Atmospheric Oxidation of Piperazine Initiated by OH: A Theoretical Kinetics Investigation

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ABSTRACT

Piperazine (Pz) mixed with other amines is a proposed carbon capture solvent, but there is concern about the impact of Pz on air quality, including the potential to produce toxic products. Here, the $\cdot\text{OH}$ initiated oxidation of Pz has been studied by *ab initio* modelling and RRKM / master equation kinetic simulations. The Pz + $\cdot\text{OH}$ reaction is found to proceed at around the capture rate, consistent with experiment, with abstraction predominantly from C—H sites, forming an alkyl radical (PzC). The subsequent reaction kinetics of carbon centred Pz radicals with O_2 are also studied, so as to determine the first-generation oxidation products. We find that the PzC radical predominantly reacts with O_2 to produce a cyclic imine product + $\text{HO}_2\cdot$ under tropospheric conditions, with the stabilized peroxy radical formed as a minor product. Subsequent reaction of the peroxy radical with NO produces an alkoxy radical that can react with O_2 to yield a cyclic amide or undergo unimolecular ring opening followed by a second O_2 addition / $\text{HO}_2\cdot$ elimination step to produce $\text{CH}_2=\text{NCH}_2\text{CH}_2\text{NHCHO}$.

KEYWORDS

Atmospheric chemistry, kinetics, piperazine, transition state theory, computational chemistry

Introduction

Carbon capture technology is being actively pursued as a means of reducing CO_2 emissions from fossil fuel burning.¹⁻⁶ Among these technologies, absorption into liquid amine solvents is currently the most mature.⁷⁻¹⁰ The amine piperazine (Pz) is one potentially attractive solvent when mixed with other compounds.^{7, 11-15} It is inevitable that significant quantities of volatile amines will be released to the atmosphere during their manufacture, transport, and use in any amine-based carbon capture process,¹⁶⁻¹⁹ and we therefore require a thorough understanding of the atmospheric chemistry of piperazine.

Pz is a nitrogen-containing heterocycle with a six-member ring and two secondary amino groups. When released into the atmosphere, Pz is expected to react predominantly with the $\cdot\text{OH}$ radical,^{20, 21} via abstraction from C—H sites to form an alkyl radical (PzC) or from N—H sites to form an aminyl radical (PzN). The extent of branching to the PzN radical is of particular interest, as aminyl radicals can react with NO and NO_2 to generate toxic nitrosamines and nitramines, respectively.²²⁻²⁹ On the other hand, α -aminoalkyl radicals such as PzC have been shown to predominantly react with O_2 to produce imines.^{30, 31} Experimentally, Pz has been shown to react with $\cdot\text{OH}$ mainly via C—H abstraction, although there is limited information on the further reaction products under atmospheric conditions.^{11, 32, 33} This

motivated us to carry out a theoretical kinetics investigation into the Pz + $\cdot$ OH reaction through multiple reaction stages, to help validate existing experimental results as well as to provide new insight into the ultimate products of atmospheric oxidation.

Methods

The G4 composite model has been used for all ab initio calculations.³⁴ It is a multistep method, in which density functional theory (B3LYP/6-31g(2df,p)) optimized geometries are used for wavefunction theory single-point energy calculations from HF to CCSD(T) paired with basis sets of incrementally decreasing size, along with added empirical corrections (using unrestricted wavefunctions for open shell species). These single-point energy steps allow for efficient approximation of the CCSD(T) energy with a complete basis set. The B3LYP method allows for computationally efficient geometry optimizations and frequency calculations, although it introduces errors on the order of 0.06 Å³⁵ for critical transition state parameters. As a result the G4 method accurately predicts barrier heights at reasonable computational cost, with mean unsigned error in barrier heights expected to be less than 1 kcal/mol.³⁶ Frequency calculations confirmed all minima to have zero imaginary frequencies and all transition states to have one imaginary frequency, with intrinsic reaction coordinate calculations used to confirm transition state connectivity. Where multiple conformations are available we refer to the lowest energy structure. Gaussian 16 was used for all reported electronic structure calculations.³⁷ Coordinates of all the wells and transition states are included in Supporting Information.

The MultiWell Program Suite (2017) was employed for statistical reaction rate simulations,³⁸ on the basis of B3LYP/6-31g(2df,p) theory moments of inertia, vibrational frequencies, and G4 theory energies. RRKM theory is used to calculate microcanonical rate coefficients, $k(E)$. In the sums and densities of state calculations, harmonic oscillators are used to describe the internal degrees of freedom and an active 1D K-rotor and inactive 2D J-rotor are used to treat external degrees of freedom. Barrierless association reactions are described using the restricted Gorin model,³⁹ where the rate of complex formation is estimated as the dipole-quadrupole capture rate, k_{cap} .⁴⁰ The equation used here is $k_{\text{cap}} = C\mu^{-0.5}|d Q|^{1/2}$, where μ is reduced mass, and d and Q are the respective dipole and quadrupole moments (all in atomic units). The constant C has a value of 4.49 when all variables are in atomic units, and arises from application of μ J-VTST on the long-range dipole – quadrupole potential.^{40, 41} All parameters used in capture rate calculation are included in Supporting Information Table S1. The capture rate of Pz and $\cdot$ OH is estimated to be $2.61 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, whereas the capture rate of PzC and O₂ is significantly lower at $3.35 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, largely due to the small quadrupole moment of O₂. Product yields are obtained from time-dependent energy grained master equation simulations. The MultiWell stochastic master equation solver simulations reaction probabilities over many trials, employing a hybrid master equation with an energy grained regime followed by a continuum regime. The energy grained master equation comprised 2000 grains with size of 10 cm⁻¹, which was then extended from 20,000 cm⁻¹ up to 150,000 cm⁻¹ for the continuum component (well above any barriers or excitation energies). Each stochastic simulation featured 10 million trials and sufficient collisions to reach steady-state. The Lennard-Jones model is used to describe the collision of wells with the bath gas, N₂. Additivity calculations were used to estimate the Lennard-Jones parameters, with $\sigma [\text{\AA}] = 1.45(\sum V_i)^{1/3}$ and $\epsilon/k [\text{K}] = 1.21T_b$, where V_i are the additive volume increments and T_b is the boiling point (K) estimated by Joback method. For the Pz–

OH adducts, Lennard-Jones parameters σ and ϵ/k_b are calculated as 6.2 Å and 584 K. For PzC–O₂ adducts, Lennard-Jones parameters σ and ϵ/k_b are 6.04 Å and 524.6 K. The average energy in deactivating collisions, ΔE_{down} , is set as 100 cm⁻¹ in the Pz + •OH reaction and 100 ± 50 cm⁻¹ for PzC + O₂.

Results and Discussion

The •OH radical can abstract H from either a N site on Pz, to form a N atom centred aminyl radical (PzN) + H₂O, or a C site on Pz, to form a C atom centred alkyl radical (PzC) + H₂O. A theoretical energy diagram of the Pz + •OH reaction is depicted in **Figure 1**. The optimised geometries of the transition states and wells in the H abstraction are shown in **Figure 2**.

The initial step begins with the approach of •OH radical to Pz, resulting in barrierless and exothermic formation of pre-reaction adduct **1** by 8.1 kcal mol⁻¹. Pre-reactant complex **1** can interconvert to **2** (4.9 kcal mol⁻¹ below the entrance) via **TS3**, which sits at close to the energy of **2**. Note that the 0 K enthalpy of **TS3** is 0.7 kcal mol⁻¹ below **2**; this indicates a small reaction barrier⁴² that is close to the zero point energies, and may also be an artefact of the multilevel calculations. This process predominantly involves rotation of the OH group; the H—O—N—H dihedral changes from almost 0° in **1** to about -112° in **2**, and is -28° in **TS3**. From **1** the C—H bond will break via **TS1** which sits 1.4 kcal mol⁻¹ above **1** (6.7 kcal mol⁻¹ below the reactants). From **2**, the N—H bond will break via transition state **TS2** which is 3.3 kcal mol⁻¹ above **2** (1.6 kcal mol⁻¹ below Pz + •OH). After H abstraction, **TS1** leads to the alkyl radical (PzC) and H₂O, whereas **TS2** goes to the aminyl radical (PzN) and H₂O in a marginally less exothermic process. According to the potential energy diagram developed here we would expect PzC to be the dominant reaction product, due to both the lower abstraction barrier and the ability for the two pre-reaction complexes to readily interconvert.

In order to quantify the Pz + •OH reaction kinetics, master equation modelling has been carried out from 300 K to 500 K at 1 atm N₂. As is shown in **Figure 3**, the calculated rate coefficient at 300 K matches the experimental result of Onel *et al.*³³ Additionally, the negative activation energy is captured reasonably well.³³ At 300 K, C—H and N—H abstraction rate coefficients are estimated to be $k_{\text{Cabst}} = k_{\text{cap}} \times y_{\text{C-H}} = 2.38 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{\text{Nabst}} = k_{\text{cap}} \times y_{\text{N-H}} = 2.66 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ respectively, where $y_{\text{C-H}}$ is the yield of C—H abstraction products and $y_{\text{N-H}}$ is the yield of N—H abstraction products. Predicted branching to C—H abstraction is $k_{\text{Cabst}} / (k_{\text{Cabst}} + k_{\text{Nabst}}) \approx 99 \%$, confirming this as the major reaction channel. As temperature increases from 300 to 500 K, the branching ratio of C—H abstraction remains as the major reaction channel and slightly decreases from 99 % to 94 %. Yields, abstraction rate coefficients, and branching ratios of both channels at 300 to 500 K are listed in Supporting information (Table S2). Thus, subsequent reactions between PzN and NO or NO₂ which may produce carcinogenic nitrosamines and nitramines are predicted to be minor in the atmospheric oxidation of piperazine initiated by •OH, although due to their potentially acute toxicity they may still need to be included in atmospheric chemical mechanisms.

Figure 1. Potential energy diagram for the piperazine + $\cdot\text{OH}$ reaction. Relative energies are 0 K enthalpies in the units of kcal mol^{-1} , at the G4 level of theory.

Figure 2. Optimized structures of the wells and transition states of Pz + $\cdot\text{OH}$ reaction at G4 level of theory. For the transition states, displacement vectors of the imaginary frequency are included.

Figure 3. Total rate coefficient (k) from calculations and experiments as a function of temperature (T) in the PzC + $\bullet$ OH reaction.

Once formed, the PzC radical will rapidly react with O_2 in the atmosphere. The energy diagram for the reaction of PzC + O_2 is shown in **Figure 4**. Energies of all the transition states, intermediates and products are below the reactants. The optimised structures of the transition states and wells in the mechanisms are illustrated in **Figure 5**. Firstly, the alkyl radical (PzC) combines with molecular O_2 to form the peroxy radical ($RO_2^\bullet$) intermediate **3**, releasing 35 kcal mol⁻¹ in energy. Relaxed potential energy scans confirmed this step to be barrierless. From here, **3** can undergo $HO_2^\bullet$ elimination via a five-member ring like transition state, **TS4**, which is 16.4 kcal mol⁻¹ below the reactant and 19 kcal mol⁻¹ above the peroxy radical **3**. Following $HO_2^\bullet$ elimination there is the formation of a weak post-reactant adduct **4**, which can dissociate to the cyclic imine 1,2,3,6-tetrahydropyrazin and $HO_2^\bullet$, whose energies are 14.4 kcal mol⁻¹ below the reactants. We preliminarily considered other isomerization and dissociation channels of the peroxy radical **3** (see Figure S1 and Table S3 in Supporting Information) although they all have substantial barriers and were subsequently excluded.

Figure 4. Potential energy diagram for the reaction of PzC + O_2 generating 1,2,3,6-tetrahydropyrazin + $HO_2^\bullet$. Relative energies are 0 K enthalpies in the units of kcal mol⁻¹, at the G4 level of theory.

Figure 5. Optimized structures of the wells and transition states of PzC + O_2 reaction at the G4 level of theory. For the transition state, displacement vectors of the imaginary frequency are included.

It is apparent from **Figure 4** that following the association of PzC with O_2 , the chemically activated peroxy radical will have sufficient energy to dissociate to 1,2,3,6-tetrahydropyrazin + $HO_2^\bullet$. This process will, however, be in competition with collisional deactivation of the peroxy radical as well as reverse dissociation to the reactants. To better understand these processes, a master equation model

has been developed, and simulations were carried out at 14 Torr (the pressure of the Onel *et al.* study) and 1 atm N₂. At 14 Torr, we predict no peroxy radical stabilization, supporting the assumption of Onel *et al.* that PzC was quantitatively oxidised to HO₂[•] in their reactor. From the 1 atm simulations the only significant product channels predicted were for dissociation to the imine + HO₂[•] plus peroxy radical stabilization; there was negligible reverse dissociation to reactants. Although peroxy radical stabilization becomes significant at atmospheric pressure, the predicted yields were sensitive to the collisional energy transfer model adopted. The time-evolution of peroxy radical **3** in the PzC + O₂ reaction at 298 K and 1 atm N₂ is plotted in **Figure 6**, for $\Delta E_{\text{down}} = 100 \pm 50 \text{ cm}^{-1}$. At 100 cm⁻¹ the steady-state peroxy radical yield is 11.3 %, increasing to 26.9 % at 150 cm⁻¹ and dropping to effectively zero at 50 cm⁻¹.

Figure 6. Predicted RO₂[•] peroxy radical yields vs. time from master equation simulations at 298 K and 1 atm N₂.

Although not the major product in the atmospheric degradation of Pz, we predict that the peroxy radical **3** will be formed to some extent, yet its further reaction pathways have to date been unexplored. In polluted environments the dominant fate will be reaction with NO to produce an alkoxy radical (RO[•]), **5**, as shown in Eqn (1). The energy release of this process is calculated as 10.0 kcal mol⁻¹, which will provide the RO[•] radical with some excess vibrational energy over that of a thermalized population.

Following the formation of RO[•], there is competition between the bimolecular reaction RO[•] + O₂ and unimolecular RO[•] chemistry. The energy diagram for the RO[•] + O₂ reaction is depicted in the Supporting Information (Figure S2); this reaction produces a cyclic amide via a transition state which is 3.1 kcal mol⁻¹ above the entrance channel. A diagram illustrating the main isomerisation and decomposition pathways of the alkoxy radical RO[•] are shown in **Figure 7**. The alkoxy radical can break

the C—N bond and form a N-centred radical $\text{HCOCH}_2\text{NHCH}_2\text{CH}_2\text{NH}^\bullet$ with a barrier of $14.3 \text{ kcal mol}^{-1}$. Direct C—H beta-scission leading to H loss, forming a cyclic amide, proceeds with a barrier of $8.9 \text{ kcal mol}^{-1}$. Intramolecular H-shifts from both neighbouring N—H and C—H groups were also investigated although the barriers were prohibitively large (20.8 and 25 kcal mol^{-1} respectively) and they are not shown. The alkoxyl radical can also break the C—C bond via a multistep process (**TS7 – TS9**) with a barrier lower than both the H loss and C—N bond breaking reactions. Firstly, the directions of the H—N bonds located at the meta and ortho N atoms sequentially change from equatorial to axial. Then C—C bond cleavage forms a ring-opened structure $\text{HCONHCH}_2\text{CH}_2\text{NHCH}_2^\bullet$ via a near-barrierless process. Subsequent H shift reactions of $\text{HCONHCH}_2\text{CH}_2\text{NHCH}_2^\bullet$ have also been explored, although all energies are significantly above the entrance channel (see Supporting Information Figure S3). Accordingly, the main alkoxyl radical product is expected to be the open chain alkyl radical $\text{HCONHCH}_2\text{CH}_2\text{NHCH}_2^\bullet$, which can undergo a second O_2 addition mechanism.

Figure 7. Potential energy diagram for PzC alkoxyl radical isomerisation. Relative energies are 0 K enthalpies in the units of kcal mol^{-1} , at the G4 level of theory.

Similar to the alkyl radical PzC, $\text{HCONHCH}_2\text{CH}_2\text{NHCH}_2^\bullet$ reacts with O_2 to form a peroxy radical (**10**), releasing $33.3 \text{ kcal mol}^{-1}$ in energy. Subsequently, **10** can undergo $\text{HO}_2^\bullet$ elimination via **TS10**, which is $19.4 \text{ kcal mol}^{-1}$ above **10** ($13.9 \text{ kcal mol}^{-1}$ below $\text{HCONHCH}_2\text{CH}_2\text{NHCH}_2^\bullet + \text{O}_2$). After $\text{HO}_2^\bullet$ elimination, **TS10** leads to the post-reactant complex **11**, which will dissociate to $\text{CH}_2=\text{NCH}_2\text{CH}_2\text{NHCHO}$ and $\text{HO}_2^\bullet$, whose energies are $12.3 \text{ kcal mol}^{-1}$ above well **11** and $13.7 \text{ kcal mol}^{-1}$ below the entrance channel. The relevant energy diagram is depicted in **Figure 8**, and a higher-energy competing process involving formyl H abstraction is shown in Figure S4 of the Supporting Information. The $\text{CH}_2=\text{NCH}_2\text{CH}_2\text{NHCHO}$ product bears an amide functional group, and the further oxidation of this species may therefore lead to toxic isocyanates.⁴³⁻⁴⁵

Based upon the results presented above, we predict that Pz will react with $^\bullet\text{OH}$ in the troposphere to almost exclusively produce the carbon-centred radical PzC. Subsequent reaction with O_2 then leads predominantly to the imine 1,2,3,6-tetrahydropyrazin (+ $\text{HO}_2^\bullet$), but with a stabilised peroxy radical yield of about 10 %. The corresponding alkoxyl radical can undergo ring opening followed by second O_2 addition to produce an open-chain imine, $\text{CH}_2=\text{NCH}_2\text{CH}_2\text{NHCHO}$. These findings are summarized in **Figure 9**. Further to this work the fate of the imines may need to be considered in order to completely appreciate the air quality impacts of piperazine.

Figure 8. Potential energy diagram for $\text{HCONHCH}_2\text{CH}_2\text{NHCH}_2^\bullet + \text{O}_2$ reaction. Relative energies are 0 K enthalpies in the units of kcal mol^{-1} , at the G4 level of theory.

Figure 9. Proposed atmospheric reaction scheme for the $^\bullet\text{OH}$ radical initiated oxidation of piperazine.

Summary and Conclusions

In this work the $\cdot\text{OH}$ initiated atmospheric oxidation of Pz has been studied. H abstraction from C—H sites is found to have a lower barrier than N—H sites, and master equation modelling confirms that H abstraction happens predominantly on C—H sites. Predicted rate coefficients for the $\text{Pz} + \cdot\text{OH}$ reaction are consistent with experiment. Reaction of the alkyl piperazine radical PzC with O_2 is also investigated, with the main product predicted to be a cyclic imine produced via a $\text{HO}_2\cdot$ elimination process, with minor yield of the stabilized peroxy radical. The alkoxy radical formed in the reaction of $\text{RO}_2\cdot + \text{NO}$ can subsequently isomerize and react with a second O_2 to produce $\text{CH}_2=\text{NCH}_2\text{CH}_2\text{NHCHO}$ and $\text{HO}_2\cdot$.

Supporting Information Available:

Potential energy diagrams for the $\text{PzC} + \text{O}_2$ reaction followed by H shift from the meta-C, $\text{RO}\cdot + \text{O}_2$ reaction, $\text{HCONHCH}_2\text{CH}_2\text{NHCH}_2\cdot$ isomerisation and formyl H abstraction in the $\text{HCONHCH}_2\text{CH}_2\text{NHCH}_2\cdot + \text{O}_2$ reaction, parameters used in capture rates calculation and calculated yields, rate coefficients, branching ratios and coordinates of the wells and transition states.

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