Theoretical studies on the kinetics and reactivity of the gas-phase addition and H-abstraction reactions of methylpyridine with atomic chlorine

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A R T I C L E   I N F O

A B S T R A C T

The atmospheric chemistry of pyridine and methylpyridine (picoline) are important because of its presence in the atmosphere from industrial sources and also from the coal combustion. Theoretical investigations are carried out on the mechanism, kinetics and thermochemistry for the reaction between methylpyridine [$C_5H_4(CH_3)N$, picoline] and atomic chlorine (Cl) using the hybrid density functional model BB1K. Thermodynamic and kinetic parameters for addition of Cl to N-atom of picoline as well as to ring carbon sites and hydrogen abstraction reactions from all the potential sites are calculated. This helps to identify the most reactive reaction channels in different temperature range.

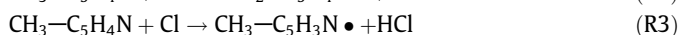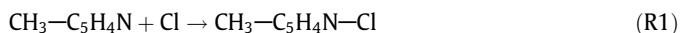© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The ion content of the troposphere influences the atmospheric electrical conductivity and ion recombination processes could trigger the formation of ultrafine aerosol particles [1]. This ion-induced nucleation process can have impact in earth's climate because of its potential role as cloud condensation nuclei [2]. The presence of the protonated ions of pyridine and its other derivatives in atmosphere have been detected by experimental measurement technique [3]. The atmospheric sources of the natural precursors of these ions are believed to be the coal combustion, tobacco burning and industrial waste [4–6].

The atmospheric chemistry of pyridine derivatives is thus important to know the degradation channels of these compounds. Reaction with OH radical is generally believed to be the major atmospheric degradation channel for pyridine. However, importance of its reaction with atomic chlorine (Cl), especially in the coastal atmosphere, has also been emphasized [7]. Several new investigations in coastal air have indeed shown that photolysis of molecular chlorine can yield sufficiently high concentrations of Cl atoms to render the oxidation of common gaseous compounds by this species to compete or even up to 100 times faster than the analogous reaction with the OH radical [8–11]. Thus reaction with Cl atom is also an important degradation channel for many atmospheric compounds and has to be considered while estimating atmospheric lifetimes of a compound [12].

The addition of OH to the ring carbon atom is known to be the dominant reaction channel at lower temperature for the pyridine + OH reactions, whereas hydrogen abstraction channel becomes important at higher temperature [13–15]. It has also been shown that OH-addition is preferred at the *meta* site, on the other hand, *ortho* site is preferred for H-abstraction reaction. Recently, Yeung and Elrod studied the kinetics of the reactions between methyl and ethyl substituted derivatives of pyridine and OH radical [14]. The hydrogen abstraction channel is likely to be competitive with the addition of OH to the ring carbons in methylpyridine (picoline) and ethylpyridine even at room temperature. This is because of the presence of an alkyl side chain from where hydrogen abstraction is likely to be much easier than that from the ring carbon. However, there are very limited data for the reaction between pyridine and its derivatives with atomic chlorine (Cl), although this reaction is believed to be important for the atmospheric degradation of pyridine derivatives, especially in coastal areas. Recently we have studied the kinetics of the reaction between pyridine and chlorine using DFT based BB1K method and the results are found to be comparable with the experimental values [16]. At lower temperature, addition of Cl-atom to the N-atom of pyridine is seen to be the major reaction channel, whereas hydrogen abstraction from ring carbon dominates at higher temperature. In this work, we have studied in detail the both addition (R1) and H-abstraction reactions (R2) and (R3) of 2-, 3- and 4-picoline with atomic chlorine using BB1K and ab initio methods:

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$$CH_3\text{—}C_5H_4N + Cl \rightarrow CH_3\text{—}C_5H_4N\text{—}Cl \qquad (R1)$$

$$CH_3\text{—}C_5H_4N + Cl \rightarrow \bullet CH_2\text{—}C_5H_4N \bullet + HCl \qquad (R2)$$

$$CH_3\text{—}C_5H_4N + Cl \rightarrow CH_3\text{—}C_5H_3N \bullet + HCl \qquad (R3)$$

To the best of our knowledge, this is the first attempt to study the kinetics of these reactions between 2-, 3- and 4-picoline and Cl atom. Theoretical studies can be very helpful to identify the actual reaction center at which addition or abstraction may occur and also to understand the reactivity and mechanism of the reaction. In this context, barrier heights for the Cl addition to all the potential sites (N-atom and ring carbons) and H-abstraction from the C–H bonds of methyl group as well as ring C–H bonds of picoline and the thermochemistry for all these possible addition and abstraction products are determined from the density functional theory (DFT) based BB1K [17]. The rate constants for these reaction channels are calculated to estimate the relative importance of these processes in the atmospheric degradation of picoline.

2. Computational method

The geometries of 2-, 3- and 4-picoline, transition states (TS) for Cl addition and H-abstraction reactions, addition products and the radicals produced after hydrogen abstraction from the methyl group of picoline were optimized using BB1K/6-31+G(d,p) method [17]. The BB1K method is specifically designed for kinetic calculations and is known to produce reliable thermodynamic and kinetic parameters for radical reactions including reactions with Cl atoms [16,18–20].

Frequency calculations were performed at each stationary point to characterize the minimum energy equilibrium structure and transition state. Single configuration ab initio calculations [like (U)MP2] may not be reliable for these systems because of high spin contamination for the open shell systems. The $\langle S^2 \rangle$ value for the doublet TS system was found to be 1.32. On the other hand the $\langle S^2 \rangle$ value for the open shell doublet systems remains within 0.78 for the BB1K method. BhandhLYP/6-311G(d,p) and single point (RO)MP2/6-311++G(d,p) calculations were also performed at selected points on the potential energy surface to check the reliability of the results.

The equilibrium constant for adduct formation was calculated from the standard statistical mechanical formula [21]:

$$K_p(T) = \frac{1}{k_B T} \frac{q_{\text{pico–Cl}}(T)}{q_{\text{pico}}(T) \cdot q_{\text{Cl}}(T)} \qquad (1)$$

where q_x represents the partition function for the species x and k_B is the Boltzmann constant. The translational partition function was evaluated per unit volume. The ground $^2P_{3/2}$ and excited $^2P_{1/2}$ electronic states of Cl atom, with a splitting of 881 cm^{-1} due to spin–orbit coupling, were used for the calculation of electronic partition function.

The rate constant for H-abstraction was estimated using the conventional transition state theory (TST) [22]:

$$k(T) = \Gamma(T) \frac{k_B T}{h} \frac{q_{TS}(T)}{q_{\text{pico}}(T) \cdot q_{\text{Cl}}(T)} e^{-\Delta E_0^{\#}/RT} \qquad (2)$$

where $\Gamma(T)$ is the transmission coefficient and $\Delta E^{\#}$ is the barrier height. The value of $\Gamma(T)$ can be approximately calculated from Wigner's empirical formula [23]. In our case, however, tunneling correction is expected to be unity, because of negligible reaction barrier. All electronic structure calculations were performed using the Gaussian 03 programme [24].

3. Results and discussion

3.1. Structure of transition states

The schematic structures of 2-, 3- and 4-picoline, TS structures for the Cl addition to ring carbons (Add-TS-CX), the structure of the adduct formed from the addition of Cl to the N-atom (henceforth referred as N-adduct) of picoline and the TS structure for H-abstraction from the CH$_3$ group (Abs-TS-me) are shown in Fig. 1(A and B). We could not locate any transition state for the N-adduct formation between Cl atom and picoline. The energy shows an asymptotic behavior when N–Cl distance is changed from its equilibrium value to a longer distance. We, therefore, consider the addition of Cl to the N-atom of picoline is a barrierless process. Addition of Cl to the *ipso* position is not considered here because it is unlikely to take place due to steric repulsion. Interestingly, we have found that two different complexes can result from the addition of Cl to each ring carbon site: one is the usual product resulting from the formation of a regular C–Cl σ-bond (Add-PD) and also another reactive complex (PR-com) with a long C–Cl distance. The transition state for addition (Add-TS-CX) actually connects this PR-com with the Add-PD as shown in Scheme 1. Some key geometrical parameters for the two types of addition complexes, TS for Cl addition to ring carbon, N-adduct and TS for H-abstraction reaction are given in Table 1. It has been observed that the N-adduct formation does not induce any significant geometrical change in the pyridine moiety. The N–Cl bond lies almost along the same line of N1–C4. Only in the case of 2-picoline the N–Cl bond is tilted slightly towards the C6 atom possibly because of steric repulsion from the CH$_3$ group. The N–Cl distance in the N-adduct for all the three picolines is found to be almost the same (2.36 Å). Similar N–Cl distance was also found in the N-adduct of pyridine and Cl atom [16]. The calculated N–Cl stretching frequency vibrations in the N-adduct of 2-, 3- and 4-picoline are 201, 196 and 192 cm^{-1}, respectively, which signifies the formation of a weak bond between N-atom of picoline and Cl. For the addition product to ring-carbons, the C–Cl distance is found to be longer than the usual C–Cl distance. The TS for hydrogen abstraction from the CH$_3$ group of picoline shows a more reactant like structure, which is of course expected from the exoergic nature of this reaction.

3.2. Addition reactions

The barrier heights and the thermochemical parameters for addition reactions of Cl-atom to different ring carbons of 2-, 3- and 4-picoline are listed in Table 2. It has been established from experimental and theoretical studies that Cl + pyridine system forms an adduct where Cl is bonded to the N atom of pyridine via a two-center-three-electron bond [25–27]. The bond dissociation energy (BDE) of this N–Cl bond at 298 K was estimated to be 11.3 kcal/mol from the G2(MP2,SVP) calculation [27]. Similar value was also predicted from the experimental study and subsequent thermochemical analysis of the adduct formation [7]. Presence of an electron donating methyl group in picoline is expected to increase the basicity of N-atom resulting greater affinity to Cl atom. This is reflected in the reaction enthalpy ($\Delta_r H$) values given in Table 2. The BB1K calculated $\Delta_r H$ values for the N-adduct formations are −13.58, −13.02 and −12.97 kcal/mol for 2-, 3- and 4-picoline, respectively, whereas the same value amounts to −12.55 kcal/mol for pyridine + Cl [16]. Since no experimental results are available for comparison, it is difficult to predict the accuracy of the BB1K calculated $\Delta_r H$ values. However, our experience with pyridine + Cl system (BB1K estimated $\Delta_r H$ value is −12.5 kcal/mol, whereas experimental value is −11.3 kcal/mol)

A

2-picoline

3-picoline

4-picoline

B

N-adduct
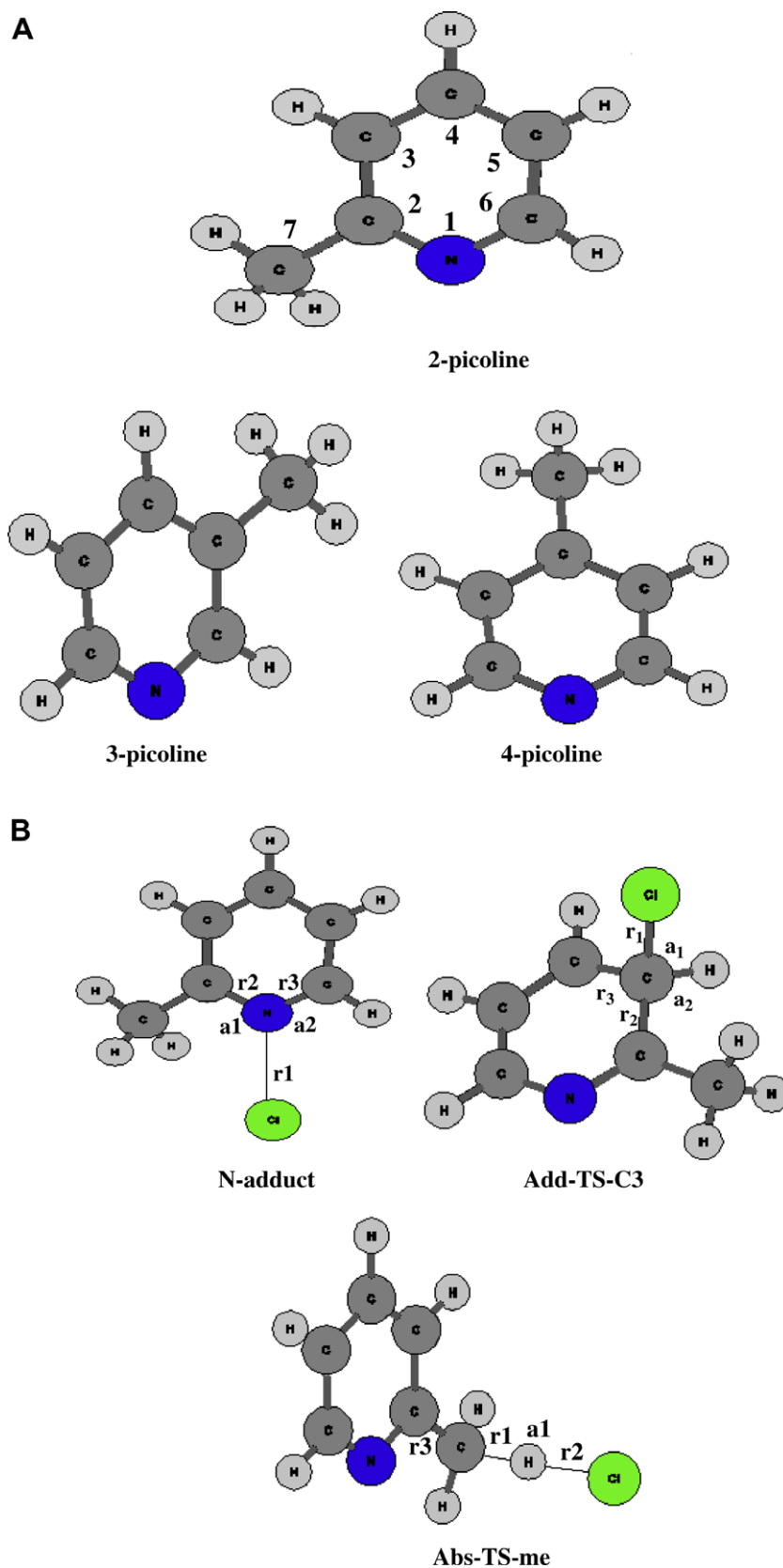
Add-TS-C3

Abs-TS-me

Fig. 1. (A) Structures of 2-, 3- and 4-picoline and the numbering system used in the text. (B) Structures of N-adduct, transition state structure (Add-TS-CX) for addition of Cl to CX ring carbon and the transition state structure (Abs-TS-me) for H-abstraction from the methyl group of 2-picoline. Similar structures are also obtained for 3- and 4-picoline and similar notations for geometrical parameters are also used for them.

suggests that the $\Delta_r H$ value obtained from the BB1K method should be within ±1 kcal/mol of the actual value. The $\Delta_r H$ value

obtained from BhandhLYP calculations is found to be close to the corresponding BB1K value and amounts to −12.74, −12.44 and
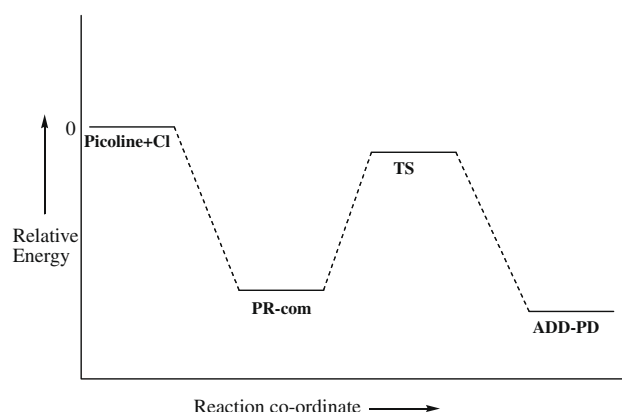
Scheme 1. Illustration of the potential energy surface for the Cl addition to ring-carbon site of picoline.

−12.49 kcal/mol, respectively, for 2, 3 and 4-picoline. The (RO)MP2 calculated $\Delta_r H$ values are seen to be almost 2 kcal/mol higher than the corresponding BB1K values.

As stated earlier, the addition of Cl to ring carbon atom results in the formation of two complexes, PR-com and Add-PD and the potential energy surface for addition reaction follows a reaction path as shown schematically in Scheme 1.

Table 1
Optimized geometrical parameters (see Fig. 1 for definition) at the BB1K level. Bond lengths are given in Å and bond angles are in degrees.

System	Adduct/TS[a]	r1	r2	r3	a1	a2
2-Picoline	N-adduct	2.361	1.326	1.319	121.9	115.6
	Add-TS-C3	2.123	1.446	1.427	92.9	102.8
	Add-PD-C3	1.898	1.461	1.483	99.9	107.6
	PR-com-C3	2.458	1.416	1.400	82.3	96.4
	Add-TS-C4	2.123	1.428	1.428	92.1	103.4
	Add-PD-C4	1.859	1.467	1.467	100.9	109.0
	Add-TS-C5	2.095	1.440	1.430	93.6	102.9
	Add-PD-C5	1.901	1.472	1.460	99.8	107.1
	PR-com-C5	2.495	1.405	1.399	85.8	92.8
	Add-TS-C6	2.155	1.428	1.377	91.8	97.7
	Add-PD-C6	1.860	1.471	1.363	101.0	106.6
	PR-com-C6	2.922	1.405	1.399	96.1	58.5
	Abs-TS-me	1.278	1.564	–	174.1	
3-Picoline	N-adduct	2.356	1.320	1.318	119.5	119.1
	Add-TS-C2	2.182	1.435	1.382	91.5	98.5
	Add-PD-C2	1.867	1.481	1.367	100.4	106.9
	PR-com-C2	2.823	1.410	1.404	96.4	65.9
	Add-TS-C4	2.140	1.434	1.427	91.9	102.5
	Add-PD-C4	1.868	1.475	1.467	100.7	109.0
	PR-com-C4	2.548	1.404	1.397	85.9	94.1
	Add-TS-C5	2.120	1.436	1.428	92.8	101.7
	Add-PD-C5	1.884	1.474	1.463	100.2	107.2
	PR-com-C5	2.547	1.403	1.397	86.0	88.1
	Add-TS-C6	2.158	1.367	1.428	91.7	98.7
	Add-PD-C6	1.864	1.414	1.471	101.0	106.8
	PR-com-C6	2.800	1.324	1.402	90.8	66.8
	Abs-TS-me	1.255	1.597	–	174.8	–
4-Picoline	N-adduct	2.356	1.319	1.319	119.7	119.7
	Add-TS-C2	2.139	1.369	1.429	92.2	98.7
	Add-PD-C2	1.857	1.415	1.472	101.1	106.9
	PR-com-C2	2.966	1.408	1.406	97.7	55.8
	Add-TS-C3	2.100	1.439	1.438	93.5	102.6
	Add-PD-C3	1.901	1.472	1.469	99.7	106.6
	PR-com-C3	2.460	1.406	1.408	86.1	95.0
	Abs-TS-me	1.276	1.562	–	175.0	–

[a] Add-TS-CX: transition state for addition of Cl at 'X' carbon atom of picoline; Add-PD-CX: product for addition of Cl at 'X' carbon atom of picoline; PR-com-CX: reactive complex for the addition of Cl at 'X' carbon atom of picoline with long C–Cl distance. PR-com-C4 for 2-picoline could not be optimized.

The barrier height for the addition of Cl-atom to ring carbons of picoline is found to be negative (listed in Table 2) relative to the energies of isolated picoline and Cl atom. As explained by Vivier-Bunge et al. [28], the final expression for the net activation energy turns out to be the usual expression for the calculation of any activation energy. Although the addition reaction barriers for the formation of the usual addition product (Add-PD) are negative with respect to $E_{reactants}$, they become positive with reference to the other complex, PR-com, and the TS actually links these two complexes for a particular carbon site. Since E_{TS} is lower than $E_{reactants}$, the addition of Cl to ring carbon is likely to have negative temperature coefficient in Arrhenius expression. The C3 and C5 positions (*meta*) are seen to be the most reactive sites for Cl-addition to ring position, except in 3-picoline where the C3 position is occupied by the CH_3 group. Similar site selectivity has also been observed for OH and Cl addition to pyridine [15,16].

Although Cl-addition to ring carbon is associated with negative activation energy and reaction energy, but the reaction free energy is positive at 240 K and above. On the other hand, the $\Delta_r E$ and $\Delta_r G$ values for the formation of N-adduct are calculated to be −13.2 and −5.3 kcal/mol, respectively. Moreover, the $\Delta_r E$ value for the N-adduct formation is found to be more than 5 kcal/mol lower than the same for Cl-addition product (Add-PD or PR-com) to ring carbon (Cl–picodienyl radical). Thus from Boltzmann distribution it can be anticipated that in thermal equilibrium and within the temperature range of our study (200–400 K), population of Cl–picodienyl radical will be negligible. Therefore the N-adduct formation is likely to be the only important addition channel for Cl-addition to picoline in tropospheric condition. Addition of Cl to ring carbon is unlikely to take place even at lower temperature. This is totally opposite to what observed for pyridine + OH and picoline + OH reactions [14,15], where addition of OH to ring carbons is the dominant reaction channel at lower temperature.

The experimental rate constant (k_{add}) for N-adduct formation for pyridine + Cl is reported to be 5×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K [7]. Similar value was also obtained from a simple collision theory based estimation and assuming that every collision to N-atom of pyridine would lead to the formation of N-adduct at lower temperature [16]. Because of slightly larger basicity of N-atom (thus likely to be more reactive) in picoline compared to pyridine, the k_{add} for N-adduct formation for picoline is expected to be little higher than that for pyridine. In fact the k_{add} values estimated from the collision frequency are 4.4×10^{-11}, 4.3×10^{-11}, 4.2×10^{-11} and 4.1×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K for 2-picoline, 3-picoline, 4-picoline and pyridine, respectively [29]. Of course, this is a very simple and qualitative estimation, but from the trend it can be stated that the actual k_{add} value for picoline should be within 5.1×10^{-11} to 5.5×10^{-11} cm^3 molecule^{-1} s^{-1}. At lower temperature, the formation of N-adduct and its unimolecular dissociation to picoline and Cl is likely to be in a rapid equilibrium. The equilibrium constant (K_P) values for the N-adduct formation calculated from Eq. (1) within a temperature range of 200–400 K are given in Table 3. The K_P values for 2-, 3- and 4-picoline at 240 K are 2.1×10^6, 4.0×10^6 and 3.9×10^6 atm^{-1}, respectively. It can be seen from Table 3 that the K_P value decreases very fast with the increase in temperature signifying the rapid unimolecular decomposition of the N-adduct to pyridine and Cl at higher temperature.

3.3. H-abstraction reactions

The barrier heights for H-abstraction from the CH_3 group of 2-, 3- and 4-picoline are tabulated in Table 2. The (RO)MP2 calculated barrier heights were seen to be quite close (within 0.2 kcal/mol) to those obtained from the BB1K method. The calculated barrier height is found to be negative relative to the energies of reactants

Table 2
Thermodynamic and kinetic parameters for the reaction between picoline with atomic chlorine (Cl) for the Cl addition channel (a) and H-atom abstraction channel (b) as obtained from the BB1K results. The values in parentheses are obtained from the BhandhLYP/6-311G(d,p) calculations. Data are in kcal/mol.

SYSTEM	Site	$\Delta E^{\#a}$	$\Delta H^{\#}$	$\Delta G^{\#}$	$\Delta_r E$	$\Delta_r H$	$\Delta_r G$
(a) Cl addition							
2-Picoline	C6	−3.65	−4.19	4.31	−5.29 [−7.12][b]	−5.70	2.74
	C3	−7.29	−7.83	0.78	−7.82 [−7.58]	−8.17	0.23
	C4	−2.19	−2.76	5.90	−3.45	−3.89	4.69
	C5	−6.46	−6.97	1.37	−6.78 [−7.12]	−7.07	0.93
	N	–	–	–	−13.20 (−12.50)	−13.58 (−12.74)	−5.35 (−4.92)
3-Picoline	C6	−4.29	−4.84	3.60	−5.81 [−6.18]	−6.18	1.91
	C2	−5.10	−5.70	3.15	−6.73 [−6.34]	−7.20	1.52
	C4	−4.44	−5.04	3.89	−5.62 [−5.09]	−6.11	2.73
	C5	−5.60	−6.09	2.17	−6.30 [−6.30]	−6.66	1.72
	N	–	–	–	−12.88 (−12.30)	−13.02	−5.84
4-Picoline	C2	−2.95	−3.53	5.27	−4.52 [−7.47]	−4.97	3.75
	C3	−7.11	−7.75	1.46	−7.48 [−7.45]	−7.91	1.01
	N	–	–	–	−12.86 (−12.36)	−12.97	−5.84
(b) H-atom abstraction by Cl							
2-Picoline	CH$_3$ group	−4.14 (−2.03)	−4.72 (−2.60)	3.48 (5.66)	−10.07 (−10.46)	−9.78 (−10.18)	−10.75 (−11.06)
3-Picoline	CH$_3$ group	−4.98 (−2.88)	−5.61 (−3.47)	2.76 (4.89)	−11.24 (−11.66)	−10.95 (−11.38)	−11.81 (−12.19)
4-Picoline	CH$_3$ group	−3.49 (−1.38)	−4.11 (−1.99)	4.47 (6.74)	−10.34 (−10.72)	−10.09 (−10.48)	−10.30 (−10.45)

[a] Relative to the energies of isolated reactants, as shown in Scheme 1.
[b] The first value corresponds to the binding energy of the usual σ-bonded complex (Add-PD) and the value within brackets corresponds to the other addition complex (PR-com) between picoline and Cl atom.

Table 3
Equilibrium constant (atm^{-1}) values for the formation of N-adduct between Cl and 2-, 3- and 4-picoline as obtained from the BB1K results.

T (°K)	2-Picoline	3-Picoline	4-Picoline
200	6.6×10^8	9.7×10^8	9.2×10^8
225	1.5×10^7	2.5×10^7	2.4×10^7
240	2.2×10^6	4.0×10^6	3.9×10^6
250	6.9×10^5	1.3×10^6	1.3×10^6
275	5.7×10^4	1.2×10^5	1.2×10^5
300	7.2×10^3	1.7×10^4	1.7×10^4
325	1.3×10^3	3.1×10^3	3.1×10^3
350	2.8×10^2	7.4×10^2	7.4×10^2
375	7.6×10^1	2.1×10^2	2.2×10^2
400	2.4×10^1	7.2×10^1	7.3×10^1

Table 4
The bond dissociation enthalpy for different ring C–H bonds and the C–H bond in the methyl group of picoline calculated at the BB1K level.

System	C2–H	C3–H	C4–H	C5–H	C6–H	CH2–H
2-Picoline	–	110.42	109.13	111.43	104.25	89.41
3-Picoline	103.96	–	108.97	110.75	105.05	87.47
4-Picoline	104.68	110.83	–	110.83	104.68	88.32

for all the three systems. But the $\Delta G^{\#}$ value given in Table 2 does show a free energy bottleneck for the H-abstraction reaction. We could not locate any pre-reactive complex associated with the abstraction process. However as stated earlier, since E_{TS} is lower than the $E_{reactants}$, activation energy for H-abstraction from the CH$_3$ group will be negative. Our results in Table 2 also show that H-abstraction from the CH$_3$ group of 2-, 3- and 4-picoline is associated with significantly negative (more than 10 kcal/mol) $\Delta_r E$ and $\Delta_r G$ values. The negative $\Delta_r G$ value along with negative or negligible activation energy suggest that H-abstraction will be one of the most important reaction channels for Cl + picoline system, especially at higher temperature. This is primarily due to the presence of a methyl (–CH$_3$) group in picoline. As the C–H bond with aromatic ring carbon is much stronger than that in the CH$_3$ group, the barrier height for hydrogen abstraction from ring C–H bond is likely to be much higher.

The calculated BDE values for the different C–H bonds in picoline are given in Table 4. The C–H bond in the CH$_3$ group is seen to be weaker by more than15 kcal/mol from the weakest C–H bond for ring-carbons. The accuracy of our reported BDE value can be judged from the calculated BDE(C–H) value for the CH$_3$ group in toluene. Our calculated BDE value for the C$_6$H$_5$CH$_2$–H bond (88.2 kcal/mol) is quite close to the experimental value of 88.5 ± 1.5 kcal/mol [30]. Comparing with the BDE(C–H) values for CH$_4$ (104.9 ± 0.1 kcal/mol) [30] and CH$_3$F (101.3 ± 0.9 kcal/mol)

[30], the C–H bond of CH$_3$ group is found to become much weaker when it is attached to an aromatic ring. The aromatic ring activates the C–H bond in the alkyl group attached to it. The barrier heights for H-abstraction reactions are known to be well correlated with the BDE values for the breaking bonds for a particular abstracting radical and the lower is the BDE the lower is the barrier height [31]. Because of higher BDE(C–H) value, abstraction of hydrogen by Cl from aromatic ring is unlikely to contribute to the H-abstraction channel. In fact, we have calculated the barrier height (2.6 kcal/mol) and reaction energy (5.7 kcal/mol) for hydrogen abstraction from the C2–H bond of 4-picoline. These values are found to be much higher than the corresponding values for H-abstraction from CH$_3$ group. It is, therefore, clear that H-abstraction from the CH$_3$ group (R2) will be only H-abstraction channel for picoline + Cl systems in the temperature range of our study (200–400 K). Results in Table 4 also show that among the aromatic hydrogens in all the three picoline systems, ortho C–H (C2–H and C6–H bonds) bond is the weakest. This is because of hyperconjugation interaction between N-atom lone pair and the antibonding orbital of the ortho C–H bonds [16].

To ascertain the accuracy of the BB1K (and ROMP2) calculated barrier heights for H-abstraction from the CH$_3$ group of picoline, we have calculated the barrier heights for H-abstraction from the CH$_3$ group of CH$_3$F and C$_6$H$_5$–CH$_3$ by Cl using the BB1K method. Our BB1K calculated barrier heights for CH$_3$F and C$_6$H$_5$–CH$_3$ amount to 1.26 and 1.07 kcal/mol, respectively. The best value for the barrier heights reported for these two systems are 3.4 and 2.81 kcal/mol, respectively [32,33]. Thus it seems that the BB1K calculated barrier height for H-abstraction from the CH$_3$ group of picoline is almost 2 kcal/mol lower than the actual value. Moreover, the BhandhLYP calculated barrier heights for H-abstrac-

tion reactions are nearly 2 kcal/mol higher than the BB1K calculated barrier heights. We have, therefore, adjusted the H-abstraction barrier heights by increasing the BB1K calculated barrier height by 2 kcal/mol to obtain better accuracy. Such shifting of calculated barrier height for obtaining better results is a standard practice in computational chemistry [33]. The adjusted barrier heights for H-abstraction from methyl group are −2.1, −2.9 and −1.4 kcal/mol for 2-, 3- and 4-picoline, respectively, which is almost the same as obtained from the BhandhLYP calculation (Table 2).

The rate constant (k_{abs}) for H-abstraction from the CH_3 group is calculated in the temperature range 200–400 K using the TST expression mentioned in Eq. (2) and the results are listed in Table 5. The k_{abs} value at 298 K amounts to 7.4×10^{-11}, 2.5×10^{-10} and 1.4×10^{-11} cm^3 molecule^{-1} s^{-1} respectively for 2-, 3- and 4-picoline. The experimental k_{abs} value for pyridine + Cl system at 299 K is 1.4×10^{-13} cm^3 molecule^{-1} s^{-1} [7]. Thus k_{abs} for picoline is much higher than that for pyridine and this is because of the presence of CH_3 side chain in picoline. The k_{abs} values calculated from the BhandhLYP results for 2-, 3- and 4-picoline are almost similar to those obtained from the BB1K results.

The Arrhenius expressions for k_{abs} of 2-, 3- and 4-picoline within a temperature range of 200–400 K are as follows:

$$k_{abs}(T) = 4.9 \times 10^{-12} \times \exp(817/T) \, cm^3 \, molecule^{-1} \, s^{-1} \quad (2-picoline)$$

$$k_{abs}(T) = 3.7 \times 10^{-12} \times \exp(1262/T) \, cm^3 \, molecule^{-1} \, s^{-1} \quad (3-picoline)$$

$$k_{abs}(T) = 2.3 \times 10^{-12} \times \exp(542/T) \, cm^3 \, molecule^{-1} \, s^{-1} \quad (4-picoline).$$

Fig. 2 shows the Arrhenius plot for k_{abs} for all the three picoline systems. Because of negative reaction barrier, the Arrhenius expression shows negative temperature coefficients of k_{abs} for all the three picoline systems.

At any given temperature, the total rate constant (k_{tot}) is the sum of the rate constant for N-adduct formation (k_{add}) and the rate constant (k_{abs}) for the H-atom abstraction from the CH_3 group,

$$k_{tot} = k_{add} + k_{abs}.$$

Since the k_{abs} value is almost an order of magnitude higher than the k_{add} value in the temperature range of 200–250 K, the total rate constant will be close to the k_{abs} value. The free energy change with temperature for the N-adduct formation and H-abstraction reaction from the CH_3 group of picoline is shown in Fig. 3. It describes that at higher temperature $\Delta_r G$ value for addition channel leading to the formation of N-adduct decreases rapidly because of negative entropy factor, whereas $\Delta_r G$ value for the abstraction reaction becomes more negative. Thus the addition reaction will no longer be important at higher temperature (>300 K) and H-abstraction will be the only major degradation channel for picolines and k_{tot} will be same as k_{abs}. Because at higher temperature, the N-adduct will be disso-
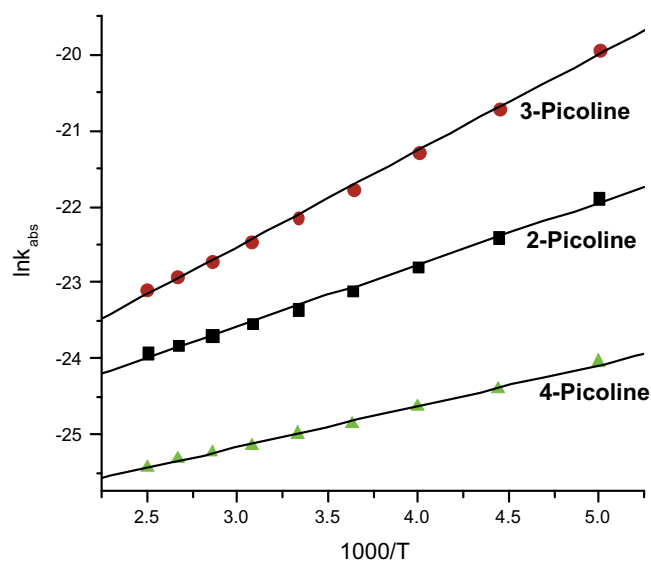

Fig. 2. Arrhenius plot for the rate constant (k_{abs} in cm^3 molecule^{-1} s^{-1}) for H-abstraction reactions from the CH_3 group of 2-, 3- and 4-picoline.
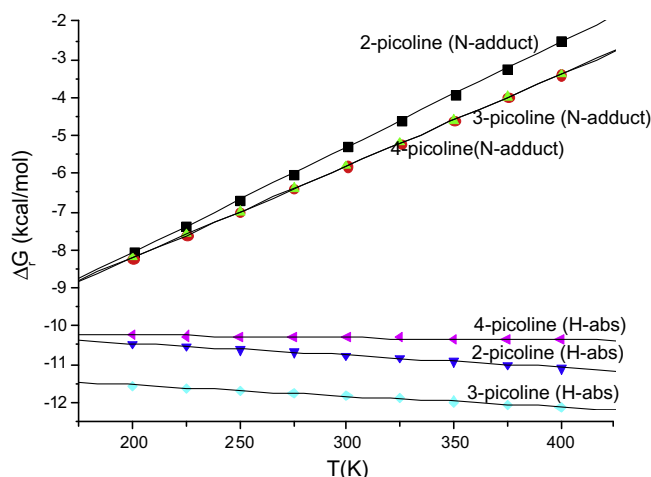

Fig. 3. Variation of reaction free energy ($\Delta_r G$) with temperature for the Cl-addition to N-atom (N-adduct) and H-abstraction reactions from the CH_3 group of 2-, 3- and 4-picoline.

ciated fast to pyridine and Cl and the addition channel will have practically no impact in the degradation of picoline.

The experimental rate constant for picoline + OH reaction is an order of magnitude greater than that for pyridine + OH reaction [14]. Our calculation shows that the rate constant of picoline + Cl reaction should be nearly an order of magnitude larger than the rate constant for pyridine + Cl reaction (5×10^{-11} cm^3 molecule^{-1} s^{-1}) at lower temperature (<240 K). At higher temperature, this difference may become higher because addition channel will not be important and k_{abs} for picoline should be at least two orders of magnitude greater than that for pyridine.

4. Summary and conclusions

The addition and H-abstraction reactions of Cl + picoline systems have been studied by using DFT methods, BB1K and BhandhLYP. Picoline is seen to form an adduct where Cl is bonded to the N atom of picoline via a two-center-three-electron (2c-3e) bond. The bond dissociation enthalpy (BDE) of this N–Cl bond at 298 K are −13.58, −13.02 and −12.97 kcal/mol for 2-, 3- and 4-picoline

Table 5
The calculated values of the rate constant for hydrogen abstraction (k_{abs}) from the CH_3-group of 2-, 3- and 4-picoline.

T (°K)	$k_{abs} \times 10^{10}$ cm^3 molecule^{-1} s^{-1}		
	2-Picoline	3-Picoline	4-Picoline
200	3.14	22.01	0.36
225	1.87	10.27	0.25
250	1.26	5.68	0.20
275	0.93	3.55	0.16
300	0.73	2.43	0.14
325	0.60	1.78	0.13
350	0.51	1.38	0.12
375	0.45	1.12	0.11
400	0.41	0.94	0.10
298	0.74	2.49	0.14

respectively. The calculated N–Cl stretching frequency vibrations in the N-adduct of 2-, 3- and 4-picoline are 201, 196 and 192 cm^{-1}, respectively, which signifies the formation of a weak bond between N-atom of picoline and Cl.

Two possible addition complexes are identified for the addition of Cl to each ring carbon site: one with the usual σ-bond between C and Cl and other with a rather long C–Cl distance (∼2.5 Å). But the Cl addition to ring carbon sites is unlikely to have any practical importance in the kinetics of picoline + Cl systems because of much lower energy N-adduct formation process. The rate constant for N-adduct formation, k_{add}, value for picoline at lower temperature (<240 K) should be within 5.1×10^{-11} to 5.5×10^{-11} cm^3 molecule^{-1} s^{-1}. The equilibrium constant (K_P) values for the N-adduct formation at 240 K are 2.1×10^6, 4.0×10^6 and 3.9×10^6 atm^{-1}, respectively, for 2-, 3- and 4-picoline. The K_P value is seen to decrease very fast with increasing temperature, indicating the increasing rate of reverse unimolecular dissociation reaction. Thus at higher temperature, the N-adduct formed will be immediately dissociated to picoline and Cl and unlikely to have any contribution in degradation of picoline.

Our results show that H-abstraction from the CH_3 group is the most important abstraction channel and abstraction from ring C–H bonds is unlikely to takes place because of greater barrier height and endothermicity of the reaction. The k_{abs} value at 298 K amounts to 7.4×10^{-11}, 2.5×10^{-10} and 1.4×10^{-11} cm^3 molecule^{-1} s^{-1} for 2-, 3- and 4-picoline, respectively, and is seen to be the most important reactive channel. It can also be concluded that the rate constant of picoline + Cl reaction should be somewhat greater than the rate constant for pyridine + Cl reaction (5×10^{-11} cm^3 molecule^{-1} s^{-1}) at lower temperature (<240 K). At higher temperature, H-abstraction channel will be the primary reaction channel for picoline + Cl system. The k_{abs} value for 2-picoline + Cl system (7.4×10^{-11} cm^3 molecule^{-1} s^{-1}) is almost two orders of magnitude higher the same for pyridine + Cl system (1.4×10^{-13} cm^3 molecule^{-1} s^{-1}). This difference in k_{abs} values is likely to decrease at higher temperature because of negative Arrhenius temperature coefficient of the former reaction. We also emphasize here that a very accurate kinetic data for these systems require high level of ab initio calculations and proper kinetic modeling especially for barrier less abstraction reactions. Our results give only a qualitative analysis of the kinetic and thermodynamic parameters of the title reactions that can be useful for further study.

Acknowledgement

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