



Determination of carboniles in the photo-oxidation reaction of benzene and toluene in the EUPHORE chambers. Comparison of SPME and PTR-MS data

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Results of the monitoring of carbonylic products of the photo-oxidation of benzene and toluene during experiments carried out in the EUPHORE chambers in September 2003 are presented in this work, which aims at contributing to a clarification of the main pathways in these reactions in order to improve their representation in atmospheric models. The reactions carried out were 1) 24/09/03, Benzene+HONO+NO_x, 1998 ppb benzene; HONO/NO/NO₂ approx. 100 ppb; 2) 25/09/03, Benzene+HONO+NO_x, 3912 ppb benzene, HONO/NO/NO₂ approx. 104 ppb; 3) 26/09/03, Toluene+HONO+NO_x, 1672 ppb toluene, HONO/NO/NO₂ approx. 170 ppb. A range of analytical instrumentation was applied to monitor the reaction. In this work, we focus on the results obtained for a number of highly reactive carbonyls, crucial in the determination of branching ratios and confirmation of the carbonylic route by PTR-MS and SPME with on-fibre derivatisation with PFBHA. The main disadvantage of the SPME methodology is the low time resolution. PTR-MS in return, provides an excellent sample throughput, but presents the problem that other compounds may give the same fragments as the measured ones and thus interfere with their determination. This study focuses particularly on butenedial, an important intermediate of the dicarbonylic route. By both methodologies the discriminated quantitation of cis- and trans-isomers was attempted. The results were compared with the model results, obtained through a simulation using the Master Chemical Mechanism, version 3.1. In the case of benzene, there was agreement between the SPME and the results predicted by PTR-MS for the cis-isomer. Model predictions of butenedial (cis-

plus trans-isomer) were in between the values obtained by the SPME and the PTR-MS measurements. In the case of toluene photo-oxidation, the agreement between SPME and the model was excellent, whereas the values measured by PTR-MS were higher. The highest observed concentrations of butenedial were in the range 5-11 ppbV, with the trans-isomer being the most important. The implication of the results for the understanding of the atmospheric oxidation pathways of benzene and toluene and the photo-isomerisation of butenedial will be discussed.