Developments of Degradation Mechanisms of Oxygenated Hydrocarbons

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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 proofed 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 of high uncertainty when the models are applied, e.g. by field modelling.

In the present work, the construction of chemical degradation schemes for single VOCs considering both experimental data and computer simulations is demonstrated. Dimethoxymethane, dimethoxyethane, 1,4-dioxane and 1,3-dioxolane were chosen as concrete examples for oxygenated VOCs, which are expected to gain importance in tropospheric photochemistry for the future. The degradation mechanisms of these compounds under urban tropospheric conditions were defined and checked by using recent experimental results from our laboratory. The importance of the individual reactions has been evaluated by means of sensitivity analyses.

Experimental Data and Computer Simulation System

The experimental data used in this work for the evaluation of the degradation mechanisms described here were obtained in our laboratory. The experimental set-up used for these experiments has been described in detail elsewhere (Barnes et al., 1994). Briefly, in a 1080 dm^3 quartz reactor, mixtures of VOC, methyl nitrite and NO in air at a total pressure of 760 Torr were irradiated with fluorescence lamps. Time resolved concentrations of VOC, primary reaction products, NO_x and ozone were measured by using long path FTIR spectroscopy.

All computer simulations were carried out by using the boxmodel SBOX by Seefeld (1997) and Seefeld and Stockwell (1999). This FORTRAN program incorporating the Gear algorithm (Gear, 1971) was operated on an SGI Origin 200 workstation running under IRIX 6.5. The program uses the public domain library VODE (Brown et al., 1989) to integrate the ordinary differential equations.

Construction of the Mechanisms

a) Photolysis reactions, inorganic chemistry and OH source

In order to describe the photolysis processes in the reaction system investigated in the present work a set of photolysis reactions taken from the RACM mechanism by Stockwell et al. (1997) was used. The only photolysis frequency, which was experimentally measured under the present conditions, was that of NO_2 for photodissociation into $O(^3P)$ and NO. All other photolysis frequencies were not measured and had to be estimated. It can be assumed, that the photolysis behaviour of the different species in the photoreactor is almost similar to that in the troposphere when suitable lamps are used. Under this assumption, photolysis frequencies can be calculated for all species relative to $J(NO_2)$ for atmospheric conditions using the algorithm of Madronich (1987). This approximation is justifiable because the radiation strength in the photoreactor is much weaker than in the atmosphere and the influence of the photolysis processes on the radical budget in the reactor is low for most of the treated species.

For the description of the inorganic processes in the model, a set of 35 inorganic reactions taken from the RACM mechanism of Stockwell et al. (1997) has been added to the chemical model used in the present study.

In the indoor photoreactor experiments relevant to this study, OH radicals were formed by the photolysis of methyl nitrite, CH_3ONO, in the presence of NO. Since it was not possible to accurately measure the initial concentration of CH_3ONO, the "real" concentration of CH_3ONO was obtained from a fit of the simulated VOC profiles to the experimental data by variation of the initial CH_3ONO concentration. Because the CH_3ONO photolysis should be the only OH source under the given conditions, this approximation can be made.

b) Dimethoxymethane (DMM)

Dimethoxymethane (DMM) is a diether which is currently used as a solvent and recently has been considered as an alternative diesel fuel. The major reaction products under urban conditions are methoxymethylformate (MMF, about 70 mol%), dimethylcarbonate (DMC, about 25 mol%) and methylformate (MF, about 5 mol%). Based on the experimental results of our laboratory, the reaction scheme was constructed as illustrated in Fig. 1. The stated branching ratios were determined by fitting the model to the experimental data. Fig. 2 illustrates comparisons of experimental and simulated data for selected reactants. Both data sets are in excellent agreement.

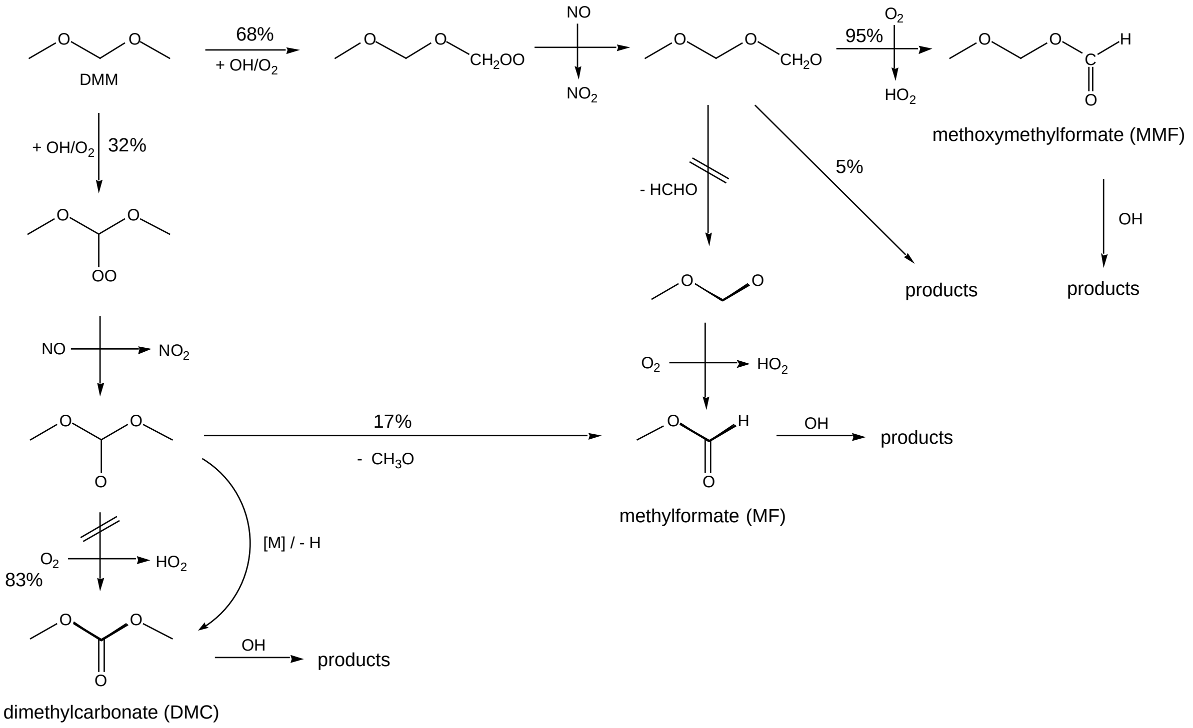

Fig. 1: Tropospheric degradation mechanism for dimethoxymethane in the presence of NO_x.

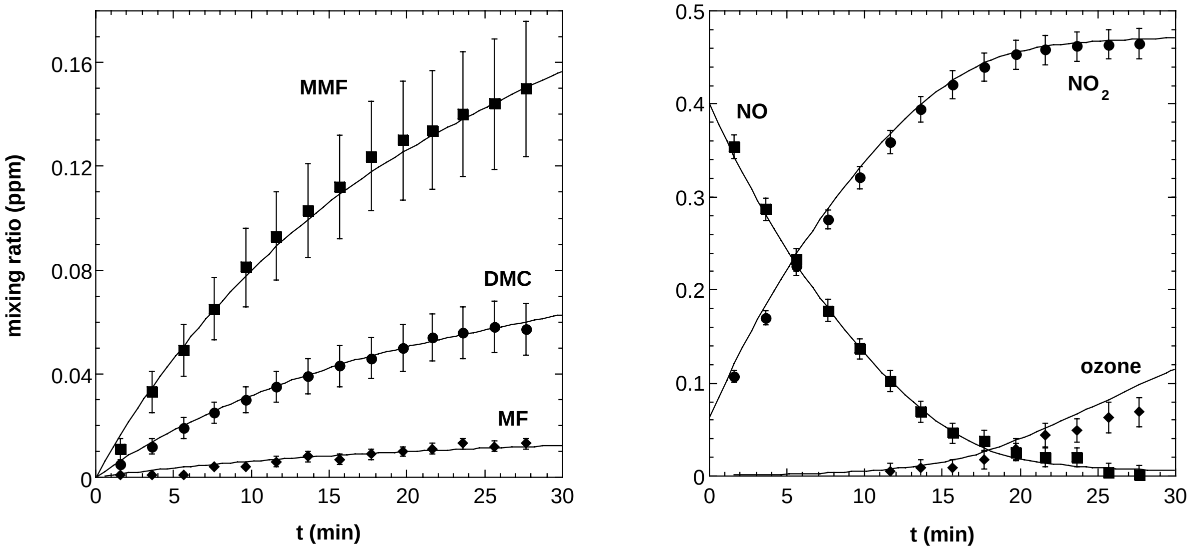

Fig. 2: Comparison of experimental (symbols) and simulated (curves) concentration-time profiles for selected reactants. Experimental conditions: 1.36 ppm DMM, 0.40 ppm NO, 0.60 ppm methyl nitrite, 760 Torr air.

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 following equation:

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

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.

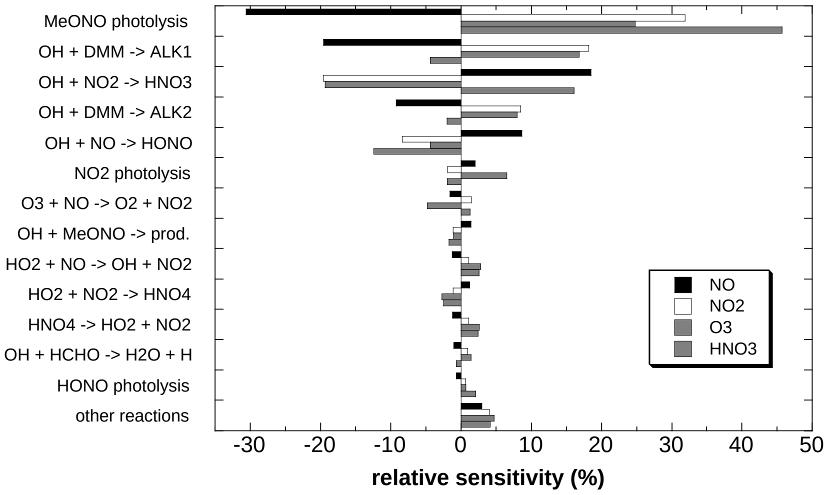

Fig. 3: Relative sensitivity of NO, NO_2, O_3 and HNO_3 to selected reaction rate coefficients of the DMM degradation scheme (ALK1 = $CH_3OCH_2OCH_2$, ALK2 = $(CH_3O)_2CH$). Experimental conditions are given in Fig. 1.

The plot illustrates, that the chemistry of the reaction system is mainly determined by CH_3ONO photolysis as the only considerable OH source and the OH reactions of DMM and NO_x. Photolysis reactions (except that of 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.

c) Dimethoxyethane (DMET)

Similar to dimethoxymethane (DMM), dimethoxyethane (DMET) is a diether which is currently used as a solvent and recently has been considered as an alternative diesel fuel. Based on experimental data of our laboratory, a tropospheric degradation scheme for DMET in the presence of NO_x was developed. The mechanism is illustrated in Fig. 4. The branching ratios given in Fig. 4 were obtained by fitting the model to the experimental results. We assume that 10% of the DMET will be consumed by OH attack on one of the terminal CH_3 groups, leading finally to methoxyethylformate (MEF). The major fraction of 90% reacts via OH attack to one of the CH_2 groups forming an alkyl radical which, after O_2 addition and NO/NO_2 conversion, leads to the corresponding $CH_3OCH(O\bullet)CH_2OCH_3$ radical. In the present mechanism, 82% of these oxy radicals decays thermally forming methylformate (MF) and a methoxymethyl radical which will finally lead to another MF molecule, as shown in Fig. 4.

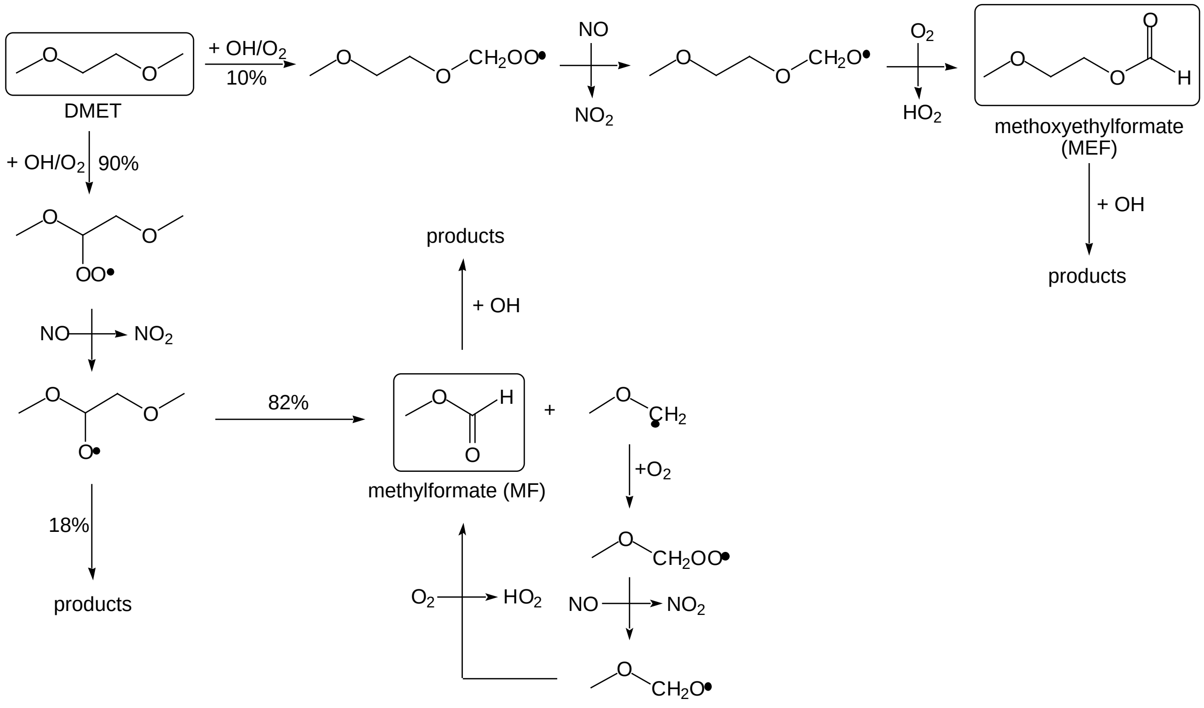

Fig. 4: Degradation scheme of the OH-initiated oxidation of dimethoxyethane in the presence of NO_x.

The remaining 18% of the $CH_3OCH(O\bullet)CH_2OCH_3$ degradation products are unknown at present. A couple of reaction pathways is conceivable, which is illustrated in Fig. 5. Besides the isomerisation leading to another alkyl radical, reaction with NO/NO_2 forming the corresponding nitrites/nitrates, H atom abstraction by O_2 leading to methoxyacetic acid methylester and decay to methoxyacetaldehyde and a methoxy radical may be possible.

Fig. 6 illustrates comparisons of experimental and simulated data for selected reactants. Both data sets are in excellent agreement.

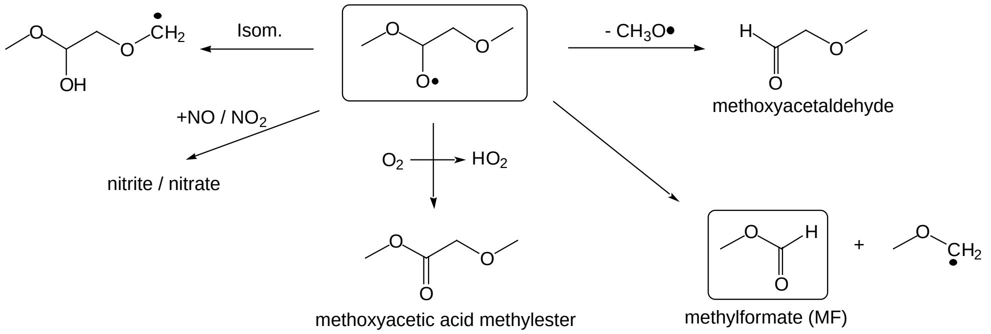

Fig. 5: Possible degradation pathways for the secondary oxy radical, $CH_3OCH(O\bullet)CH_2OCH_3$.

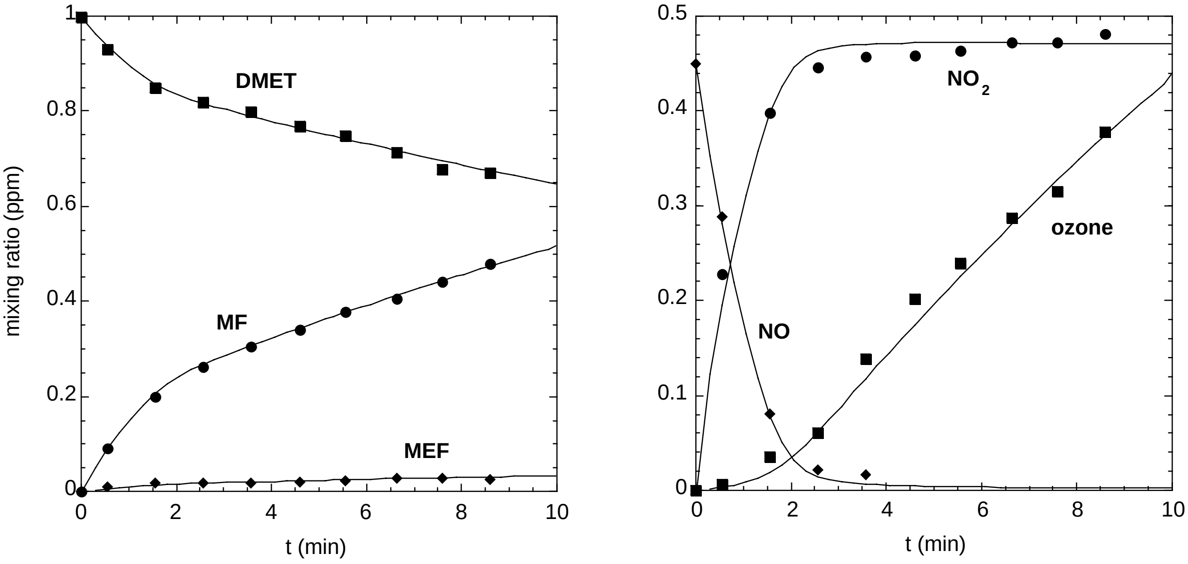

Fig. 6: Comparison of experimental (symbols) and simulated (curves) concentration-time profiles for selected reactants. Experimental conditions: 1.00 ppm DMET, 0.45 ppm NO, 0.45 ppm methyl nitrite, 760 Torr air.

d) 1,4-Dioxane

1,4-Dioxane is a cyclic diether which is currently used as a solvent and recently has been considered as a fuel additive. The only primary reaction product of the OH-initiated degradation specified in the experiments is ethylene glycol diformate (EDF). The carbon yield is more than 95 mol%. The remaining few mol% are unknown. Based on the experimental results of our laboratory, the reaction scheme was constructed as illustrated in Fig. 7. Fig. 8 illustrates a comparison of experimental and simulated data for selected reactants. Both data sets are in excellent agreement. It was shown, that consideration of nitrate formation with ratios of 2.5% for each peroxy radical reaction in the model led to a much better agreement of experimental and simulated data (see Fig. 8).

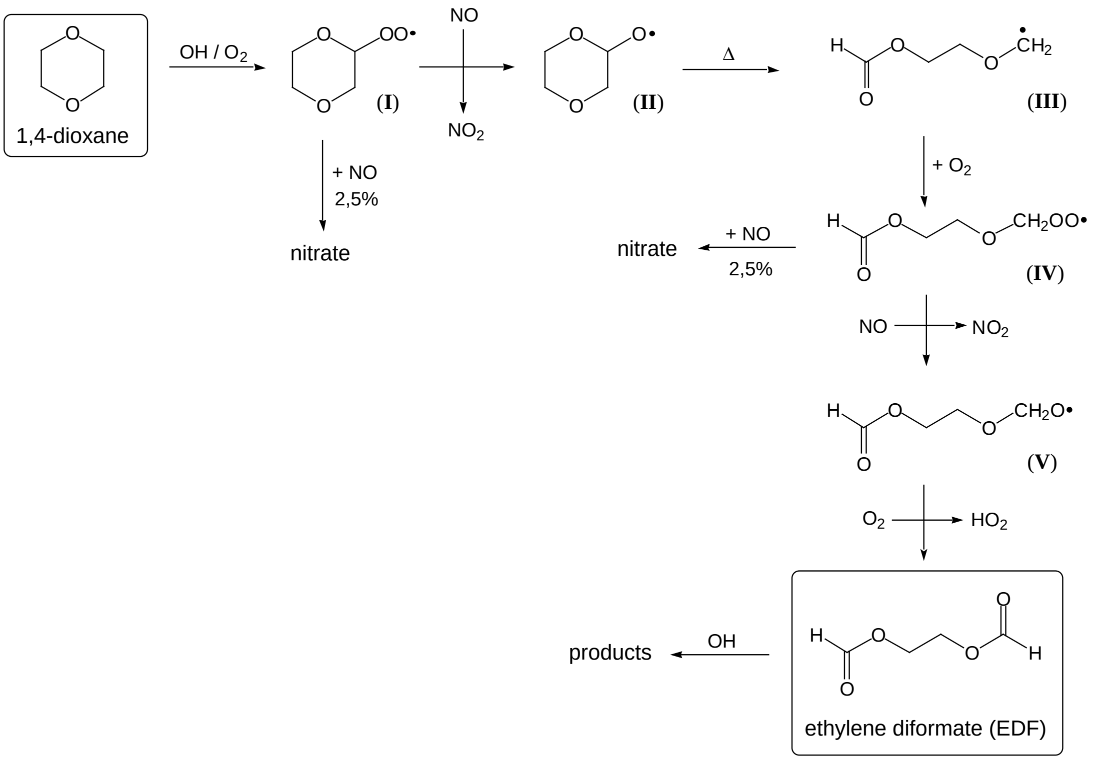

Fig. 7: Degradation scheme of the OH-initiated oxidation of 1,4-dioxane in the presence of NO_x.

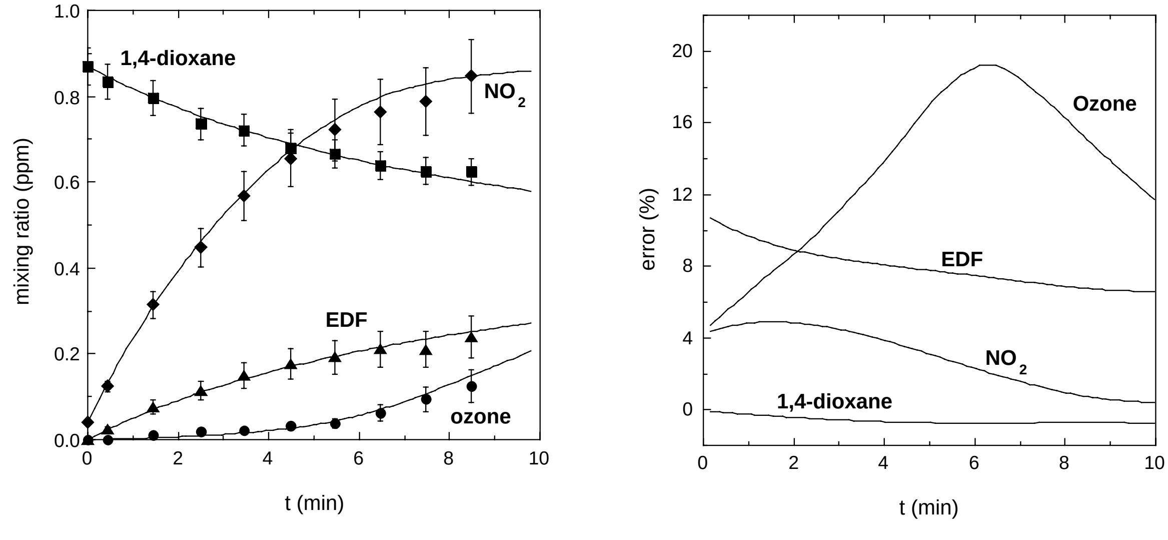

Fig. 8: Left: Comparison of experimental (symbols) and simulated (curves) concentration-time profiles for selected reactants. Experimental conditions: 0.87 ppm 1,4-dioxane, 0.80 ppm NO, 1.15 ppm methyl nitrite, 760 Torr air. Right: Deviations of the simulation, if nitrate formation is not considered in the model.

e) 1,3-Dioxolane

1,3-Dioxolane is a cyclic diether, which is currently used as a solvent. Based on the experimental results of our laboratory, the reaction scheme was constructed as illustrated in Fig. 9. The branching ratio for the OH reaction of 1,3-dioxolane was determined by fitting the model to the experimental data.

In the modelling exercise the NO and NO_2 profiles were sensitive to the nitrate yield. It was found that the best fits were achieved using a nitrate formation yield of 2.5% for reaction of NO with each of the peroxy radicals (see Fig. 9). Fig.10 shows as an example the results of the computer simulations in comparison with the experimental data. Both data sets are in excellent agreement.

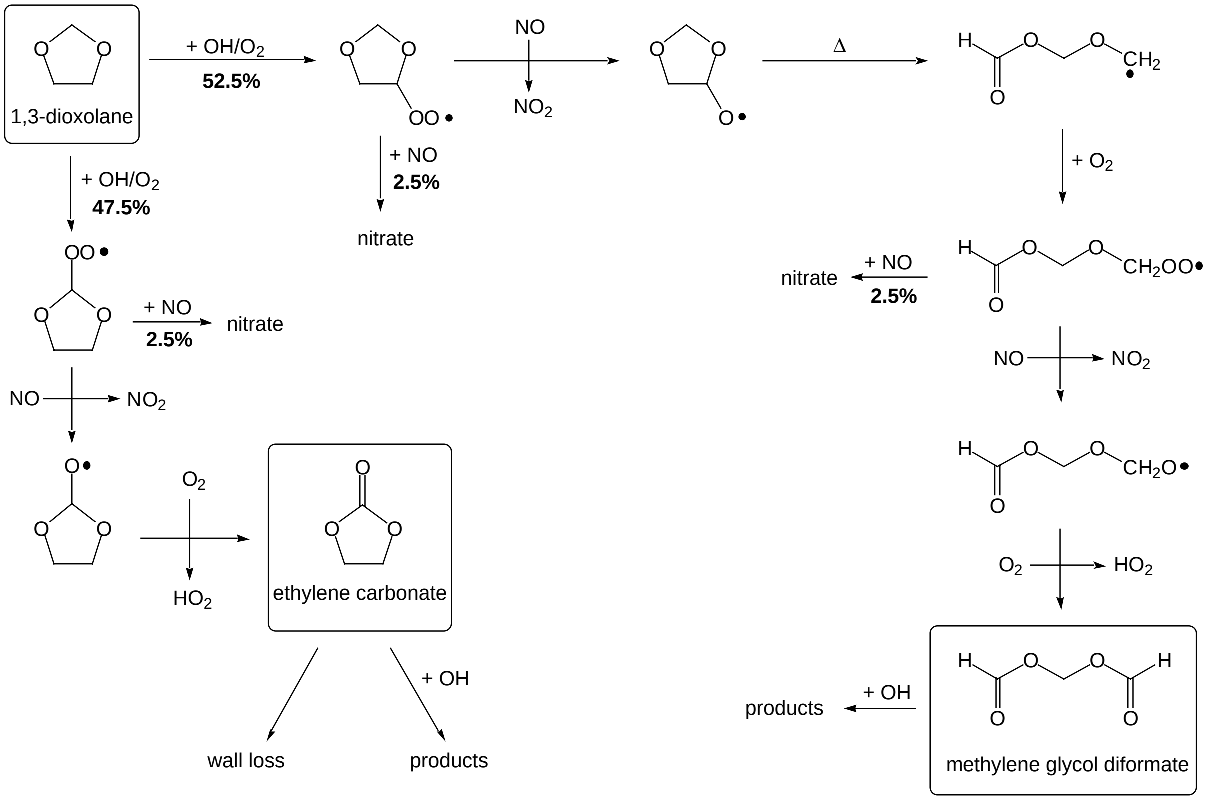

Fig. 9: Degradation scheme of the OH-initiated oxidation of 1,3-dioxolane in the presence of NO_x.

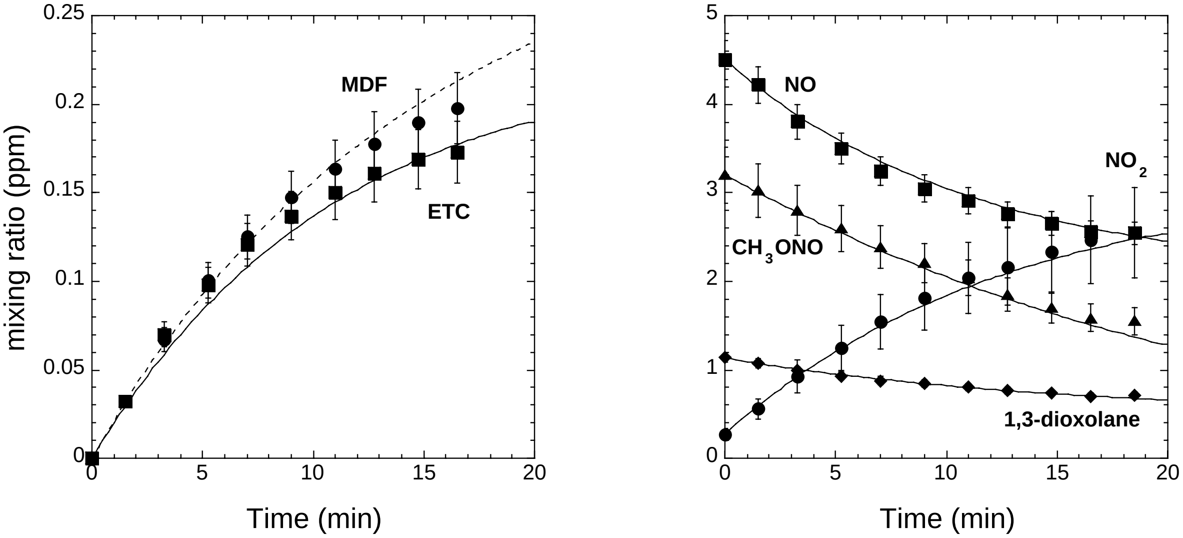

Fig. 10: Comparison of experimental (symbols) and simulated (curves) concentration-time profiles for selected reactants. Experimental conditions: 1.14 ppm 1,3-dioxolane, 4.50 ppm NO, 0.28 ppm NO_2, 3.20 ppm methyl nitrite, 760 Torr air.

Conclusions

In the present work, urban tropospheric degradation mechanisms for dimethoxymethane (DMM), dimethoxyethane (DMET), 1,4-dioxane and 1,3-dioxolane were postulated and checked by comparison with suitable laboratory data. For all compounds, experimental and modelling results are in excellent agreement. This leads to the possibility that these reaction schemes might be used successfully in further applications, e.g. field modelling.

The results of the sensitivity analyses carried out for the investigated reaction systems indicate that photoreactor experiments using methyl nitrite as OH precursor and relatively high concentrations of NO_x are characterised by well-defined conditions, which can be modelled with high accuracy. As a consequence, such experiments are highly suitable for mechanism validation procedures for degradation schemes of VOC under urban conditions.

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