5.2. Related mechanisms of halogen chemistry

A large variety of organic reactions involving different halogen species is known within the basic organic chemistry literature (e.g. March, 1992). Those reactions can be divided into two groups: carbon skeleton affecting and functionality modifying reactions. The halogen species discussed here are the species which are supposed to be present during the molecular halogen photochemical experiments: X_2, HOX and HX, where X is chlorine or bromine. XO radicals formed by the rapid reactions of halogen atoms with ozone are considered to be unreactive against the organic precursors and to be converted to HOX via reaction with HO_2, thus keeping the levels low (Mellouki et al., 1994; Bedjanian et al., 2001). The chosen precursors for the SOA represent different structural elements like an aliphatic structure with ring strain, comprising primary, secondary and tertiary C-H bonds, and an olefinic double bond (α-pinene) and substituted aromatic/phenolic structures (catechol and its methyl-ether modification guaiacol), where ring opening upon oxidation and possibly aldol condensation lead to further olefinic and conjugated structures. Those different organic precursors result in a different chemical structure of the related SOA. The SOA is considered to be still highly reactive and thus will offer a different chemical environment for RHS chemistry.

The change of carbon-hydrogen bonds, observed by long-path FTIR spectroscopy upon halogenation (Fig. 4), can be related to the abstraction reaction of H atoms by chlorine atoms from C-H bonds of the methyl groups of the carbon structure (2A).

$$R - CH_3 + Cl \cdot \rightarrow R - CH_2 \cdot + HCl \tag{2A}$$

Molecular chlorine might then react with the aliphatic radical in the well-known chain propagation of photochlorination according to equation (2B) in the initial phase of chlorine injection.

$$R - CH_2 \cdot + Cl_2 \rightarrow R - CH_2Cl + Cl \cdot \tag{2B}$$

Furthermore, addition of a chlorine atom to the aliphatic radical might form saturated carbon-chlorine bonds, as suggested in figure 5 if not enough unsaturated/aromatic double bonds for addition are available (see below). On the other hand, the FTIR and UV/Vis spectra indicate the sufficient presence of such sites for addition, and such radical-radical reactions are suppressed by the presence and predominance of O_2 in the reactivity by its concentration, forming RO_2 radicals (2C) (Wallington et al., 1989; Carr et al., 2003).

$$R - CH_2 \cdot + O_2 + M \rightarrow R - CH_2O_2 \cdot + M \qquad (2C)$$

The abstraction reaction can concern our model aerosols formed from α-pinene and guaiacol (indicated by the long-path FTIR spectra), where methyl groups occur (even more so with the methyl group of guaiacol that has a minor benzylic character because of the lone-pair electrons of the ether oxygen). Abstraction of hydrogen from the two CH_2 groups and even more so the tertiary C-H bonds of α-pinene (if all of them persist in the SOA) is expected as well. Hydrogen abstraction from methyl groups located close to oxygen or halogen containing functional groups was discussed in detail by Carr et al. (2003).

Halogen addition to unsaturated bonds is the preferred pathway for bromine atoms (3) since their abstraction reactions are much slower than those chlorine atoms. This reaction might be the most important reaction for formation of brominated compounds from SOA of the chosen precursors. Wallington et al. (1989) studied the addition of atomic bromine to several alkenes. Nordmeyer et al. (1997) studied the chlorination of isoprene and suggested an addition of chlorine to double bonds (equation (3)) and a quenching of the bond by oxygen (equation (2C)). A series of unsaturated hydrocarbons were used by Orlando et al. (2003), identifying the same reaction path-way.

$$R - CH = CH - R + Br \cdot \rightarrow R - CBrH - CH \cdot - R \qquad (3)$$

Bierbach et al. (1996) compared the reaction of chlorine and bromine atoms with the (in our case) competing reaction of OH radicals. While the reaction with chlorine atoms (hydrogen abstraction) is expected to be faster than the reaction with OH radicals, the reaction with bromine appears to be in the same temporal regime compared to the reaction with OH especially for terpenes and dienes. These authors state that the reaction of bromine atoms with especially alkenes and dienes might be an effective tropospheric sink for bromine atoms. The high reactivity of terpenes towards halogenation is indicated by the amount of halogenated compounds related to the organic bulk of SOA from α-pinene (Table 2 and table 3 for bromine). The amount of halogenated species caused by reaction of RHS with SOA from the aromatic precursors is significantly lower.
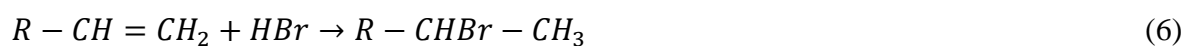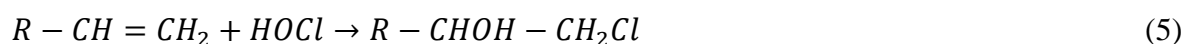
Atomic bromine is also known to abstract hydrogen atoms at tertiary C-H bonds (4).

$$H_3C - CH(CH_3) - CH_3 + Br \cdot \rightarrow H_3C - C \cdot (CH_3) - CH_3 + HBr \qquad (4)$$
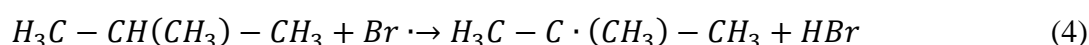
While this reaction is known to produce tertiary halogenated aliphatic compounds by abstracting a second bromine atom from molecular bromine, quenching of this reaction center by oxygen molecules (2C) seems to be more likely. Electron-rich tertiary reaction centers like

α-pinene-induced structures are likely to undergo this abstraction. SOA from catechol or guaiacol are not supposed to exhibit those centers, although aldehydes, derived from ring opening, have weak C-H bonds as well (see also below).

Apart from the reaction of atomic halogens with saturated or unsaturated structural elements, HOX or HX are able to undergo a heterolysis and an addition to unsaturated bonds, where the more electrophilic part is added to the stabilized carbocation. Hypochlorous acid (HOCl), which is formed during the homogeneous gas-phase reactions and by reaction of molecular chlorine with liquid or surface-adsorbed water, is known to add to unsaturated bonds, forming an alcohol group in α-position (5). HBr causes the formation of a brominated carbon in α-position (6).

$$R - CH = CH_2 + HOCl \rightarrow R - CHOH - CH_2Cl \tag{5}$$

$$R - CH = CH_2 + HBr \rightarrow R - CHBr - CH_3 \tag{6}$$

While no terminal unsaturated bonds are available by the chosen precursors, these reactions can also occur at other unsaturated bonds of the reactive SOA or at aromatic systems. α-pinene induced SOA is suspected to be rather poor on unsaturated bonds. SOA from catechol and guaiacol still exhibits a large amount of unsaturated or aromatic structural elements. Furthermore, these reactions take also place in the quasi-liquid phase of the aerosol. Chlorination of substituted alkanes with HOCl in CCl_4 is reported by Tanner and Nychka (1967). Carpenter et al. (2005) related brominated humic material, sampled in the Hudson Bay, to the reaction with HOBr. Halogenation by HOCl and HOBr of aromatic compounds was studied by Voudrias and Reinhard (1988), where the acid catalyzed bromination with HOBr exhibits significant reaction rates. Vione et al. (2005 and 2008) investigated the halogenation of phenols at simulated atmospheric aerosol conditions in the presence of H_2O_2, X^- and H^+ where HOX is reported as the main halogenating reagent. Aromatic compounds (formed from catechol or guaiacol as precursors), are also suspected to undergo electrophilic aromatic substitutions and hence an increase of the decree of substitution. The substituents OH- and CH_3O- on benzenes activate the aromatic for the addition of further functional groups according to the Hammett-equation (Zetzsch, 1982). Hence, any substituted aromatic structure on SOA from catechol or guaiacol is available for further substitution reactions by RHS to form aromatic C-X bonds.

While reactions (2) to (6) modify the carbon structure of the macromolecules of the preformed SOA, other reactions are suspected to influence functional groups and hence

related aerosol parameters like the average carbon oxidation state or vibrational features related to carbonyls or other oxygen containing functional groups. The NO_X-free formed SOA in this study is suspected to not contain any different chemical element than carbon, hydrogen and oxygen. Furthermore, in the oxidizing environment of the smog-chamber atmosphere, no chemical reduction will occur. The following part discusses reactions which influence oxygen containing functional groups. However, since there are no metals present in the gas phase or particle phase, reactions which depend on inorganic catalysts like the Hunsdiecker reaction (e.g. March, 1992) are not discussed.

HOX species are also suspected to form gaseous halogen containing methanes (like e.g. trihalomethanes) by haloform-type reactions (Carpenter et al., 2005; Mok et al., 2005). In these reactions, a methyl group in α-position of a carbonyl containing functional group is substituted by a halogen atom (with HOX as reacting agent) and separated by forming gaseous CH_nX_{4-n}-species. The carbonyl group is simultaneously oxidized to a carboxylic acid. Although the α-pinene and guaiacol (and their related aerosols) exhibit reaction centers for haloform-type reactions, no related gaseous halogen-species were detected by FTIR spectroscopy.

Alcohols are affected by halogen atoms either by hydrogen abstraction in α-position (Wu et al., 2003) or by oxidation to aldehydes (Hurley et al., 2004).

The reaction of aldehydes with halogens (Wallington et al., 1989; Ramacher et al., 2000) is dominated by the abstraction of the relatively weak bonded hydrogen of the aldehyde. A subsequent addition of oxygen (according to equation 2C) will cause a one-carbon shorter aldehyde and the release of CO_2 (Ramacher et al., 2000). The remaining carbonyl can be separated from the organic molecule (CO release) or be oxidized to a carboxylic acid. A corresponding release of CO and CO_2 was measured for all three types of SOA using long-path absorption FTIR spectroscopy.

HOBr (and maybe HOCl) is also suspected to cause decarboxylation by formation of an acyl hypohalite. Organic acyl hypohalites are discussed e.g. by Anbar and Ginsburg (1954). Pink and Steward (1971) report oxidative decarboxylation caused by bromine water. Formation of acyl hypohalites is also discussed by Skell and May (1983). These reactions explain a possible decarboxylation of the organic aerosols.

The formation of gaseous phosgene during the reaction of RHS with SOA can be explained by several basic reaction path-ways. Chlorine is able to react with released carbon monoxide (e.g. from the oxidation of aldehydes) similar to equations (3) and (2B). The decomposition of

chloroalkanes and chloroalkenes is reported as the main phosgene source in the troposphere by Helas and Wilson (1992). The temporal resolution of the applied methods of the present study is too low to determine the significant source of phosgene, measured using FTIR spectroscopy in the aerosol smog-chamber. A further processing of haloform-type reaction products to phosgene cannot be excluded.

The reactions mentioned above can explain several changes observed while processing the preformed organic aerosols from α-pinene, catechol and guaiacol with reactive halogen species. However, there is still lack of literature on heterogeneous gas-phase reactions of halogen species with organic compounds (in the aerosol phase) and how basic organic reaction mechanisms can be applied to atmospheric conditions in the boundary layer.

New Literature:

Anbar, M., and Ginsburg, D.: Organic hypohalites, Chem. Rev., 54, 925-958, 1954.

Bedjanian, Y., Riffault, V., and Poulet, G.: Kinetic study of the reactions of Br with HO_2 and DO_2, J. Phys. Chem. A, 105, 573-578, 2001.

Bierbach, A., Barnes, I., and Becker, K. H.: Rate coefficients for the gas-phase reactions of bromine radicals with a series of alkenes, dienes, and aromatic hydrocarbons at 298 ± 2 K, Int. J. Chem. Kinet., 28, 565-577, 1996.

Carr, S., Shallcross, D. E., Canosa-Mas, C. E., Wenger, J. C., Sidebottom, H. W., Treacy, J. J., and Wayne, R. P.: A kinetic and mechanistic study of the gas-phase reactions of OH radicals and Cl atoms with some halogenated acetones and their atmospheric implications, Phys. Chem. Chem. Phys., 5, 3874-3883, 2003.

Helas, G., and Wilson, S. R.: On sources and sinks of phosgene in the troposphere, Amos. Environ., 26A, 2975-2982, 1992.

Hurley, M. D., Wallington, T. J., Sulbaek Andersen, M. P., Ellis, D. A., Martin, J. W., and Mabury, S. A.: Atmospheric chemistry of fluorinated alcohols: Reaction with Cl atoms and OH radicals and atmospheric lifetimes, J. Phys. Chem. A, 108, 1973-1979, 2004.

March, J.: Advanced organic chemistry, John Wiley & Sons, New York, 1992.

Mellouki, A., Talukdar, R. K., and Howard, C. J.: Kinetics of the reactions of HBr with O3 and HO2: The yield of HBr from HO2 + BrO, J. Geophys. Res., 99, 22949-22954, DOI: 10.1029/94JD02144, 1994.

Mok, K. M., Wong, H., and Fan, X. J.: Modeling bromide effects on the speciation of trihalomethanes formation in chlorinated drinking water, Global Nest J., 7, 1-16, 2005.

Nordmeyer, T., Wang, W., Ragains, M. L., Finlayson-Pitts, B. J., Spicer, C. W., and Plastridge, R. A.: Unique products of the reaction of isoprene with atomic chlorine: Potential markers of chlorine atom chemistry. Geophys. Res. Lett., 24, 1615-1618, 1997.

Orlando, J. J., Tyndall, G. S., Apel, E. C., Riemer, D. D., and Paulson, S. E.: Rate coefficients and mechansims of the reaction of Cl-atoms with a series of unsaturated hydrocarbons under atmospheric conditions, Int. J. Chem. Kinet., 35, 334-353, 2003.

Pink, J. M., and Stewart, R.: Mechanism of oxidative decarboxylation of α-hydroxy acids by bromine water. Part I. Oxidation in neutral and alkaline medium, Can. J. Chemistry, 49, 649-653, 1971.

Ramacher, B., Orlando, J. J., and Tyndall, G. S.: Temperature-dependent rate coefficient measurements for the reaction of bromine atoms with a series of aldehydes, Int. J. Chem. Kinet., 32, 460-465, 2000.

Shell, P. S., and May, D. D.: Ground- and excited-state carboxylate radical chain carriers. Radical chain substitution reactions with acyl hypohalites, J. Am. Chem. Soc., 105, 3999-4008,1983.

Tanner, D. D., and Nychka, N.: Radical chain halogenation reactions of chlorine monoxide, J. Am. Chem. Soc., 89, 121-125, 1967.

Vione, D., Maurino, V., Minero, C., Calza, P., and Pelizzetti, E.: Phenol chlorination and photochlorination in the presence of chloride ions in homogeneous aqueous solutions, Environ. Sci. Technol., 39, 5066-5075, 2005.

Vione, D., Maurino, V., Man, S. C., Khanra, S., Arsene, C., Olariu, R.-I., and Minero, C.: Formation of organobrominated compounds in the presence of bromide under simulated atmospheric aerosol conditions, Chemsuschem, 1, 197-204, 2008.

Voudrias, E. A., and Reinhard, M.: Reactivities of hypochlorous and hypobromous acid, chlrine monoxide, hypobromous acidium ion, chlorine, bromine, and bromine chloride in electrophilic aromatic substitution reactions with p-xylene in water, Environ. Sci. Technol., 22, 1049-1056, 1988.

Wallington, T. J., Skewes, L. M., Siegl, W. O., and Japar, S. M.: A relative rate study oft he reaction of bromine atoms with a variety of organic compounds at 295 K, Int. J. Chem. Kinet., 21, 1069-1076, 1989.

Wu, H., Mu, Y., Zhang, X., and Jiang, G.: Relative rate constants for the reactions of hydroxyl radicals and chlorine atoms with a series of aliphatic alcohols, Int. J. Chem. Kinet., 35, 81-87, 2003.

Zetzsch, C.: Predicting the rate of OH-addition to aromatics using σ^+-electrophilic substituent constants for mono- and polysubstituted benzene, XVth Informal Conference on Photochemistry, 27.06.-01.07.1982, Stanford, USA.