



Effect of basicity and acidity on hydrolysis of methyl nitrate in aqueous aerosols

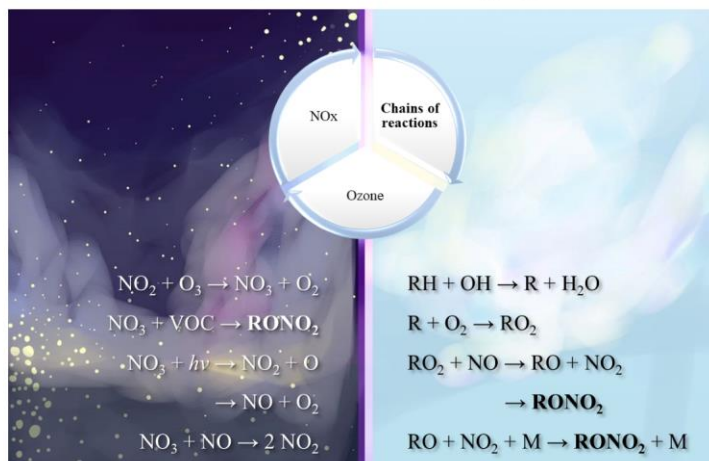
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Outline

- The sources and removal pathways of alkyl nitrates
- Facts about alkyl nitrate hydrolysis
- Details of the kinetics study
- Reaction mechanisms
- Rate coefficient calculations and results
- Key findings

Nitrogen cycle and alkyl nitrate (AN; RONO_2) generation



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The nitrogen cycle starts with NO_x species, continues through multiple reactions, gives different nitrogen-containing compounds and ends up with ozone formation. Therefore, the nitrogen cycle plays a key role in regional air quality, human health and climate.

In daytime and at night, alkyl nitrates (ANs; RONO_2) can be generated through the outlined reactions.

References:

J. D. Rindelaub, et al., *Atmospheric Chemistry and Physics Discussions* 14.3 (2014): 3301-3335.

N. Sobanski, et al., *Atmospheric Chemistry and Physics* 17 (2017) 4115–4130.

J. Liebmann, et al., *Atmospheric Chemistry and Physics* 19.15 (2019) 10391-10403.

The background picture taken from:
<https://www.deviantart.com/funriltheflower/art/Night-and-Day-Background-762041411>

Other sources of atmospheric ANs



Marine sources

* The main source of methyl nitrate



Anthropogenic activities:

Biomass burning and nitrogen-rich explosives

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Reference:

S. He, et al., *Environmental Chemistry* 8.6 (2011) 529-542.

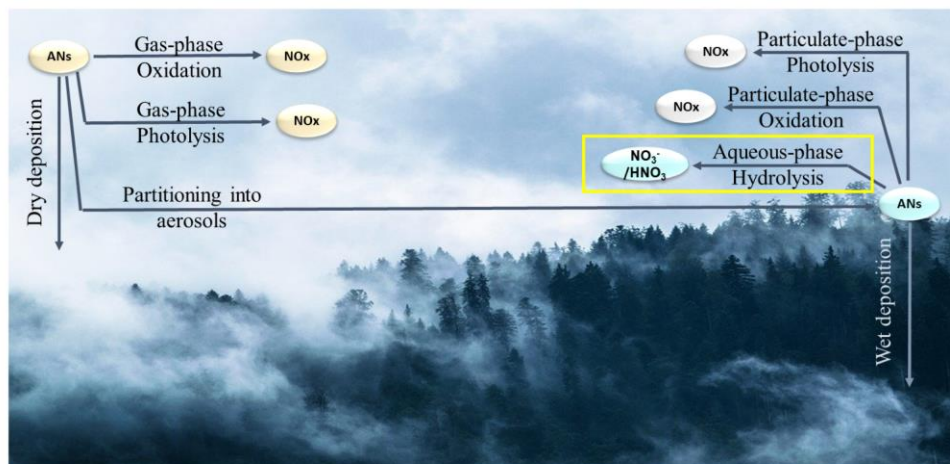
Pictures taken from:

https://gamespot1.cbsistatic.com/uploads/original/57/579912/2936482-memorial_day_2-4x3-6.jpg

<https://www.borgenmagazine.com/consequences-biomass-burning-india/>

<https://www.businessinsider.com/most-powerful-explosives-2017-2?r=US&IR=T>

AN removal from the atmosphere



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References:

A. Zare, et al., *Atmospheric Chemistry and Physics* 18.20 (2018) 15419-15436.

A. G. Carlton, et al., *Atmospheric Chemistry and Physics Discussions* 13.5 (2013) 12743-12770.

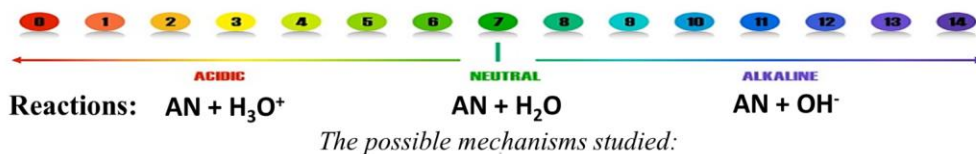
Forest picture taken from: <https://www.piqsels.com/en/public-domain-photo-frbox>

Facts about AN hydrolysis



- › Some potential products known
- › Detailed mechanism unknown
- › Rate coefficients limitedly known
- › Effect of acidity and basicity (un)known: conflict!

Kinetics study and conflict resolution: reaction scenarios



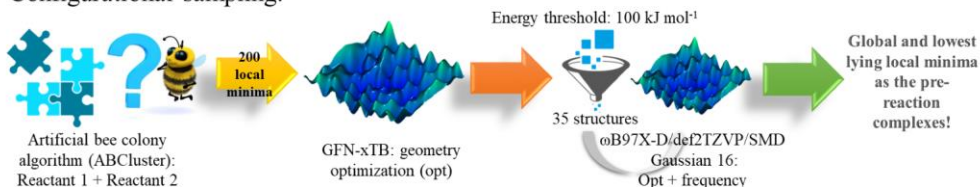
- | | | |
|--|---|--|
| ▪ Nucleophilic substitution | ▪ Nucleophilic substitution | ▪ Nucleophilic substitution |
| ▪ Nucleophilic substitution + O-H bond cleavage in H ₃ O ⁺ | ▪ Nucleophilic substitution + O-H bond cleavage in H ₂ O | ▪ Nucleophilic substitution + O-H bond cleavage in OH ⁻ |
| ▪ Catalytic/inhibitory role for H ₃ O ⁺ | ▪ Catalytic/inhibitory role for water | ▪ Hydrogen abstraction |
| ▪ Reaction of protonated AN + H ₂ O: nucleophilic substitution and unimolecular dissociation of protonated AN | | |

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To start the mechanistic study, at each pH, the reaction was supposed to be represented by a single reaction at the basic, acidic and neutral pH ranges. So, for basic conditions (basic hydrolysis) the reaction of ANs with OH⁻ was studied. For neutral hydrolysis the AN + H₂O reaction was considered and for acidic hydrolysis the presence of H⁺ and H₃O⁺ was taken into account.

Kinetics study and conflict resolution: Technical details

Configurational sampling:



- Solvent effect: implicit solvent using the SMD model
- Computational level: CCSD(T)/cc-pVDZ// ω B97X-D/def2-TZVP
- Quantum mechanical package: Gaussian 16
- Reaction path: scanning using the pre-reaction complexes as the starting points
- Stationary point approval: harmonic frequency calculation
- Reaction path and transition state approval: intrinsic reaction path analysis

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References to packages and computational methods:

The configurational sampling method: J. Kubečka, et al., *The Journal of Physical Chemistry A* 123.28 (2019) 6022-6033.

ABCluster: J. Zhang, M. Dolg, *Physical Chemistry Chemical Physics* 18.4 (2016) 3003-3010.

XTB calculation: S. Grimme, et al., *Journal of chemical theory and computation* 13.5 (2017) 1989-2009.

GFN-xTB: C. Bannwarth, et al., *Journal of chemical theory and computation* 15.3 (2019) 1652-1671.

Gaussian 16: M. J. Frisch, et al., Gaussian, Inc., Wallingford CT, 2016.

SMD: A. V. Marenich, et al., *The Journal of Physical Chemistry B* 113.18 (2009) 6378-6396.

Pictures taken from various sources and then combined!

Mechanism of neutral hydrolysis

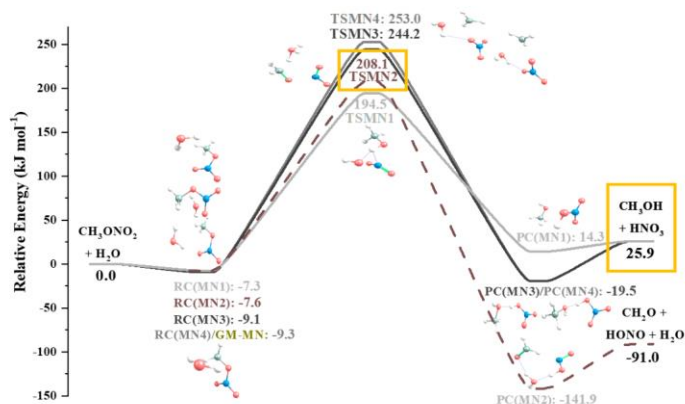


Figure 1. The zero-point energy corrected potential energy surface of neutral methyl nitrate hydrolysis (0 K).

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GM: the global minima structure

Here, different configurations of the pre-reaction complexes (RC complexes) and transition states (TSs) lead to the same main product, i.e. methanol + nitric acid. The main product is thermodynamically unstable relative to the reactants.

There is also the reaction path related to TSMN2. Along this path, the water molecule is not consumed but its presence is involved in the intramolecular break down of methyl nitrate into formaldehyde and nitrous acid (HONO). So, does water catalyze this reaction? Does it inhibit it? It will be discussed in the following slides.

In general, the most important point is that all transition states are so high in energy and all barriers are above 190 kJ/mol high.

Mechanism of basic hydrolysis

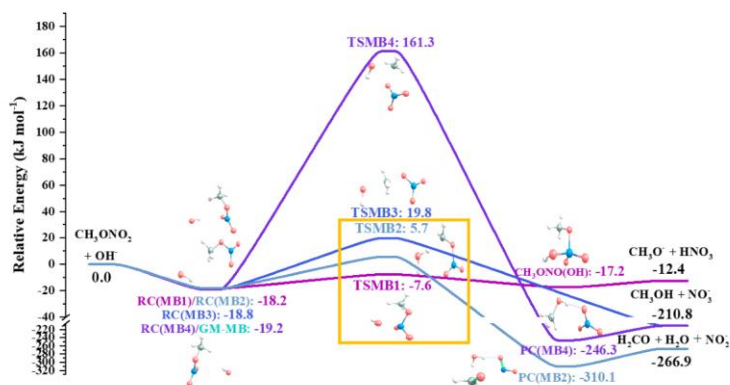


Figure 2. The zero-point energy corrected potential energy surface of basic methyl nitrate hydrolysis (0 K).

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When we shift from neutral hydrolysis to basic hydrolysis, suddenly the reaction barriers decrease so noticeably that we can see reaction paths with approximately zero apparent activation energy (check the yellow square). Also, the diversity of products increases and all reaction products become thermodynamically stable relative to the reactants.

Here, the lowest energy path (TSMB1) leads to the formation of methoxy ion and nitric acid.

Mechanism of acidic hydrolysis

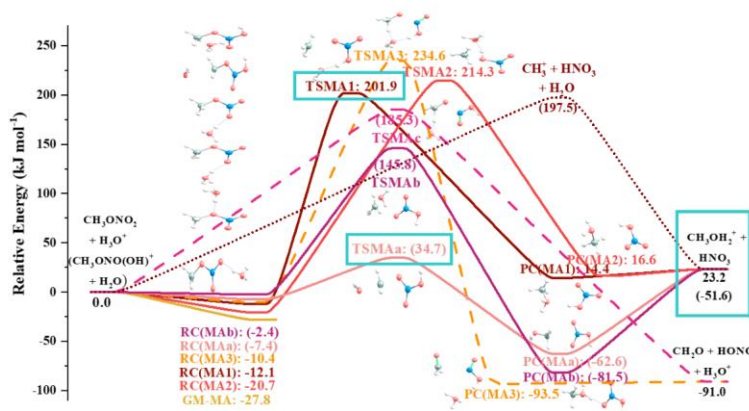
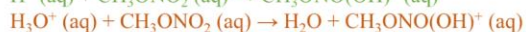


Figure 3. The zero-point energy corrected potential energy surface of acidic methyl nitrate hydrolysis (0 K).



$$\Delta G = -429.1 \text{ kJ mol}^{-1}$$



$$\Delta G = +77.5 \text{ kJ mol}^{-1}$$

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ΔG : Gibbs free energy of protonation at 298.15 K and 1 atm calculated at the ω B97X-D/def2-TZVP level

As aforementioned, 4 different reaction scenarios are possible for acidic hydrolysis. Though these paths are mechanistically different, most of them have ultimately ended up with the production of protonated methanol and nitric acid.

The most important point is that the barrier height of the reaction paths of methyl nitrate + H_3O^+ are higher than their neutral hydrolysis counterparts. So that, the acidic hydrolysis transition states (methyl nitrate + H_3O^+) are all above 200 kJ/mol (see TSMA1). It is while the barrier heights related to the reaction of H_2O with protonated methyl nitrate can be as low as 34.7 kJ/mol (for TSMAa). So, can we say acidity catalyzes the hydrolysis reaction? No!!!! Look at the reaction Gibbs free energies. Thermodynamically speaking, the protonation of methyl nitrate by free H^+ is spontaneous. But, free H^+ does not exist and free protons are always combined with water molecules or the other solution components and protonation of methyl nitrate by H_3O^+ is NOT spontaneous! So, acidity increases the barrier heights while basicity was shown to reduce the reaction barriers.

This qualitative finding solves out the conflict about the effect of acidity and basicity and will be further approved by pH-dependent rate coefficients. It should be kept in

mind that just one experimental study has mentioned basicity improves AN hydrolysis and the other studies have stated that acidity improves the reaction.

Supporting basicity effect:

R. Boschan, et al. *Chemical Reviews* 55.3 (1955) 485-510.

Studies stating acidity catalyzes AN hydrolysis:

K. S. Hu, et al., *Atmospheric Chemistry and Physics* 11.16 (2011) 8307-8320.

J. D. Rindelaub, et al., *Atmospheric Environment* 100 (2015) 193-201.

J. D. Rindelaub, et al., *Atmospheric Chemistry and Physics* 16, no. 23 (2016): 15425-15432.

A. Zare, *ACS Earth and Space Chemistry* 3.8 (2019) 1426-1437.

Last point: Similar to what we saw for neutral hydrolysis, here H_3O^+ can intervene in degradation of methyl nitrate into formaldehyde and nitrous acid. So, catalysis or inhibition? It would be answered in the next slide.

Catalysis or inhibition?

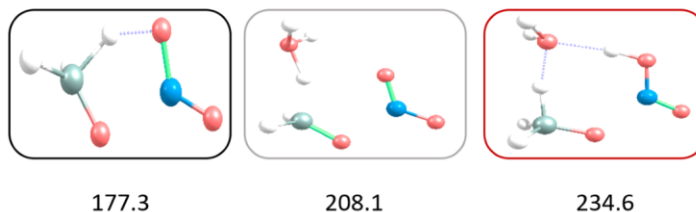


Figure 4. The transition state geometries and barrier heights (kJ mol^{-1}) of methyl nitrate degradation into formaldehyde and HONO in the absence (the black panel) and presence of water (the grey panel) and hydronium ion (the red panel).

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As it can be seen, the intervention of both H_2O and H_3O^+ increases the reaction barrier. So, they INHIBIT degradation of methyl nitrate into formaldehyde and nitrous acid.

Casting the reaction mechanisms into pH-dependent rate coefficients

$$k_{uni,r} = \kappa_r \times \frac{k_B T}{h} e^{-\Delta_r^\ddagger G / RT} \quad (1) \quad \leftarrow \text{Eckart tunneling } (\kappa)\text{-corrected unimolecular transition state theory applied to every reaction path } r \text{ separately}$$

$$k_{diff} = \frac{8 k_B T}{3 \eta} \quad (2) \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} \text{Including the effect of solution dynamics by incorporating the effect of diffusion on the rate coefficients of each individual reaction path}$$

$$k_{uni,r}^{mod} = \frac{k_{uni,r} \times k_{diff}}{k_{uni,r} + k_{diff}} \quad (3)$$

$$k_{uni,i}^{mod} = \sum_r k_{uni,r}^{mod} \quad (4) \quad \leftarrow \text{Total diffusion-modified pseudo-unimolecular rate coefficients related to each reaction set } i \text{ (reaction of methyl nitrate with OH}^-, \text{H}_3\text{O}^+, \text{ or H}_2\text{O) obtained by summing over all reaction paths}$$

$$k_{uni}^{tot} = \sum_i \left(k_{uni,i}^{mod} / \sum_i C_i \right) \quad (5) \quad \leftarrow \text{Total pseudo-unimolecular rate coefficient at each pH obtained using the concentration of each reacting species } i \text{ at each specific pH: } C_{H_3O^+} = 10^{-pH}; C_{H_2O} = 46.1\text{-}55.5 \text{ mol L}^{-1}; \text{ and } C_{OH^-} = 10^{pH-14}$$

$$k_{bi}^{tot} = k_{uni}^{tot} / \sum_i C_i \quad (6) \quad \leftarrow \text{Total bimolecular rate coefficient at each pH}$$

$$\tau = 0.693 / k_{uni}^{tot} \quad (7) \quad \leftarrow \text{Half-life of methyl nitrate hydrolysis at each pH}$$

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The rate coefficient calculations were based on Eckart tunneling (κ)-corrected unimolecular transition state theory (Equation 1). Here, $\Delta_r^\ddagger G$ is the energy difference between the transition state and the reactants.

T : temperature = 298 K

k_B : Boltzman constant

h : Plank's constant

η : viscosity of solvent (water)

Water concentration in aqueous aerosols (46.1-55.5 mol/L) taken from: W. G. et al., *Atmosphere* 10.11 (2019) 666.

The half-life values are calculated based on the pseudo-unimolecular rate coefficients.

Acidity and basicity effects on the rate coefficient and half-life of methyl nitrate hydrolysis

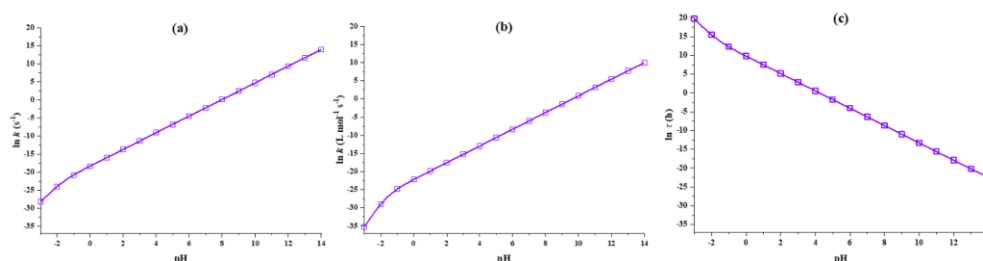


Figure 6. pH dependency of the pseudo-unimolecular (a) and bimolecular (b) total rate coefficients of methyl nitrate hydrolysis at 298 K and 1 atm, along with the corresponding half-lives (c).

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In line with the potential energy surfaces, the rate coefficients clarify that basicity increases methyl nitrate hydrolysis and acidity suppresses the process. Careful analysis of concentrations and energy profiles (not shown here) suggests that the reason is the high barriers of neutral and acidic hydrolysis. In fact, it is the basic hydrolysis reaction that controls the rate coefficients all over the pH range. Therefore, acidity, which restricts the number of available OH^- ions, prevents the hydrolysis reaction.

Key findings

- § In contrast with the belief that acidity improves AN hydrolysis, the results confirm that acidity suppresses methyl nitrate hydrolysis.
- § Basic hydrolysis is the reaction that controls the extent of methyl nitrate hydrolysis over the -3 to 14 pH range.
- § Over the most common range of aqueous aerosol pH (pH: 2-6), methyl nitrate hydrolysis is significant enough to alter the chemistry of aerosols.
- § Methyl nitrate hydrolysis should be particularly concerned when studying the marine (pH: -1-10) and haze (pH: -2.5-8) basic aerosols.

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To understand the key findings consider these pH ranges: rain (pH: 3.5-6.5), marine/polluted cloud (pH: 3.6-6), remote cloud (pH: 4-6), continental cloud (pH: 3.9-5.0), polluted cloud (pH: 2-5), polluted fog (pH: 2-7), continental fog (pH: 3.8-7.2), remote fog (pH: 3.1-7.4), sea fog: 4.8-6.1, marine aerosols (pH: -1-10), urban aerosol (pH: -2-5), continental aerosols (pH: -0.8-4.5) and haze (pH: -2.5-8).

Reference:

H. Herrmann, et al., *Chemical reviews* 115.10 (2015) 4259-4334.



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