Phototransformation of Air Pollutants: Rapid Test for the Determination of k_{OH}

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Dedicated to Professor Schulte-Frohlinde on the occasion of his 60th anniversary

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An empirical correlation between the k_{OH} rate constants in air and in water is derived from literature values. A simple method to measure k_{OH} in water has been used. In addition, it is demonstrated that the reactivity of organic chemicals with the OH radical in Freon 113 is proportional to their reactivity in air.

1. Introduction

The reaction with the OH radical is the major sink for most air pollutants in the troposphere. The rate constant k_{OH} of this reaction is measured in smog chambers or by various flash photolysis methods [1]. One limiting factor in these measurements is the vapour pressure of the substances which should be greater than approximately 10^{-2} Pa; however, substances with vapour pressures down to about 10^{-6} Pa have been reported to occur in the trophosphere in molecular form [2, 3]. It therefore would be desirable to have a method for measuring or at least estimating k_{OH} for these compounds. Furthermore, chemical legislation demands an estimate of abiotic degradation, including data on the lifetime of chemicals in the troposphere. Clearly, for an estimate of a chemical's tropospheric liefetime, k_{OH} and the concentration of the OH radical in the troposphere have to be known. A rapid and comparatively inexpensiv test method is therefore wanted in order to determine k_{OH} during initial testing of "new substances" and screening of large numbers of "old substances".

In this paper, a suitable rapid test for water-soluble substances is described, which is based on the work by Walling [4]. The measurement is performed in aqueous, acidic solution and thus is primarily relevant to the phototransformation in water (e.g. in clouds). In order to estimate the gasphase data of k_{OH}, a correlation with k_{OH} data valid for the aqueous phase has to be used [5].

The method is not suitable for water-insoluble substances. For such substances we have explored a different technique. The method uses F 113 as an inert solvent and H_2O_2 as a source of photochemically generated OH radicals. First results also reported in this paper.

2. Methods

2.1. Correlation Between k_{OH} Measured in Water and in the Gasphase

The rapid test described in this paper is based on the determination of k_{OH} in an inert solvent. Using a correlation between the rate constants in the liquid phase k_{OH} (liquid) and in the gas phase k_{OH} (air), the unknown rate constant of a substance in the gas phase can be estimated if the rate constant is measured in the same solvent [5]. Güsten et al. [6] found the following correlation for water as solvent:

$$\log k_{OH}\,(\text{air}) = -21.9 + 1.14 \log k_{OH}\,(\text{water}),$$

where k_{OH} (water) is in $M^{-1}\,s^{-1}$ and k_{OH} (air) in $cm^3\,mol.^{-1}\,s^{-1}$. The different units are due to the use of the most frequent units for liquid solution and gas phase measurements, respectively, in [6].

Using more data, Klöpffer et al. [7, 8] found

$$\log k_{OH}\,(\text{air}) = 1.29 + 0.891 \log k_{OH}\,(\text{water}),$$

where both rate constants are given in the "liquid phase unit" $M^{-1}\,s^{-1}$. The data are compiled in Table 1 and presented graphically in Figure 1. The correlation appears to be invalid only for very small molecules and for aromatics with electron-withdrawing substituents. It will be used for estimating gas phase data from k_{OH} (water) in Section 3.

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Table 1. Decadic logarithms of recommended k_{OH} rate constants ($M^{-1} s^{-1}$).

Substance	log k_{OH} (water)	Ref.	log k_{OH} (air)	Ref.
i-Propanol	9.3	[9]	9.6	[1, 15]
Aniline	10.23	[10]	10.85	[1]
Formaldehyde	9.1	[9]	9.89	[1]
Anisol	10.08	[9]	10.07	[15]
o-Xylene	9.83	[11, 12]	9.95	[15]
m-Xylene	9.88	[11, 12]	10.16	[15]
p-Xylene	9.85	[11, 12]	9.92	[1, 15]
Mesitylene	9.81	[12]	10.57	[15]
Phenol	10.2	[9, 11]	10.22	[1]
Methylamine	9.84	[10]	10.12	[15]
Ethylene	9.45	[9, 11]	9.70	[1, 15]
Dimethyl sulphide	9.72	[9]	10.4	[1, 15]
Acetonitrile	6.54	[9]	7.18	[1]
Biacetyl	8.23	[13, 9]	8.16	[15]
Ethyleneoxide	7.59	[14]	7.78	[1]
Acrylonitrile	9.53	[9]	9.38	[1]
t-Butanol	8.7	[11]	8.8	[15]
Naphtalene	10.07	[11]	10.06	[1]
Diphenyl	9.87	[11]	9.66	[1]
Carbon disulphide	9.91	[11]	9.12	[1]
Benzonitrile	9.7	[11]	8.3	[1]
Chlorobenzene	9.65	[11]	9.81	[1]
Nitrobenzene	9.5	[11]	7.95	[1]
o-Nitrophenol	9.96	[11]	8.75	[1]
Benzene	9.89	[9]	8.84	[1, 15]
Chloroform	6.93	[14]	8.1	[1, 15]
p-Cresol	10.08	[14]	10.5	[15]
Ethanol	9.26	[9]	9.3	[1, 15]
Ethyl acetate	8.38	[14]	9.06	[15]
Methanol	8.95	[9, 11]	8.82	[1, 15]
Propanol	9.45	[9, 11]	9.55	[1, 15]
n-Propyl acetate	9.15	[9]	9.41	[15]
Toluene	9.48	[9]	9.57	[1, 15]
Methyl ethyl ketone	8.95	[9]	9.32	[15]
Tetrahydrofuran	9.43	[9]	9.95	[15]
Methyl acetate	8.08	[9]	8.04	[15]
Methyl propionate	8.65	[9]	8.23	[15]
Ethyl propionate	8.94	[9]	9.03	[15]
1,2-Epoxybutane	8.65	[14]	8.89	[15]
Epoxypropane	8.15	[14]	8.89	[15]
Diethyl ether	9.37	[14]	9.73	[15]
Nitromethane	8.28	[14]	8.81	[15]
Cyclohexane	9.94	[9]	10.61	[15]
Acetone	7.95	[9, 11]	8.15	[1]
n-Butanol	9.63	[9, 11]	9.7	[1, 15]
Allyl alcohol	9.77	[16]	10.19	[15]
Benzaldehyde	9.64	[11]	9.86	[17]
Cyclopentane	9.48	[11]	9.5	[18]
Acrolein	9.85	[11]	10.06	[17]
Thiophene	9.52	[11]	9.76	[1]
Trichloroethylene	9.48	[11]	9.2	[1]
Vinyl chloride	9.85	[11]	9.6	[1]
Methyl mercaptan	10.5	[9]	10.9	[1]
Butyraldehyd	9.55	[9]	9.2	[1]
Methane	8.08	[11]	6.69	[1, 19]
Acetaldehyde	8.7	[11]	9.94	[1]
Glycol	9.3	[11]	9.68	[1]
1-Butene	9.89	[11]	10.33	[1]
1,3-Butadiene	9.89	[11]	10.61	[1]
Cyclohexene	9.94	[9, 11]	10.63	[1]
Propylene oxide	8.38	[11]	8.5	[15]

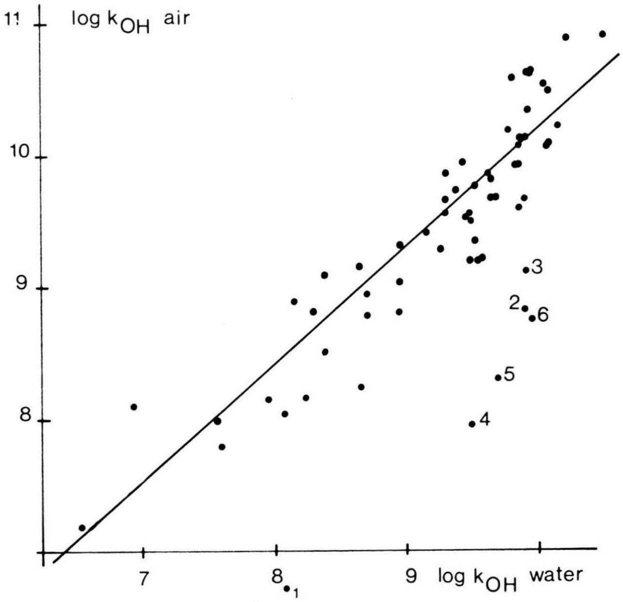

Fig. 1. Correlation between k_{OH}(water) and k_{OH}(air); 1 methane, 2 benzene, 3 carbon disulphide, 4 nitrobenzene, 5 benzonitrile, 6 o-nitrophenol.

2.2. Determination of k_{OH} in Water

2.2.1. Measuring Principle and Evaluation

The rate constant k_{OH} is determined according to Walling's method [4, 13] in which OH radicals are generated by the reaction of H_2O_2 with Fe(II). Walling proposed the following reaction scheme for the kinetic analysis:

$$H_2O_2 + Fe^{++} \xrightarrow{k_1} Fe^{+++} + OH^- + \cdot OH; \quad k_1 = 76 \; M^{-1} s^{-1}, \tag{1}$$

$$\cdot OH + Fe^{++} \xrightarrow{k_2} Fe^{3+} + OH^-; \quad k_2 = 3 \cdot 10^8 \; M^{-1} s^{-1}, \tag{2}$$

$$\cdot OH + R_1H \xrightarrow{k_{31}} H_2O + R_1^{\cdot}, \tag{3.1}$$

$$\cdot OH + R_2H \xrightarrow{k_{32}} H_2O + R_2^{\cdot}, \tag{3.2}$$

$$\cdot OH + R_3H \xrightarrow{k_{33}} H_2O + R_3^{\cdot}, \tag{3.3}$$

$$R_1^{\cdot} + Fe^{+++} \xrightarrow{k_4} Fe^{++} + \text{Prod.}, \tag{4}$$

$$2\,R_2^{\cdot} \xrightarrow{k_5} \text{Dimer}, \tag{5}$$

$$R_3^{\cdot} + Fe^{++} \xrightarrow[H^+]{k_6} Fe^{+++} + R_3H. \tag{6}$$

The rate constant $k_{OH}(\text{water}) = k_{31} + k_{32} + k_{33} = k_3$ has to be determined for the chemical RH. The Eqs. (3.1) to (3.3) represent different reaction possibilities for RH. $k_{OH}(\text{water})$ is determined from the slope of a plot of R versus $2r(1-R)$ according to

$$R = 2ar(1-R) + b; \tag{7}$$

$$R = \frac{[\text{Fe}^{++}]}{2\,[\text{H}_2\text{O}_2]}, \quad r = \frac{[\text{Fe}^{++}]_0}{2\,[\text{RH}]_0},$$

$$a = \frac{k_2}{k_{31} + k_{32} + k_{33}} = \frac{k_2}{k_3},$$

$$b = \frac{k_{32} + 2k_{33}}{2(k_{31} + k_{32} + k_{33})}.$$

The slope a should be determined using at least 3 or 4 different values of r (ratio of the initial concentrations of Fe(II) and RH). The intercept b shows the relative importance of the reactions (3.2) and (3.3). If oxidation of the primarily produced alkyl radicals is the main process, the rate constants k_{32} and k_3 become equal to zero and the observed intercept b becomes zero, too. $k_{OH}(\text{water}) = k_3$ is determined from slope a, using the known rate constant k_2.

Possible side reactions like

$$\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^{\cdot}; \quad k = (1.2-4.5)\cdot 10^7\ \text{M}^{-1}\,\text{s}^{-1};$$

$$2\cdot\text{OH} \rightarrow \text{H}_2\text{O}_2; \quad k = 5.3\cdot 10^9\ \text{M}^{-1}\,\text{s}^{-1}$$

are eliminated by suitable reaction conditions (see Experimental).

2.2.2. Experimental (Wallings' Method)

Reagents: $\text{Fe(ClO}_4)_2 \times 6\,\text{H}_2\text{O}$ purchased from Ventron, Karlsruhe. Purity and concentration were checked by AAS. The crystals contained additional water but only traces of Fe(III). $5\cdot 10^{-2}$ M solutions in 0.1 M HClO_4 were used. HClO_4 and H_2O_2 (p.a. grade) were used. The grades of the other chemicals were Ökanal, p.a. or nanograde. All experiments were performed in an inert N_2 atmosphere.

Performance of the test: The chemical for which the k_{OH} rate constant has to be determined is dissolved in such an amount of 0.1 M HClO_4 that a volume of 60 ml is obtained after addition of the H_2O_2 solution. The reaction vessel is thermostated at 30 °C and flushed with N_2. The H_2O_2 solution is slowly added from a burette. To evaluate the kinetic parameters, the concentrations of Fe and H_2O_2 have to be determined when the reaction is finished.

The concentration of Fe ions can be measured photometrically: Fe(III) by the absorption of its thiocyanate complex, Fe(II) by its 1,10-phenanthrolin complex. The concentration of H_2O_2 is determined by titration with KMnO_4.

2.3. Determination of k_{OH} Rate Constants in F 113

2.3.1. Measuring Principle

The k_{OH} rate constants of chemicals which are not soluble in water have to be measured in a nonpolar solvent. This solvent has to be capable of dissolving the chemical and H_2O_2, so that photochemical generation of OH radicals and their reaction with the chemical is possible. Furthermore, the solvent has to be inert toward OH radicals and must not react with any of the intermediate radicals, e.g. those created by abstracting H-atoms from the test substance ($\text{Rh} + \cdot\text{OH} \rightarrow \text{R}^{\cdot} + \text{H}_2\text{O}$). After testing, several chloro- and fluoroalkanes, F 113 (1,1,2-trichloro-1,2,2-trifluoro ethane) turned out to be sufficiently stable. This corresponds to the result of Katz et al., who found that alkyl radicals cannot abstract halogen atoms from Freon 113 but are capable of abstracting chlorine from tetrachloromethane [27].

For the solvent F 113, no correlation between $k_{OH}(\text{air})$ and $k_{OH}(\text{F 113})$ can be established since no k_{OH} rate constants have been measured in this solvent. Therefore it is necessary first to test wether k_{OH} rate constants in F 113 are proportional to the rate constants in air. These experiments are described in Section 3.2.

In principle, OH radicals are created photochemically at wavelengths > 300 nm,

$$\text{H}_2\text{O}_2 \xrightarrow{h\nu} 2\cdot\text{OH}; \quad \text{rate: } k_1\,[\text{H}_2\text{O}_2], \tag{8}$$

using H_2O_2 as the radical source. The solubility of H_2O_2 in F 113 is $1.5\cdot 10^{-3}$ M if the equilibrium is established with 30% aqueous solution of H_2O_2. The OH radicals created are consumed by the test substance added in different concentration,

$$\cdot\text{OH} + \text{RH} \xrightarrow{k_{OH}} \text{Prod.}; \quad \text{rate: } k_{OH}[\text{OH}][\text{RH}], \tag{9}$$

and by side reactions (e.g. $\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \cdot\text{OOH}$) combined in the equation

$$\cdot\text{OH} + \text{X} \xrightarrow{k_X'} \text{Prod.}; \quad \text{rate: } k_X[\text{OH}]. \tag{10}$$

2.3.2. Experimental (Test in F 113)

An aqueous solution of H_2O_2 (30%) and F 113 were shaken to prepare a solution of H_2O_2 in F 113. The maximum concentration of H_2O_2 in F 113 is $1.5 \cdot 10^{-3}$ M. The concentration of H_2O_2 was determined by the absorption of the Ti(IV) H_2O_2 complex at 419 nm. 1 ml of F 113 containing H_2O_2 was mixed with 5 ml of acetic acid (100%). After the addition of 1 ml of the Ti(IV) solution (Merck Titrisol; 1 g Ti(IV) l^{-1} in diluted HCl) the volume was adjusted to 10 ml with acetic acid. The concentrations of the various substances in F 113 were determined by gas chromatography. The experiments were conducted in a photochemical apparatus. For the generation of the OH-radicals the solutions were irradiated with UV-light ($\lambda \gtrsim 290$ nm). A high pressure mercury lamp TQ from Heraeus was used for the irradiation. All experiments were conducted under an inert nitrogen atmosphere.

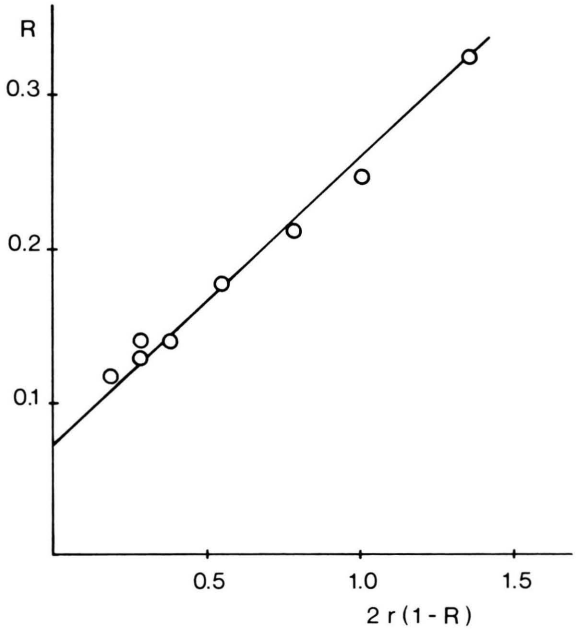

Fig. 2. Plot of R versus $2r(1-R)$. Substance: isopropanol.

3. Results

3.1. *Walling's Method*

The results of the measurements using 7 test substances are summarised in Table 2. Figure 2 shows a typical plot of R versus $2r(1-R)$ used for evaluation according to (7).

For ethylacetate, the measured k_{OH}(water) is considerably higher than data reported previously [9]. This may be due to difficulties encountered in measuring substances which are volatile from aqueous solution.

Urea reacts very slowly with OH radicals [20]. The evaluation of data according to (7) is not possible in this case, since most values of R fall in the range 0.9 to 1.0, so that the $(1-R)$ correction is subject to serious errors. A simplified plot of $1/R$ vs. $1/2r$ can be tried in these cases [4], which is strictly valid only if $k_3 = k_{31}$. In the case of urea, the lower limit of the range of applicability of Walling's method is clearly reached. Correspondingly, the estimate of k_{OH} (air) is a very rough one.

Isopropanol, which had been investigated by Walling and Kato [13] behaves good-natured in water as well as with regard to extrapolation to the gas phase.

Table 2. Measured and estimated k_{OH} rate constants.

Substance	k_{OH}(water) $[M^{-1} s^{-1}]$		Ref.	k_{OH}(air) [mol. $cm^{-3} s^{-1}$]		Ref.
	Measured (this work)	Literature		Estimated[a]	Literature	
Ethylacetate	$1.22 \cdot 10^9$	$2.4-4.0 \cdot 10^8$	[9]	$4.0 \cdot 10^{-12}$	$1.0 \cdot 10^{-12}$	[15]
Urea	$2.1 \cdot 10^6$	$<1.25 \cdot 10^6$	[14]	$1.4 \cdot 10^{-14}$		
Isopropanol	$1.6 \cdot 19^9$	$2.0 \cdot 10^9$	[13, 9]	$5.1 \cdot 10^{-12}$	$5.48 \cdot 10^{-12}$	[15]
Methanol	$1.23 \cdot 10^9$	$0.85 \cdot 10^9$	[9]	$4.1 \cdot 10^{-12}$	$1.0 \cdot 10^{-12}$	[15]
Dichloromethane	$2.2 \cdot 10^7$	–		$1.1 \cdot 10^{-13}$	$1.5 \cdot 10^{-13}$	[15]
p-Nitrophenol	$3 \cdot 10^9$	$3.8 \cdot 10^9$	[11]	$9 \cdot 10^{-1}$		
Phenol	$> 3 \cdot 10^9$	$1.4 \cdot 10^{10}$	[9]	$3.5 \cdot 10^{11}$	$2.8 \cdot 10^{-11}$	[1]

[a] according to log k_{OH}(air) = 1.29 + 0.891 k_{OH}(water) [7, 8] from data obtained in this work except for phenol.

Methanol is kinetically simple since only one C-radical can be formed ($CH_3OH + \cdot OH \rightarrow H_2O + \cdot CH_2OH$); the alcoholic H is more strongly bound and practically does not react. A plot according to (7) yields $b = 0$, i.e. $k_{32} = k_{33} = 0$.

Dichloromethane is volatile and slowly reacting; the evaluation can be done, as in the case of urea, only using the simplified plot. The coincidence with gas phase literature data is good.

High reactivity toward OH is indicated by p-nitro phenol; the coincidence with k_{OH}(water) data is satisfactory. No gas phase data are available for comparison with the extrapolated value. Only the lower limit of k_{OH}(water) could be established for phenol ($a \approx 0$; $k_3 \gg k_2$). The extrapolation of literature data of k_{OH}(water) is in very good agreement with k_{OH}(air).

3.2. *Hydrogen Peroxide in F 113*

The reaction of photolytically generated OH radicals in F 113 has been studied with four substances of widely different OH-reactivity, as measured in the gas phase (k_{OH} given in parentheses, $M^{-1} s^{-1}$): limonene ($8.4 \cdot 10^{10}$ [7]), phenol ($1.7 \cdot 10^{10}$ [1]), toluene ($3.7 \cdot 10^9$ [1, 15]) and 1,2,4-trichlorobenzene ($3.8 \cdot 10^8$ [7]).

The initial concentrations $[RH]_0$ of the test substances were 10^{-4} to 10^{-3} M for limonene, toluene and 1,2,4-trichlorobenzene, and 10^{-5} to 10^{-4} M for phenole. The initial concentration of hydrogen peroxide $[H_2O_2]$ was approximately $1.5 \cdot 10^{-3}$ M. The experiments showed that the testsubstances disappeared exponentially as a function of irradiation time, indicating an approximately stationary concentration of OH radicals:

$$\ln [RH] = \ln [RH]_0 - k_{OH} [OH]\, t. \tag{11}$$

Evidently, $k_{OH}[OH]$ can be determined from the slope of semilogarithmic plots according to (11). The concentration of OH radicals can only be estimated, using the gas phase reaction constants. The OH concentrations in F 113 estimated in this way range from 10^{-16} to 10^{-14} M.

Assuming stationary conditions, the equation

$$\frac{1}{[OH]} = \frac{k_{OH}[RH]}{k_1 [H_2O_2]} + \frac{k_X}{k_1 [H_2O_2]} \tag{12}$$

is derived from (8) to (11).

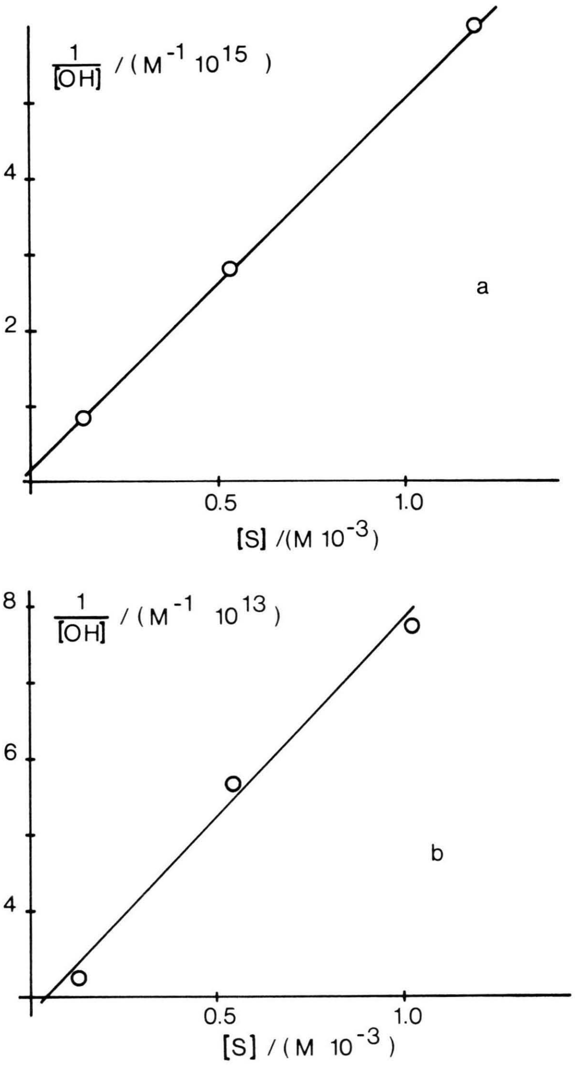

Fig. 3. Plots of 1/[OH] versus initial concentration of RH. a) Limonene, b) 1,2,4-trichlorobenzene.

According to (12) a linear correlation should exist between 1/[OH] and [RH]. Using the estimated [OH] values, 1/[OH] can be plotted versus the initial concentrations of the substances $[RH]_0$. All plots yield straight lines (Figure 3). Equation (12) can also be used to test whether the rate constants in Freon 113 are proportional to the k_{OH}(air) rate constants plotting 1/[OH] versus k_{OH}(air). The values of 1/[OH] have to be determined for equal concentrations of RH and H_2O_2 and with equal irradiation intensity. Figure 4 shows the plot obtained. The data points lie on a straight line. Although further chemicals have to be measured in

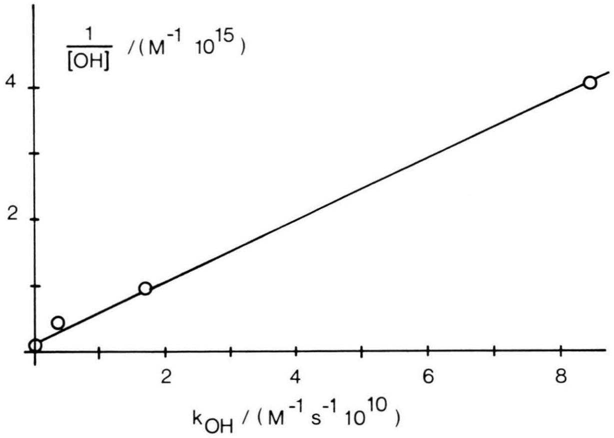

Fig. 4. Plot of 1/[OH] versus k_{OH}(air).

order to test the reliability of the method, it appears that k_{OH} rate constants between $4 \cdot 10^8$ and $8.5 \cdot 10^{10}$ $M^{-1} s^{-1}$ will be measurable.

4. Discussion

The main advantage of Walling's method is its simplicity, only conventional laboratory equipment being required so that the test can be performed in any laboratory. The correlations between the values measured in water and extrapolated to the gas phase and the values measured in the gas phase is sufficiently exact for the estimation of tropospheric lifetimes. The optimum range for determining rate constants k_{OH}(water) is between $3 \cdot 10^7$ and $3 \cdot 10^9$ $M^{-1} s^{-1}$. The upper limit is due to diffusion control. Extrapolation to the gas phase of that region corresponds to rate constants between $5 \cdot 10^{-14}$ and $5 \cdot 10^{-12}$ cm^3 mol.$^{-1}$ s^{-1}. The rate constants of many air pollutants are situated in this region.

The use of Walling's method is limited by several constraints which determine the number of substances which can be tested. (i) The water solubility of the substances under concern should exceed 10 g dm^{-3}. (ii) The pH of the test solution is very low so that bases and salts of weak acids will be protonated in contrast to ordinary environmental conditions. (iii) The substances should not form strong complexes with Fe(II) or Fe(III). (iv) Coloured oxidation products may disturb the photomeric determination of concentration.

The measurement of volatile components still has to be improved.

In order to overcome these problems in the future, other simple methods for the production of OH radicals should be investigated additionally, e.g. photochemical generation from H_2O_2 (a similar method is already being applied in polarographic analysis for the destruction of disturbing organic chemicals). For the determination of k_{OH} rate constants, this procedure has to be combined with efficient analytical methods which allow the disappearance of the test chemicals to be measured relative to suitable reference substances.

The same is true for F 113 as an inert solvent for non-polar compounds. The first results presented here indicate that at least a ranking of different chemicals with regard to OH-reactivity is possible. Relative rate constants k_{OH}(F 113) can be determined as soon as at least one reliable absolute k_{OH} will have been measured in this solvent.

The suggested rapid test would be especially suited to investigate the environmental fate of less volatile substances ($P_{25} < 10^{-2}$ Pa), e.g. DDT and other molecularly dispersed environmental chemicals. As it is not possible to measure the rate constants of these chemicals in the gas phase, the measurement should be performed in an inert solvent, or in more than one solvent preferably. Comparison of the results of the different experiments may then be used to evaluate k_{OH} rate constants which are good estimates of the exact values. Water and Freon 113 have been shown to be suitable solvents in this work.

For calculations of the atmospheric lifetime

$$t_{1/2} = \ln 2/(k_{OH}(\text{air})\,[OH]), \qquad (13)$$

OH radical concentrations of approximately $5 \cdot 10^5$ to 10^6 mol. cm^{-3} are used.

If (13) is used for estimating the atmospheric lifetime, it is assumed that the reaction with OH radicals is the most efficient sink of the chemical. The actual tropospheric residence time may be much shorter due to wash out, dry deposition and other transfer processes.

The measurement of tropospheric OH radical concentrations is still a problem; values between 10^5 and 10^7 mol./cm^3 have been reported [1, 21–25]. For a preliminary estimate of a chemical's tropospheric lifetime, approximate k_{OH} values are sufficiently correct. The suggested rapid test is therefore especially useful to fulfil the demands of chemicals legislation (abiotic degradation) in its low tiers.

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