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Measurement of Surface Residence Times of Halogen-Containing Molecules on Sea-Salt Mimics

A contribution to subproject CMD

Thomas G. Koch and Michel J. Rossi

Laboratoire de la Pollution Atmosphèrique et Sol (LPAS), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Introduction

Heterogeneous reactions of halogen containing atmospheric trace gases, such as $ClONO_2$ and $ClNO_2$ on sea-salt aerosols, have been shown to play an important role in the marine troposphere as they may change the oxidative capacity of the troposphere (Versino, 1996). $ClONO_2$ is a reservoir for active chlorine which is formed in the gas phase in the presence of NO_x; $ClNO_2$ is produced *via* the heterogeneous reaction of N_2O_5 on NaCl. Either compound may interact with alkali halide surfaces to produce a more readily photolysable halogen-containing gas:

$$ClNO_2 + KBr \rightarrow BrNO_2 + KCl \quad (1)$$

$$ClONO_2 + NaCl \rightarrow Cl_2 + NaNO_3 \quad (2)$$

The reaction probabilities for reactions (1) and (2) are 2×10^{-4} and 0.1, respectively, as determined in Knudsen Cell studies (Caloz *et al.*, 1996, 1998).

The primary aim of this study was to develop and apply a *novel technique* which enables the first real-time surface residence time measurement of adsorbates on unreactive as well as reactive substrates. The surface residence time is a parameter fundamental to the understanding of gas-surface interactions and provides additional information on the reaction mechanism. Furthermore, it complements 'pure' uptake studies carried out in Knudsen cell or laminar flow tube reactors.

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Experimental

The experiment involves sending a pulse of molecules (0.2–10 × 10^{15} #) through a tube coated with a material of interest. The arrival time ($t_{arrival}$), defined as the inverse of the decay constant (k), is recorded using the time-dependent mass spectrometric (MS) signal. The mass spectrometer is mounted at the tube exit on a high vacuum chamber ($p < 1 \times 10^{-8}$ mbar). Since the number of wall collisions (Z) is only determined by the tube geometry under molecular flow conditions (Dushman, 1964), the surface residence time can be calculated by comparing the arrival time distribution of an interactive gas-surface system (k_{sticky}) to that of an ideal, non-interactive system (k_{ideal}). In practice a second, Teflon-coated tube serves as a reference for the measurement of k_{ideal}.

$$t_{surf} = \frac{\frac{1}{k_{sticky}} - \frac{1}{k_{ideal}}}{Z} \tag{3}$$

The number of collisions (Z) is computed numerically. Fig. 1 illustrates the delayed arrival time of water vapour passing through a Pyrex tube when compared to a Teflon tube. The yield at the tube exit is 100% in both cases, *i.e.* irreversible loss of H_2O does not occur.

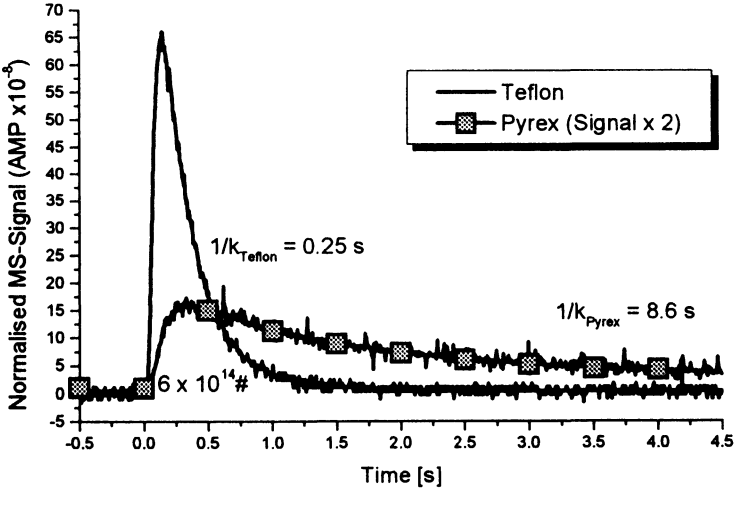

Fig. 1: Experimental MS signal of a pulse of H_2O molecules after passage through a 1.2 × 100 cm tube (Z = 10000)

A Monte Carlo (MC) simulation, which determines random trajectories of individual molecules), is used to model the experimental results (Fenter *et al.*, 1997; Koch *et al.*, 1997). The algorithm is based on the assumption that the molecules are reflected upon collision with a cosine directional distribution (Boeckmann, 1961). Individual trajectory times are stored in a histogram which can be compared directly to the experimentally observed MS signal. Real reactor geometries are used in these calculations. The excellent agreement between experiment and simulation is demonstrated in Fig. 2. For interactive or reactive systems, the only adjustable parameters introduced are the reaction probability (γ) and the surface residence time.

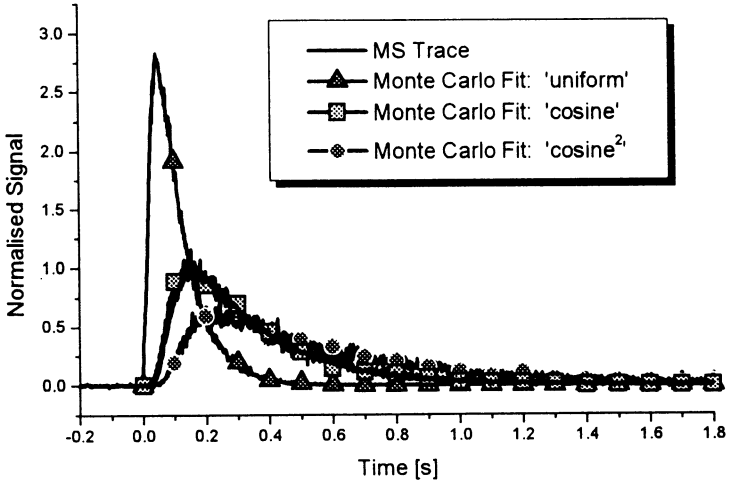

Fig. 2: Algorithm test: non-interactive N_2 molecules passing through a 1.05 × 100 cm tube (Z = 14000).

Results and discussion

The study of surface residence times in reactive systems poses a new challenge since kinetic analysis is no longer trivial: irreversible uptake of the reactant molecule on the coated diffusion tube walls may lead to an apparent $1/k_{sticky}$ value shorter than $1/k_{ideal}$ due to the loss process which may partially or even totally counteract the 'delaying' effect of the surface residence time. To determine the extent of either process we must first know the reaction probability. This can be achieved by using mass balance arguments or by Knudsen cell experiments. The arrival time MS signal for a 'non-sticky'

surviving fraction of molecules may be calculated using the Monte Carlo simulation. Any differences to the observed signal are then attributed to the surface residence time which is fitted to the observed arrival time.

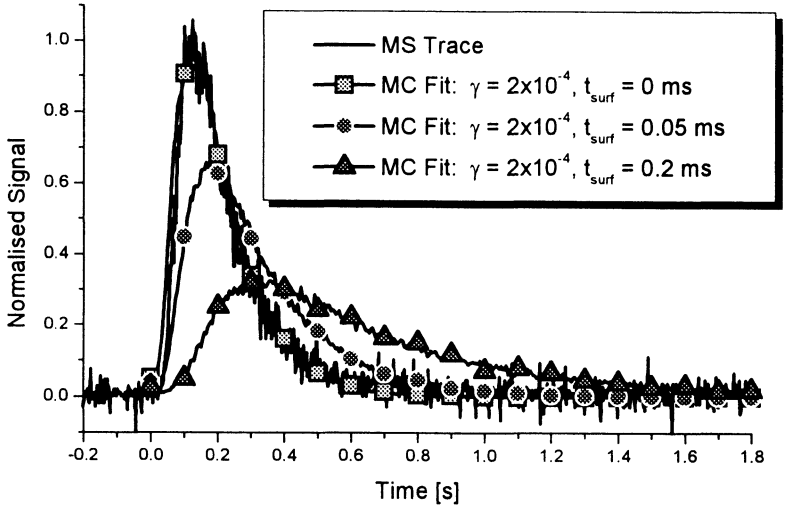

Fig. 3: $ClNO_2$ after passage through a 2 × 90 cm tube (Z = 3250) coated with KBr

Fig. 3 shows the arrival time of a pulse of $ClNO_2$ molecules after passage through a 2 × 90 cm tube internally coated with KBr. Only 23 % of the injected molecules survived, causing a decrease in the arrival time from 0.2 (Teflon) to 0.13 s (KBr). The Monte Carlo fit obained for a γ of 2×10^{-4} (Caloz *et al.*, 1998) without adding a surface residence time is excellent. A summary of the results for all the reactor geometries used is presented in Table 1.

Table 1: $ClNO_2$ Results

Tube [cm]	Z	Surface	$\#_{in}$ [$\times 10^{15}$]	$\#_{out}$ [%]	1/k [s]	γ	t_{surf} [ms]
2 × 120	5700	Teflon	0.5–10	REF	0.348 ± 0.04	–	–
2 × 120	5700	KBr	1–10	18.7 ± 4.2	0.150 ± 0.03	2×10^{-4}	< 0.02
2 × 90	3250	Teflon	0.5–10	REF	0.201 ± 0.02	–	–
2 × 90	3250	KBr	0.5–5	22.9 ± 7.6	0.131 ± 0.02	2×10^{-4}	< 0.03
2 × 60	1480	Teflon	0.5–2.5	REF	0.092 ± 0.01	–	–
2 × 60	1480	KBr	0.5–5	36.2 ± 9.5	0.074 ± 0.08	2×10^{-4}	< 0.04

A similar series of experiments has been carried out for $ClONO_2$ on NaCl. However, due to the considerably higher reaction probability (γ = 0.1), much shorter diffusion tubes had to be used in order to ensure a 'surviving fraction' of molecules large enough to be observed. The arrival time distribution of a pulse of $ClONO_2$ molecules passing through a 2 × 20 cm tube coated with NaCl is shown in Fig. 2. Typically, only 5 % of the injected molecules survive the Z collisions across the NaCl coated tube. Although the rapid heterogeneous loss inevitably leads to a faster decay constant, the observed arrival time for $ClONO_2$ on NaCl (0.049s) is actually greater than that for $ClONO_2$ interacting with Teflon (0.023s). This clearly suggests a significant surface residence time. The Monte Carlo fits (Fig. 4) indicate that t_{surf} is of the order of 0.7 ms, which we confirmed using other tube geometries. A summary of all results is listed in Table 2.

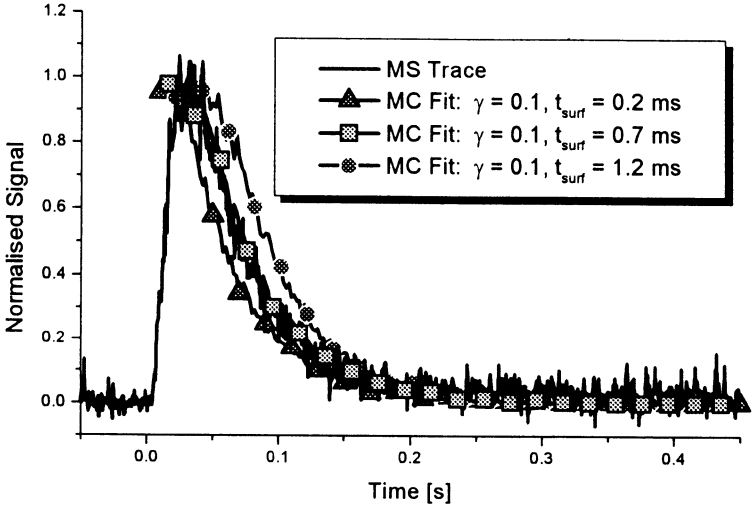

Fig. 4: $ClONO_2$ after passage through a 2 × 20 cm tube (Z = 280) coated with NaCl

Our results show that the surface residence time of the highly reactive $ClONO_2$ on NaCl (γ = 0.1; t_{surf} = 0.7 ms) is at least 30 times larger than that of the much less reactive $ClNO_2$ on KBr ($\gamma = 2 \times 10^{-4}$; $t_{surf} < 30$ μs). This is presumably due to a strong Cl^----$^{\delta+}ClONO_2$ interaction. These results suggest that long surface residence times pertaining to sticky moelcules may be related to high uptake probabilities. Further work is planned to resolve this issue.

Table 2: $ClONO_2$ Results

Tube [cm]	Z	Surface	$\#_{in}$ [$\times 10^{15}$]	$\#_{out}$ [%]	1/k [s]	γ	t_{surf} [ms]
2 × 30	390	Teflon	1	REF	0.035 ± 0.004	–	–
2 × 30	390	KBr	1	4.2 ± 2.4	0.057 ± 0.006	0.1	1.2 ± 0.5
2 × 25	280	Teflon	1–2.5	REF	0.027 ± 0.003	–	–
2 × 25	280	KBr	1–2.5	5.8 ± 2.7	0.044 ± 0.005	0.1	1.0 ± 0.4
2 × 20	180	Teflon	1–10	REF	0.023 ± 0.002	–	–
2 × 20	180	KBr	1–10	5.0 ± 2.6	0.049 ± 0.005	0.1	0.7 ± 0.2

Acknowledgements

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