Theoretical study on the reactions of CH₃NHNH₂ with ground state O(³P) atom and excited state O(¹D) atom

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(Received 9 May 2013; accepted 13 September 2013)

The reaction mechanisms of methylhydrazine (CH₃NHNH₂) with O(³P) and O(¹D) atoms have been explored theoretically at the MPW1K/6-311+G(d,p), MP2/6-311+G(d,p), MCG3-MPW91 (single-point), and CCSD(T)/cc-pVTZ (single-point) levels. The triplet potential energy surface for the reaction of CH₃NHNH₂ with O(³P) includes seven stable isomers and eight transition states. When the O(³P) atom approaches CH₃NHNH₂, the heavy atoms, namely N and C atoms, are the favourable combining points. O(³P) atom attacking the middle-N atom in CH₃NHNH₂ results in the formation of an energy-rich isomer (CH₃NHONH₂) followed by migration of O(³P) atom from middle-N atom to middle-H atom leading to the product P₆ (CH₃NNH₂⁺OH), which is one of the most favourable routes. The estimated major product CH₃NNH₂ is consistent with the experimental measurements. Reaction of O(¹D) + CH₃NHNH₂ presents different features as compared with O(³P) + CH₃NHNH₂. O(¹D) atom will first insert into C–H₂, N₁–H₄, and N₂–H₅ bonds barrierlessly to form the three adducts, respectively. There are two most favourable paths for O(¹D) + CH₃NHNH₂. One is that the C–N bond cleavage accompanied by a concerted H shift from O atom to N atom (mid-N) leads to the product P₁ (CH₂O⁺NH₂NH₂), and the other is that the N–N bond rupture along with a concerted H shift from O to N (end-N) forms P₄IV (CH₃NH₂⁺HNO). The similarities and discrepancies between two reactions are discussed.

Keywords: reaction mechanism; CH₃NHNH₂; O(³P); O(¹D)

1. Introduction

Hydrazine (N₂H₄) is the classical rocket fuel with notable advantages such as high reaction capabilities, high energy density, low molecular weight of the combustion products, and no special requirement for the production bases [1]. However, the thermodynamic stability of N₂H₄ is not good enough, and N₂H₄ is hard to remain in the liquid state over a wide temperature range. With the substitution of methyl for one hydrogen in N₂H₄, the formed compound methylhydrazine (CH₃NHNH₂) presents better thermodynamic stability and better remaining-liquid-state ability over a wide temperature range [1]. Thus, it drew much more attention as an important rocket propellant. Rocket exhaust effluent including raw fuel fragments will not only contaminate the surface of the onboard instrumentation to reduce the lifetime or performance [2], but also degrade the ambient atmospheric optical environment due to chemiluminescent interactions both in the near- and far-fields of the expanding plume [3]. Oxidation by O atoms is one of the main processes that determine the fate of the diamine fuel fragments within the thermospheric plume. As stated by Vaghjiani [3], it is desirable to accurately determine the product distributions and the reactivity trends in O atom reactions with diamines, not only for carrying out reliable plume-radiance calculations but also for properly simulating the combustion of these fuels in N₂O₄. Therefore, chemical kinetics studies of CH₃NHNH₂ with O(³P) atoms have attracted lots of attentions.

According to the Lang’s report [4], the rate constants for the reaction of CH₃NHNH₂ + O are larger than those of reaction N₂H₄ + O. Moreover, it was estimated that the primary reaction step should be hydrogen abstraction or the attacking of methyl group by O atoms. In addition, Vaghjiani [3] pointed out that direct H abstraction by the O atom from N–H or C–H bonds plays a relatively minor role in the overall reaction mechanism since low OH yields are determined. Removal of hydrogen atom may occur in other processes such as addition, elimination, etc. The mechanism and rate constants of H-abstraction process have been studied in our other work [5], but the discrepancy between the theoretical and experimental values in higher temperatures is large beyond the acceptable scope. Therefore, other feasible pathways should be considered for the reaction of CH₃NHNH₂ + O. Products CH₃NNH (not CH₃NNH₂) and CH₃NHNH or CH₃NNH₂ were detected [3]. However, no actual yields for the carbonaceous species and...
detailed mechanisms were reported in both literatures [3,4]. It is important and desirable to exactly identify the product distributions and the detailed reaction mechanism of O atom with CH₃NHNH₂ for elucidating the combustion and oxidation processes. Except for the O(3P) atom, excited O(1D) species is also a primary component in the atmosphere. Therefore, the reaction of CH₃NHNH₂ + O(1D) should also be considered to obtain more reliable and more complete reaction mechanisms. To our best knowledge, no experimental or theoretical study has focused on the reaction of CH₃NHNH₂ with O(1D). The general purposes of this paper are to provide the detailed information of isomerisation or dissociation pathways for both reactions of CH₃NHNH₂ + O(3P) and CH₃NHNH₂ + O(1D), to determine the products to assist further experiments, and to make a comparison between two title reactions in order to deeply understand the combustion process of CH₃NHNH₂.

2. Computational methods

All electronic calculations were carried out using the GAUSSIAN 09 program package [6]. The geometries of stationary points including reactants, minimum isomers, transition states, and products were fully optimised by modified Perdew–Wang one-parameter model for kinetics (MPW1K) [7] with the 6-311 + G(d,p) basis set (MPW1K/6-311 + G(d,p)) and restricted or unrestricted second-order Møller–Plesset perturbation theory (MP2) [8] with the same basis set (MP2/6-311 + G(d,p)). The stationary nature of structure is identified by the number of imaginary frequency, i.e. 0 is for the local minimum and 1 is for the transition state. The zero-point energy (ZPE) corrections were obtained at the same level of theory. Single-point calculation was performed at the MCG3-MPWPW91 [9] level (a multi-coefficient modification of the Gaussian-3 electronic structure method by empirically mixing correlated wave-function methods and density-functional methods) and CCSD(T) level [10] (coupled-cluster approach with single and double substitutions including a perturbative estimate of connected triple substitutions) with the cc-pVTZ basis set. Note that an unrestricted Hartree–Fock based treatment is being used. The minimum energy path was performed by the intrinsic coordinate theory at the MPW1K/6-311 + G(d,p) and MP2/6-311 + G(d,p) levels to confirm that the obtained transition states really connect the designated intermediates.

3. Results and discussions

Optimised geometries of some local minimum and transition states involved in two reactions O(3P) + CH₃NHNH₂ (R1) and O(1D) + CH₃NHNH₂ (R2) at the MPW1K/6-311 + G(d,p) level are displayed in Figures S1 and S2, respectively, of the Supporting Information. The optimised geometries of OH radical and CH₄ molecule agree well with the experimental values [11,12]. The calculated coordinates and harmonic frequencies of all species involved in the two reactions are given in Tables S1–S4 of the Supporting Information. In addition, the (S¹) values are also listed in Table S3. The (S²) values for the triplet range from 2.01 to 2.08 at the MPW1K/6-311 + G(d,p) level, which are slightly higher than the value of a pure triplet (the exact value for a pure triplet is 2.0) with a maximum error within 4%. Since the calculated values of (S²) differ from s(s + 1) (s equals 1/2 times the number of unpaired electrons) by less than the permitted criterion of 10% [13], the spin contamination can be negligible. Similar behaviour is observed for the doublet, which will not be discussed again.

The energetic profiles of two reactions obtained at the MCG3-MPWPW91/MPW1K/6-311 + G(d,p) level are presented in Figures 1 and 2. The ZPE correction is included and the energy of reactants is set to be zero for reference. In this work, the energy of reactant R is set to be zero for reference to calculate the relative energy, while the barrier height is measured from the corresponding complex energy level.

3.1. Reaction O(3P) + CH₃NHNH₂ (R1)

3.1.1. Reaction pathways

There are four potential kinds of binding sites in the course of O(3P) atom attacking CH₃NHNH₂: H atoms and three heavy atoms in CH₃NHNH₂. It is an elementary reaction when O(3P) atom abstract one of the H atoms in CH₃NHNH₂, which is studied in detail in our other work [5]. Therefore, the primary aim of this work is to provide a deep insight into the detailed mechanism of O(3P) atom approaching three heavy atoms, i.e. middle-N attack, end-N attack, and end-C attack. The reaction of O(3P) + CH₃NHNH₂ is classified into seven paths, denoted as routes 1–7, leading to six products, as follows:

When O(3P) atom nears the N atom in the amino group of CH₃NHNH₂, a pre-reaction complex is formed barrierlessly. We have failed to locate the transition state from R to a at the MPW1K/6-311 + G(d,p) level. The relaxed potential energy curve for the formative process of CH₃NHNH₂O at the MPW1K/6-311 + G(d,p) level of theory is calculated to further confirm whether this process possesses a barrier.
The forming N–O bond is fixed at the values from 2.2 to 7.0 Å with an interval of 0.05 Å, and the other geometric parameters are optimised for each value of the N–O distance. The minimum point with a N–O distance of 2.35 Å in Figure S3 of the Supporting Information corresponds to complex a at the MPW1K/6-311 + G(d,p) level. In complex a, the bond distance of O–N2 is 2.37 Å, which is longer than the equilibrium O–N covalent bond length (1.26 Å) but shorter than the sum of the van der Waals radii of N and O atoms (3.07 Å). It suggests that the weak interaction is formed between O and N2 atoms, which are easy to take isomerisation. There is no big change between the structure of complex a and TSaa1, only with a bit turning of the O atom from N2 atom to the H6 atom to facilitate the H6 shifting between N2 atom and O atom. The bond length of O–H (0.98 Å) in complex a1 is almost equal to that of O–H bond length in the isolated OH radical, which indicates that the OH radical is combined with the end-N atom through the weak interaction. Consequently, complex a1 would dissociate easily to form product P1 (CH3NNH + OH). The geometry parameters of a1 are close to those of CH3NNH.

Only one transition state is included in the whole process from adduct a to product P1 with the relative energy of 6.60 kcal mol$^{-1}$. Thus, route 1 will be one of the most favourable pathways. Alternatively, a can isomerise to another isomer a2 via N–N bond rupture with the relative energy of 24.03 kcal mol$^{-1}$, which indicates that the cleavage of N–N bond is hard to happen.

In contrast, no adduct is located when O(3P) atom approaches the C atom (route 3) and the imino-N atom (routes 4–7). Route 3 is an elementary reaction corresponding to the break of C–N bond via the transition state TSRb with much high relative energy of 32.94 kcal mol$^{-1}$ to produce adduct b. Then, adduct b directly dissociates to produce P3 (CH3O + NH2NH) without any barrier height. Therefore, route 3 has little opportunity to occur.

The association of O(3P) atom with the nitrogen of imino group will form an adduct c via the transition state TSRc with a small barrier height of 1.24 kcal mol$^{-1}$ followed by four routes. The adduct c will either dissociate to product P4 (CH3NONH2 + H) via N1–H4 bond cleavage through transition state TScP4 (route 4), or undergo...
displacement to form $c_1$ via C–N bond rupture through transition state $TSc{c}1$ leading to product $P5$ ($CH_3 + NOHNH_2$) (route 5).

In route 6, three steps are developed by adduct $c$, i.e. $c \rightarrow c_2 \rightarrow a_1 \rightarrow P1$ ($CH_3NHNH + OH$). The O atom transfers from N1 atom to H4 atom through $TSc{c}2$ to form intermediate $c_2$. The structure of $TSc{c}2$ is similar to that of $c$ except that the N1–O bond length is increased and O–H4 bond distance is decreased to promote the O–H4 bond formation. Subsequently, the complex $c_2$ takes O migration from H4 to H6 atom associated with the N2–H6 bond rupture via transition state $TSc{c}2a_1$. The relative energies of $TSc{c}2$ and $TSc{c}2a_1$ are 5.98 and $-4.61$ kcal mol$^{-1}$ with respect to the reactants, respectively.

As to the route 7, three steps are included. The first two steps are the same with those of route 6, i.e. (1) $CH_3NHNH_2 + O(3P) \rightarrow c$ and (2) $c \rightarrow c_2$. The third step is a process to obtain $P6$ ($CH_3NNH_2 + OH$) barrierlessly. Among routes 4–7, routes 4 and 5 have little opportunity to occur because of higher barrier, especially for route 4. As to routes 6 and 7, they have the same rate-determining step. However, the reaction steps of route 6 are one more than those of route 7. Therefore, the more competitive pathway should be route 7 leading to product $P6$ ($CH_3NNH_2 + OH$) due to less reaction steps and lower overall barrier from the intermediate $c$ to the final dissociation products.

3.1.2. Experiments and implications

Lang [4] performed the kinetic study for the reaction of $O(3P) + CH_3NHNH_2$ and pointed out that it was premature to think that just the simple hydrogen abstraction was involved in the reaction mechanism. Attacking of the methyl group and other possible channels should be considered. However, the product identification had not been obtained by him. Products $CH_3NNNH$, $CH_3NHNH$, and $CH_3NNH_2$ were detected by another group [14]. Observed product $CH_3NNH_2$ is one species of the favourable product $P6$ ($CH_3NNH_2 + OH$). The product $CH_3NNH$ is not found in our calculations, but the product $CH_3NNH_2$ will react with OH leading to $CH_3NNH$ via a simple H abstraction. Another product $CH_3NHNH$ is confirmed as one species of the feasible product $P1$ ($CH_3NHNH + OH$). Except
products, the theoretical mechanism is also in line with the experimental assumption. First, both the experimental studies indicate that removal of hydrogen atom could also well occur in an addition–elimination process except abstraction of a single H atom by atomic oxygen, which should be a complex reaction mechanism involving the formation of an initial adduct that then rapidly dissociated into a variety of products. In routes 1–2, an initial adduct indeed exists, which is formed when O atom attacks end-N in CH$_3$NHNH$_2$. Next, adduct a will rapidly dissociate into products with lower relative energy and the simplest steps, which is similar to experimental estimation. Second, experimental studies [14,15] pointed out that O-atom migration can take place either across two H atoms at the same nitrogen or between two H atoms, each one of which is situated at the two different nitrogen atoms. In route 6, O atom shifts across two H atoms belonging to different N atoms via a bridging structure of TSc2a1, which is consistent with Foner and Hudson’s conclusion [14,15]. They also stated that different-N type of bridging is favourable in O + CH$_3$NHNH$_2$ reaction. Our results present the same conclusion that route 6 is one of the most favourable pathways with the lower barrier height for rate-determining step.

3.2. Reaction O($^1$D) + CH$_3$NHNH$_2$ (R2)

Note that the relative energy discussed in Section 3.2 is relative to the energies of corresponding reactants O($^1$D) + CH$_3$NHNH$_2$.

3.2.1. Reaction pathways

The first step for reaction of CH$_3$NHNH$_2$ + O($^1$D) is different from that of the triplet potential energy surface. There are three possible insert modes for the O($^1$D) atom approaching CH$_3$NHNH$_2$, i.e. C–H bond, N(–NH–)–H bond, and N(–NH$_2$)–H bond. Three separate isomers 1a, 2a, and 3a are formed barrierlessly correlating with the following disparate steps and products. The O($^1$D) atom inserts into C–H bond to form 1a with the relative energy of $-150.85$ kcal mol$^{-1}$ at the MCG3-PMWPW91/MPW1K level. The insertion provides the intermediate 1a enough energy to take subsequent isomerisation or dissociation reactions. Similarly, O($^1$D) atom will insert into N–H bonds to form 2a and 3a corresponding to middle-N insert and end-N insert, respectively. Subsequently, various isomerisations or dissociations are identified from the initial isomers. There exists total five channels for reaction of O($^1$D) + CH$_3$NHNH$_2$. Path A is confirmed starting from 1a; paths B and C are confirmed starting from 2a; and 3a is prophase complex for paths D and E. For clarity, these processes are simply written as follows:

Path A: R → 1a → TS1aPI → P1 (CH$_2$O + NH$_2$NH$_2$) 

Path B: R → 2a → TS2a2b → 2b → TS2b2c → 2c → $P_{1\Pi}$ (CH$_3$NO + NH$_3$) 

Path C: R → 2a → TS2a2d → 2d → TS2d2e → 2e → $P_{1\Pi}$ (CH$_4$ + NONH$_2$) 

Path D: R → 3a → TS3a3b → 3b → $P_{1\Pi}$ (CH$_3$NH$_2$ + HNO) 

Path E: R → 3a → TS3a3c → 3c → TS3c3d → 3d → $P_Y$ (CH$_2$NHNHO + NH$_2$OH) 

3.2.1.1. Path A. For path A, adduct 1a can undergo C–N bond cleavage accompanied by a concerted H1 shift from O atom to N1 atom via transition state TS1aP1 leading to product P1 (CH$_2$O + NH$_2$NH$_2$). In transition state TS1aP1, the lengths of active bonds N1–H1 (1.18 Å), O–H1 (1.39 Å), and C–N1 (1.54 Å) are longer than the respective normal covalent bond distance especially for the O–H1 bond. The relative energy of TS1aP1 to the reactants (O($^1$D) + CH$_3$NHNH$_2$) is $-109.94$ kcal mol$^{-1}$ and the overall exothermicity is $-135.91$ kcal mol$^{-1}$ for path A.

3.2.1.2. Paths B and C. Two paths, i.e. paths B and C are followed after complex 2a. With respect to path B, the isomeric pair 2a and 2b can be converted to each other via a O–H single bond rotation with the barrier heights of 7.55 kcal mol$^{-1}$ (2a → 2b) and 2.23 kcal mol$^{-1}$ (2b → 2a), respectively. Subsequently, 2b will pass a transition
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3.2.1.3 Paths D and E. Similar to 2a, two paths, i.e. paths D and E, are located starting from 3a. In path D, adduct 3a can change to intermediate 3b via the N–N bond rupture along with N1–H5 bond formation. Then, hydrogen-bond complex 3b splits to PIV (CH$_3$NH$_2$ + HNO) spontaneously.

With respect to path E, 3a first isomerises to isomer 3c, followed by a concerted N1–N2 bond rupture and H migration from C to O via transition state TS2d2e (45.59 kcal mol$^{-1}$) to form 2d, followed by a concerted process of the cleavage of C–N1 bond and H4 shifting from N1 to C via transition state TS2d2e (47.98 kcal mol$^{-1}$); intermediate 2e will continue to form product PIV (CH$_4$ + NONH$_2$) barrierlessly. Therefore, path C is less favoured as compared with path B because of overcoming two high-energy transition states. Note that the barrier heights listed in the parentheses are calculated relative to the corresponding intermediate.

3.2.2. Reaction mechanism

O(3P) can barrierlessly insert into C–H, N1–H, and N2–H bonds to form the low-lying isomers 1a, 2a, and 3a respectively. There are total five energetically accessible paths starting from respective isomers. Among these channels, paths A and D should be the most two competitive pathways because the energies of rate-determining transition states TS1aP1 in path A and TS3a3b in path D are much lower than those involved in other three paths. The barrier heights of TS1aP1 and TS3a3b are 40.91 and 36.94 kcal mol$^{-1}$. Moreover, both paths A and D are one-step pathways. Therefore, two products, P1 (CH$_3$O + NH$_3$) and PIV (CH$_3$NH$_2$ + HNO) corresponding to path D, may have comparable branching ratios, while other products produced via paths B, C, and E may have less yields.

Multi-coefficient correlation methods [16–21] have proven to be very efficient for the computation of thermochemical properties and potential energy surfaces, and require significantly less computational time and disk storage than brute force methods [22–26]. To testify the accuracy of mechanism obtained at the MCG3-MPWPW91//MPW1K/6-311+G(d,p) level, all the stationary points involved in the reaction O(3P) + CH$_3$NNH$_2$ (R1) are optimised at the MP2/6-311 + G(d,p) level. It is unfortunate that the TSaa1 is not located since MP2 method is not good to search for a looser transition state. Since the barrier heights of other routes are much higher than those of routes 1 and 7, they are impossible to be favourable reaction routes. As a consequence, only the energies of route 1, route 7, and all products are refined at MCG3-MPWPW91 and CCSD(T)/cc-pVTZ levels based on the optimised geometries. The relative energies (the energy of reactants is set to be zero) obtained at various levels are summarised in Table 1. Due to the absence of the TSaa1 it is difficult to compare the relative activity of routes 1 and 7 based on the MP2-optimised geometries. The energies refined at MCG3-MPWPW91//MPW1K/6-311+G(d,p) and CCSD(T)/cc-pVTZ//MPW1K/6-311+G(d,p) levels present different results. At the MCG3-MPWPW91//MPW1K/6-311+G(d,p) level, routes 1 and 7 are competitive with the similar barrier height. However, route 7 is more favourable than route 1 with relative lower barrier height at the CCSD(T)/cc-pVTZ//MPW1K/6-311+G(d,p) level. We are struggled by the question which result is more reliable. Therefore, the reaction energies are calculated at the following levels, i.e. MCG3-MPWPW91//MPW1K/6-311 + G(d,p), CCSD(T)/cc-pVTZ//MPW1K/6-311 + G(d,p), MCG3-

| Species       | CCSD(T)//MP2 | CCSD(T)//MPW1K | MCG3//MP2 | MCG3//MPW1K |
|---------------|--------------|----------------|-----------|-------------|
| a             | --           | --0.03         | --        | --1.72      |
| TSaa1         | --           | --8.16         | --        | 6.60        |
| a1            | --           | --24.73        | --        | --27.82     |
| P1            | -18.02       | -18.57         | -21.61    | -22.10      |
| TSRc          | 3.88         | 2.49           | 2.73      | 1.24        |
| c             | -2.13        | -1.64          | -2.18     | -2.68       |
| TSec2         | 0.57         | 1.42           | 1.42      | 5.98        |
| c2            | -26.72       | -26.92         | -29.95    | -30.60      |
| P6            | -20.80       | -21.19         | -24.36    | -24.69      |
MPWPW91//MP2/6-311 + G(d,p), and CCSD(T)/cc-pVTZ//MP2/6-311 + G(d,p). The reaction energies calculated at the same higher level based on the different geometries for all products (P1 (CH3NHNH + OH), P2 (NH2O + CH3NH), P3 (CH3O + NH2NH), P4 (CH3NONH2 + H), P5 (NOHNH2 + CH3), and P6 (CH3NHNH2 + OH)) agree well with each other. Therefore, the energy is slightly affected by the different geometries. However, the reaction energies calculated at the CCSD(T) level are higher than those obtained at the MCG3-MPWPW91 level. Moreover, the reaction enthalpies ($\Delta H^{0}_{298}$) of P1 ($-21.50/-21.05$ kcal mol$^{-1}$) and P6 ($-24.05/-23.74$ kcal mol$^{-1}$) calculated at the MCG3-MPWPW91 level based on MPW1K- and MP2-optimised geometries are in good accordance with the experimental values $-21.25 \pm 2.32$ and $-23.85 \pm 2.32$ kcal mol$^{-1}$ deduced from the known experimental heats of formation: (OH, 8.85 kcal mol$^{-1}$; CH3NHNH2, 21.6 $\pm$ 0.5 kcal mol$^{-1}$; CH3NNH2, 48.5 $\pm$ 1.8 kcal mol$^{-1}$; CH3NNH, 51.1 $\pm$ 1.8 kcal mol$^{-1}$; O, 59.6 $\pm$ 0.02 kcal mol$^{-1}$) [27–30]. The reaction energies calculated at the CCSD(T)/cc-pVTZ levels based on different optimised geometries are much higher than the experimental values. Thus, it is reasonable to infer that the energies obtained at the MCG3-MPWPW91 level are reliable for title reactions.

4. Summary
The detailed mechanisms of atomic O(3P) and O(1D) with CH3NNH2 are theoretically investigated by MPW1K/6-311 + G(d,p) and MCG3-MPWPW91 (single-point) methods. The processes include insertion, association, dissociation, and isomerisation.

For the reaction of O(3P) + CH3NNH2, O(3P) atom will approach three heavy atoms, i.e. middle-N, end-N, and end-C to form seven routes and six products. Products CH3NNH2 and CH3NNH will have more yields. In contrast, reaction of O(1D) + CH3NNH2 presents totally different mechanism and products. O(1D) can barrierlessly insert into C–H, N1–H, and N2–H bonds to form the low-lying isomers 1a, 2a, and 3a: then, five reaction pathways are located. P1 (CH3O + NH2NH2) is the most favourable product and P2 (CH3NH2 + HNO) is the secondary feasible product. The present work is expected to be useful and helpful for deeply understanding the mechanism of title reactions and CH3NNH2-combustion chemistry.

Acknowledgements
We thank the State Key Laboratory of Physical Chemistry of Solid Surfaces for providing computational resources.

Funding
This work was supported by the National Natural Science Foundation of China [grant number 21003036]; the Foundation for University Key Teachers from the He’nan Educational Committee, Science Foundation of He’nan Educational Committee [grant number 2008A150005]; grant number 2011B150003; Science Foundation of Henan University [grant number SBGJ090507]; Doctor Foundation of Henan University.

Supplemental data
Supplemental data for this article can be accessed here.

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