Tropospheric Degradation of Dimethoxymethane under Urban Conditions: Validation of the Chemical Mechanism

A contribution to subproject CMD

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Introduction

The increasing use of oxygenated organic compounds like ethers, esters and alcohols as fuel additives, alternative fuels or solvents during the last years may lead to a higher influence of these species on tropospheric chemistry. While the rate coefficients for the OH reactions of the relevant oxygenated VOCs are mostly well established, the knowledge of the detailed atmospheric degradation pathways for these compounds is relatively poor. The mechanistic studies are very often confined to the detection of the primary reaction products. Reaction mechanisms which are derived from these data are usually not validated by comparison of the measured product concentrations and the model. In other cases, where no suitable experimental results are available, reaction mechanisms are postulated without any further verification. Both methods are characterised by high uncertainty when the models are applied, *e.g.* iny field modelling.

In the present work, we demonstrate the construction of chemical degradation schemes for single VOCs considering both experimental data and computer simulations. Dimethoxymethane (DMM) was chosen as a concrete example for an oxygenated VOC which is expected to gain importance in tropospheric photochemistry for the future.

The degradation mechanism of DMM under urban tropospheric conditions is defined and validated by using recent experimental results from Hass (1998).

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The validated model has been subjected to a sensitivity analysis. Finally, the scheme is reduced by using objective methods (Zeng *et al.*, 1997).

Mechanism construction and validation

Dimethoxymethane (DMM) is a diether which is currently used as a solvent and recently has been considered as an alternative diesel fuel. The OH rate coefficient was determined by several authors (Hass, 1998, Porter *et al.*, 1997, Sidebottom *et al.*, 1997, Wallington *et al.*, 1997). Hass, Wallington *et al.*, and Sidebottom *et al.*, carried out product studies of the OH initiated DMM degradation in the laboratory. The major reaction products under urban conditions are methoxymethylformate (MMF) (about 70 mol %) and dimethylcarbonate (DMC, about 25 mol %). Hass and Sidebottom *et al.* also observed the formation of a small fraction of methylformate (MF, about 5 mol %), as a consequence, the carbon yield in this case is nearly 100 %.

Based on the experimental results of the studies cited above, the reaction scheme was constructed as illustrated in Fig. 1. The branching ratios for the OH reaction of DMM and the reaction of the $CH_3OC(O)OCH_3$ radical were determined by fitting the model to the experimental data generated by Hass (1998).

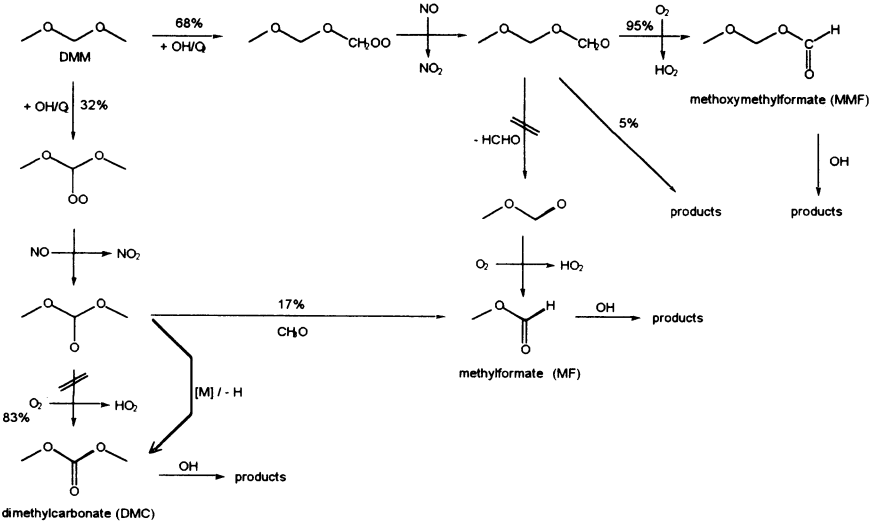

Fig. 1: Tropospheric degradation mechanism for dimethoxymethane (DMM) under urban conditions

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The chemical mechanism also includes a set of reactions in order to describe the inorganic chemistry. This part of the model was taken from the new RACM mechanism of Stockwell *et al.* (1997).

The initial concentration of methyl nitrite (MeONO) as OH precursor in the experiments is not known, since its direct determination is not possible with sufficient accuracy. As a consequence, the "real" concentration of MeONO was obtained from fitting the simulated DMM profiles to the experimental data by variation of the initial MeONO concentration. Since the MeONO photolysis should be the only OH source in the reaction system, this approximation can be made.

Fig. 2 shows as an example a comparison between experimental and simulated c/t profiles for the primary reaction products of the OH initiated oxidation of DMM and NO, NO_2 and O_3. Both data sets are in excellent agreement.

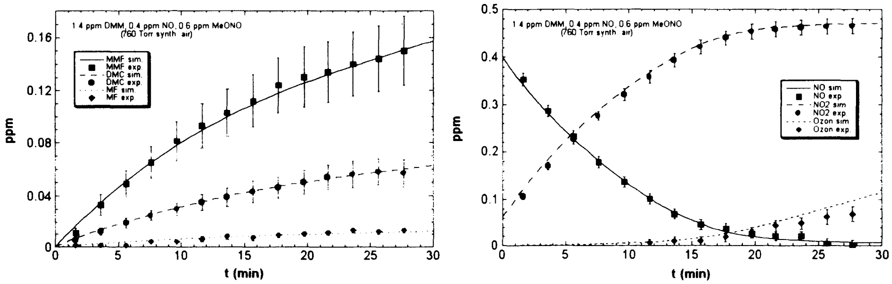

Fig. 2: OH-initiated degradation of DMM in the presence of NO_x. Comparison between experimental and simulated c/t profiles. Left plot: MMF, DMC and MF; right plot: NO, NO_2 and O_3.

Sensitivity Analysis

A sensitivity analysis was carried out for the DMM degradation scheme in order to rate the importance of the single reaction steps. Relative sensitivities S_{ri} were calculated by using time-averaged normalised sensitivity coefficients S_{ai} (Stockwell *et al.*, 1995) as shown by the equation (1):

$$S_{ri} = \frac{S_{ai}}{\sum S_{ai}} \tag{1}$$

Fig. 3 shows as an example the relative sensitivities of NO, NO_2, O_3 and HNO_3 to the most important rate coefficients of the DMM degradation scheme.

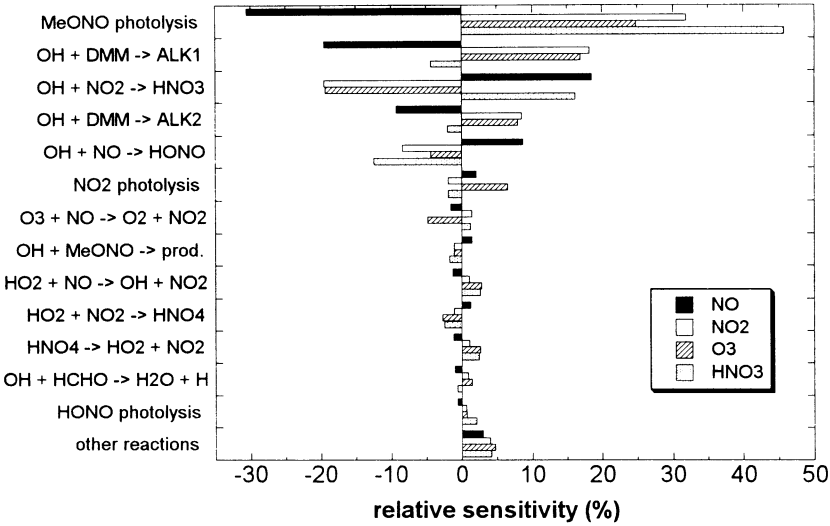

Fig. 3: Relative sensitivity of NO, NO_2, O_3 and HNO_3 to selected reaction rate coefficients of the DMM degradation scheme (ALK1 = $CH_3OCH_2OCH_2$, ALK2 = $(CH_3O)_2CH$).

The plot illustrates, that the chemistry of the reaction system is mainly determined by MeONO photolysis as the only significant OH source and the OH reactions of DMM and NO_X. Photolysis reactions (except methyl nitrite) are of minor importance under the present conditions. The values for S_{ri} of DMM and the primary reaction products lead to the same result. It can be followed, that such well-defined conditions are an excellent basis for the validation of degradation schemes for single VOCs.

Mechanism reduction

Finally, the DMM degradation scheme was reduced by using objective methods (Zeng *et al.*, 1997) The reduction criteria were focused on a minimum error for the calculation of the concentrations of the primary degradation products, MMF, DMC and MF as well as NO, NO_2 and O_3. The table shows the results for a run with the initial conditions given in Figs. 1– 3. The percentage errors for the reactants mentioned above in the reduced model were in the range of 0.5 %–3 %.

Table: Results of reduction of the DMM degradation scheme by using objective methods (Zeng *et al.*, 1997)

	no. of reactions	distribution of redundant reactions:	
full scheme	**71**		
redundant species (7)	−11	photolysis reactions:	−8
principal component analysis (PCA)	−18	inorganic reactions:	−27
rate of production analysis (ROPA)	−3	DMM scheme:	−3
QSSA species (5)	−6	**total:**	**−38**
reduced scheme	**33**		

Acknowledgements

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