Detailed modelling of the mechanism of the atmospheric degradation of brominated very-short lived substances

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2.4 Estimation method of the Henry's law constants

Some of the halogenated organics intermediate products are soluble. The Henry's law constants are not known for complex halogenated products. Consequently, we used the Bond Contribution Method (BCM) (Meylan and Howard, 1991) or the Molecular Connectivity Index (MCI) method (Nirmalakhandan and Speece, 1988) to estimate them. These methods attribute a "contribution value" for each different atom and/or each bond present in the molecule, depending on the chemical nature, and estimate the Henry's law constant from these values. Before estimating the Henry's law constant of our bromine products, we have tested the two methods by comparisons with well-known Henry's law constants (referenced by Sander et al., 1999). Table 4 shows these comparisons. For small peroxides and alcohols, BCM is better than MCI method, which overestimates the values for peroxides and underestimates them for alcohols. So we used this method for brominated peroxides and alcohols ($CH_nBr_{3-n}OOH$ and $CH_nBr_{3-n}OH$, with n = 0, 1, or 2). Both methods are in excellent agreement for the estimation of aldehydes and ketones Henry's law constants, except for formaldehyde. However, BCM estimates the constant from the bond between each atom and treats carbonyl groups (C=O) as single atoms. Their authors (Meylan and Howard, 1991) established the values of each bond as C-C bond, C-H bond or CO-C bond but with no value for the bond CO-Br. So we used the MCI method to estimate the Henry's law constant of the brominated aldehydes and ketones. MCI method uses the contribution of each atom of the molecule and considers aldehydes and ketones as subgroups of the molecule for which an additional contribution to the Henry's law constant is attributed. These two estimation methods allow us to derive an order of magnitude for the Henry's law constant. Seinfeld and Pandis (2006) proposed that species with a Henry's law constant lower than 1000 $mol.L^{-1}.atm^{-1}$ are considered insoluble, species with constants between 1000 and 10^4 $mol\ L^{-1}\ atm^{-1}$ are

moderately soluble and species with constants higher than 10^4 mol L^{-1} atm^{-1} are very soluble. For our study we considered only two classes: species with constants lower than 10^4 mol L^{-1} atm^{-1} as not very soluble and species with constants higher than 10^4 mol L^{-1} atm^{-1} as very soluble. Indeed, for a cloud with a typical water content of 1 g m^{-3} of air (Seinfeld and Pandis, 2006), a constant of 10^4 mol L^{-1} atm^{-1} corresponds to a mass aqueous fraction of 20%.

The results of the estimation Henry's law constant for bromine compounds are reported in Table 5. The most soluble organic species are CBr_3O_2H and CBr_3OH with Henry law's constants higher than 10^5 mol L^{-1} atm^{-1}, whereas the less soluble organics are CBr_2O and CHBrO.

Table 1: Comparisons of well known Henry's law constants (referenced by Sander et al. 1999) with estimated Henry's law constant for the two methods, Bond Contribution Method (BCM) and Molecular connectivity index method (MCI)

	BCM	MCI	Experimental (Sander et al., 1999)
Aldehydes			
HCHO	10	18	3000
CH_3CHO	15	15	17
C_2H_5CHO	11	12	13
C_4H_9CHO	4.8	7.5	6.4
Ketones			
CH_3COCH_3	20	18	27
$C_2H_5COCH_3$	15	15	20
Peroxides			
CH_3O_2H	147	1501.18	310
$C_2H_5O_2H$	110	1326.7	340
$OHCH_2O_2H$	$4x10^6$	$7.54x10^6$	$1.7x10^6$
Alcohols			
CH_3OH	235	195	230
C_2H_5OH	176	167	160
C_3H_7OH	132	131	130
Compounds with bromine			
$CHBr_3$	8.9	2.4	2.1
CH_2Br_2	1.0	1	1.1
$C_2H_4Br_2$	0.8	0.8	1.5

Table 2: Henry law's constants $k°_H$ of the intermediate products (PGs)

Species	$k°_H$ (298K) (mol L^{-1} atm^{-1})
HBr	0.71 (1)
HOBr	$6.1x10^3$ (1)
CBr_3O_2H	$1.9x10^5$ (2)
$CHBr_2O_2H$	$2.24x10^4$ (2)
CH_2BrO_2H	$2.58x10^3$ (2)
CHBrO	74 (3)
CBr_2O	21.5 (3)
$CBr_3O_2NO_2$	401 (2)
$CHBr_2O_2NO_2$	304 (2)
$CH_2BrO_2NO_2$	35 (2)
CBr_3OH	$1.5x10^5$ (2)
$CHBr_2OH$	$1.73x10^4$ (2)
CH_2BrOH	$2.0x10^3$ (2)

(1)Sander et al., 1999
(2) Bond Contribution Method (Meylan and Howard, 1991)
(3) Molecular Connectivity Index (Nirmalakhandan and Speece, 1988)