Tropospheric Photooxidation of Perchloroethene and Trichloroacetyl Chloride and the Role of Aerosols

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Our present knowledge of the degradation products of chlorinated organic compounds in the atmosphere is still limited. Most of the chlorinated solvents emitted are degraded in the troposphere by attack of OH, and only minor portions can reach the stratosphere (leading to low atmospheric chlorine loading potentials and consequently low stratospheric ozone depletion potentials). On the other hand, a significant formation of CCl_4, persistent in the troposphere, has been reported in an earlier smog chamber study of perchloroethene (PER) at yields up to 9%[1]. The formation of this product has not been confirmed in later smog chamber studies of the OH-initiated degradation of PER[2], and it was observed that attack by atomic Cl may contribute to attack by OH[3-5]. In the present study, the tropospheric photooxidation of PER is investigated in a smog chamber[6] in the absence and presence of NaCl aerosol, a model for sea-spray[7], in order to clarify the occurrence of CCl_4 and to assess its atmospheric yield[8].

In the homogeneous gas-phase, the OH-initiated degradation of PER leads to the formation of phosgene ($COCl_2$)[1-5], and a production of atomic Cl is observed at high yields[5,8] and traces of the epoxide, C_2Cl_4O, of about 0.1% of the PER consumed (identified by GC/MS and comparison with a sample provided by courtesy of H. Frank, Tübingen), probably by reaction with HO_2. Because of the extremely high reactivity of PER against atomic Cl (more than 200 times higher than OH[4]) the Cl-initiated degradation predominates in the smog chamber experiments in the absence of specific scavengers of atomic Cl. In the Cl-initiated degradation, trichloroacetyl chloride (TCAC) is identified as a major intermediate[5,8] and CCl_4 as a minor product[8] that had already been observed by Singh et al. (1975)[1] in early smog chamber investigations of PER. Fig. 1 shows the yield of CCl_4 from the OH-initiated degradation of PER as a function of the PER consumed by attack of atomic Cl (computed from the time profiles of PER and time integrals of atomic Cl, determined from the consumption of selected alkanes and aromatics in the system[9]) in various smog chamber runs after 45h. It can be seen in fig. 1 that a fairly constant portion of 0.5% of the PER attacked by Cl is converted to CCl_4.

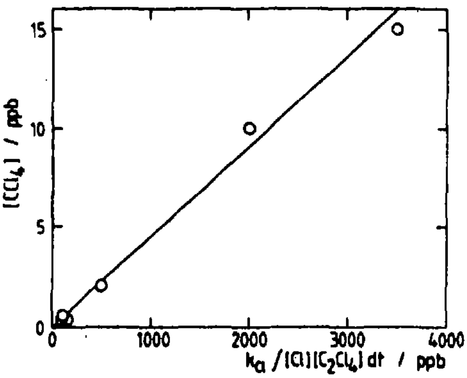

Fig. 1: Formation of CCl_4 from the degradation of PER ($[PER]_0$ = 4 ppm) in various smog chamber runs (in teflon film at 50% rel. humidity and producing OH by photolysis of H_2O_2 at $[H_2O_2]_0$ = 2 ppm)) as a function of the portion of PER consumed by attack of atomic Cl

Further experiments showed that the yields of CCl_4 rise to almost 2 % when the irradiation is continued for up to 140 h and that there is a delay of CCl_4 formation compared to the consumption of PER with TCAC as the major intermediate. The formation of TCAC can be explained from the mechanism[10-12]

$$
\begin{array}{llr}
Cl\cdot + CCl_2{=}CCl_2 & \rightarrow CCl_3\text{-}CCl_2\cdot & (1) \\
CCl_3\text{-}CCl_2\cdot + O_2 & \rightarrow CCl_3\text{-}CCl_2O_2\cdot & (2) \\
CCl_3\text{-}CCl_2O_2\cdot + NO & \rightarrow CCl_3\text{-}CCl_2O\cdot + NO_2 & (3) \\
CCl_3\text{-}CCl_2O\cdot & \rightarrow CCl_3COCl\ (\text{TCAC}) + Cl\cdot & (4a) \\
 & \rightarrow COCl_2 + CCl_3\cdot & (4b) \\
CCl_3\cdot + O_2 & \rightarrow CCl_3O_2\cdot & (5) \\
CCl_3O_2\cdot + NO & \rightarrow CCl_3O\cdot + NO_2 & (6) \\
CCl_3O\cdot & \rightarrow COCl_2 + Cl\cdot & (7)
\end{array}
$$

where the temperature dependence of the branching ratio k_{4a}/k_{4b} can be described by the expression[11,12] $\log (k_{4a}/k_{4b}) = 2.59 - 558\ K/T$, leading to yields of TCAC around 84 % at 300 K. A formation of CCl_4 might be explained by photolysis of TCAC according to:

$$
\begin{array}{llr}
CCl_3COCl + h\nu & \rightarrow COCl_2 + \text{products} & (8a) \\
 & \rightarrow CCl_4 + CO & (8b)
\end{array}
$$

These channels were investigated by direct photolysis of TCAC in the smog chamber[13]. The UV absorption spectrum of TCAC was determined in the gas phase in agreement with another recent study[14]. It overlaps only weakly with the spectrum of the solar simulator above 300 nm. $COCl_2$ is observed as a main product, indicating $\phi_{8a} \approx 1$ and that the other product(s) of photolysis (8a), possibly CCl_2 radicals, lead to $COCl_2$ as well. A minor formation of CCl_4 was observed, corresponding to a quantum yield of $\phi_{8b} = 0.03$. In contrast to the constant yield of $COCl_2$ with time, the yield of CCl_4 increased with time and was observed to be favoured by humidity, indicating that the hydrolysis product of TCAC, trichloroacetic acid (TCA) is responsible for the production of CCl_4 (although the these experiments were started in the absence of humidity, water vapour is known to permeate through the teflon film). Our value for the quantum yield ϕ_{8b} should therefore be considered as an upper limit. Uptake of TCAC by aerosols and clouds, leading to hydrolysis, is expected to occur within the order of a few days in the troposphere (as concluded from recent measurements of the uptake of TCAC[15,16], similar to the uptake of phosgene[17] (with Henry's law and hydrolysis constants of $H \cdot k = 5 \cdot 10^3\ l\ mol^{-1} atm^{-1} s^{-1}$). Direct photolysis of TCA was consequently investigated in the chamber. It formed $COCl_2$ and atomic Cl and again traces of CCl_4, which increased markedly upon addition of 1 ppm HCl (about 50% of which is immediately adsorbed on the teflon film).

This observation lead us to investigate the impact of NaCl aerosol (that is the dominating aerosol in the troposphere on a global scale, arising from sea-spray and carried over the continents) on the formation of CCl_4 by dissolving TCA in NaCl solution and atomising this to produce an aerosol (1.5 mg m^{-3} at 50 % r.h.). The initial conversion rate of TCA to CCl_4 was observed to be 2% per hour but fell off sharply with time. Yields of about 8% of the initial TCA converted to CCl_4 were observed after 30 h.

The contribution of atomic Cl to the degradation of PER in the troposphere may be considerable because of natural sources of atomic Cl. A widely accepted source of atomic Cl is the reaction of OH with HCl according to:

$$
\begin{array}{llr}
OH + HCl & \rightarrow H_2O + Cl & (9)
\end{array}
$$

Model calculations of this source in the gas phase[18] (assuming HCl-levels of 1ppb in the marine boundary layer) showed that reaction (9) leads to Cl-levels of $[Cl = 3 \cdot 10^3$ cm^{-3} at $[OH] = 1.3 \cdot 10^6$cm^{-3}. *An additional source of atomic Cl is the reaction of* N_2O_5 with NaCl aerosol, that has been observed to form $ClNO_2$ not only from dry NaCl but from deliquescent aerosol as well. $ClNO_2$ is readily photolysed leading to the sequence:

$$N_2O_5 + NaCl \rightarrow ClNO_2 + NaNO_3 \qquad (10)$$

$$ClNO_2 + h\nu \rightarrow Cl + NO_2 \qquad (11)$$

This source of atomic Cl is expected to contribute in the early morning hours in the marine troposphere of the northern hemisphere at high latitudes, where NO_x-levels and wind speeds (and thus aerosol densities) are high and temperatures are low (thereby leading to long lifetimes of N_2O_5). A model calculation, taking these environmental conditions into account and assuming a preliminary uptake coefficient of 0.01 for N_2O_5 on deliquescent sea-salt aerosol leads to a diurnal average of $[Cl] = 4 \cdot 10^3$ cm^{-3} (compared to $[OH] = 5 \cdot 10^5$ cm^{-3}) at 60° latitude north for January, where more than 60% of the PER are consumed by Cl instead of OH. In the meanwhile, the uptake coefficient has been determined to be 0.032 ± 0.03[19]. Employing a wetted-wall flow tube technique the yields of $ClNO_2$ have shown to be higher than those of HNO_3 from the competing reaction of N_2O_5 with H_2O, even in dilute NaCl solutions[20].

Further sources of atomic Cl, such as the reaction of O_3 with HCl (or Cl^- from NaCl) on insoluble solid, inorganic aerosol particles and with aerosol from genuine sea-water have been identified[21] . These have not been quantified yet, although direct observations of photolytic precursors of atomic Cl now exist[22,23].

Conclusions from the experimental observations The formation of CCl_4 as a product from the photochemical degradation of PER in air is confirmed in smog-chamber experiments performed in teflon film.

In the absence of aerosol, the yields of CCl_4 from PER increased with time up to about 2% after 140 h irradiation. A correlation was observed between the amount of CCl_4 formed and the amount of PER reacted with atomic chlorine.

In smog-chamber experiments on the photolysis of TCAC (known to arise from Cl-atom initiated degradation of PER) and its hydrolysis product, TCA, CCl_4 was again observed to be a minor product. In the case of TCA, the formation of CCl_4 was further enhanced by the addition of HCl gas or of NaCl aerosol (the latter at a concentration about 100 times that of the atmospheric marine boundary layer) leading to yields of up to 8%.

These observations suggest that CCl_4 is formed by heterogeneous photochemical processes (occurring on the reactor walls or on the surface of the aerosols, as suggested by photolysis experiments of TCA in the aqueous phase in the presence of Cl^- at low pH, less than about 3).

Atmospheric implications The experimental observations lead to the conclusion that the tropospheric yield of CCl_4 from PER will depend on the concentration level of atomic Cl in the troposphere (which will determine the portion of PER converted to TCAC) and on the concentration, nature and pH of aerosols.

In the homogeneous gas phase in remote regions of the troposphere an estimated 50% of PER may be consumed by atomic Cl at 265 K, and 75% of the resulting pentachloroethoxy radicals will decompose to TCAC.

The globally averaged photolytic lifetime of TCAC is about 2 months with an upper limit for the quantum yield of $CCl_4 < 3 \cdot 10^{-3}$ (uptake by aerosols, hydrolysis and rainout are known to shorten the lifetime of TCAC considerably), i.e. an upper limit of 0.1 % of PER converted to CCl_4.

A considerable additional contribution by the heterogeneous formation of CCl_4 from TCA dissolved in sea-salt aerosol (or other aerosols containing Cl^-) is expected, since such a process predominates in the smog chamber even on the teflon walls. The present data base does not however enable us to make a quantitative evaluation of the atmospheric importance of this process, and additional research will be needed to clarify this point.

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