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MEASUREMENT OF PHOTODEGRADATION OF CHEMICALS IN A CASCADE-FLOW REACTOR

by

R.M. van Aalst et al.

organization for
industrial research

TNO

p.o. box 217
2600 AE delft

address
schoemakerstraat 97

telex 31453 zptno
phone 015 - 56 93 30

Authors:

R.M. van Aalst
J.H. Duyzer
H. Nieboer

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R.M. van Aalst, J.H. Duyzer and H. Nieboer
(Division of Technology for Society, TNO
P.O. Box 217,
2600 AE Delft, The Netherlands)

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ABSTRACT

A photochemical cascade-flow reactor is described. The reactor can be used for the determination of the degradation behaviour of chemical substances under well-controlled simulated tropospheric conditions. Specifically, the OH-reactivity of the test chemical can be measured accurately and reproducibly for a wide range of substances. The expected maximum atmospheric lifetime may be calculated directly from these measurements.

The use of this technique is illustrated for the case of dimethylether (DME), an alternative propellant for aerosol spray cans. On the basis of measured OH-reactivity, model calculations have been performed to obtain the expected concentration of DME in the atmosphere as a function of height up to 20 km, assuming that all chlorofluorocarbons used at the present time as propellants in aerosol cans would be replaced by DME.

1. INTRODUCTION

We describe here a method for the assessment of the degradation of chemicals in the atmosphere. As a consequence of legislation, interest in test methods for degradation of chemicals in the environment is increasing [1, 2, 3].

In general, the removal of a substance from the atmosphere can be effected by wet or dry deposition, or by (photo)chemical degradation. Deposition can only be considered as effective in removing the substance from the environment, if it is follwed by degradation in water or soil.
Moreover, deposition may be a reversible process. (Photo)chemical degradation in the atmosphere is, however, in most cases irreversible. The degradation can take place by direct photolysis or by reaction with photochemical species, such as ozone or radicals. Moreover, degradation may take place by hydrolysis or reactions in cloud or rain droplets and in or on the surface of aerosol particles.

Of course, in a testing programme, not all possible degradation routes can be investigated. However, in order to estimate the maximum range of dispersion in horizontal and vertical directions, it is sufficient to obtain an upper limit of the residence time, and to determine only the degradation rate for a dominant process. For many organic substances, reaction with OH-radicals has been shown to be the most important removal process from the atmosphere [1, 4]. Accurate techniques for the measurement of OH-reactivity, both on an absolute and on a relative basis have been developed [5, 6, 7, 8]. At the present time, our knowledge of the concentration of OH-radicals in the troposphere sets a limit to the accuracy in calculated life times, since few reliable measurements of OH-concentrations have been reported [9, 10, 11, 12].

Because the contributions of other degradation processes as mentioned earlier may also be important, it is desirable to determine the OH-reactivity under conditions of temperature, pressure, relative humidity, light intensity and spectral distribution and reactant concentrations that simulate the conditions in the troposhere as closely as possible. The relative determination of OH-reactivity as described by Lloyd et al. [6] is well-suited for that purpose. In this method, the OH-reactivity is determined from the ratio of the degradation rates of the test substance and a reference substance upon irradiation with NO_x in air in a smog chamber.

We describe here a cascade-flow reactor that can be used for the determination of OH-reactivity by this method. As an illustration, some results are presented on dimethylether (DME), an alternative for chlorofluorocarbons (CFC) as propellant for aerosol spray cans. The results have been used as input for model calculations of the concentration of DME in the atmosphere as a function of height. This work was part of a more extensive test programme that has been performed by TNO under contract with Aerofako BV, sponsored by the Netherland's Ministry of Health and Environmental Protection.

2. THE CASCADE-FLOW REACTOR; EXPERIMENTAL PROCEDURE

The cascade-flow reactor [13,14] consists of a number of compartments interconnected by narrow orifices. The advantage of this type of reactor over conventional flow reactors is that the residence time is fairly well-defined even at low flow rates, where diffusion and convective mixing play a role. Therefore, long reaction times can be achieved in relatively small reactors. This is an advantage in view of the high costs involved in irradiation and temperature control equipment of large systems. The cascade-flow reactor offers, moreover, the advantages of flow reactors over the more commonly used batch reactor type-smog chambers. Wall effects are more easily reproducible because equilibrium between the reactant in the gas phase and absorbed on the wall can be attained. The size of a sample taken for measurements is, in principle, unlimited, and does not depend on reactor volume.

The cascade reactor consists of a Pyrex-glass tube (length 1.7 m; internal diameter 0.23 m; wall thickness 0.008 m) divided into seven compartments by Pyrex partitions with small orifices (see Fig. 1).

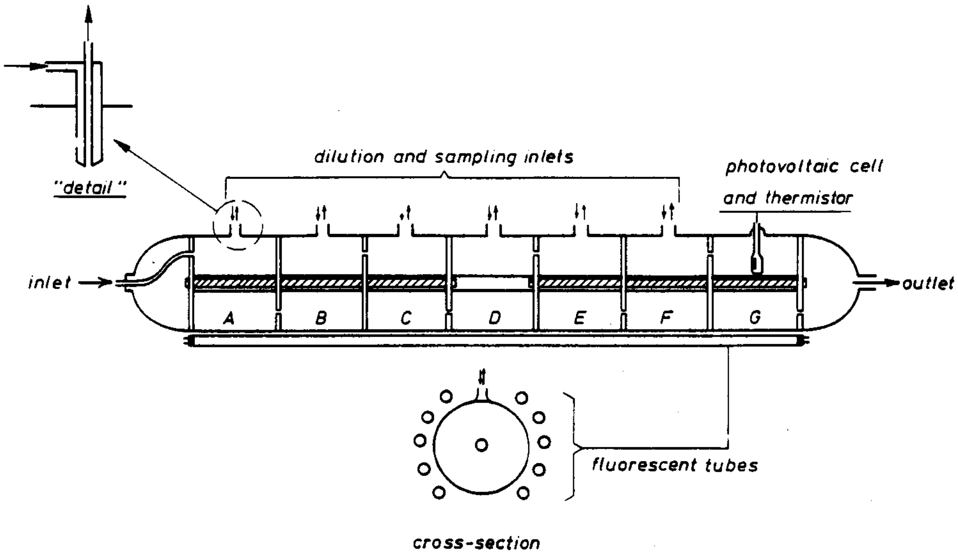

Fig. 1. Cascade reactor for the measurement of atmospheric degradation.

Each compartment has a volume of $(9.35 \pm 0.02) \times 10^{-3}$ m^3 and an internal surface area of (0.30 ± 0.01) m^2 (ratio of surface area to volume 32 m^{-1}). Each compartment has an opening at the top through which samples can be taken or air introduced. The reactor is surrounded by ten fluorescent tubes (Philips TL 05, 120 W) with a stabilized voltage supply and a continuously variable light intensity. The spectral energy distribution matches closely that of natural sun light in the atmosphere (Fig. 2). Compartment G contains a platinum resistance thermometer and a photovoltaic cell (Black Ray J-221, UV Products) for routine measurement of the relative light intensity. The cell was calibrated by NO_2 actinometry. The reactor and the fluorescent tubes are mounted in a heat-insulated box provided with a closed cooling circuit. The cooling capacity can be adjusted continuously to a maximum of 1200 kcal per hour.

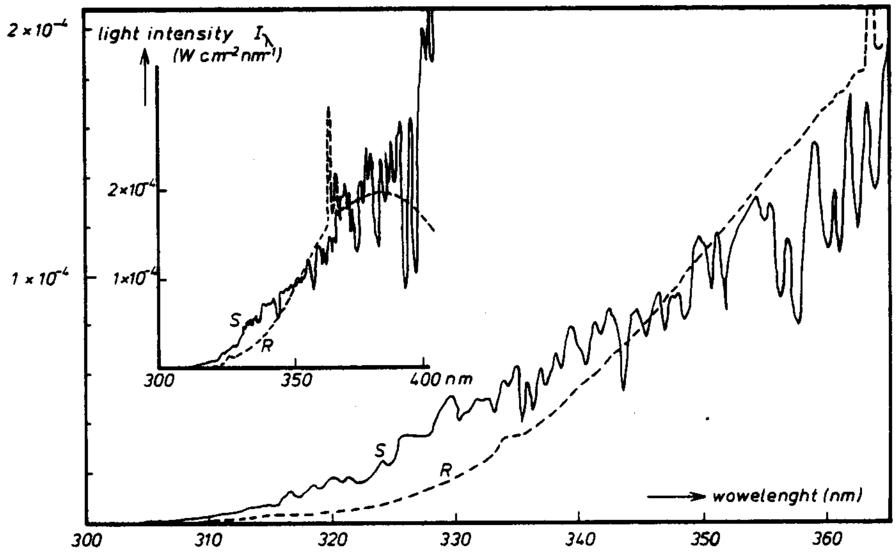

Fig. 2. Spectral energy distribution of sunlight at a zenith angle of 40° (S) and of the light in the cascade-flow reactor (R).

The average residence time per compartment, τ is given by

$$\tau = V / v + v_d$$

where V is the volume of the compartment, v the main gas flow rate and v_d the dilution gas flow rate. In our experiments, τ is usually equal to 1 hour.

Precursors are to be dosed at a constant rate in a stream of clean air, for instance from permeation or diffusion tubes. For details, we refer to refs. 13 and 14. Clean air is prepared by passing compressed air successively over activated carbon, 0.5 % Pt/Al at 300 °C, a heat exchanger, mol. sieve 5 A and a Cambridge glass fiber filter. The relative humidity is adjusted by bubbling the air through destilled water and then passing it through a reflux condenser at controlled temperature.

Measurements of concentrations in the compartments can be started after the concentration in each compartment has reached a steady state. In the last compartment of our reactor, the steady state concentration is reached to within 1 % in 15 hours, unless slow gas-wall reactions play a role.

If it is desired to calculate the OH-reactivity of the compound, the degradation rate as observed in the irradiation experiment has to be corrected for degradation by wall reactions, hydrolysis, reaction with ozone, and the like. This is most conveniently done by performing an experiment without irradiation, if necessary in the presence of ozone. If the test substance is expected to react with ozone, the concentration of ozone has to be measured during both the irradiation and the dark experiment.

The system described here is suitable for the measurement of degradation rates of 0.5 - 50 % per hour, provided that analytical accuracy is sufficiently high, and the test- and reference substance can be dosed at constant concentration. If the OH-concentration is about 5×10^{6} molecules/cm³, as is commonly encountered in these measurements, OH-reaction rate constants in the range 3.10^{-13} - 3.10^{-11} cm³ molecule^{-1} s^{-1} can be measured. This covers class III and part of classes II and IV in the reactivity classification as proposed by Darnall et al. $^{4)}$. The range can easily be extended to the rate constants of the more reactive compounds of class IV and V by lowering the residence time per compartment. Extension to compounds of lower reactivity is limited by the degree of temperature control. The relative variation of the residence time as a consequence of temperature variations is given by:

$$\frac{\Delta\tau}{\tau} \cong \tau \frac{dT}{dt} \frac{1}{273}$$

If temperature is controlled to within 1 °C, and the allowed uncertainty in residence time is 5 %, residence times of up to 14 hours per compartment may be realized. Then, degradation rates as low as 0.05 % per hour could be detected, corresponding to an OH-reaction rate constant of 3×10^{-14} cm^3 $molecule^{-1}$ s^{-1}. In these cases, an appropriate reference substance has to be chosen, and the dilution system of the reactor should be used to introduce precursors of OH-radicals, for instance butane and NO_x or HNO_2.

Building a cascade-flow reactor for testing purposes is rather easy and not very expensive. It can easily be assembled from pyrex glass vessels joined by short, narrow tubing of pyrex or teflon. The most costly part is the temperature control unit, especially if measurements at low temperature are needed.

3. DETERMINATION OF THE DEGRADATION BEHAVIOUR OF DIMETHYLETHER

The method as described was used for the determination of the degradation behaviour of dimethylether (DME). Air, containing 85 ppbv NO, 30 ppbv NO_2, 250 ppbv n-butane and 820 ppbv DME was irradiated in the cascade reactor at temperatures of 25 °C and 12.5 °C. The relative humidity was 50 %, the volumetric UV light intensity was 100 W/m^2. DME was released at a constant rate from a permeation tube held at 14 ± 0.2 °C. The concentration of DME and butane was measured by gas chromatography. The results are depicted in Fig. 3.

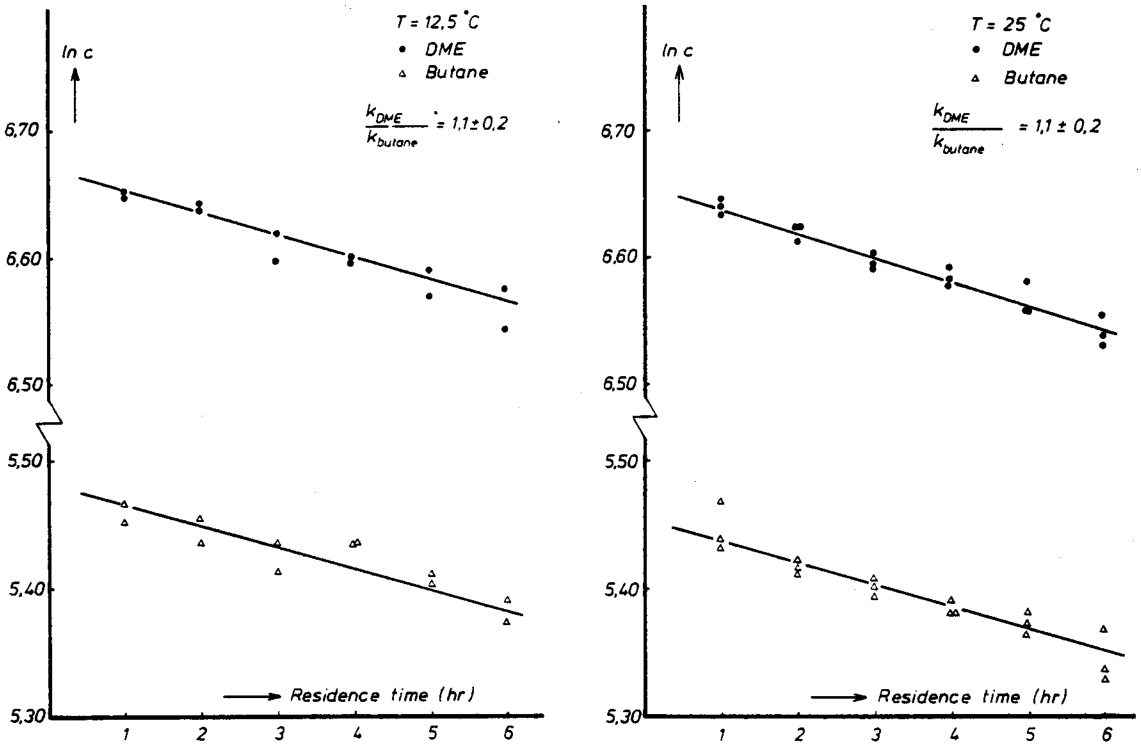

Fig. 3. Concentration of n-butane and of DME as measured in the cascade-flow reactor as a function of residence time.

The linearity of a plot of the logarithm of the concentration c_n in the n'th compartment vs. n shows that the decay is pseudo-first order, and that, therefore, the OH-concentration is approximately constant. From mass balance considerations it follows that

$$c_n = c_{n-1} (1 + k_{OH} \tau [OH])$$

and therefore,

$$\ln c_n = \ln c_o - n \ln (1 + k_{OH}\tau\,[OH])$$

From the measured slopes, it was found that $\frac{k_{OH}\ (DME)}{k_{OH}\ (Butane)} = 1.1 \pm 0.2$ both for 25 °C and 12.5 °C.

The absolute rate constant for n-butane has been measured as a function of temperature by Perry et al. 15) to be

$^{k}K_{OH}$ (Butane) = $1.76\ 10^{-11}\ e^{-(1110 \pm 300)/RT}$ $cm^3\ molecule^{-1}\ s^{-1}$.

Therefore, the values of k_{OH} (DME) could be calculated from our measurements as shown in Table 1. After we had finished our measurements, data on the absolute rate constant for DME k_{OH}(DME) in the temperature range 299 - 427 K were reported 16). From these data we calculated the values also shown in Table 1. There is satisfactory agreement with our results.

Table 1 Rate constants for the reaction of DME with OH-radicals, calculated from our measurements and from ref. 16

	rate constants ($cm^3\ molecule^{-1}\ s^{-1}$)	
temperature (K)	k_{OH}(DME) from this work	k_{OH}(DME) from ref. 16
298	$(3.0 \pm .5) \times 10^{-12}$	$(3.50 \pm .35) \times 10^{-12}$
285.5	$(2.7 \pm .5) \times 10^{-12}$	$(3.30 \pm .33) \times 10^{-12}$

4. MODEL CALCULATIONS OF THE ATMOSPHERIC BEHAVIOUR OF DIMETHYLETHER

From the measured reaction constants, the average residence time in the lower troposphere can be estimated to be at most 6.5 days, if it is assumed that the average OH-concentration in the troposphere is about 6.10^5 molecules cm^{-3} 17). In order to assess the potential of DME to reach the stratosphere, model calculations were performed of the atmospheric concentration of DME as a function of height up to 20 km. under average climatic conditions in the northern hemisphere. We used a one-dimensional tropospheric model developed by Gravenhorst et al. 18) which was adapted for our purposes *). Removal processes for DME considered in the model were reactions with OH-radicals and incorporation into liquid water. Profiles of OH-concentration were calculated from a set of reactions describing the (photo)chemistry of the various chemical species 19). To this chemical model, some reactions describing the degradation of DME and its products were added. The calculated OH-profile is shown in Fig. 4.

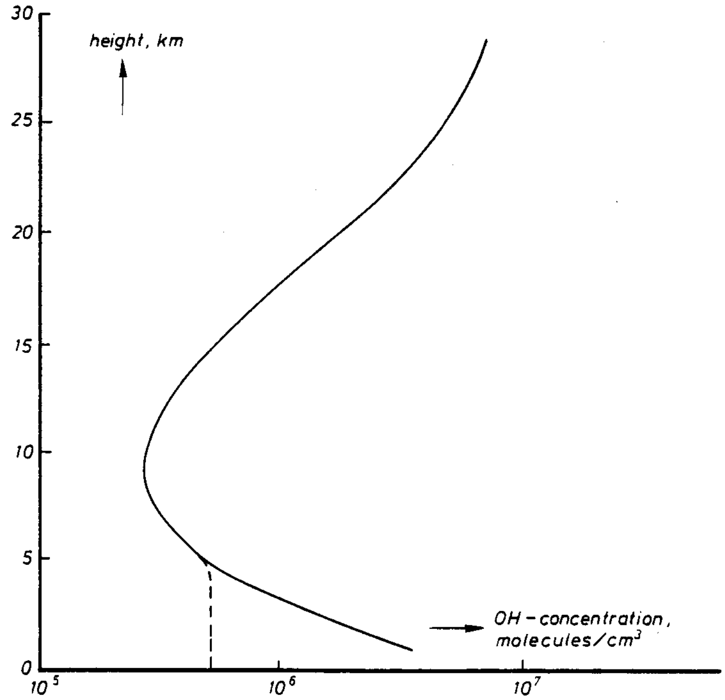

Fig. 4. Calculated OH-profile (——) and the OH-profile in the lower troposphere adapted to recent theoretical and experimental indications (---).

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*) We are greatly indebted to Professor dr D.H. Ehhalt who provided all facilities needed for this study and to Dr E.P. Röth for helping us to adapt the model.

In order to estimate the wet removal, it was assumed that at every height equilibrium of DME in gas- and liquid phase exists. The wet removal rate was calculated from the amount of rainfall, and from the estimated liquid water content of the atmosphere as a function of height using Henry's constant. Henry's constant was determined from measurements to be $4.3 \times 10^{-6} e^{4650/T} \frac{\text{cm}^3 \text{ gas}}{\text{cm}^3 \text{ water}}$ for DME. For detailed descriptions of the model calculations, we refer to ref. 20. Calculations were performed for F 11 ($CFCL_3$), assuming a global flux of 3.2×10^8 kg/year and for DME, assuming fluxes of 1.6, 5.4 and 20.5×10^8 kg/year. The results are shown in Fig. 5.

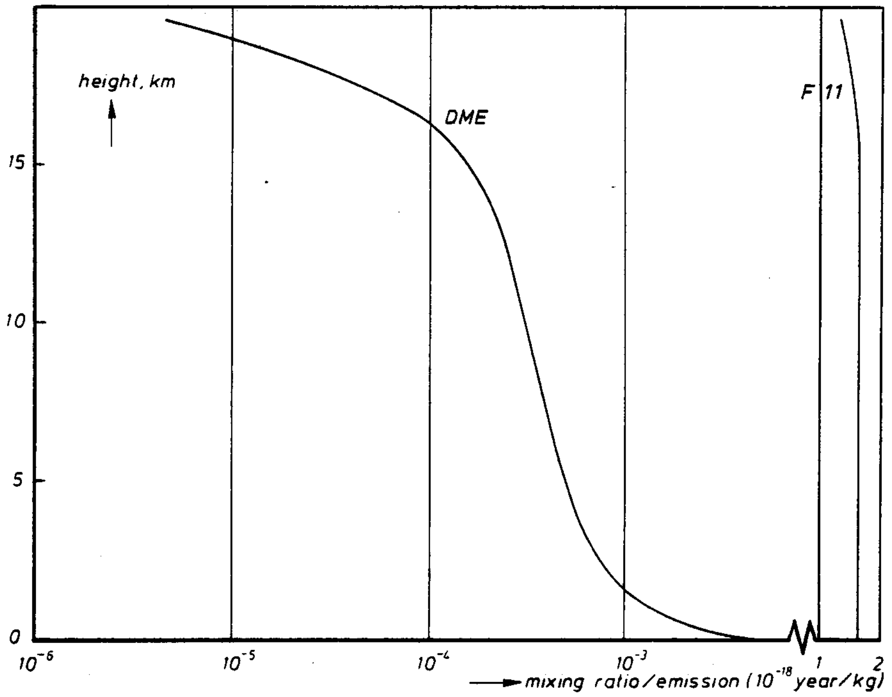

Fig. 5. Calculated mixing ratios of DME normalized by the emission (10^{-18} year/kg) vs. height (km). F 11 is $CFCL_3$.

From the study, it could be calculated that the concentration of DME at a height of 15 km would be 10^3 - 10^4 times less than current concentrations of F 11, if all chlorofluocarbons used as propellant were to be replaced by DME. Damage to the ozone layer would very probably be negligible, even if DME would be as effective in removing ozone as the chlorine atoms produced by photolysis of CFC's. From sensitivity analysis, the OH-concentration turned out to be by far the most important uncertainty in the model. Including wet removal had little effect on the calculated concentration profiles. The amount of DME annually transported by rainfall to the aquatic environment could be estimated to be roughly 0.02 % of the annual production.

5. CONCLUSIONS

Measurement of the OH-reactivity of chemical substances under controlled simulated tropospheric conditions is a valuable procedure for estimating their atmospheric life times. A cascade-flow reactor is an adequate instrument to perform such measurements in an accurate and reproducible way, for a wide range of reactivities. This type of reactor offers several advantages over the conventionally used smog chambers, and the system may be useful as a relatively cheap and simple means for the routine testing of OH reactivity and degradation behaviour of chemicals. Measurement results may be directly used to estimate atmospheric life times, or can serve as input data for more elaborate model calculations to assess the range of horizontal and vertical dispersion of the chemicals in the atmosphere.

Several of these aspects are illustrated in this paper for the case of dimethylether.

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