Atmospheric Chlorine Reaction with N-methyl-2-pyrrolidinone (NMP)

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ABSTRACT:

Density functional theory (DFT) and Complete Basis Scale methods (CBS-QB3, G3B3) are used to investigate the reactivity, the mechanism, structure-reactivity relationship and the kinetics of N-methyl-2-pyrrolidinone (NMP) with Cl atom. To obtain rate constants of the reaction, the RRKM theory is employed at atmospheric pressure and temperature range 273–380 K. This study provides the rate coefficients and detailed H-abstraction mechanism for the reaction of Cl with NMP at high level of theoretical methods. The obtained rate constant ~ 0.92 x 10^{-10} to 8.98 × 10^{-10} cm³ molecule⁻¹ s⁻¹ at 298 K agreed with those obtained previously for N,N-dimethyl formamide (DMF) and N,N-dimethyl acetamide (DMA). The study shows that the reaction mechanism of Cl with NMP goes favorably through an H-abstraction from N-methyl groups and adjacent CH₂. The rates constants obtained for the three amides confirm our prediction regarding the structure-reactivity relationship where \( \frac{1000}{T} \).

1. Introduction

Chlorine reactions with volatile organic compounds (VOCs) are important for the atmospheric observations regarding the pollution of the troposphere and has provided models for studies of dynamics and kinetics of reactions in gas phases. In the troposphere, VOCs constitute a major class of chemicals emitted directly into the earth’s troposphere. The H-abstraction from these compounds provides an important source of O₃ and other photochemical pollutants in coastal and industrialized areas [1].

Amides form a wide variety of volatile organic nitrogen compounds (NVOCs). They are considered as primary pollutants or secondary pollutants [2]. Amides reactions with atmospheric radicals shows the involvement of these contaminants relative to the tropospheric lifetime in relation to each atmospheric photo-oxidant [1–5].
Koch et al. [6], Aschmann et al. [7] Solignac et al. [8], and El Dib et al [9] carried out the reaction of amides with atmospheric oxidants. Koch et al. [6] used flash/fluorescence resonance photolysis to study the oxidation kinetics of amides by OH radicals at various temperatures. Aschmann et al. [7] used the relative rate technique to study the OH and NO₃ homogeneous oxidation kinetics of N-methyl-2-pyrrolidinone. Solignac et al. [8] have determined the kinetics reactions of the amide with OH radical and Cl at room temperature. G. El Dib et al. [9] studied the radical reaction of NO₃ with certain amides at different temperatures and determined the rate coefficient by laser photolysis coupled with UV-visible spectroscopy and time resolved absorption. The kinetic results without a mechanism investigation (isotope labelling) seems indicate that the reactions of amides with atmospheric oxidants is sensitive to the amide structure.

NMP, with low volatility and high chemical and thermal stability, is considered to replace some organic solvents[6]. Few information exist concerning the mechanisms of amides degradation by atmospheric oxidants. Mechanistic and theoretical studies are useful to give an understanding of the mechanism involved in reaction process with atmospheric radicals. This study reports a theoretical investigation of the kinetics and structure-reactivity mechanism of Cl atom with NMP a cyclic amide.

The results reported provide additional information on the kinetics of the reaction with atmospheric oxidants to understand the tropospheric implication of NMP and its importance as a primary or secondary pollutant.

2. Theoretical Methods

2.1. Quantum Chemistry Calculations

The calculations obtained using the Gaussian 09 package[10] available at the URCA-France and the data analysis were done on the CPO platform at the U-BATNA-1 in Algeria. Geometries and electronic structures for all minima and transition states (TS) were calculated with density functional theory DFT B3LYP/6-311++G(2d, pd) level of theory[11].

Each stationary point was determined by calculating the frequencies harmonic vibration and the minimum is characterized by real frequency, the reaction TS’s are localized with the “quasi-Newton guided by
synchronous transit” procedure for the search for the saddle point (QST3). The Hessian matrix of TS has a one negative frequency. The localization of the TS as recommended in a previous criticism were confirmed with intrinsic reaction coordinates calculations (IRC)[12].

As B3LYP method overestimates H-abstraction barriers and provides unreliable thermochemical values. The neutrals, radicals, and transition-states geometries were optimized using B3LYP method, CBS-QB3 model of Petersson et al [13-23] was used to calculate the energies of the different species involved. In fact, current studies show that the CBS-QB3 method frequently gives good agreement with experimental reaction energies and barriers for molecules having same size to those involved in this work [24-26]. Heats of formation for all gaseous species involved in the reaction were calculated based on the procedure defined in the literature [24-25].

G3B3 (or G3//B3LYP), a variant of G3 method, is useful for larger open-shell systems with a very low spin contamination (~1 kcal/mol for the neutral set of molecule)[26]. Enthalpies of formation at 0 K and 298 K were calculated as defined in our previous work [26-29].

2.2. Rate Calculations.

The rate constants were carried out using RRKM theory[30-32] counting the required sums, density of states, frequencies, zero-point energies and moments of inertia. Kinetics calculations were done with reactants, TSs, and products optimized at B3LYP/6-311++G(2d,pd) level of theory. Enthalpies calculated from both CBS-QB3//B3LYP/6-311++G(2d,pd) and G3B3// B3LYP/6-311++G(2d,pd) for all gaseous species injected in the Master equation (ME in Chemrate) permit to obtain the rates constants including the temperature dependence for each reaction involved in the global mechanism[33-41]. Our simulations take the most stable conformer. These simplifications will have little effect on numerical precision but should affect the validity of the rates values obtained.

3. Structural calculations

Five stationary points on the profile energy surface (PES) have been localized, with a competition of four H-abstraction pathways, for each path: the reactants, the reactant complex, the transition state, the product complex and the products respectively NMP, HCL, CR1-CR4, TS1-TS4, CP1-CP4 and P1-P4.
For N-methyl-2-pyrrolidinone (NMP), H-abstraction may take place (Figure1) at several sites. The reaction is estimated to process with H- abstraction from the three –CH2 – groups of the pentacycle, or –CH3 adjacent to the Nitrogen. The TS’s geometry consist of a near-linear alignment of the Cl atom, the H atom to be abstracted, and the atom to which the H atom is attached in the neutral structure. Four channels have been modeled for NMP +Cl.

The reaction H-abstraction pathways progress via three-steps, namely: (i) the formation of the complex CR1-CR4 from the isolated reactants NMP+Cl, (ii) the formation of the complex CP1-CP4 from the reactant complex through the TS1-TS4 and (iii) the formation of the consistent radical and HCl from the product complex Fig 1–4. Table 1-6 regroup the energies of reactants, complex reactants, Ts’s, complex products and products species involved in the mechanism.

The experimental and theoretical enthalpies are in good agreement except for R1–R4 species Fig 1 for which the experimental enthalpies are not available in the literature as mentionned previously in [26-29].

3.1 H-Abstraction from –N-CH3 group.
The H abstraction in this path includes only one H from the CH₃ of the –N-CH₃ group of the amide. The TS1 characterized by a single imaginary frequency of -534.94 cm⁻¹ is confirmed by the IRC calculation (see supporting information). The reactive complex CR1 is energetically stable, The C-H bond distance in this reactive complex (RC1) is ~1.20 Å and the intermediate hydrogen bond C-H…Cl is ~1.82 Å, while for TS1, the distances of identical bond are respectively ~1.41 and ~1.42 Å. The CP1 involve an intermolecular H bond between the carbon atom and HCl with a distance of ~1.62 Å. This path involves an energy barrier of ~6.44 (6.17) kcal / mol. (in parentheses and bold the energy barrier at G3B3 // B3LYP / 6-311 G- (2d, pd) level) The reaction path is exothermic and exergonic see Table 4.

3.2 H-Abstraction from –CH₂ adjacent to the N-CH₃ group

In this path the H- abstraction process includes the hydrogen of the –CH₂- group adjacent to the N-CH₃. The CP2 structure shows an intermolecular H-bond between the carbon of the group -CH₂- adjacent to the N-CH₃ and HCl with a bond distance of ~1.66 Å. The C-H bond in the CR2 is ~1.20 Å, the like bond H…Cl distance is ~1.81 Å while for the TS2 the distances bonds involved in the coordinate reaction are, respectively, ~1.40 and ~1.42 Å. The CP2 via dissociation of the intermolecular H-bond gives rise to the product P2 and HCl. This path involves an energy barrier of ~12.70 (8.33) kcal / mol. The reaction process is exothermic and exergonic (see Table 4) as in the previous path.

3.3 H-Abstraction from Group –CH₂ central and –CH₂ adjacent to the C=O group

The H- abstraction process in this path includes the hydrogen of the CH₂- group central in the NMP structure. The products complex involve an intermolecular hydrogen bond between the carbon atom of the CH₂ and HCl with a bond distance of ~1.66 and 1.68 respectively for CP3 and CP4. The bond distance C-H in the reactive complex is ~1.27 Å while the like bond H…Cl distance is ~1.80 to 1.81 Å for both. The distances bonds involved in the two TSs are, respectively, ~1.40 and ~1.45 Å. These reactions involves energies barriers of ~20.97 (32.72) kcal / mole for TS3 and ~19.99 (31.11) kcal / mole for TS4. For these path’s, although the reactions process are lightly exothermic and exergonic see (see Table 4), the calculations shows a very high barrier compared to the other paths and were not taken in
consideration in the Kinetic calculations without considering the tunneling effect that may occur in these cases.

4. KINETICS

The mechanism of H-abstraction reaction of NMP with Cl is studied as a competition between two H-abstractions as follows.

\[ \text{NMP} + \text{Cl} \xrightarrow{k_{\text{Ia}}} (CR) \xrightarrow{k_{\text{lb}}} (CP) \xrightarrow{k_{\text{Ic}}} \text{P1} + \text{HCl} \]

\[ \xrightarrow{k_{\text{Ia}}} (CR) \xrightarrow{k_{\text{lb}}} (CP) \xrightarrow{k_{\text{Ic}}} \text{P2} + \text{HCl} \]

as seen previously in the Cl reaction with DMF and DMA, and according to the PES’s, the rate constant (k) of the four channels can be analyzed in terms of conventional transition-state theory (CTST) or RRKM/ME calculations. \( k_{\text{Ia}}, k_{\text{IIa}} \) represent the forward rates, \( k_{-\text{Ia}}, k_{-\text{IIa}} \) the reverse ones for the first step and the second step respectively for channel Ia, while \( k_{\text{Ic}}, k_{\text{IIc}} \) represent the forward rates and \( k_{-\text{Ic}}, k_{-\text{IIc}} \) the reverse ones for channels Ib.

Rate constants \( (k_I, k_{II}) \) of channels Ia–Ib can be obtained according to this hypothesis, as:

\[ k_I = k_{\text{eqIa}} \times k_{\text{lb}} \times k_{\text{eqIc}} \quad (a) \]

\[ k_{II} = k_{\text{eqIIa}} \times k_{\text{lb}} \times k_{\text{eqIIc}} \quad (b) \]
Where \( k_{eqIa}, k_{eqIia}, k_{eqIc}, k_{eqIIc} \) represent the equilibrium constants connecting the isolated reactants and the complexes for channel I and channel II respectively.

The rates constants involved in the H-abstraction mechanism were carried out with ChemRate program [14]. Simulations were determined at 1atm and 273-380 K. Collision energy transfer was designated by an exponential-down model, with \( \Delta E_{\text{down}}=300 \text{ cm}^{-1} \). Ar (argon) considered as bath gas with lennard-jones parameters of \( \sigma=4.4 \) and \( \xi=216 \text{ K} \) [38-39]. All rate constants obtained in this study are in \( \text{s}^{-1} \) or \( \text{cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1} \) units.

The overall rate constant (c), the branching ratios (d) obtained from the kinetic simulation model are calculated as follow:

\[
k_{\text{overall}} \leq k_I+k_{II} \quad (c)
\]

\[
\beta_I = \frac{k_I}{k_I+k_{II}}, \beta_{II} = 1 - \beta_I \quad (d)
\]

The calculations of the transmission coefficients (using the Wigner, Skodje, and Truhler formalisms[42-43]) were obtained in the range 278–400 K. Small tunneling effect was observed (0.994 to 1.004) saying no effect on the rate constant values calculated in this study as seen in our previous work for DMF and DMA[28].

**5. RESULTS AND DISCUSSION**

The H-abstraction from N-methyl -2-pyrrolidinone (NMP) reaction as described above, has been modeled according to a complex mechanism in the entrance channel: two complexes CR1 and CR2 have been considered with the lowest two transition states TS1 and TS2 respectively followed by two complexes CP1 and CP2 for each reaction profile.

The H-abstraction from the –N-CH\(_3\) group site leads to the species PC1. This path was found to be slightly dominant with a branching ratio \( \beta_I = 0.55 \), as for DMA, toward electrophilic attack due to the positive inductive effect of these groups can be stated for this reaction. Significant negative temperature effect was
noted for \( k_1 \) and \( k_{II} \). \( k_{overall} \) vary from 8.87(E-10) to 1.05(E-09) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) in the temperature range 273-380 K (see Table 5-6). The linear fit of all the data carried out using the calculation at different temperatures; leads to the Arrhenius expression at CBS-QB3 and G3B3 level of theory equation e and f (see Fig 5):

\[
k_{overall}(T) = 8.89 \times 10^{-10} \times \exp \left( -163.8/T \right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (e)
\]

\[
k_{overall}(T) = 3.70 \times 10^{-11} \times \exp \left( 63.8/T \right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (f)
\]

Previous studies have focused on the reactivity of DMF (N,N-dimethyl formamide (CH\(_3\)_2NCOH)) and DMA (N,N-dimethyl acetamide (CH\(_3\)_2NC(O)CH\(_3\))) with OH radical and Cl. Only one experimental study on the reactivity of NMP was carried out by Aschmann et al.[7], the relative rate technique was used for the homogeneous oxidation kinetics of NMP with OH and NO\(_3\).

Theoretical and mechanistic investigation of the reactions of DMF and DMA with Cl, OH and NO\(_3\) published previously[28] gives rate constants of 4.45 \times 10^{-10} and 9.92 \times 10^{-10} cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) at 298 K respectively obtained with the DFT/CBS-QB3//B3LYP/6-311++G(2d,pd) level of theory. The results are in the same order with the ones observed for NMP and shows that there is a relation between the rate constant and the structure of the amides (reactivity-structure relationship): \( k_{NMP} > k_{DMF} > k_{DMA} \)

The rate constant of the reaction of Cl with NMP decrease as the temperature increases in the range 273-380 K and are in good agreement with the results of the reaction Cl with DMF and DMA[28]. In the literature the reaction of DMA and DMF with Cl [8], state that for DMA and DMF, abstraction occur with a branching ratio of 55 %, in N-CH\(_3\) groups [28]. This mechanistic tendency is also observed in the theoretical calculations, where the H-abstraction from the –N-CH\(_3\) group appeared to be slightly dominant channel with small barrier energy and negative temperature dependence. For the reaction of NMP with Cl over the temperature range explored, an important effect of the temperature is observed.

6. Conclusion
This study represents a theoretical determination of the rate coefficients and detailed H-abstraction mechanism for the reaction of the Chlorine atom with one cyclic amide (NMP), within the temperature range 273–380 K. This work has been achieved using high level of theory DFT, CBS-QB3 and G3B3 methods considered to be the most efficient and accurate computational methods for the study of this kind of reactions. The reaction of NMP with Cl is exothermic and exergonic taking place in five steps as mentioned in our previous work for DMF and DMA. Kinetic and mechanistic results show that the mechanism of the Cl reaction with NMP goes with small barriers through H-atom transfer from –N-CH$_3$ group and -CH$_2$ adjacent to the N-CH3 site within a branching ration slightly in favor of the N-CH3 site. The suggested mechanism is maintained by the results for reactions of DMF and DMA with chlorine [28]. The rate constants determined in this study present a troposphere lifetime of 3 to 10 days which could be seen as affect the chemistry of the troposphere on local and regional scales.

Supporting Informations

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Figure 1. Structures of key species (1-methyl-2-pyrrolidinone – NMP-) and P1–P4 (radicals obtained via channels Ia–Id)) considered for kinetics simulations determined by B3LYP/6-311++G(2d,pd); bond lengths in angstroms.
Figure 2. Structures of key species CR1–CR4 (radicals obtained via channels Ia–Id) considered for kinetics simulations determined by B3LYP/6-311++G(2d,pd); bond lengths in angstroms.
Figure 3. Structures of key species TS1−TS4 (Transitions stat obtained via channels Ia–Id) considered for kinetics simulations determined by B3LYP/6-311++G(2d,pd); bond lengths in angstroms.
Figure 4. Structures of key species CP1–CP4 obtained via channels Ia–Id considered for kinetics simulations determined by B3LYP/6-311++G(2d,pd); bond lengths in angstroms.
Figure 5. Arrhenius plot ln(koverall) versus 1000/T for NMP + Cl reaction at CBS-QB3 and G3B3
Table 1: Energies (Hartree) of reactants and products species involved in the mechanism: In hartree(u,a) as obtained from the DFT calculation. CBS-H enthalpy at 298.15 K. CBS-G Gibbs free energy at 298.15 K. CBS-E energy. CBS (0 K) energy at 0 K. a Atomization energy in kcal mol⁻¹ at 0 K. b Heat of formation at 0 K in kcal mol⁻¹. c Heat of formation at 298.15 K in kcal mol⁻¹. d Experimental Heat of formation at 298.15 K in kcal mol⁻¹. (1) CRC Handbook of Chemistry and Physics New York October 2003.

|       | E-DFT  | CBS-H   | CBS-G   | CBS-E   | CBS-0K | ΔH°f(0K) | ΔH°f(298K) | ΔH°f(298K) |
|-------|--------|---------|---------|---------|--------|----------|------------|------------|
| NMP   | -326.049078 | -325.365587 | -325.408694 | -325.366531 | -325.374519 | 1591.38 | -105.29 | -112.10 | -107.51 |
| R1    | -325.3920739 | -324.719681 | -324.75868 | -324.720625 | -324.727539 | 1499.03 | -64.57 | -71.05 | / |
| R2    | -325.3939165 | -324.720451 | 324.764413 | -324.721395 | -324.72952 | 1500.27 | -65.81 | -71.53 | / |
| R3    | -325.3672691 | -324.693336 | -324.732936 | -324.69428 | -324.701326 | 1482.58 | -48.12 | -54.52 | / |
| R4    | -325.3723767 | -324.699291 | -324.740413 | -324.700235 | -324.7078 | 1486.64 | -52.18 | -58.26 | / |
| CL    | -459.477436 | -459.681285 | -459.699322 | -459.67646 | -459.683645 | 0.00 | 28.59 | 28.61 | 28.97 |
| HCL   | -460.100058 | -460.344912 | -460.366099 | -460.345856 | -460.348216 | 103.38 | -23.16 | -23.20 | -23.04 |
Table 2: Energies (Hartree) of species involved in the Mechanism Obtained at CBS-QB3//B3LYP/6-311G++(2d,pd) Level. CBS-H enthalpy at 298.15 K. CBS-G Gibbs free energy at 298.15 K. CBS-E energy. CBS (0 K) energy at 0 K.\(^a\) Atomization energy in kcal mol\(^{-1}\) at 0 K.\(^b\) Heat of formation at 0 K in kcal mol\(^{-1}\).\(^c\) Heat of formation at 298.15 K in kcal mol\(^{-1}\).

| Species          | E-DFT  | CBS-H   | CBS-G   | CBS-E   | CBS-0K | \(\Delta H^a_{\theta f}(0K)\)^b | \(\Delta H^c_{\theta f}(298K)\)^c | \(\gamma\) |
|------------------|--------|---------|---------|---------|--------|-------------------------------|---------------------------------|-------|
| NMP+CL           | -785.52651 | -785.046872 | -785.10801 | -785.04299 | -785.05816 | 1591.38 | -76.70 | -83.13  |
| RC1              | -786.22495 | -785.049597 | -785.09697 | -785.05054 | -785.05961 | 1592.29 | -77.61 | -84.84  |
| RC2              | -786.20098 | -785.048959 | -785.07562 | -785.03140 | -785.05975 | 1592.37 | -77.69 | -84.44  |
| RC3              | -786.19258 | -785.046565 | -785.06583 | -785.02063 | -785.01488 | 1576.77 | -62.09 | -84.82  |
| RC4              | -786.18839 | -785.046707 | -785.06661 | -785.02165 | -785.01027 | 1573.87 | -59.19 | -84.91  |
| TS1              | -786.22013 | -785.036605 | -785.10076 | -785.06557 | 1596.03   | -81.35  | -76.69 | -534.94 |
| TS2              | -786.19486 | -785.036199 | -785.07739 | -785.03414 | -785.04222 | 1581.38 | -66.70 | -70.43  | -732.70 |
| TS3              | -786.18378 | -785.013008 | -785.05664 | -785.01395 | -785.02207 | 1566.01 | -52.33 | -62.16  | -1220.71 |
| TS4              | -786.17631 | -785.015014 | -785.059003 | -785.01595 | -785.02416 | 1570.04 | -55.36 | -63.14  | -1402.26 |
| PC1              | -785.54166 | -785.06813  | -785.08211 | -785.08413 | -785.07825 | 1603.98 | -89.30 | -96.47  |
| PC2              | -785.54235 | -785.06801  | -785.10205 | -785.08725 | -785.05207 | 1587.55 | -72.87 | -96.39  |
| PC3              | -785.56214 | -785.04135  | -785.11012 | -785.05625 | -785.04094 | 1580.56 | -65.88 | -79.66  |
| PC4              | -785.54258 | -785.04552  | -785.11327 | -785.05844 | -785.01287 | 1562.95 | -66.27 | -82.28  |
| R1+HCL           | -785.49213 | -785.06459  | -785.12477 | -785.10664 | -785.07575 | 1602.42 | -87.74 | -94.25  |
| R2+HCL           | -785.49397 | -785.065363 | -785.60168 | -135.62446 | -785.07773 | 1603.66 | -88.98 | -94.73  |
| R3+HCL           | -785.46732 | -785.038248 | -785.09903 | -785.04013 | -785.04954 | 1585.97 | -71.29 | -77.72  |
| R4+HCL           | -785.47279 | -785.044203 | -785.10651 | -785.04609 | -785.05601 | 1590.03 | -75.35 | -81.46  |
Table 3: Energies (Hartree) of species involved in the Mechanism Obtained at G3B3//B3LYP/6-311G++(2d,pd) Level. CBS-H enthalpy at 298.15 K. CBS-G Gibbs free energy at 298.15 K. CBS-E energy, CBS (0K) energy at 0 K. a Atomization energy in kcal mol\(^{-1}\) at 0 K. b Heat of formation at 0 K in kcal mol\(^{-1}\). c Heat of formation at 298.15 K in kcal mol\(^{-1}\).

|       | E-DFT  | CBS-H          | CBS-G          | CBS-E          | CBS-0K         | \(\Delta H^\circ\)\(^{0K}\) | \(\Delta H^\circ\)\(^{298K}\) | \(\gamma\) (cm\(^{-1}\)) |
|-------|--------|----------------|----------------|----------------|----------------|--------------------------|--------------------------|--------------------------|
| NMP+CL| -785.52651 | -785.046435 | -785.069202 | -785.03657 | -785.045215 | 1583.25 | -68.57 | -82.86 |
| RC1   | -786.22495 | -785.07103 | -785.04125 | -785.04622 | -785.05961 | 1583.88 | -69.20 | -86.92 |
| RC2   | -786.20098 | -785.04622 | -785.04622 | -785.04622 | -785.04622 | 1587.03 | -72.35 | -85.49 |
| RC3   | -786.19258 | -785.070252 | -785.02371 | -785.046135 | -785.01488 | 1583.83 | -69.15 | -85.04 |
| RC4   | -786.18339 | -785.070285 | -785.02551 | -785.051941 | -785.01027 | 1587.47 | -72.79 | -86.16 |
| TS1   | -786.22013 | -785.03661 | -785.10076 | -785.06557 | 1596.03 | -81.35 | -76.69 | -534.94 |
| TS2   | -786.21486 | -785.03404 | -785.09858 | -785.09499 | -785.06326 | 1594.57 | -80.89 | -74.53 | -732.70 |
| TS3   | -786.18378 | -785.01254 | -785.01532 | -785.01209 | -785.0207 | 1577.46 | -41.13 | -50.41 | -1220.71 |
| TS4   | -786.17631 | -785.01204 | -785.02395 | -785.01236 | -785.02416 | 1572.63 | -42.21 | -52.02 | -1402.26 |
| PC1   | -785.54166 | -785.06176 | -785.07396 | -785.06122 | -785.07019 | 1598.92 | -84.24 | -92.47 |
| PC2   | -785.54235 | -785.06146 | -785.07439 | -785.06256 | -785.07054 | 1599.14 | -84.46 | -92.29 |
| PC3   | -785.56214 | -785.06042 | -785.07439 | -785.06959 | -785.07014 | 1598.89 | -84.21 | -91.63 |
| PC4   | -785.54258 | -785.06018 | -785.07454 | -785.06978 | -785.07006 | 1598.84 | -84.16 | -91.48 |
| R1+HCL| -785.49213 | -785.052482 | -785.081619 | -785.059396 | -785.058793 | 1591.77 | -77.09 | -86.65 |
| R2+HCL| -785.49397 | -785.052162 | -785.076229 | -135.635732 | -785.058571 | 1591.63 | -76.95 | -86.45 |
| R3+HCL| -785.47632 | -785.055322 | -785.079735 | -785.028996 | -785.05736 | 1590.32 | -71.64 | -85.61 |
| R4+HCL| -785.47279 | -785.027262 | -785.075412 | -785.026844 | -785.033426 | 1590.85 | -73.17 | -83.83 |
Table 4: $\Delta H$-CBS/ $\Delta H$-G3B3 enthalpy at 298.15 K of reaction NMP+ Cl Obtained at CBS-QB3//B3LYP/6-311G++(2d,pd) / Obtained at G3B3//B3LYP/6-311G++(2d,pd)

|       | $\Delta H$-CBS | $\Delta H$-G3B3 |
|-------|----------------|-----------------|
| NMP+Cl | 0              | 0               |
| RC1    | -1.71          | -4.06           |
| RC2    | -1.31          | -2.63           |
| RC3    | -1.69          | -2.18           |
| RC4    | -1.78          | -3.30           |
| TS1    | 6.44           | 6.17            |
| TS2    | 12.7           | 8.33            |
| TS3    | 20.97          | 32.72           |
| TS4    | 19.99          | 31.11           |
| PC1    | -13.34         | -9.61           |
| PC2    | -13.26         | -9.43           |
| PC3    | 3.47           | -8.77           |
| PC4    | 0.85           | -8.62           |
| R1+HCl | -11.12         | -3.79           |
| R2+HCl | -11.6          | -3.59           |
| R3+HCl | 5.41           | -2.75           |
| R4+HCl | 1.67           | -0.97           |
Table 5. Rate Constants (cm$^3$ molecule$^{-1}$ s$^{-1}$) and Branching Ratio ($\beta$) within the Temperature Range 273–380 K for Reaction NMP + Cl at CBS-QB3//B3LYP/6-311G++(2d,pd).

| T   | $K_I$       | $K_{II}$  | $K_{overall}$ | $\beta$ |
|-----|-------------|-----------|---------------|---------|
| 273 | 4.87E-10    | 3.99E-10  | 8.87E-10      | 0.55    |
| 280 | 4.93E-10    | 4.04E-10  | 8.98E-10      | 0.55    |
| 290 | 5.02E-10    | 4.12E-10  | 9.14E-10      | 0.55    |
| 298 | 5.09E-10    | 4.17E-10  | 9.27E-10      | 0.55    |
| 300 | 5.11E-10    | 4.19E-10  | 9.30E-10      | 0.55    |
| 310 | 5.20E-10    | 4.26E-10  | 9.46E-10      | 0.55    |
| 313 | 5.22E-10    | 4.28E-10  | 9.50E-10      | 0.55    |
| 320 | 5.28E-10    | 4.33E-10  | 9.61E-10      | 0.55    |
| 330 | 5.37E-10    | 4.40E-10  | 9.76E-10      | 0.55    |
| 333 | 5.39E-10    | 4.41E-10  | 9.81E-10      | 0.55    |
| 340 | 5.45E-10    | 4.46E-10  | 9.91E-10      | 0.55    |
| 350 | 5.53E-10    | 4.53E-10  | 1.01E-09      | 0.55    |
| 353 | 5.55E-10    | 4.55E-10  | 1.01E-09      | 0.55    |
| 360 | 5.61E-10    | 4.59E-10  | 1.02E-09      | 0.55    |
| 380 | 5.77E-10    | 4.72E-10  | 1.05E-09      | 0.55    |
Table 6. Rate Constants (cm$^3$ molecule$^{-1}$ s$^{-1}$) and Branching Ratio ($\beta$) within the Temperature Range 273–380 K for Reaction NMP + Cl at G3B3//B3LYP/6-311G++(2d,pd)

| T   | $K_1$   | $K_2$   | $K_{overall}$ | $\beta_1$ |
|-----|---------|---------|---------------|-----------|
| 273 | 4.62E-11| 4.62E-11| 9.24E-11      | 0.5       |
| 280 | 4.60E-11| 4.62E-11| 9.22E-11      | 0.5       |
| 290 | 4.57E-11| 4.61E-11| 9.18E-11      | 0.5       |
| 298 | 4.55E-11| 4.60E-11| 9.16E-11      | 0.5       |
| 300 | 4.55E-11| 4.60E-11| 9.15E-11      | 0.5       |
| 310 | 4.52E-11| 4.59E-11| 9.11E-11      | 0.5       |
| 313 | 4.51E-11| 4.59E-11| 9.10E-11      | 0.5       |
| 320 | 4.49E-11| 4.58E-11| 9.07E-11      | 0.5       |
| 330 | 4.46E-11| 4.57E-11| 9.03E-11      | 0.49      |
| 333 | 4.46E-11| 4.56E-11| 9.02E-11      | 0.49      |
| 340 | 4.44E-11| 4.55E-11| 8.99E-11      | 0.49      |
| 350 | 4.41E-11| 4.54E-11| 8.94E-11      | 0.49      |
| 353 | 4.40E-11| 4.53E-11| 8.93E-11      | 0.49      |
| 360 | 4.38E-11| 4.52E-11| 8.90E-11      | 0.49      |
| 380 | 4.32E-11| 4.48E-11| 8.81E-11      | 0.49      |