Building and Environment 44 (2009) 1343–1349

Contents lists available at ScienceDirect

Building and Environment

journal homepage: www.elsevier.com/locate/buildenv

Modeling of the production of secondary gaseous products in confined atmospheres

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ARTICLE INFO

Article history:
Received 13 March 2008
Received in revised form
25 July 2008
Accepted 31 August 2008

Keywords:
Indoor chemistry
Confined atmosphere
Homogeneous/heterogeneous chemistry
Secondary products

ABSTRACT

Confined environments are indoor spaces in which the air is not renewed or very poorly renewed by fresh outdoor air (spacecraft, submarines, etc.). In these environments, indoor air quality (IAQ) is expected to be highly influenced by homogeneous and heterogeneous chemistry. This paper presents a representative example of the contribution of these two phenomena to the production of secondary gaseous pollutants indoors by analyzing the chemical degradation of isoprene. An indoor air quality model was developed in the Matlab environment to compute the concentrations of both organic and nonorganic gaseous species involved in this mechanism. Two kinds of initial conditions (concentrations of nitrogen oxides, ozone and isoprene) were considered for the simulations. The results show strong interactions between homogeneous and heterogeneous reactions. Especially, the integrated reaction rate (IRR) of the heterogeneous hydrolysis of nitrogen dioxide emerges very high. Demonstration of strong interactions between inorganic and organic chemistries is also made, the conversion between NO and NO_2 being of central importance in the degradation cycle of isoprene. The type and amount of secondary products obtained are assessed. The results emphasize the strong influence of ozone and nitric oxide concentration levels indoors.

1. Introduction

Indoor chemistry has been shown to play a significant role in the fate of indoor gaseous pollutants [1,2]. In confined indoor environments indoor chemistry may have an even greater influence due to the absence of dilution by ventilation. Here confined atmospheres are defined as indoor environments isolated from outdoors that has no air change rate or very low air change rates. A concealed indoor environment with no air change rate is considered in this work. Insofar as air change rates in buildings are getting lower, this limit case has been chosen in order to underline the role of indoor chemistry and to describe its specific mechanisms.

To be able to model indoor chemistry, chemical mechanisms have to be taken into account. However gas phase atmospheric chemistry of organic compounds is very complex. The numbers of compounds and reactions involved are potentially huge. Taking into account every single species and reaction in numerical simulations would be too wasteful from the computing time point of view. To solve this problem, atmospheric air quality models use simplified mechanism. These mechanisms are built on the fact that gaseous molecules belonging to the same class react in a similar way. It is therefore possible to noticeably reduce the number of both species and reactions by grouping molecules. Differences between the photochemical mechanisms available are mainly due to the way that real mechanisms are simplified.

Nazaroff and Cass [3] first used a complete photochemical mechanism (31 species, 56 reactions) to model indoor air quality. Their simulations show noticeable indoor production of HONO, HNO_3, NO_3 and N_2O_5 due to homogeneous chemical reactions.

Later on, Axley and coworkers [4] used a more reduced mechanism (8 species, 9 reactions) to study nitric acid production from reactions involving NO_3 and N_2O_5. This study shows that indoor concentrations of O_3, NO and NO_2 are strongly influenced by homogeneous chemical reactions.

Blondeau [5] took into account a chemical mechanism (13 species, 23 reactions) in an indoor air quality model applied to a room enlightened by natural radiation. It has shown that the dynamic of pollutant concentrations is strongly related to the dynamic of light intensity.

A chemical mechanism taking into account 116 species and 198 reactions has been used by Sarwar et al. [6] to evaluate indoor hydroxyl radical (OH) in a typical indoor environment.

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0360-1323/$ – see front matter © 2008 Published by Elsevier Ltd.
doi:10.1016/j.buildenv.2008.08.015

Pommer et al. [7] studied the behavior of an atmosphere composed by ozone, nitrogen oxides and two terpenes using a mechanism involving 23 species and 34 reactions.

Courtey et al. [8] compared three state of the art chemical mechanisms in order to model a typical indoor environment. Whereas no differences were found concerning inorganic compounds, higher discrepancies were found concerning secondary organic gaseous species.

Finally, Carslaw [9] simulated an indoor environment with a nonsimplified mechanism involving 15 400 reactions and 4700 species.

Moreover, indoor chemistry modeled in these studies involved mainly homogeneous reactions. Heterogeneous reactions are usually not modeled with accuracy; the only heterogeneous phenomenon to be modeled being the irreversible deposition of gaseous molecules onto walls.

Interactions between gaseous pollutants and indoor surfaces may play a huge role due to higher surface/volume ratio indoors. Surfaces involved are associated either with the room (floor, ceiling, walls, furniture and occupants) or with particulate matters. However this last type of surfaces is a minority in most indoor environments [1,2]. Heterogeneous processes may be crucial, especially for inorganic species thanks to the heterogeneous hydrolysis of NO_2.

Heterogeneous hydrolysis of NO_2 has been recognized as one of the major heterogeneous phenomena occurring indoors. It has been shown for years that NO_2 hydrolysis indoors preferably occurs on surfaces rather than in the bulk air. This reaction is the result of complex chemical mechanisms of which some steps remain still unknown [10,11]. However the balance and stoichiometry of this mechanism are known for a long time and can be sum up by the following reaction:

$$2NO_2 + H_2O \xrightarrow{\text{surface}} HONO + HNO_3 \qquad (R1)$$

This reaction has been particularly studied in the field of tropospheric chemistry at urban scale since nitrous acid HONO photolysis to form the hydroxyl radical OH, a critical oxidant in tropospheric chemistry. This reaction has also been studied in indoor environments [12–15]. From these studies, it appears that HONO concentration indoors is mainly due to sources indoors rather than to the transport from the outside. However combustion sources cannot explain entirely the levels of HONO observed indoors [15]. Spengler et al. [14] have thus shown a strong correlation between indoor concentration of HONO and NO_2, nitrous acid having a concentration lying between 5 and 15% of NO_2 concentration.

Studies carried out in experimental chambers or in real indoor settings don't match quantitatively, in particular concerning the rate constant of reaction (R1). However numerous common observations come up from these studies. Finlayson-Pitts et al. [10] enumerated five of them:

1. HONO and NO are the two main gaseous products observed. Yield of HONO observed is always less than 50% which would be expected from the stoichiometry of reaction (R1) [13];
2. The rate of generation of HONO and the rate of removal of NO_2 are first order in gas phase nitrogen dioxide contrary to the stoichiometry of reaction (R1) and first order in gas phase water vapor [16–19];
3. The HNO_3 produced isn't observed in the gas phase but in the adsorbed phase or in solution in aqueous films [11,19,20];
4. The kinetic of this reaction is higher in clean rooms than in conditioned chambers [19];
5. The rate constant become less sensible to the nature of the surface with time [19].

Moreover Syomin and Finlayson-Pitts [21] underlined the fact that there is a competition for the adsorption sites between the water vapor, HONO and HNO_3.

There are more uncertainties concerning quantitative data. The surface/volume (S/V) ratio would be expected to be a crucial parameter because of the heterogeneous nature of this reaction. However this is far from being obvious. Thus England and Corcoran [22] observed a slight increase of the rate constant when S/V is multiplied by 3.4. Svensson et al. [19] observed a more important influence of S/V although less important than expected for a heterogeneous reaction. Svensson even proposed an expression of the rate constant functions of S/V. Interestingly this function gives a nonzero reaction rate when $S/V = 0$. Data gathered from some studies [16–19] exhibits however that the trend is a linear increase of the rate constant with S/V (see Fig. 1 in Ref. [10]). Regrettably, no author since Svensson et al. in 1987 [19] ventured to propose an expression of the rate constant functions of S/V, showing that quantitative data available in the literature are too scattered to allow this kind of exercise.

Other heterogeneous reactions have been identified in the literature. For instance, ozone can react with indoor materials like filters [23], ventilation ducts [24] or any building materials that contain unsaturated organic chemicals [25] to produce secondary VOCs, especially aldehydes. However, the data available for ozone concentrations typically observed indoors are scarce.

The present study aims to investigate the influence of indoor chemistry in confined atmosphere and to assess the respective role of homogeneous and heterogeneous reactions and their interactions concerning the production of secondary gaseous pollutants. The specific goals are the following:

1) describe the chemical mechanisms leading to the yield of secondary gaseous products in confined atmospheres,
2) assess the contributions and interactions between organic and inorganic chemistry and
3) evaluate the type and amount of the secondary products originating from the decomposition of a representative VOC indoors, isoprene.

Isoprene has been taken as a representative primary VOC in this study because isoprene is a very reactive species and is likely to be found in confined indoor environments as it is produced by human breath [26].

2. Method

A confined indoor environment was simulated with an indoor air quality (IAQ) model developed under the Matlab environment. This model is described more precisely in Ref. [27]. The indoor air is assumed to be perfectly and instantaneously mixed during the simulations. The model considers homogeneous and heterogeneous reactions (including irreversible deposition on building materials). Ventilation and direct emissions can also be modeled although they weren't considered in this study.

Homogeneous reactions were taken from the tropospheric chemical mechanism MELCHIOR2 developed for the chemistry-transport model Chimere [28]. This mechanism involves 50 species (Table 1) and 117 reactions.

Two types of heterogeneous processes were considered: irreversible deposition on building materials characterized by a deposition velocity and heterogeneous hydrolysis of NO_2.

The rate of deposition on building materials D_i [ppb s^{-1}] for each species i is given by the following equation:

$$D_i = -\frac{A}{V} v_d C_i \qquad (1)$$