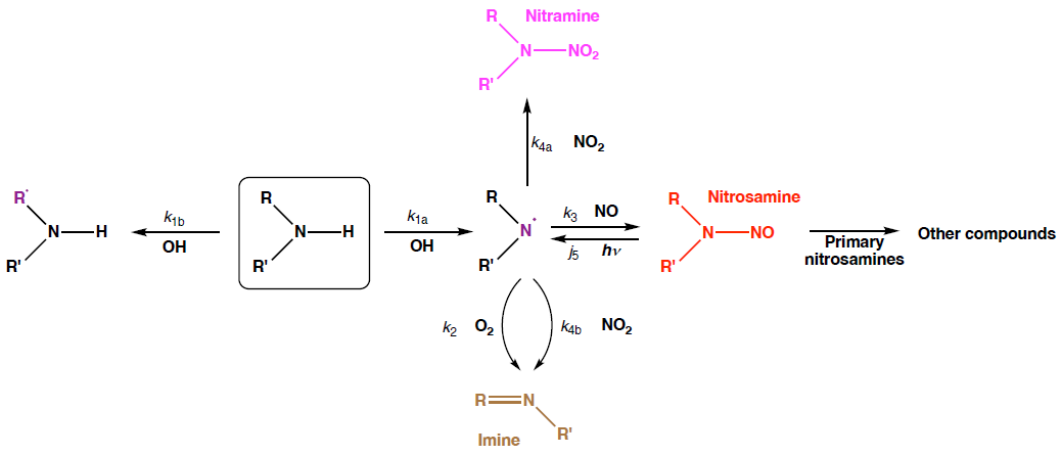
Support for proposed ADMS amine chemistry parameters used for dispersion modelling of flue gas from CANSOLV units

Background Information

The ADMS amine chemistry module requires as input values for kinetic constants of the reaction mechanism used (and widely accepted as best representative of the available experimental results):



Since the rate limiting step of the reaction mechanism is the initial reaction of the amine with OH radicals, the relative amounts of the different products formed depend on the ratios of the respective kinetic constants as follows:

- k_{1a}/k_1
- k_2/k_{4a}
- k_3/k_{4a}
- k_{4a}/k_{4b}

For the CANSOLV DC-103 constant values are required for:

- Piperazine (Amine 2)
- HEP (Amine 1)

While some proposed values for piperazine can be found in the literature, none are available for HEP. In 2014 Pr. Nielsen, University of Oslo, was mandated to recommend values for HEP for the Boundary Dam project. This information was utilized in the dispersion modelling

carried out for the original Environmental Permit Variations submitted by VPI and Phillips 66, and was provided in Annex A of the respective Air Quality Assessment.

In 2024 Shell mandated Pr. Nielsen to reassess the findings of his original report based on new data available in the literature (where available), as well as progress in theoretical tools since the 2014 work.

In 2025 Pr. Nielsen completed a full literature review of the atmospheric chemistry of piperazine and reviewed the theoretical quantum chemistry calculations to provide a proposed set of rate constants for HEP. The review demonstrates that piperazine is a good read-across for HEP.

Proposed Rate Constants

As the rate limiting step of the reaction mechanism is the initial reaction of the amine with OH radicals, the relative amounts of the different products formed depend on the ratios of the respective kinetic constants. This means that atmospheric chamber experimental studies can only access these ratios and cannot provide absolute rate constant values. It is therefore not considered appropriate to select individual rate constants from different literature sources, such as the proposed k_2 value of 1.3×10^{-21} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ from Liu et al., 2019 and a k_3 value of 7.2×10^{-11} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ from Ma et al., 2018 as detailed in the CERC report[1].

Additionally, whilst the CERC report details a value for k_2 from Liu et al., 2019, and this was identified by the EA as being the most conservative value for use in the ADMS amines module, Pr. Nielsen has expressed caution over the use of this value as the calculations are ill-documented and difficult to peer review, and display a wide scatter of values. It should also be noted that the value of 1.24×10^{-20} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ for k_2 provided in Table 3.8 of the CERC report is incorrect, and based on the ratio of k_2/k_{4a} should be 4.99×10^{-20}.

The branching ratios are usually specified relative to k_{4a}, and constants can be obtained by setting an arbitrary value of k_{4a} consistent with the aminyl radical being the limiting step, i.e. ensuring that:

$$k_2 \cdot [O_2] + k_3 \cdot [NO] + k_{4a} \cdot [NO_2] + k_{4b} \cdot [NO_2] \approx 1 \text{ s}^{-1} \text{ (or larger)}.$$

Pr. Nielsen advises that the value used for k_{4a} to derive proposed values for the kinetic constants correspond to the experimental value obtained by Lazarou et al[2] (3.18×10^{-13} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$).

It follows from the above that:

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[1] CERC (2024). Improving Post-Combustion Carbon Capture Air Quality Risk Assessment Techniques. Available: Contents

[2] Lazarou, Y.G., K.G. Kambanis, and P. Papagiannakopoulos, *Gas-Phase Reactions of $(CH_3)_2N$ Radicals with NO and NO_2.* Journal of Physical Chemistry, 1994. **98**(8): p. 2110-2115.

- Direct specification of individual constants from different sources will lead to an inconsistent set of constants for the overall mechanism.
- Unless it is clearly established that the value of the arbitrary fixed constant is identical, comparison of constants is irrelevant and only branching ratios should be compared.

Only specification of a consistent full set of constants, derived from a full set of branching ratios, is considered meaningful, and should be used in the ADMS chemistry module.

Several of the values reported in the literature for piperazine, and resulting from theoretical studies, should be considered with caution. The most reliable source is considered to be the article of Tan et al.[3], which states:

Table 1: Tan et al 2021 Reaction Ratios ($cm^3 \cdot molecule^{-1} \cdot s^{-1}$) for Piperazine

k_{1a}/k_1	k_2/k_{4a}	k_3/k_{4a}	k_{4b}/k_{4a}
0.18	1.57×10^{-7}	1.7	0

The k_1 value reported in Tan et al. (2.80×10^{-10} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ report is not considered to be accurate as particle formation was experienced during the experiments, and therefore the values of 2.38×10^{-10} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ from Onel et al., 2014 based on experimental studies is considered to be the most appropriate value to use.

The full set of rate constants for the ADMS Amines Module for Piperazine is shown in Table 2.

Table 2: Rate Constants for use in ADMS for Piperazine ($cm^3 \cdot molecule^{-1} \cdot s^{-1}$)

k_1	j_{rel}	k_{1a}/k_1	k_2	k_3	k_{4a}	k_4
2.38×10^{-10}	0.34	0.18	4.99×10^{-20}	5.41×10^{-13}	3.18×10^{-13}	3.18×10^{-13}

Table 3: Rate Constants for use in ADMS for Piperazine ($ppb^{-1} \cdot s^{-1}$)

k_1	j_{rel}	k_{1a}/k_1	k_2	k_3	k_{4a}	k_4
5.95	0.34	0.18	1.25×10^{-9}	0.0135	0.00795	0.00795

The 2025 theoretical study shows that for HEP:

- Three aminyl radicals can be formed with a total yield of 17% ($k_{1a}/k_1 = 0.17$).

[3] Tan, W., et al., *Experimental and Theoretical Study of the OH-Initiated Degradation of Piperazine under Simulated Atmospheric Conditions.* The Journal of Physical Chemistry A, 2021. **125**(1): p. 411-422.

- Two of those are similar to the radical formed by piperazine and quantum potential are shown to be similar, supporting also similar branching ratios.
- The third aminyl radical is formed with an about 200 times lower yield than for the two other radicals, leading to a negligible contribution to the total nitrosamines and nitramines yield.
    - the aminyl group structure is similar to the diethyl aminyl radical structure and potentials are expected to be similar.
    - The yield of this aminyl radical is predicted to be about 200 times lower than for the two other radicals, leading to a negligible contribution to the total nitrosamines and nitramines yield.

The contribution from the third radical can thus be ignored and again a single reaction mechanism can be considered with the aggregated piperazine radicals branching ratios, which form a consistent set of data.

The proposed rate constants for the ADMS amine model are therefore the same as those proposed for piperazine shown in Table 3 above, however the value for k_1 from Pr. Nielsen's 2014 study should be applied (i.e. 6.25 $ppb^{-1} \cdot s^{-1}$) with the k_{1a}/k_1 branching ratio of 0.17.