride. Since solvent effects cannot be predicted, at least two solvents that result in very similar absorption spectra should be used. Generally, solvents that tend to associate such as H₂O, alcohols, carboxylic acids, and nitriles should be avoided if possible.

As for the gas phase spectrum determination, a 10 cm cell should be used for the solution spectrum, if possible. The procedure is also analogous to that for the gas phase determination. The solution can be made up and thoroughly mixed using appropriate analytical glassware and techniques. The cell to be used and another matching cell, if necessary, are filled with solvent, and a blank spectrum is run. Absorbances obtained must be subtracted from the spectrum measured with the test compound present. The blank run and reference cell are more important with solution phase spectroscopy than gas phase spectroscopy because the solvents may absorb at solar spectral wavelengths as a result of dissolved impurities or surface reflection or refractions (due to the typically large index of refraction difference between air and liquid).

After the sample cell is rinsed three times with the solution containing the compound under investigation at the desired concentration, a spectrum is obtained. Two spectra, taken 15 minutes apart, should be obtained on the first sample only, to determine if the compound is reacting. Subsequently, spectra should be recorded for at least two other concentrations, covering an order of magnitude if possible. The blank run and rinsing processes are then repeated, and the whole process is repeated with a second solvent.

2.3.4 Calculation of the Maximum Rate of Direct Photo-transformation

The absorption cross section for a compound at a given wavelength may be derived from absorbance in the following manner. The Beer-Lambert Law may be expressed as

$$2.303 A(\lambda) = \sigma(\lambda) C l \quad (7)$$

where $A(\lambda)$ is the absorbance at wavelength λ , $\sigma(\lambda)$ the absorption cross section at wavelength λ (cm² molecule⁻¹), C the concentration of the absorbing species (molecules cm⁻³) and l the pathlength of the absorption cell (cm). From Equation 7, $\sigma(\lambda)$ is given by

$$\sigma(\lambda) = 2.303 A(\lambda) / C l$$

From the consistency of the data at three pressures plus estimates of possible deviations, it will be possible to determine whether there is deviation from the Beer-Lambert law. In cases where there is a consistent variation between absorption cross sections determined at different pressures, the low pressure values are preferred, providing that the instrumental precision is better than $\pm 25\%$ at the low pressure.

Pathlength error contributes directly to the error in $\sigma(\lambda)$, but fortunately it can be controlled relatively easily. For 10cm absorption cells, direct measurement with calipers should be adequate to obtain pathlengths accurate to within ± 2 mm or 2%. For cells with smaller pathlengths especially those with 1cm pathlengths sometimes used for solution phase work, special calipers are necessary for direct measurement. Often the manufacturers of such cells are in a better position to determine the pathlength to within 0.2 mm or 2%.

Combining $\sigma(\lambda)$ with $J(\lambda)$ and assuming $\phi(\lambda) = 1$ as in Equation (6) an estimate may be obtained of the rate constant for direct phototransformation at wavelength λ . The $J(\lambda)$ values in Appendix 2 refer to the summer solstice, equinox, winter solstice, as well as average values for the autumn/winter period, and spring/summer period. Thus estimates of $k_p(\lambda)$ generated using data from Appendix 2 will be relevant only for the time period or season associated with $J(\lambda)$. To estimate the overall rate constant for direct phototransformation in the troposphere, k_p , values of $k_p(\lambda)$ are summed over the wavelength range

characteristic of the solar radiation in the troposphere. Because of the assumption of a quantum yield of 1, this method calculates a maximum rate constant for direct phototransformation in the troposphere.

3. EXPERIMENTAL METHODS

3.1 Absolute Methods to Determine the Rate of Reaction with OH-Radicals

3.1.1 Introduction

Absolute experimental methods to determine the rate of reaction with OH-Radicals are generally carried out with the reactant i.e. the gaseous organic compound, in large excess over the initial OH-Radical concentration (Atkinson, 1985). Under such conditions, the decay of the OH-Radical concentration can be considered to be pseudo first order. The decreasing OH-Radical concentration is monitored using optical detection methods in the UV region.

Two common experimental techniques are the discharge flow and flash photolysis techniques. These techniques are complementary in the sense that with the flash photolysis technique a pressure range up to atmospheric pressure or greater can be employed whereas with the discharge flow technique pressure is limited to $\leq 1.5 \times 10^3$ Pa. Only the flash photolysis technique is described in more detail in the remainder of this section. For further information on this and other techniques the reader is referred to the review by Atkinson (1985) and the references cited therein.

With the flash photolysis technique, OH-Radicals are produced by pulsed photolysis of precursors. The technique requires the introduction of gaseous organic compounds into a reaction cell or chamber at a partial pressure of the organic compound sufficient to measurably increase the decay rate of OH-Radicals above that of the background.

Relatively small ($< 10^{-12}$ cm³ molecule⁻¹ s⁻¹) rate constants may be difficult to measure accurately due to direct phototransformation of the organic compound under investigation itself or direct phototransformation of more reactive and/or more volatile impurities. The lower limit for determination of k_{OH} by the flash photolysis technique may be derived from the following expression (Zetzsch, 1982):

$$P_s \cdot k_{OH} = 10^{-13} \text{ Pa cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

where P_s is the vapour pressure of the organic compound at the lowest temperature in the experimental system, i.e., gas saturation system, reaction cell and connecting lines.

In order to detect any pressure dependence of the reaction, experiments need to be conducted with a variation in total pressure (a factor of at least 10 is sufficient). If a dependence is discovered, this information can be employed to predict k_{OH} under tropospheric conditions (10^5 Pa).

3.1.2 Equipment and Materials

Experimental System

Slow flow conditions where the gaseous mixture (containing a diluent gas such as Ar if necessary) is swept out of the reaction chamber to prevent accumulation of photolysis and reaction products are generally employed.

A number of different precursors may be used as OH-Radical sources including H₂O, HNO₃, HNO₂, HCOOH, O₃ and H₂ mixtures.

With the exception of H₂O, these precursors can be photodissociated by electromagnetic radiation with one of the following wavelengths: 193, 248 and 351 nm.

Flash lamps with typical flash energies of 2 Joules or excimer lasers may be used as light sources for the photolysis of OH-Radical precursors. The duration of the light pulses should not exceed the time resolution of the OH-Radical monitoring system which should be in the range of 10 μ s. Initial OH-Radical concentrations should be smaller than 5×10^{12} molecules cm^{-3} in order to avoid interferences by radical-radical reactions. Since OH-Radical concentrations are determined using various optical methods, depending on the photolysis light source, special precautions such as light baffles, spectral filters etc. may need to be employed to avoid stray light.

Techniques to measure OH-Radical concentrations include conventional resonance fluorescence or absorption. Higher sensitivity may be achieved by laser techniques such as laser induced fluorescence. In the case of fluorescence detection, the reaction chamber may be as small as a few hundred cm^3 , allowing simple temperature control. CW-laser long path absorption, incorporating a multipath reflection system in the photolysis cell may also be employed to measure OH-Radical concentrations. With all OH-Radical monitoring techniques a lower detection limit of $\leq 10^{10}$ molecules cm^{-3} is necessary to enable the concentration decay to be followed over at least 3 lifetimes. A lifetime is defined as the time period for the concentration to fall to 1/e of its initial value. For the gaseous organic compound, concentrations are usually determined by volume and flow measurements, and the absolute pressure in the reaction chamber.

3.1.3 Experimental Procedure

Under pseudo first order conditions, with the gaseous organic compound in excess, an exponential decay of OH-Radical concentration should be observed. A plot of $\log [\text{OH}]$ versus time, such as that in Figure 9 should afford a linear relationship, with an intercept of the initial OH-Radical concentration, and a slope of $k'_{\text{OH}}/2.303$ where k'_{OH} is the pseudo first order rate constant (s^{-1})

Fig. 9: A plot of the logarithm of the OH-Radical concentration versus time from a typical exponential decay under pseudo first order conditions.

The bimolecular rate constant for reaction with OH-Radicals, k_{OH} , may be determined using differing excess concentrations of the test organic compound under pseudo first order conditions, from the following equation

$$k'_{\text{OH}} = k_{\text{OH}} [S] + k_b \quad (8)$$

where [S] is the concentration of the organic reactant. The intercept of Equation (8) is k_b which is the background rate constant (first order) for OH-Radical concentration decay in the absence of organic compound.

3.1.4 Reproducibility

Using the equipment, materials and general procedure outlined, data repeatability of $2\sigma < 10\%$ might be expected from a single laboratory. Results from different laboratories are expected to agree to within $\pm 20\%$.

3.2 Relative Methods to Determine the Rate of Reaction with OH-Radicals

3.2.1 Introduction

With relative experimental methods one or more reference compounds (with known values of k_{OH}) and one or more test compounds (with unknown k_{OH} values) are vapourized in a reaction chamber (Nolting et al., 1985). Thereafter, OH-Radicals are produced in the reaction chamber by a suitable method. The decay of each of the compounds is measured by appropriate analytical procedures as a function of time. The k_{OH} rate constants of the test compounds are obtained from kinetic analysis of the concentration time profiles as outlined later in this section.

The method described in this section is applicable generally to substances whose vapour pressure at 298 K exceeds 1 Pa. For further detail, the reader should consult Pitts et al. (1985). The lower limit of k_{OH} values as determined by this method is about $3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$. This corresponds to a maximum or upper tropospheric half-life of approximately 27 days (assuming $[OH] = 10^6 \text{ molecules cm}^{-3}$).

For substances with relatively low vapour pressure ($<1 \text{ Pa}$), a special vapourizer (Klöpffer et al., 1985) or heat regulated chamber (Becker, 1986; Atkinson, 1985) should be used.

Experiments can be conducted at room temperature or elevated temperatures. If the experiments are conducted at elevated temperatures, they should be performed at several temperatures using one or more reference compounds (Atkinson et al., 1979; Becker, 1986; Atkinson, 1985 and Nolting et al., 1988). Checks should be carried out to ensure that test and reference compounds react essentially only with OH-Radicals, or that the rate of other loss processes such as reaction with Cl-Radicals, NO_3 -Radicals, ozone or direct phototransformation can be accurately accounted for.

3.2.2 Equipment and Materials

The reaction chamber should be sufficiently large (generally $> 20 \text{ litre volume}$) to minimize the influence of wall reactions on measured rate constants. For highly volatile organic compounds, reaction chambers with smaller volumes can be used (Fujiki, 1986). Teflon, Tedlar and borosilicate glass have been employed successfully as reaction chamber materials. The chamber may be operated with heating equipment for experiments involving elevated temperatures (Becker, 1986), and to investigate the humidity dependence of the reaction rate, the relative humidity of the reaction chamber contents may be varied. Before commencing an experiment it is important to ensure homogeneous mixing of the contents of the reaction chamber. Following completion of an experiment, an appropriate cleaning technique for the reaction chamber is necessary in order to avoid "memory" effects.

OH-Radicals may be generated by photolytic processes from a number of precursors including

- HONO which is prepared by mixing H_2SO_4 with NaNO_2 (Cox, 1974; Klöpffer et al., 1985)
- CH_3ONO and other alkyl nitrites (Tuazon et al., 1983) which are prepared from reaction of the corresponding alcohol with NaNO_2 in H_2SO_4 solution (Taylor et al., 1980)
- Photosmog system (Carter et al., 1979)

OH-Radical generation processes not involving photolysis include

- the thermal decomposition of HO_2NO_2 prepared from the reaction of H_2O_2 with HNO_3 at 0°C (Barnes et al., 1982)
- the reaction of NH_2NH_2 with O_3 leading to the formation of OH-Radicals by a series of complex reactions (Tuazon et al., 1983)

Reference compounds employed should be of the highest purity possible, and should have well characterized values of k_{OH} , as well as of rate constants for other possible loss processes. The following list of possible reference compounds, are taken from Becker et al. (1984) and Atkinson (1985). Where reaction with ozone is sufficiently rapid to interfere with measurement of k_{OH} , values of k_{O_3} are provided (Tuazon et al., 1983).

T a b l e 8 :
 Values of k_{OH} and where appropriate k_{O_3} for possible reference compounds. Data are taken from Becker et al. (1984), and Atkinson (1985) and Tuazon et al. (1983)

Reference Compounds	k_{OH}	k_{O_3}
	$(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	$(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$
Hexafluorobenzene	0.219×10^{-12}	
n-Butane	2.53×10^{-12}	
Propane	1.20×10^{-12}	
n-Pentane	4.13×10^{-12}	
Ethane	2.80×10^{-12}	
Ethene	8.54×10^{-12}	1.75×10^{-18}
Propene	26.3×10^{-12}	11.3×10^{-18}
n-Hexane	5.58×10^{-12}	
Cyclohexane	7.38×10^{-12}	
2-Methyl-1,3-butadiene	101×10^{-12}	14.3×10^{-18}
2,2,3,3-Tetra-methylbutane	1.06×10^{-12}	
Toluene	6.10×10^{-12}	
Mesitylene	55.0×10^{-12}	

Using the procedures outlined in this section, the dynamic range for evaluation of rate constants of test compounds is limited to a factor of 5 relative to that of the chosen reference compound.

The decrease in concentration of the test and reference compounds should be measured at regular intervals by a suitable analytical technique. Continuous measurement, e.g., *in situ* spectro-photometric techniques such as FT-IR, is possible in some cases. Analytical methods which allow the simultaneous determination of concentrations of a test and reference compounds are to be preferred. The decrease of the concentration of test and reference compounds should be monitored over at least an order of magnitude.

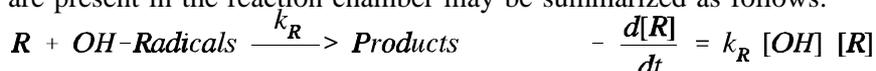
3.2.3 Experimental Procedure

The reaction chamber is filled with synthetic or purified natural air and the organic reactants are injected or flushed into the chamber with the air. Initial concentrations of reference compounds $[R]_0$ and test compounds $[S]_0$ are determined several times. Equilibrium between adsorption on the walls and the gas phase must be achieved before commencing the experiment. It should be ascertained whether the compounds interact with the OH-Radical precursor. In these cases dilution experiments or other OH-Radical precursors should be employed.

If the test compound absorbs light emitted from the light source used to generate OH-Radicals photolytically, the influence of direct photo-transformation should be determined before k_{OH} is measured. This can be done in the reaction chamber in a separate experiment ensuring traces of NO_x are carefully avoided so that formation of OH-Radicals and O_3 can be neglected. The absence of OH-Radicals and O_3 should be checked by also adding a reference compound which does not absorb light in the wavelength range of the emission spectrum of the light source, and which is highly reactive towards OH-Radicals and ozone. Constant temperatures should be maintained inside the reaction chamber during all experiments.

Experimental procedure with one reference compound:

The kinetic analysis of this situation, where the test compound, S, and one reference compound with known k_{OH} are present in the reaction chamber may be summarized as follows: (8)



(9)

where R and S are the reference and test compounds respectively and k_R and k_S the respective rate constants for reaction with OH-Radicals. The value of k_R is known, whereas that for k_S is not.

For pseudo first order conditions, with constant $[OH]$, values of $k_R [OH]$ and $k_S [OH]$ can be evaluated by plotting $\ln([R]_t/[R]_0)$ and $\ln([S]_t/[S]_0)$ versus reaction time. An example is shown in Figure 10. Initial concentrations of R and S are denoted $[R]_0$ and $[S]_0$ respectively, while concentrations at time t are denoted $[R]_t$ and $[S]_t$ respectively.

Fig 10: Plots for evaluating $k_R [OH]$ and $k_S [OH]$ from the decay of reference and test compound concentrations as a function of time with constant $[OH]$.

The slopes of the plots, b_R and b_S are equivalent to $-k_R[\text{OH}]$ and $-k_S[\text{OH}]$ respectively. The unknown k_S is then calculated from

$$k_S = k_R \ b_S / b_R$$

If pseudo first order assumptions are not applicable, and the concentration of OH-Radicals varies significantly during the reaction time, the data points in $\ln([\text{R}]_t/[\text{R}]_o)$ versus t plots will not fit a straight line.

In such cases the formal solutions of the differential equations (8) and (9) are

$$\ln [\text{R}]_t / [\text{R}]_o = - k_{R_o} \int^t [\text{OH}] \ dt$$

and

$$\ln [\text{S}]_t / [\text{S}]_o = -k_{S_o} \int^t [\text{OH}] \ dt$$

Combination of these two equations and rearrangement of terms yields

$$\ln \frac{[\text{S}]_o}{[\text{S}]_t} = \frac{k_s}{k_R} \ln \frac{[\text{R}]_o}{[\text{R}]_t}$$

The data points in a plot of $\ln([\text{S}]_o/[\text{S}]_t)$ versus $\ln([\text{R}]_o/[\text{R}]_t)$ can be fitted to a straight line with zero intercept and a slope of k_S/k_R . This is illustrated below in Figure 11.

Fig. 11: A plot of $\ln([\text{S}]_o/[\text{S}]_t)$ versus $\ln([\text{R}]_o/[\text{R}]_t)$ for evaluating k_S if $[\text{OH}]$ is not constant.

The unknown k_S can be calculated from the slope, and k_R . It should be noted that the above discussion is only applicable if the contents of the reaction chamber are well mixed.

Experimental procedure with several reference compounds

The simultaneous employment of several reference compounds requires a more sophisticated data treatment. Because several reference compounds are used, individual concentrations may be relatively small, and dilution effects resulting from sampling for example need to be taken into account (Lloyd et al., 1976). For a reference compound concentration decay including dilution effects may be represented by the following kinetic scheme



where k_R represents k_{OH} for a reference compound, and d_i is the first order dilution rate constant. This leads to the differential equation

$$-\frac{[R]}{dt} = k_R [OH][R] + d_i [R] \quad (10)$$

Assuming the contents of the reaction chamber are ideally mixed, Equation (10) may be integrated to

$$\ln \left(\frac{[R]_t}{[R]_0} \right) = -k_{R_0} \int_0^t [OH] dt - \int_0^t d_i dt$$

For checking the validity and consistency of data at least five reference compounds are necessary. For each time a measurement is made, a plot of $\ln([R]_t/[R]_0)$ versus k_R for all reference compounds should yield a straight line with a slope of

$$-\int_0^t [OH] dt$$

and an intercept of

$$-\int_0^t d_i dt$$

An example is shown in Figure 12 below.

Fig. 12: A plot of $\ln([R]_t/[R]_o)$ versus the value of k_{OH} for each reference compound, k_R , at one measurement time. The reference compounds are hexafluorobenzene, 2,2,3,3-tetramethyl-butane, n-butane, 2,2,4-trimethylpentane, n-hexane and n-octane.

The above procedure enables the determination of

$$\int_0^t [OH] dt \text{ and } \int_0^t d_i dt$$

for each sampling time. Following completion of the experiment, the value of k_{OH} for the test compound (S) can be obtained by plotting

$$\ln ([S]_t / [S]_o) + \int_0^t d_i dt \text{ versus } \int_0^t [OH] dt$$

for each sampling time. Since the decay of the test compound concentration is described by an expression analogous to Equation (11), the intercept of such a plot is zero, and the slope $-k_{OH}$ for the test compound. An example is shown below.

Fig. 13: A plot of $\ln([S]_t / [S]_o) + \int_0^t d_i dt$ versus $\int_0^t [OH] dt$ for the test compound at all sampling times.

3.2.4 Reproducibility

Using the equipment, material and general procedures outlined, repeatability of the determined rate constant is approximately 10 to 20% or better. Reproducibility (between different laboratories) may be expected to be within a factor of two. It should be noted that greater variability has been observed with certain S, N and Cl containing compounds.

3.3 Absolute Methods to Determine the Rate of Reaction with Ozone

3.3.1 Introduction

Absolute methods to determine the rate of reaction with ozone have been reviewed by Atkinson and Carter (1984). The method outlined in this section is based upon those originally described by Pitts et al. (1981) and Mill et al. (1982). For further specific detail the reader should consult these references. Inert (Tedlar or FEP Teflon) bags are filled with either ozone or the test organic compound in relative excess and the other reactant at less than one-tenth the concentration. If the test compound is present in relative excess (the recommended situation in order to minimize the importance of secondary reactions leading to enhanced consumption of ozone, the ozone concentration is monitored in the dark, and the loss of ozone can be considered a pseudo first order process. Standard kinetic analysis affords a pseudo first order rate k'_{O_3} constant from which the true bimolecular rate constant k_{O_3} can be derived by taking into account the background disappearance rate constant of ozone.

If ozone is the reactant in relative excess or if ozone and the test compound are present in comparable concentration, alternative kinetic analyses are employed. These situations are not considered further in this document.

The method described is not applicable where the partial pressure of the test compound is sufficiently low that significant wall sorption occurs. In practical terms, this limits the method to compounds with vapour pressures greater than about 10Pa. Rate constants as small as $10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ may be measured with this method. Assuming an ozone concentration of $7 \times 10^{11} \text{ molecules cm}^{-3}$ (Atkinson and Carter, 1984), this corresponds to a tropospheric half-life of 3.13 years.

3.3.2 Equipment and Materials

To determine the rate constant for reaction of the test compound with ozone an ozone generator capable of producing up to 1 ppm ozone in a dried air stream is necessary. To determine ozone concentrations an ozone monitor or a suitable wet method such as that proposed by Bader and Hoignè (1982) is required.

Two 50 to 100 litre Teflon bags connected by a 10 mm stopcock, or alternatively one Teflon bag of approximately 160 litre volume which can be divided into two sub-chambers of equal volume are used. The bags or sub-chambers are fitted with manifolds permitting the addition of ozone/ air and test compound/air mixtures, and the withdrawal of samples for analysis. The volumes of both bags or sub-chambers should be known. The reaction of ozone and the test compound occurs in one bag or sub-chamber. The other bag or sub-chamber is used to prepare the test compound/air mixture.

3.3.3 Experimental Procedure

The bag or sub-chamber to be used as the reaction chamber is first filled with dry air containing about 1 ppm of O_3 . The ozone concentration is monitored for one hour in the absence of direct illumination.

A plot of the natural logarithm of the ozone concentration as a function of time is then made. The slope is equal to $-k_b$, where k_b is the first order background disappearance rate constant for ozone.

If k_b is greater than 0.01 min^{-1} , the bag may be contaminated, in which case the bag should be allowed to stand overnight with approximately 1 ppm O_3 . This treatment should be repeated until the background rate constant reaches the indicated limit.

The reaction chamber is then filled to approximately three-quarters of the maximum capacity with 1 ppm O_3 in dry air and the ozone concentration is monitored. In the second bag, which should be connected to the first bag with a freshly cleaned 10 mm stopcock, the test compound/air mixture is prepared by injecting a sufficient amount of liquid test compound into the second bag or sub-chamber. The syringe should be weighed before and after injection to obtain an accurate measure of the amount injected. The bag or sub-chamber is mixed by alternately pushing in the sides and ends for several minutes. Once the compound is totally vapourized, the stopcock is opened and the mixture is forced totally (> 95%) into the reaction chamber.

It may be necessary to vent some of the ozone/air mixture before adding the test compound/air mixture to ensure sufficient space in the reaction chamber. There will be a reduction in the ozone concentration reflecting the dilution that has occurred, and this should be measured.

At least 3 runs using a different initial excess concentration of the test compound must be performed. For each run the pseudo first order rate constant for reaction with ozone, k'_{O_3} , is defined by the relationship

$$\ln \frac{[\text{O}_3]_t}{[\text{O}_3]_o} = -k_{\text{O}_3} t = -(k_b + k_{\text{O}_3} [\text{S}]) t$$

where $[\text{S}]$ is the concentration of the test substance, which should be varied by a factor of at least 3. If less than 50% of the ozone disappears during the experiment, then additional experiments should be made with higher concentrations of the test substance. If all the ozone disappears in less than an hour, then $[\text{S}]$ should be decreased. However, it is important to keep the ratio of $[\text{S}]/[\text{O}_3]_o$ greater than 10 if at all possible; therefore, if $[\text{S}]$ is reduced, the initial $[\text{O}_3]$ should be reduced accordingly.

Since $k'_{\text{O}_3} = k_b + k_{\text{O}_3} [\text{S}]$, the value of k_{O_3} may be determined by plotting k'_{O_3} versus the various excess concentrations of the test substance. The intercept of such a plot will be k_b , and the slope k_{O_3} .

3.3.4 Repeatability and Reproducibility

Using the equipment, materials and general procedure outlined, data repeatability of < 10 to 20%, and data reproducibility of the order of 100% or less may be expected.

3.4 Methods to Determine the Rate of Direct Photo-transformation

3.4.1 Introduction

Depending on the calculated maximum rate of direct phototransformation (as outlined in Section 2.3), it may be decided to measure the actual quantum yield for direct phototransformation of the test compound. This will enable the evaluation of the rate of direct phototransformation in the troposphere.

Briefly, the method described in this section involves the test compound and an actinometer being exposed to light at one or more monochromatic wavelengths depending on the extent of the test compound's absorption in the solar spectral range. An actinometer is a compound that has a relatively high

vapour pressure, precisely known quantum yield ($\phi(\lambda)$) and absorption cross section ($\sigma(\lambda)$) at all photolysis wavelengths.

By monitoring the decrease in test compound and actinometer concentrations, disappearance rate constants for the test compound and actinometer under the experimental conditions employed can be determined. Using this data, together with absorption cross sections for both test compound and actinometer and the quantum yield of the actinometer, the quantum yield of the test substance can be determined. This can be combined with the absorption cross section and solar light intensity in the manner outlined in Section 2.3 to afford k_p , the rate constant for direct phototransformation.

The method described in this section is based on that described by Hendry in Mill et al. (1982). An action coefficient (defined as $\phi(\lambda) \sigma(\lambda)$) with units of $\text{cm}^2 \text{ photon}^{-1}$) as low as 10^{-22} can be measured using this method. This limit assumes that a $(40 \pm 2)\%$ disappearance of the test compound occurs within 10 days using an average light intensity of $10^{15} \text{ photons s}^{-1}$ for wavelengths in the solar spectral range through a 20 cm^3 , 10 cm long cell. Thus for an absorption cross section $\sigma(\lambda) = 3.9 \times 10^{-21} \text{ cm}^2 \text{ molecule}^{-1}$ (equivalent to $\epsilon = 1 \text{ l mole}^{-1} \text{ cm}^{-1}$) quantum yields ($\phi(\lambda)$) as small as 2.6×10^{-2} photons molecule⁻¹ can be determined. Lower quantum yields can be determined for compounds with larger absorption cross sections. The method is not applicable where the partial pressure of the test compound is sufficiently low that significant wall sorption occurs. In practical terms, this limits the method to compounds with vapour pressures greater than about 10 Pa.

3.4.2 Equipment and Materials

Light sources

A mercury monochromatic source, using the filtered lines at 297-302 nm, 313 nm, 334 nm, 365-366 nm, 405-407 nm, 424-436 nm, 546 nm, and 577 nm is often used, but other lines sources are available and may be used (e.g., Kr, Ar, and CW dye laser and narrow band pass filtered Xe lamps).

Use of broadband radiation is also acceptable but there are several extra considerations. First, the light source must be confirmed by emission spectrum measurements to approximate the solar spectrum over the wavelength region above 290 nm in which the test compound absorbs. Second, because the emission spectra of broadband light sources are variable frequent checks must be made of the emission spectrum. These conditions require fairly sophisticated equipment and procedures.

Both types of light sources can yield excellent results under ideal conditions. However, it is not clear which of the two methods yields the best general results under practical conditions.

Optical train

A typical optical train configuration for determining quantum yields is shown below in Figure 14.

Fig. 14: The essential features of an optical train for determining quantum yields (Mill et al., 1982), where

- S denotes collimator openings
- L denotes an optional collimating lens system
- F denotes a wavelength filter system
- P denotes a photodetector to monitor lamp intensity

The optical train must have a light source capable of emitting a useful constant intensity at several wavelengths above 290 nm as discussed above.

Normally, significant temperature increases in the cell may be expected if heat (IR) filters are not used with high power lamps. If any special conditions such as these apply or if room temperature is outside the 18-25° C range, a jacketed cell and thermostat must be used to control the bulk gas temperature to within this range.

A filter is needed to isolate radiation or light of the desired wavelength. The filter requirements vary somewhat depending on the nature of the test compound's absorption spectrum and the light source used. Ideally, the lamp and filter should allow no more than 0.5% for the total transmitted intensity to be outside a 5 nm wide band, and none of the 0.5% should be in a region where the test compound strongly absorbs. This should be checked with a monochromator. Interference filters, coloured glass filters, solution, gas or gelatin filters, or combinations of these types are all satisfactory. A water filter is very useful in significantly reducing the amount of IR radiation reaching the cell.

If an *in situ* analytical method such as UV absorption spectroscopy is employed, the reaction cell depicted in Figure 8 (Section 2.3) is suitable. If an *ex situ* method is employed, a cell such as that depicted in Figure 8 may require another side arm.

The reaction cell should be placed in the collimated beam so that no part of the beam touches the cylindrical walls of the cell. The cell should rest so that both quartz windows are perpendicular to the collimated light beam. The cell can be aligned before filling by temporarily using a filter that passes visible light. If the lamp emits only in the UV, then the lamp, collimator, and cell holder (with cell) should be

aligned on a pencil of collimated light such as that obtained from a low-power helium neon laser or small collimated incandescent source.

Determination of quantum yield can be accomplished in either of two configurations. If the phototransformation rate constants of actinometer and test compound are similar under the experimental conditions employed, the test compound reaction cell may be placed behind the actinometer cell (See Figure 14). The light intensity incident on the reaction cell will be reduced due to absorption of the actinometer. A correction factor must be applied. This is easily determined as the ratio of the rate of phototransformation of the actinometer in the two cells.

Otherwise, after the lamp has been turned on and stabilized, an actinometer cell can be placed in the single cell holder to determine the lamp intensity before or after the sample is irradiated. If the lamp intensity is monitored electronically, only one actinometer measurement per run or set of runs is necessary.

A photodetector may be placed anywhere in the beam to monitor the monochromatic intensity. If sample and actinometer initial transmittance is under 95 %, a quartz disc reflector may be used to reflect some light (~10%) out of the beam before it impinges on the first cell window. The deflected beam can be used to monitor the lamp intensity without interference from sample or actinometer absorption. The optical train is most conveniently set up on an optical bench, but a solid metal rod lattice could also be used. Ring stands, because of their instability, are not satisfactory for these optical measurements.

Actinometer

Any compound with a well defined and documented quantum yield, absorption cross section and analytical method may be used. Four are recommended here. NO_2 is easily obtained and purified (Mill et al., 1982) and is useful at wavelengths in the solar region below 390 nm ($\phi = 1.9 \pm 0.1$ photons molecule⁻¹). The absorption spectrum is precisely given in Bass et al. (1976). NOCl is also available and easily purified to levels 98% or better. Its absorption spectrum is given in Goodeve et al. (1939). It is best used at wavelengths 380 nm to 600 nm ($\phi = 2.0$ photons molecule⁻¹) though it is also useful in the 290-380 region where a reaction product, Cl_2 , absorbs light and causes further reaction. The first 10% of NOCl disappearance will follow first order kinetics, even in the worst case (approximately 340-360 nm) where the Cl_2 absorption maximum occurs. These two actinometers may be used neat, with no air component.

Two other substances that are useful as actinometers, but with much slower phototransformation rates than NO_2 or NOCl , are sec-butyl iodide and mesityl oxide. Sec-butyl iodide has a useful absorption spectrum up to 350 nm (Davenport et al., 1984) and a quantum yield of 0.42 photons molecule⁻¹ in that region. It is readily available and can usually be used without further purification. An absorption maximum at 255 nm makes it convenient for analysis. An I_2 impurity, which may be present, and the product formed during photolysis has been shown not to interfere with the first order decrease of [s-BI] over 1.5 orders of magnitude (Mill et al., 1982). Mesityl oxide has useful absorption from 290 to almost 400 nm. It is readily available in liquid form (greater than 98% purity) and can normally be used without further purification. Reaction products do not interfere (Mill et al., 1982) with the phototransformation rate or disappearance of the mesityl oxide, but they do interfere somewhat with the absorption spectrum; thus, UV analysis is difficult, and GC or some other analytical method is preferred. The quantum yield of mesityl oxide is 0.011 photons molecule⁻¹ in the 290-400 nm region (Mill et al., 1982). Both sec-butyl iodide and mesityl oxide are used in air at atmospheric pressure.

3.4.3 Experimental Procedure

Three sets of experiments are necessary to determine the quantum yield. First, the phototransformation rate constant of the actinometer under the experimental conditions employed (k_A) must be measured. It should be noted that k_A is not generally equal to k_p , the rate constant for phototransformation in the troposphere. This is because the light intensity in the optical train is not generally equal to solar light intensity.

The logarithm of the observed concentration of the actinometer is plotted against time. From the relationship

$$\ln \frac{[A]_t}{[A]_0} = -k_A t$$

where $[A]_t$ and $[A]_0$ are actinometer concentrations at time t and zero, it can be seen that k_A can be derived from the slope.

If the slope of the plot gives no evidence of curvature, the reproducibility of the actinometer and light source have been demonstrated. If the rate constant increases with time, the light source may not have been allowed to stabilize sufficiently. If it decreases, the phototransformation of the actinometer may be too extensive or reaction products are influencing the reaction. From these experiments, an optimum time for measuring the light flux can be determined.

If the light intensity is being monitored electronically, stabilization can be attained before k_A is determined as described above.

In the second series of experiments, test compound is introduced into the reaction cell at a pressure that does not exceed 50% of its vapour pressure at the experimental temperature, while keeping the absorbance below 0.02 at the phototransformation wavelength. Then phototransformation is allowed to proceed until the initial test compound concentration has decreased by approximately 10%, and the reaction time noted. Three additional runs are then made for time periods two, three, and four times longer and the extent of phototransformation noted. The lamp should always be allowed to stabilize before beginning the experiment. Alternatively, phototransformation and analysis of the test compound using an *in situ* measurement method may be conducted simultaneously, or the phototransformation may be interrupted to make the *in situ* concentration determination. The first method described above (using separate runs for each time determination) is the more general method when a significant portion of the test compound must be used for analysis.

By plotting the logarithm of the test compound concentration against time, the phototransformation rate constant under the experimental conditions (k_C) may be determined. If the plot shows a noticeable curvature suggesting a slower rate at the later stages, one of the reaction products may be quenching the reaction; if the curvature suggests a faster rate, a reaction product may be sensitizing the reaction. In either case, the initial slope will give the most reliable value of k_C .

From the above experiments, the optimum conditions may be selected for measuring the light flux and photo-transforming the test compound. A third series of experiments should then be performed consisting of an actinometer run, a test compound run, and a second actinometer run using these optimal

conditions and the same cell. From each experiment a phototransformation rate should be determined. Those from the two actinometer runs should be averaged, correcting for lamp aging during the series of experiment.

Since the experimental light intensity ($I(\lambda)$) was the same for actinometer and test compound, from $k_A(\lambda) = \phi_A(\lambda) \sigma_A(\lambda) I(\lambda)$ and $k_c(\lambda) = \phi_c(\lambda) \sigma_c(\lambda) I(\lambda)$, the following equation is derived:

$$\phi_c(\lambda) = \frac{k_c(\lambda) \sigma_A(\lambda) \phi_A(\lambda)}{k_A(\lambda) \sigma_c(\lambda)}$$

The quantum yield $\phi_c(\lambda)$ should be determined at at least 2 wavelengths where the test compound absorbs light to be sure that it is independent of wavelength. Wavelengths in the solar region are preferred, but if the absorption spectrum cuts off too soon above 300 nm, the mercury lines at 297 or 275 nm may be used.

If $\phi_c(\lambda)$ is found to vary with wavelengths, measurements should be taken at at least 3 wavelengths so that the $\phi_c(\lambda)$ values for the test compound in the solar spectral range can be determined. The first order rate constant for direct phototransformation in the troposphere (k_p) is then given by

$$k_p = \sum \phi_c(\lambda) \sigma_c(\lambda) J(\lambda)$$

where $J(\lambda)$ is the solar light intensity at wavelength.

3.4.4 Repeatability and Reproducibility

Using the equipment, materials and general procedure outlined, repeatability within a factor of about 10% should be easily attainable.

4. REFERENCES

- Atkinson, R. (1985) Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions. *Chem. Rev.* 85, 69-201.
- Atkinson, R. (1987) *Int. J. Chem. Kinetics*, 19, 799-828
- Atkinson, R. (1988) *Environ. Tox. and Chemistry*, 7, 435-442
- Atkinson, R.; Ashman S.M. (1989) *Int. J. Chem. Kinetics*, 21, 1123-1129
- Atkinson, R.; Carter, W.P.L. (1984) Kinetics and mechanisms of the gas-phase reactions of ozone with organic compounds under atmospheric conditions. *Chem. Rev.*, 84, 437-470.
- Bader, H.; Hoigné, J. (1982) Determination of ozone in water by the indigo method; a submitted standard method. *Ozone Sci. Eng.*, 4, 169-176.
- Barnes, I.; Bastian, V.; Becker, K.H.; Fink, E.H.; Zabel, F. (1982) Studies of organic substances toward hydroxyl radicals under atmospheric conditions. *Atmos. Env.*, 16, 545-550.
- Bass, A.M.; Ledford, A.E.; Laufer, A.H. (1976) Extinction coefficients of NO₂ and N₂O₄. *J. Res. Nat. Bur. Stand.*, 80, 143-166.
- Becker, K.H. (1986) Aufbau einer Reaktionskammer für Testverfahren zum abiotischen Abbau bei 500 K. GSF Abschlußbericht Juni 1986.
- Becker, K.H.; Biehl, H.M.; Bruckmann, P.; Fin, E.H.; Führ, F.; Klöpffer, W.; Zellner, R.; Zetzsch, C. (1984) Methods for the Ecotoxicological Evaluation of Chemicals: Photochemical Degradation in the Gas Phase, Volume 6: OH Reaction Rate Constants and Tropospheric Lifetimes of Selected Environmental Chemicals. Report 1980-1983 KFA-Jülich, Jül-Spez. 279, Nov. 1984.
- Brown, H.C.; Okamoto, Y. (1958) Directive effects in aromatic substitution. XXX Electrophilic substituent constants. *J. Am. Chem. Soc.*, 80, 4979-4987.
- Carter, W.P.L.; Lloyd, A.C., Sprung, J.L.; Pitts, J.R., Jr. (1979) Computer modeling of smog chamber data - Progress on validation of a detailed mechanism for the photo-oxidation of propene and normal-butane in photochemical smog. *Int. J. Chem. Kinetics*, 11, 45-101.
- Cox, R.A. (1974) Photolysis of gaseous nitrous acid. *J. Photochem.*, 3, 175-188.
- Davenport, J.E.; Mill, T.; Johnson, R.M.; Gu, C.-L. (1984) Part 3 of Development of a Tiered Test System for Photochemical Degradability of New Chemicals in the Atmosphere, Phase I. Umweltbundesamt, Berlin. Project No. 106-02-017.

Fujiki, M. (1986) Draft test guideline for Laboratory gas phase photodegradation. OECD Meeting Oct 6 to 8, Berlin, FRG.

Goodeve, C.F.; Katz, S. (1939) The adsorption spectrum of nitrosyl chloride. Proc. Royal Soc. (London), 172, 432-444.

Heicklen, J. (1981) The correlation of rate coefficients for H-atom abstraction by HO radicals with C-H bond dissociation enthalpies, Int. J. Chem. Kinetics, 13, 651-665.

Hendry, D.G.; Kenley, R.A. (1979) Atmospheric reaction products of organic compounds. US Environmental Protection Agency Report. EPA - 560/12-79-001. 40pp.

Klöpffer, W.; Kaufmann, G.; Frank, R. (1985) Phototransformation of air pollutants - Rapid test for the determination of k_{OH} . Z. Naturforsch. 40, 686-692.

Lloyd, A.C.; Darnall, K.R.; Winer, A.M.; Pitts, J.R., Jr. (1976) Relative rate constants for reaction of the hydroxyl radical with a series of alkanes, alkenes and aromatic hydrocarbons. J. Phys. Chem. 80, 789-794.

Mill, T.; Mabey, W.R.; Bomberger, D.C.; Chou, T.W.; Hendry, D.G. (1982) Laboratory protocols for evaluating the fate of organic chemicals in air and water. US Environmental Protection Agency Report EPA-600/3-82-022. 338pp.

Nolting, F.; Behnke, W.; Zetzsch, C. (1988) A smog chamber for studies of the reactions of terpenes and alkanes with ozone and OH. J. Atmos. Chem., 6, 47-59.

Pitts, J. N., Jr.; Winer, A.M.; Fitz, D.R.; Aschmann, S.M.; Atkinson, R. (1981) Experimental protocol for determining ozone reaction rate constants. US Environmental Protection Agency Report EPA-600/53-81-024.

Pitts, J.N., Jr.; Winer, A.M.; Aschmann, S.M.; Carter, W.P.L.; Atkinson, R. (1985) Experimental protocol for determining hydroxyl radical reaction rate constants for organic compounds: Estimation of atmospheric reactivity. US Environmental Protection Agency Report EPA-600/53-85-058.

Taylor, W.D.; Allston, T.D.; Moscato, M.J.; Fazekas, G.B.; Kozlowski, R.; Takacs, G.A. (1980) Atmospheric photodissociation lifetimes for nitromethane, methyl nitrite and methyl nitrate. Int. J. Chem. Kinetics, 12, 231-240.

Tuazon, E.C.; Carter, W.P.L.; Atkinson, R.; Pitts, J.N., Jr. (1983) Reaction of hydrazine and ozone - A non-photolytic source of OH radicals for measurement of relative OH radical rate constants. Int. J. Chem. Kinetics, 15, 619-629.

Zetzsch, C. (1982) Predicting the rate of OH addition to aromatics using σ^+ electrophilic substituent constants for mono- and polysubstituted benzenes. Abstract A-11, XVth Informal Conference on Photochemistry, Stanford, California, June 27 to July 1, 1982.

