Formation of small alkyl nitrates in RO_2 + NO reactions and its significance in gas phase tropospheric chemistry

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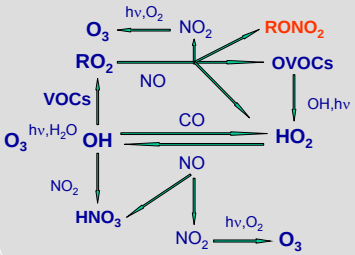
Introduction



Reactions of alkyl peroxy radicals with NO are recognized to potentially reduce tropospheric ozone formation through their minor channel (b) producing organic nitrates, which are both ROx and NOx reservoir or sink species:

$RO_2 + NO \rightarrow RO + NO_2$ **(a)**

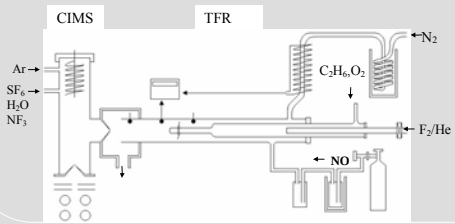
$\rightarrow RONO_2$ **(b)**

The available nitrate yields measured in these reactions range from ≈ 4% for propyl nitrate to ≈ 30% for long-chain alkyl nitrates (C ≥ 7) at T = 298 K and P = 760 Torr [eg. 1]. The yields also increase with increasing pressure and with decreasing temperature. For the short-chain alkyl nitrates (C ≤ 4), very few data are available due to the difficulties to precisely measure low nitrate yields. Yield data are reported here for ethyl nitrate, as a function of pressure and temperature, and for iso-propyl nitrate and methyl nitrate as a function of pressure at ambiant temperature.

Turbulent Flow Reactor (TFR) with Chemical Ionization Mass Spectrometer (CIMS)

Reactor conditions:

P = 50-600 Torr; T = 220-298 K; Re = 4700-12000.



- CIMS detection of the species in positive (PTR, DTR) and/or negative (NICI) mode:
  - PTR (H_3O^+): CH_2O, CH_3OH, CH_3ONO, CH_3ONO_2, CH_3CHO, C_2H_5OH, C_2H_5ONO, $C_2H_5ONO_2$
  - DTR (D_3O^+): CH_2O, CH_3OH, CH_3ONO, CH_3ONO_2
  - NICI (SF_6^-): NO_2
  - NICI (F^- from NF_3): C_2H_5OH, CH_3CHO, $CH_3C(O)CH_3$, $C_2H_5ONO_2$, i-$C_3H_7ONO_2$ (a new sensitive method)
- Calibration of the species using commercial compounds or producing them *in situ*.

Formation of ethyl nitrate (reaction 1b)

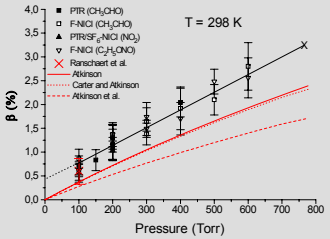


Figure 1. Pressure dependence of β for ethyl nitrate formation. Red lines are calculated values from empirical functions [4, 5, 6].

Main reactions in the TFR:

$C_2H_6 + F\ (+ O_2) \rightarrow C_2H_5O_2 + HF$

$C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$ **(1a)**

$\rightarrow C_2H_5ONO_2$ **(1b)**

$C_2H_5O + NO \rightarrow C_2H_5ONO$ (1-α)

$\rightarrow CH_3CHO + HNO$ (α)

Determination of the branching ratio

$\beta = k_{1b}/k_{1a}$:

$\beta = \Delta[C_2H_5ONO_2] / \Delta[NO_2]$

$\beta = \alpha \cdot \Delta[C_2H_5ONO_2] / \Delta[CH_3CHO]$

$\beta = (1-\alpha) \cdot \Delta[C_2H_5ONO_2] / \Delta[C_2H_5ONO]$

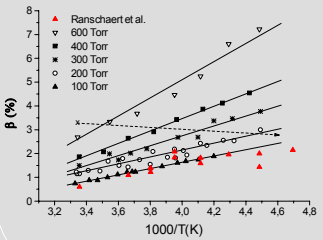


Figure 2. Temperature dependence of β for ethyl nitrate formation at different pressures.

The overall P and T dependence of β is expressed as [2]:

$\beta(P,T)(\%) = k_{1b}/k_{1a} = (3.88 \times 10^{-3} \cdot P(Torr) + 0.365) \cdot (1 + 1500(1/T(K) - 1/298))$

(100 ≤ P ≤760 Torr and 215 ≤ T ≤300 K)

➞ Only small changes of β and $k_{1b} \approx 0.01 \cdot k_1(T) \cdot \beta(P,T)$ throughout the whole troposphere:

β ≈ 3.3% $k_{1b} \approx 2.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at the Earth surface

β ≈ 2.8% $k_{1b} \approx 3.9 \times 10^{-13}$ " " in the upper troposphere

Formation of iso-propyl nitrate (reaction 2b)

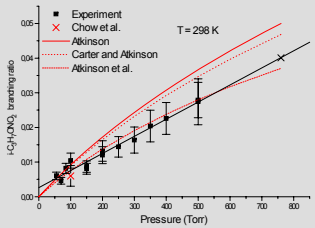


Figure 3. Pressure dependence of β for iso-propyl nitrate formation. Red lines are calculated values from empirical functions [4, 5, 6].

Main reactions in the TFR:

$C_3H_6 + H + M\ (+ O_2) \rightarrow$ i-$C_3H_7O_2$ + M

i-$C_3H_7O_2$ + NO → i-C_3H_7O + NO_2 **(2a)**

→ i-$C_3H_7ONO_2$ **(2b)**

i-C_3H_7O + NO → i-C_3H_7ONO (1-γ)

→ **$CH_3C(O)CH_3$** + HNO (γ)

Determination of the branching ratio

$\beta = k_{2b}/k_{2a}$:

$\beta = \gamma \cdot \Delta[\text{i-}C_3H_7ONO_2] / \Delta[CH_3COCH_3]$

A linear pressure dependence of β is observed providing the following expression [7]:

$\beta(P)(\%) = k_{2b}/k_{2a} = (4.93 \pm 0.24) \times 10^{-3} \cdot P(Torr) + (0.265 \pm 0.067)$

(55 ≤ P ≤ 500 Torr, T = 298 K)

➞ Only small changes of $k_{2b} \approx 0.01 \cdot k_2(T) \cdot \beta(P,T)$ are expected throughout the whole troposphere by combining our value of β ≈ 4% at 760 Torr and 298 K and that of Chow et al. [8], β ≈ 2% at 100 Torr and 210 K:

β ≈ 4% $k_{2b} \approx 3.6 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at the Earth surface

β ≈ 2% $k_{2b} \approx 3.0 \times 10^{-13}$ " " in the upper troposphere

Formation of methyl nitrate (reaction 3b) *(preliminary results)*

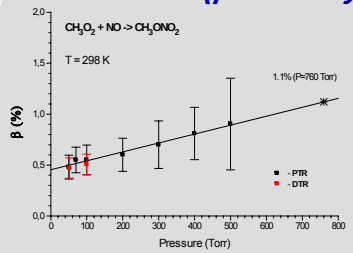


Figure 4. Pressure dependence of β for methyl nitrate formation.

Main reactions in the TFR:

$CH_4 + F\ (+ O_2) \rightarrow CH_3O_2 + HF$

CH_3O_2 + NO → CH_3O + NO_2 **(3a)**

→ CH_3ONO_2 **(3b)**

$CH_3O + NO \rightarrow$ **CH_3ONO** (1-δ)

→ **CH_2O** + HNO (δ)

Determination of the branching ratio

$\beta = k_{3b}/k_{3a}$:

$\beta = \delta \cdot \Delta[CH_3ONO_2] / \Delta[CH_2O]$

$\beta = (1-\delta) \cdot \Delta[CH_3ONO_2] / \Delta[CH_3ONO]$

PTR detection of methyl nitrate ($CH_3ONO_2 \cdot H^+$ ion, m/z 78) was complicated by formation of $CH_2O \cdot NO^+ \cdot H_2O$ complex with the same mass. Its contribution was determined separately and subtracted from the reaction signal. Deuteron Transfer Reaction (DTR) was used along with PTR detection in order to avoid this interference by detection of methyl nitrate at m/z 79 ($CH_3ONO_2 \cdot D^+$ ion), while the complex is moved to mass m/z 80 ($CH_2O \cdot NO^+ \cdot D_2O$ ion).

A linear pressure dependence of β is observed providing the following expression:

$\beta(P)(\%) = k_{3b}/k_{3a} = (8.8 \pm 0.7) \times 10^{-4} \cdot P(Torr) + (0.45 \pm 0.03)$

(50 ≤ P ≤ 500 Torr, T = 298 K)

➞ β ≈ 1% $k_{3b} \approx 7 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at the Earth surface

Atmospheric application

The present work provides values of k_{1b}, k_{2b} and k_{3b} for use in chemistry-transport models to calculate the impact of chain termination reactions 1b, 2b and 3b on the tropospheric composition, in particular for species involved in the VOC/NOx/ozone chain mechanism. This impact is likely to be not negligible considering both the efficiency of radical chain termination reactions in this mechanism and the rather long lifetimes of methyl-, ethyl- and i-propyl nitrate as NO_x reservoirs (typical lifetimes of 1 month, 2 weeks and 1 week, respectively, controlled mainly by photolysis [9]). Besides, the apparent inconsistency between the k_{3b}/k_{3a} ratio obtained in this work and atmospheric measurements of methyl nitrate requires further investigation.

References:

[1] Atkinson R. et al., *J. Phys. Chem.* 1982, 86, 4563; [2] Butkovskaya N. et al., *J. Phys. Chem. A* 2010, 114, 956; [3] Ranschaert D.L. et al., *J. Phys. Chem. A* 2000, 104, 5758; [4] Atkinson R. et al., *J. Phys. Chem.* 1983, 87, 2012; [5] Carter W.P.L. and Atkinson R., *J. Atmos. Chem.* 1989, 8, 165; [6] Atkinson R., *Phys. Chem. Ref. Data* 1994, 1, Monograph 2; [7] Butkovskaya et al. *Z. Phys. Chem.* 2010, 224, 1025; [8] Chow J.M. et al., *J. Phys. Chem. A* 2003, 107, 3040; [9] Talukdar R. et al., *J. Chem. Soc. Faraday Trans.* 1997, 93, 2797

Acknowledgement

These studies have been carried out within the French PRIMEQUAL Programme of the Ministry of Energy, Ecology, Sustainable Development and Sea.