

## Heterogeneous processes involving atmospheric particulate matter

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**Abstract:** Atmospheric aerosol particles differ widely by size, surface area, and chemical composition. The particles are either dry solid or deliquescent, depending on relative humidity. According to their surface properties, aerosol particles are suspected, and in a number of cases have been shown, to interact with gaseous environmental chemicals, radicals, and other reactive intermediates. However, for many potential surface reactions the reaction probabilities are still unknown. Reaction probabilities which were determined under typical laboratory conditions may differ from reaction probabilities under real atmospheric conditions. The following classes of heterogeneous reactions, which directly or indirectly affect the degradation rates of airborne environmental chemicals and/or modify their atmospheric residence times, will be reviewed: hydrolysis of  $N_2O_5$  on atmospheric aerosols; reactions of soot and other oxidising compounds on soot particles which exhibit pronounced surface ageing effects; reactions of  $NO_x$  and water vapour on soot and other particulate matter which generate HONO as a photochemical OH source; reactions of OH radicals with surface-adsorbed non-volatile environmental chemicals on aerosol particles, as well as their impact on atmospheric residence times.

### INTRODUCTION

Degradation rates of volatile environmental chemicals in the gas phase can be calculated on the basis of photolysis frequencies and rate constants  $k(T)$  of their gas phase reactions with important atmospheric oxidants (OH radicals, ozone,  $NO_3$ , Cl). Where measurements are unavailable, upper limits of photolysis frequencies may be obtained from absorption spectra, while structure-reactivity relationships have been developed to predict rate constants with OH. These pieces of information, combined with Chemistry and Transport Models (CTMs) to create representative concentration fields of OH and ozone in the atmosphere, yield removal rates of environmental chemicals by gas phase processes. Additional losses by wet removal, sometimes enhanced by hydrolysis in cloud and fog water, can be quantified if the solubilities or Henry's law constants (ref. 1) of the compounds in water as well as their hydrolysis rate constants are known as functions of temperature. Degradation reactions in the aqueous phase are also possible (ref. 2). However, tested mechanisms of cloud water chemistry to be included in CMTs are not yet routinely available.

Among the processes contributing to the degradation and eventual removal of environmental chemicals from the atmosphere, heterogeneous reactions on aerosol particles have attracted much less attention than reactions in the gas phase and in cloud water. Prototypical heterogeneous processes of atmospheric relevance were first discovered to be important in the polar winter stratosphere, where they occur on either solid or supercooled liquid cryoaerosols. Extensive laboratory studies (ref. 3,4) have confirmed that these reactions convert chlorine and bromine reservoir species into photoactive halogen compounds, and  $N_2O_5$  into particle-bound nitric acid, thus setting the scene for the well known chlorine and bromine catalysed homogeneous destruction of ozone under the action of sunlight.

Heterogeneous reactions of trace gases on particulate matter must also be considered in the troposphere, particularly in the polluted boundary layer where aerosol particles are most abundant (ref. 5). Strictly speaking only those trace gas reactions should be classed as heterogeneous which involve adsorption of reactants at phase boundaries, *i.e.* on solid surfaces of dry particles at low relative humidities, or on ice crystals, or perhaps at the gas-liquid interface, although examples for the latter type of heterogeneous interaction are scarce (ref. 6). Furthermore, some non-volatile environmental chemicals already exist in the atmosphere as aerosols, or adsorbed on the surface of particulates (ref. 7). If this is the case, the following questions arise: 1.) can the particulates (or their surface films) be degraded (*e.g.* oxidised and/or volatilised) by surface chemical reactions with species from the gas phase? 2.) can modifications to the physico-chemical and other properties of the chemicals in particulate form influence (shorten) their residence time in the atmosphere, or affect their respirable properties?

Table 1 combines, in the form of a matrix, various reactive species in the gas phase with various types of condensed particulate matter which may be important under atmospheric conditions. The entries in the table give short-hand information about our state of knowledge (or ignorance) with respect to each interaction. It should be noted that the entries are biased by the limited experience of the author.

### REACTION PROBABILITIES OF REACTIVE SPECIES ON PARTICULATE MATTER

The simplest rate equation describing heterogeneous loss of gaseous species X on aerosol particles is

$$-\left(\frac{d \ln[X]}{dt}\right) \approx \gamma_X \cdot \frac{\langle c_X \rangle}{4} \cdot S,$$

where  $\gamma_X$  denotes the reaction probability per collision of X with the surface of the condensed phase (which must be determined in the laboratory),  $\langle c_X \rangle$  is the mean molecular speed, [X] is the concentration in [molecule  $\text{cm}^{-3}$ ], and S is the specific surface area of the aerosol in [ $\text{cm}^2$  per  $\text{cm}^3$ ]. The formula is approximately valid for particle radii  $R$  (in  $\mu\text{m}$ )  $< \frac{0.1}{\gamma} \cdot \frac{p}{p_0}$ ; a correction factor  $< 1$  must be added for diffusion limited reaction rates on larger particles (ref. 8).

### HETEROGENEOUS REACTIONS OF $\text{N}_2\text{O}_5$

Perhaps one of the most important heterogeneous reactions in the troposphere is the hydrolysis of  $\text{N}_2\text{O}_5$  on aerosol particles.  $\text{N}_2\text{O}_5$  exists in equilibrium with  $\text{NO}_3$ , according to  $\text{NO}_2 + \text{NO}_3 \leftrightarrow \text{N}_2\text{O}_5$ . Since  $\text{NO}_3$  (which forms in a slow reaction of ozone with  $\text{NO}_2$ ) photolyses extremely rapidly, its existence (and thus the coupled existence of  $\text{N}_2\text{O}_5$ ) is limited to night-time hours. The impact of  $\text{N}_2\text{O}_5$  hydrolysis at the surface of aerosol particles on the oxidising capacity of the troposphere (in terms of  $\text{NO}_x$ , ozone, and OH distributions in time and space) has been demonstrated by Dentener and Crutzen in a pioneering modelling study (ref. 9). The work was, however, published *before* extensive laboratory measurements of reaction probabilities of  $\text{N}_2\text{O}_5$  on tropospheric aerosols became available, and a value  $\gamma_X = 0.1$  was adopted, only slightly larger than reaction probabilities which had been reported for  $\text{N}_2\text{O}_5$  on  $(\text{NH}_4)\text{HSO}_4$  particles (ref. 10). Furthermore, the slow but non-negligible homogeneous hydrolysis of  $\text{N}_2\text{O}_5$  in the gas phase (ref. 11) was omitted, while fast direct loss of  $\text{NO}_3$  on particles was assumed to occur, which should, however, be considerably less important owing to solubility limitations (ref. 12). The assumed reaction probability of  $\text{N}_2\text{O}_5$  was probably too large for an average atmospheric aerosol, because values of  $0.017 \leq \gamma \leq 0.053$  were subsequently measured on  $(\text{NH}_4)_2\text{SO}_4$  particles between 93.5 and 50 % r.h. in a flow tube study (ref. 13). More recently, a huge Teflon-lined aerosol chamber was used to study reaction

Table 1: Possible interactions of reactive gaseous species with various types of condensed particulate matter

substrate reactant	Diesel or air- craft soot	mineral dust	particles coated with organics	sulphates, nitrates, bisulphates	deliquescent sea salt particles	sulphuric acid droplets	cloud droplets, ice particles
<b>OH</b>	reactive loss likely	unknown	H abstraction, addition	unknown	reactive loss likely	uptake?	Uptake?
<b>HO<sub>2</sub></b>	reactive loss	unknown, may depend on composition	uptake and reac- tion?	unknown	uptake and reac- tion likely		uptake, loss on ice surface
<b>RO<sub>2</sub></b>	reactive loss likely	unknown	uptake	unknown	solubility limited uptake?		solubility limited uptake
<b>ozone</b>	reactive loss, surface ageing, competition?	unlikely to be important, but unknown	reaction, depend- ing on structure	unknown	importance of direct uptake to be established		fast reactive loss, solubility limited
<b>NO<sub>2</sub></b>	chemisorption, reduction, HONO format.	HONO forma- tion?	Nitration (more likely by N <sub>2</sub> O <sub>5</sub> /NO <sub>2</sub> <sup>+</sup> )	unknown	ClNO formation on dry NaCl		HONO formation on ice? On water?
<b>NO<sub>3</sub></b>	reactive loss	unlikely to be important, but unknown	reaction, e.g. with aromatics	unknown	solubility limited reaction with I etc.		solubility is low
<b>N<sub>2</sub>O<sub>5</sub></b>	hydrolysis or reaction as NO <sub>2</sub> <sup>+</sup> , reaction probabilities seem to be very variable;	depending on the substrate; formation of particulate nitrate or gaseous HNO <sub>3</sub>			ClNO <sub>2</sub> , other halogen com- pounds formed	hydrolysis	
<b>SO<sub>2</sub></b>	catalytic oxida- tion slow	catalytic oxida- tion likely			oxidation in pol- luted marine at- mosphere	unimportant	oxidation by H <sub>2</sub> O <sub>2</sub> , ozone, etc.
<b>other relevant processes</b>	chemisorption of radicals at radical sites	solubilisation of catalytic metals	gas-to-particle conversion, parti- cle coating	pH dependent of acidic / alkaline gases	uptake of am- monia, change of pH	aerosol process- ing, interface phenomena	

probabilities of  $N_2O_5$  on  $NaNO_3$  and  $NaHSO_4$  aerosols under simulated atmospheric conditions in complete darkness. A preliminary value  $\gamma_X \approx 0.03$  on  $NaNO_3$  at 61 % r.h. was published (ref. 14). However this value should be regarded as an upper limit for this material (ref. 15). To our knowledge no reaction probabilities of  $N_2O_5$  on other inorganic tropospheric aerosol materials have been reported (with the exception of reactions with dry and deliquescent alkali halides which will not be discussed in this context), and temperature dependencies are also unknown.

In a subsequent global modelling study, Dentener et al. (ref. 16) have included (in addition to  $N_2O_5$ ) heterogeneous reactions of other gas phase species (ozone,  $HO_2$  radicals,  $SO_2$  and  $HNO_3$ ) on mineral dust. Obviously, these reactions have a direct impact on the environmental chemicals  $SO_2$  and  $NO_x$ . However, they will also be modifying the oxidising capacity of the troposphere. This latter effect is of more general importance, because it changes the lifetimes of numerous other environmental chemicals as well. The authors point out that the results of their study depend critically on the largely unknown reaction probabilities of the species involved. Even such simple reactions as the loss of ozone on mineral dust have not been studied in the laboratory.

## REACTIONS ON SOOT PARTICLES

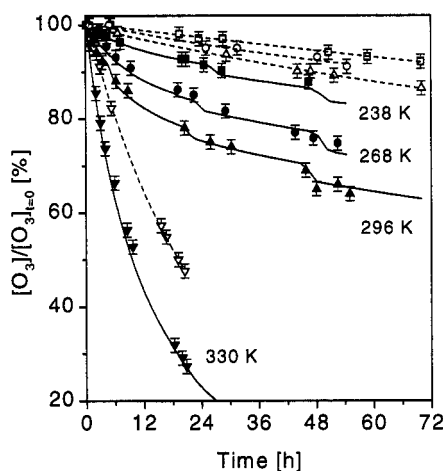
While reaction probabilities of ozone on most other atmospheric aerosols are unknown to date, heterogeneous losses of ozone on soot particles have been repeatedly studied in several laboratories, and by a number of different techniques. Soot, which is a carrier of carcinogenic

**Table 2:** Observed reaction probabilities for ozone loss on black carbon

$\gamma_{eff}$ for ozone on soot	experimental technique/conditions; remarks	ref.
$\approx 10^{-3}$ on fresh surface $\approx 10^{-5}$ on oxidised surface	soot layer exposed in a Knudsen reactor; exposure time dependence was observed	19
$1.4 \times 10^{-4}$ on fresh surface $6.4 \times 10^{-6}$ on oxidised surface	flame soot coating in a flow tube, $T$ -dependency reported	21
$2 \times 10^{-4} - 3 \times 10^{-3}$ , depending on ozone concentration	spark generator soot in an aerosol flow tube; interaction times 15 - 30 s	20
$\approx 2 \times 10^{-5}$ , assuming 1 <sup>st</sup> order kinetics	4 m <sup>3</sup> aerosol chamber, fast initial reaction could not be observed, interaction times 2 - 3 h	22
$(1 \pm 0.5) \times 10^{-3}$	soot layer exposed in a Knudsen reactor; exposure time of a few minutes	23
$\gamma_{eff} = f(t, [O_3], T)$ ; severe passivation observed: $\gamma_{eff} < 10^{-7}$ after 2 days	airborne spark generator soot, $[O_3]_0 = 100$ ppb - 10 ppm in $\approx 80$ m <sup>3</sup> evacuable aerosol chamber, decay measured between 238 K and 330 K	24

chemicals like polycyclic aromatic hydrocarbons (PAHs), is an important by-product of fossil fuel combustion. The toxic PAHs are thought to condense on the particles when the temperature drops after the soot particles have been formed at very high temperatures. Prominent sources of very small soot particles in the polluted boundary layer are Diesel engines, and jet engines in the upper troposphere/lower stratosphere. Some more recent studies were motivated by model calculations which indicate that reactions on soot particles from aircraft can lead to significant ozone reductions near the stratopause, and to a shift of the tropospheric  $NO_x/NO_y$  ratio, if the reaction probabilities of ozone,  $NO_x$  and  $HNO_3$  on soot are high (ref. 17,18). Table 2 summarises some of the results which have been obtained for ozone. Very surprising is the extreme variability of the reported reaction probabilities. Relatively large initial reactivities,  $\gamma(O_3) \approx 10^{-3}$ , were repeatedly measured on freshly prepared soot samples. These decreased to much lower values after exposure times between a few minutes and a few hours. In our own laboratory, the ageing behaviour of airborne soot (about 200  $\mu$ g

$\text{m}^{-3}$ , corresponding to  $2.7 \text{ m}^2$  accessible surface area of the fractal agglomerates, primary particle diameter ca.  $5 \text{ nm}$ ) has recently been studied on time scales of several days in a large evacuable aerosol chamber of ca.  $80 \text{ m}^3$  volume which can be temperature controlled in the range  $183 \text{ K} - 333 \text{ K}$ . Ozone mixing ratios between  $100 \text{ ppb}$  and  $1 \text{ ppm}$  were used. The relatively long mixing times (ozone was added after soot had been introduced into the dry chamber) obscured the initially rapid reaction which has been reported by several other investigators (ref. 19,20). It can, however, be reconstructed from the amount of ozone which is lost during the mixing phase. Some typical observational data, ozone decaying in the absence/presence of soot particles, are shown in Fig. 1. Clearly the decay rate of ozone in the presence of soot is initially much faster than without soot. However, after about 2 days the enhancement of the decay rate by soot becomes immeasurable at all temperatures, implying  $\gamma_{\text{eff}} < 10^{-7}$  for aged soot particles. All observations (ageing, dependence on ozone mixing ratio) can be consistently explained with a minimal set of pseudo-elementary surface reactions which are listed in Table 3. The sticking coefficient of reaction 1, which proceeds until about a monolayer of ozone has been consumed, was taken from the literature. The temperature dependence evidenced in Fig. 1 can be explained by assuming that the loss of ozone (essentially due to reactions 2a,b) has an *effective* activation energy in the order of some  $20 \text{ kJ mole}^{-1}$ . Surprisingly, surface passivation by reaction 3 seems to be temperature independent.



**Fig. 1:** Ozone decay in the absence (open symbols) and presence (black symbols) of airborne soot, initial ozone mixing ratios  $100 - 120 \text{ ppb}$

This mechanism yields an interaction time dependent *effective* reaction probability:

$$\gamma_{\text{eff}}(t) = \frac{2\gamma_{2a,b} + 2.6 \times 10^{15} k_{2c}}{[\text{O}_3] \times \langle c_{\text{O}_3} \rangle} \times e^{-k_3 t}$$

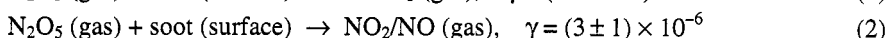
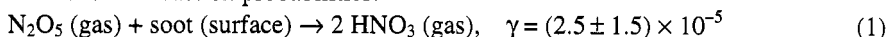
With this result it can be easily shown that ozone loss on soot particles is negligible under all atmospheric conditions. While the detailed surface reaction mechanism is only of academic interest, it implies that reaction probabilities of other atmospheric species on solid surfaces, which have been measured in the laboratory on short time scales only, should also be used with caution, because surface ageing on atmospherically relevant time scales is likely to induce significantly lower reactivities.

Using the same large evacuable aerosol chamber as described above, we also investigated reactions of  $\text{N}_2\text{O}_5/\text{NO}_3$  with soot particles, either by adding  $\text{N}_2\text{O}_5$  vapour in an inert carrier, or by generating the reactants *in situ* from  $1 \text{ ppm}$  ozone and  $1 \text{ ppm}$   $\text{NO}_2$ .  $\text{N}_2\text{O}_5$  and other reactants/products were measured by *in situ* long path FTIR, combined with FT-VIS

**Table 3:** Pseudo-elementary reactions of ozone on soot (SS denotes a reactive site on the particle surface), needed to fit observed ozone decays in the absence and presence of soot

No.	Reaction	Rate at 296 K	comment
1	$SS + O_3 \rightarrow SSO + O_2$	$\alpha_1 \approx 10^{-3}$ (ref. 19,20)	one monolayer
2a	$SSO + O_3 \rightarrow SS + 2 O_2$	$\gamma_{2a} + \gamma_{2b} =$ $(1.0 \pm 0.3) \times 10^{-7}$	slow reactivation, indistinguishable
2b	$SSO + O_3 \rightarrow SS + CO_2 + O_2$		
2c	$SSO \rightarrow SS + CO$	$k_{2c} = (4.5 \pm 1.0) \times 10^{-5} s^{-1}$	slow reactivation
3	$SSO \rightarrow$ passivation	$k_3 = (2.3 \pm 1.0) \times 10^{-5} s^{-1}$	„irreversible“ passivation
4	$O_3 + \text{wall} \rightarrow$ loss	$k_4 = (6.8 \pm 2.0) \times 10^{-7} s^{-1}$	depends on preconditioning

spectrometry for  $NO_3$ . The room temperature results could be consistently described by the following reactions and reaction probabilities:

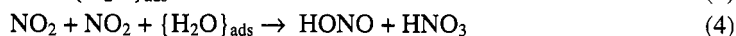


The relatively large hydrolysis rate, reaction 1, compared with the soot surface oxidation/ $NO_x$  reduction step 2, is surprising in view of the very dry conditions and the often assumed hydrophobic nature of the soot surface. Although the participation of  $NO_3$  as a surface oxidant in the second reaction could not be ruled out entirely, an upper limit of  $\gamma(NO_3/\text{soot}) \leq 10^{-3}$  could be deduced. We also found no evidence of  $NO_2 \rightarrow NO$  reduction ( $[NO_2]_0 = 100$  ppm) on airborne dry soot during interaction times of up to 6 days, which sets an upper limit of  $\gamma(NO_2/\text{soot}) \leq 2 \times 10^{-8}$  for the interaction time averaged reaction probability, excluding the mixing time during which our experiment is blind for small but rapid concentration changes. This sheds some doubt on the hypothesised impact of soot particles on the  $NO_x$  budget of the atmosphere (ref. 17,18).

### HONO AS A HETEROGENEOUS SOURCE OF OH RADICALS

Heterogeneous interactions of  $NO_2$  with aerosol particles are of extreme interest because they are a likely night-time source of HONO, which has been repeatedly detected by differential optical absorption spectrometry and also by denuder techniques in polluted urban atmospheres (ref. 25-28). After sunrise HONO is photolysed (photolysis frequency in bright sunshine ca.  $1.3 \times 10^{-3} s^{-1}$  (ref. 29,30)), yielding OH radicals with a quantum yield of unity. These OH radicals trigger degradation processes of environmental chemicals long before other radical sources (e.g. the photolysis of ozone, followed by the reaction of  $O(^1D)$  with water vapour) generate OH radicals at a significant rate.

Very recently, HONO formation was observed under laboratory conditions when  $NO_2$  was adsorbed on soot particles in the presence of water vapour (ref. 31,32). It was shown that  $NO_2$  can be hydrated in a redox step which involves reactive centers (possibly adsorbed hydrogen atoms) on fresh soot particles. The maximum number of  $NO_2$  molecules which can be hydrated on the surface of soot particles is limited to less than a monolayer. Therefore, soot cannot be the exclusive source of HONO in the polluted boundary layer, and other heterogeneous reactions must be invoked. Two alternatives have been proposed to occur on wet aerosol particles or at the ground:



There is now convincing evidence from field and laboratory studies (ref. 28,34) that HONO formation is insensitive to the presence or absence of NO. This eliminates reaction 3, which was favoured in earlier studies (ref. 33), leaving reaction 4 as an alternative. However, according to field observations (ref. 28) HONO concentrations during night-time hours correlate better with  $[NO_2]$  than with  $[NO_2]^2$ , which would be consistent with a hydration mechanism of  $NO_2$  on soot, while being inconsistent with reaction 4 as the rate limiting step.

We propose an alternative interpretation of these experimental observations, which does not seem to have been considered by other investigators: the free enthalpy change of reaction 4 is *positive*,  $\Delta_r G \approx +6 \text{ kJ mol}^{-1}$ . This yields an equilibrium constant  $K_4$  at 298 K which is rather unfavourable for the formation of HONO *via* reaction 4:

$$K_4 = \frac{[\text{HONO}][\text{HNO}_3]}{[\text{H}_2\text{O}][\text{NO}_2]^2} \approx 4 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1}$$

Although no simultaneous field measurements of all involved trace gases are available, the reported HONO mixing ratios before sunrise are often quite close to estimated equilibrium concentrations (ref. 25-28). Considering the small amount of liquid water on wet aerosol particles, most of the nitric and nitrous acid formed *via* reaction 4 will evaporate. If the [HONO]:[HNO<sub>3</sub>] = 1:1 ratio based on the stoichiometry of reaction 4 is roughly maintained in the gas phase, the following approximation is valid at equilibrium:

$$[\text{HONO}]_{\text{equilibrium}} \approx \sqrt{[\text{HONO}][\text{HNO}_3]} = [\text{NO}_2] \times \sqrt{K_2 \times [\text{H}_2\text{O}]}$$

This shows that the often observed nearly first order dependence of [HONO] on [NO<sub>2</sub>] may arise from a significant contribution of the reverse of reaction 4, which cannot be neglected when equilibrium conditions are approached.

## HETEROGENEOUS DEGRADATION OF ENVIRONMENTAL CHEMICALS ON AEROSOLS

The heterogeneous loss of reactive species (radicals, higher oxides of nitrogen) and the formation of photoactive radical precursors (e.g. HONO) on aerosol particles affects the fate of other environmental chemicals rather indirectly. It is, however, also conceivable that environmental chemicals are directly involved in heterogeneous reactions. This happens if particles - or coatings on particles - are composed of environmental chemicals which can react with OH radicals or be degraded by other reactive gas phase intermediates.

An example is the oxidation of soot particles by ozone. This reaction was first studied nearly 10 years ago (ref. 35). Although the results of the study are difficult to extrapolate to atmospheric conditions, they leave little doubt that the removal rate of airborne soot is too slow to be important under atmospheric conditions. This is consistent with the very low reaction probability for ozone on aged soot particles reported above.

While the bulk oxidation of soot particles or of other environmental chemicals in particulate form is unlikely to be important, reactions of OH radicals and other very reactive gas phase species with certain environmental chemicals which are adsorbed on the surface of aerosol particles are more likely to occur. Non-volatile environmental chemicals (vapour pressures in the order of  $10^{-5}$  mbar or less) often exist as adsorbates on aerosol particles (e.g., PAHs on soot particles). There are few quantitative investigations of reactions with adsorbates on airborne particles. Zetzsch and co-workers (ref. 36) have recently studied the heterogeneous reaction of an adsorbed pesticide (terbutylazine = TBA, molecular weight 231) with OH radicals. The compound was deposited on aerosol particles, forming less than a monolayer on the dry SiO<sub>2</sub> surface. The particles, approximately 1  $\mu\text{m}$  in diameter, were agglomerates of spherical primary particles of about 12 nm diameter. The coated particles were suspended in a 2.4 m<sup>3</sup> aerosol chamber which could be illuminated to form OH radicals from various precursor systems. The OH radical dose rate was monitored by measuring the removal rate of several selected hydrocarbons with known OH rate constants. Filter samples of the coated aerosol particles were taken at regular intervals, extracted with a suitable solvent, and analysed by GC-MS. From the removal rate of TBA, a bimolecular rate constant of  $k = (1.1 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  was deduced.

The bimolecular rate constant for the gas phase reaction of a species Y (= TBA in this case) with OH is defined by the rate equation  $-d[Y]/dt = k \cdot [Y][\text{OH}]$ . However, the gas phase concentration [Y], which appears in this equation, is not really defined for an adsorbate, and therefore a rate equation describing the loss of a gaseous reactant X (= OH in this case) adsorbed on reactive surfaces of very small aerosol particles is preferred:

$$-\frac{d[X]}{dt} = -\frac{d[Y]_{\text{surface}}}{dt} = \gamma_{XY} \times \frac{\langle c_{\text{OH}} \rangle}{4} \Omega_X [Y]_{\text{surface}} [\text{OH}].$$

In this equation,  $\Omega_Y$  is the surface area extended by a single adsorbate molecule,  $[Y]_{\text{surface}}$  is the number of adsorbed TBA molecules in one  $\text{cm}^3$  of air, and  $\gamma_{XY}$  is the reaction probability of OH per collision with an adsorbed TBA molecule. Palm et al. (ref. 36) estimate  $\Omega_{\text{TBA}} \approx 64 \text{ \AA}^2$ . This yields  $\gamma_{XY} = 4k / \langle c_{\text{OH}} \rangle \Omega_Y = 0.11$ . In other words: OH radicals react with an adsorbed TBA molecule in more than one out of 10 collisions! The reaction probability may even be somewhat larger, because for reaction probabilities  $\gamma > 0.01$  on particles of  $1 \text{ }\mu\text{m}$  diameter the Knudsen correction is no longer negligible (ref. 8), unless only very few TBA molecules are adsorbed on the aerosil particles, while the remainder of the surface is unreactive.

Although the result of this study cannot be generalised, it certainly implies that surface adsorbed molecules on aerosol particles can be as reactive as their more volatile homologues in the gas phase. It is thus very likely that organic coatings on aerosol particles become continuously more oxidised when exposed to OH radicals and other reactive species ( $\text{NO}_3$ , ozone) in the atmosphere. Surface reactions will turn initially hydrophobic particles into more and more hydrophilic („surface soluble“) particles. These will eventually become cloud condensation nuclei, which are rapidly removed from the atmosphere by cloud droplet formation and rainout.

## SUMMARY AND CONCLUSIONS

A few gaseous environmental chemicals ( $\text{SO}_2$ ,  $\text{NO}_x$ ) can be directly degraded by heterogeneous processes on particles. In most other cases, reactions involving aerosols are important because they affect the oxidising capacity of the atmosphere, and thus the lifetimes of many environmental chemicals which can undergo oxidation. Of particular importance may be losses of peroxy radicals on particulate matter which are, however, difficult to study under realistic atmospheric conditions. Only some representative examples of the many possible interactions listed in Table 1 could be discussed, because many gaps are still wide open. Heterogeneous reactions with sea salt particles, which are known to generate photoactive precursor gases of Cl atoms, have not been discussed in this article, although Cl atoms may be lifetime limiting for some persistent chemicals. Also the impact of heterogeneous reactions on the lifetime of aerosol particles has not been treated in detail, although it should be clear from the last section of this paper that surface reactions are likely to enhance the hygroscopic properties, and thus shorten atmospheric residence times, in particular of initially hydrophobic particles like soot.

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