**Atmospheric
Chemistry
and Physics
Discussions**

# *Interactive comment on* "Peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) in urban and suburban atmospheres of Beijing, China" *by* J. B. Zhang et al.

**X. Xu**

xuxb@cams.cma.gov.cn

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This is an interesting paper, but I feel some more attention should be paid to the derivation of equations that are used for your calculations. For example, the equation (5) may not be correct. Because the estimation of the termal decomposition of PAN and PPN is not limited to nighttime, the photochemical sources of the key radicals for PAN and PPN should be included in the derivation. For PAN, this source is the reaction: $CH_3CHO + OH + O_2 \rightarrow CH_3C(O)OO + H_2O$. Together with the reactions (1), (2) and (4) on page 8185 of the manuscript, the following equation can be obtained:

$$-d[PAN]/dt = k_4[PAN] - k_1(k_4[PAN] + k_5[CH_3CHO][OH])[NO_2]/(k_1[NO_2] + k_2[NO]),$$

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where, $k_5$ is the reaction constant for $CH_3CHO + OH$, and $k_1$, $k_2$, and $k_4$ are the reaction constants for the reactions (1), (2), and (4), respectively (see page 8185 of the manuscript). This equation is different from your equation (5), but it can be simplified to obtain equation (5) if $k_4[PAN] \gg k_5[CH_3CHO][OH]$. However, $k_5[CH_3HO][OH]$ may not always be negligible. Taking your average PAN (1.41 ppb), the average $CH_3CHO$ for PKU (3.6 ppb, Shao et al., 2009), and the values of $k_4$ (3.77x10^-4 /s) and $k_5$ (9.55x10^12 cm^3/mol/s) (298K, Atkinson et al., 1997), I obtained 2.17x10^-17 mol/cm^3/s for $k_4[PAN]$ and 2.33x10^-18 to 2.33x10^-17 mol/cm^3/s for $k_5[CH_3CHO][OH]$ for OH varying from 1x10^6 to 1x10^7 cm^-3. Note that the conditions are close to the normal summer conditions in Beijing. Therefore, $k_4[PAN]$ and $k_5[CH_3CHO][OH]$ should be comparable, at least for the daytime period, and omitting the later one may results in significant errors in your results.

Another point, you get loss rate of PAN using the thermal decomposition equation (say eq.(5)) but not the loss itself. You compare the absolute losses of PAN and PPN with their ambient concentrations in Fig. 9. However, it is not stated in the manuscript how are the absolute losses calculated. Integration over a certain period?

References

Shao, M., et al., Volatile organic compounds measured in summer in Beijing and their role in ground-level ozone formation, J. Geophys. Res., 114, D00G06, doi:10.1029/2008JD010863, 2009.

Atkinson,R., et al, Evaluated kinetic, photochemical and heterogeneous data for atmospheric chemistry: supplement V, IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry, J. Phys. Chem. Ref. Data 26, 521-1011, 1997.

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