Pressure and temperature dependence of methyl nitrate formation in the CH_3O_2 + NO reaction

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Reactions of alkyl peroxy radicals, RO_2, with NO are recognized to potentially reduce tropospheric ozone formation through their minor channel producing organic nitrates, acting as both RO_x and NO_x reservoir or sink species. The nitrate yields previously measured for these reactions range from a few percents for small alkyl nitrates ($C \geq 2$) to ≈ 30% for long-chain alkyl nitrates ($C \geq 7$), at room temperature and atmospheric pressure. For the methyl nitrate yield in the reaction:

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \quad (1a)$$
$$\rightarrow CH_3ONO_2 \quad (1b)$$

only an upper limit of 3% has been determined so far at 295 K and 100 Torr (1). However, even at a lower CH_3ONO_2 yield, channel (b) may still be of tropospheric significance considering both the importance of the CH_3O_2 radical as intermediate in the oxidation of methane and other major VOCs, and the long lifetime of CH_3ONO_2 (one week to one month).

The study of methyl nitrate formation in reaction (1) has been carried out using a turbulent flow reactor coupled with a chemical ionisation mass spectrometer (TFR-CIMS). This set up has been previously used to investigate the formation of ethyl nitrate and isopropyl nitrate in reactions of NO with ethyl peroxy and isopropyl peroxy radicals, respectively (2, 3). The branching ratio $\beta = k_{1b}/k_{1a}$ has been determined over the pressure and temperature ranges 50-500 Torr and 220-300 K, respectively. Methyl nitrate was generated in the TFR from $F/CH_4/O_2/NO$ mixtures where CH_3O produced reacted predominantly with NO. β was determined from the CH_3ONO_2/CH_2O and CH_3ONO_2/CH_3ONO product concentration ratios where CH_2O and CH_3ONO were produced in the two channels of the CH_3O + NO reaction. These three products were calibrated by generating them *in situ* from $F/CH_3OH/NO_2$ and $F/CH_3OH/NO$ mixtures. All the species were detected by PTR from H_3O^+ and its water clusters, except NO_2 detected by electron transfer from SF_6^-. At 298 K, the branching ratio β has been found to increase linearly with pressure from (0.33 ± 0.16)% at 50 Torr to (0.80 ± 0.54)% at 500 Torr. Decrease of temperature from 300 K to 220 K leads to an increase of β by a factor of about 3 in the 100-200 Torr range. These data correspond to a value of β ≈ (1.0 ± 0.7)% over the pressure and temperature ranges of the whole troposphere.
The atmospheric concentrations of methyl nitrate estimated using these results have been compared to those measured in different atmospheric environments.

THURSDAY

References

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