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Atmospheric Chemistry and Physics Discussions

Interactive comment on "HONO and NO_2 evolution from irradiated nitrate-doped ice and frozen nitrate solutions" *by* T. Bartels-Rausch and D. J. Donaldson

Anonymous Referee #1

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Nitrate photolysis on ice was investigated, over a wide wavelength range, as a potential source of nitrous acid (HONO) and nitrogen dioxide at low temperature by means of well designed experimental techniques. The outcomes of this study are not only of high quality but also very interesting.

Nevertheless, I still have a set of questions that I would like to see discussed.

First of all, concerning the experimental procedure, it is stated that the ice films were made at the bottom of the chamber and its walls. However, it is not clear if the whole surface is irradiated by the output of the Xenon lamp. In addition, as this beam is focussed down to a diameter of ca. 2 cm, it would be interesting to have more information about the ratio of ice on which photochemistry may occur, compared to the surface being not illuminated. Maybe adding a picture of the setup would help understanding how this was made.

How thick were the ice films? Could they be influenced by the underlying Pyrex?

The infrared output of the lamp is filtered out by a water film whereas the UV part is partly removed by the Pyrex walls. Therefore, which range of wavelengths may initiate nitrate photolysis (UV and vibrational overtones)?

In the CIMS analysis, NO2- is used to analyse two different species. Were possible interferences removed? Was NO detected? In fact, nitrogen monoxide is a by-product of both nitrate and HONO photolysis. Knowing its production may help for understanding the reaction mechanism.

Different time behaviours were observed for HONO and NO2. But how was the pH changing at the same time?

Also, did you observe any dependence on the initial nitric acid concentration on the ice surface? In fact, some of the acid may interact and be partially protonated which in turn will modify the possible sources of NO2. By the way, how will vibrational-overtone induced photodissociation be affected by the protonation of the acid?

As both nitric acid doped surface and frozen nitrate solutions were used. Maybe you could comment slightly more on the differences, if any, between these two set of experiments as they may be linked to the HNO3 dynamics on the ice.

Another possible link to NOx chemistry is found again through HNO3 photochemistry which is known to produce OH radicals, reacting with nitric acid to produce NO3 radicals. The later may then undergo various chemical pathways including vibrational-overtone induced photodissociation.

Clearly, this is a short report providing some new and more or less unique information about ice (or nitrate) photochemistry. It is not presenting a complete set of experiments

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but rather initiating new possible research.

In conclusion, this is an excellent paper that opens a series of questions that will be certainly addressed in future studies. I recommend its publication.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 10713, 2006.