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Theoretical study on the mechanism of the NCO + CH_3 reaction

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ABSTRACT

The reaction of NCO with CH_3 is studied at B3LYP/6-11G(d,p) and CCSD(T)/6-311++G(3df,2pd)(single-point) levels. On the singlet potential energy surface (PES), the most feasible channel is direct radical–radical recombination leading to isomers $OCNCH_3$ and $NCOCH_3$. Further isomerization and dissociation of $OCNCH_3$ and $NCOCH_3$ to yield the dissociation products need to surmount the energy barrier at least 4.7 kcal/mol with respect to reactant, which indicate that these processes are kinetically unfeasible at normal temperatures and may become feasible only at high temperatures. Compared with the singlet pathways, the triplet pathways may have less contribution to the title reaction.

1. Introduction

Methyl radical CH_3 is an important intermediate in the oxidation of methane in the atmosphere and also in combustion system [1]. On the other hand, the isocyanate radical NCO is also an important combustion intermediate because this radical contributes to the conversion of fuel nitrogen to NO*x* and to the so-called "prompt" NO formation [2]. It can be produced by HCN reactions with oxygen atoms or by CN reactions with OH or molecular oxygen. In addition, NCO radical is important in NO*x* reduction processes with cyanic acid $(HONC)_3$ or urea $((NH_2)_2CO)$ suggesting its relevance in life cycles and biochemistry [3]. Up to now, a large number of experimental studies have been reported on the NCO reactions with various species, such as Cl, NO, NO_2, CH_3OH, CH_3NO_2, CH_4–*n*Cl*n*, CCl_2F_2, CH_3CH_2OH, C_2H_2, C_2H_4, alkanes, alkenes, CH_3, etc. [4–13]. Theoretical studies of NCO with F, ^3O, NO, NO_2, OH, and C_2H_2 have also been reported [14–19]. Among these reactions, the reaction of NCO with CH_3 attracts our attention. Yet, to our best knowledge, only one experimental study has been reported up to now. The experimental study was conducted by Yide et al. over a pressure range of 2.8–4.3 Torr of CH_4 at a temperature of 293 ± 2 K. Based on the experimental studies, the most likely products are CH_3NCO and CH_3OCN via direct recombination.

In view of the absence of the mechanistic information of the NCO + CH_3 reaction, we performed a detailed theoretical study of the title reaction by constructing both singlet and triplet potential energy surfaces.

2. Computation methods

All calculations are carried out using the GAUSSIAN98 program package [20]. The optimized geometries and harmonic frequencies of the reactant, products, intermediates, and transition states are obtained at the B3LYP/6-311G(d,p) [21] level. Connections of the transition states between designated isomers or products are confirmed by intrinsic reaction coordinate (IRC) [22,23] calculations at the same level of theory. Single-point calculations are performed at CCSD(T)/6-311++G(3df,2pd) [24] level using the B3LYP/6-311G(d,p)-optimized geometries. For the species involved in the singlet PES, additional single-point calculations are performed using the composite G3B3 scheme [25,26].

3. Results and discussion

The optimized structures of reactant and products are shown in Fig. 1. For the singlet $[NOC_2H_3]$ system, the optimized structures of isomers and transition states are depicted in Figs. 2 and 3, respectively, while the energies of all species are shown in Table 1. For those of the triplet system the structures and energies are shown in Figs. 4 and 5, and Table 2, respectively. The schematic profiles of the potential energy surfaces (PES) for the NCO + CH_3 reaction at CCSD(T) level are plotted in Fig. 6a (singlet) and Fig. 6b (triplet). The total energy of the reactant **R**(NCO + CH_3) is set as zero for reference, and the symbol ^{s}**TSm/n** is used to denote the transition state connecting isomers **m** and **n**. Unless specified otherwise,

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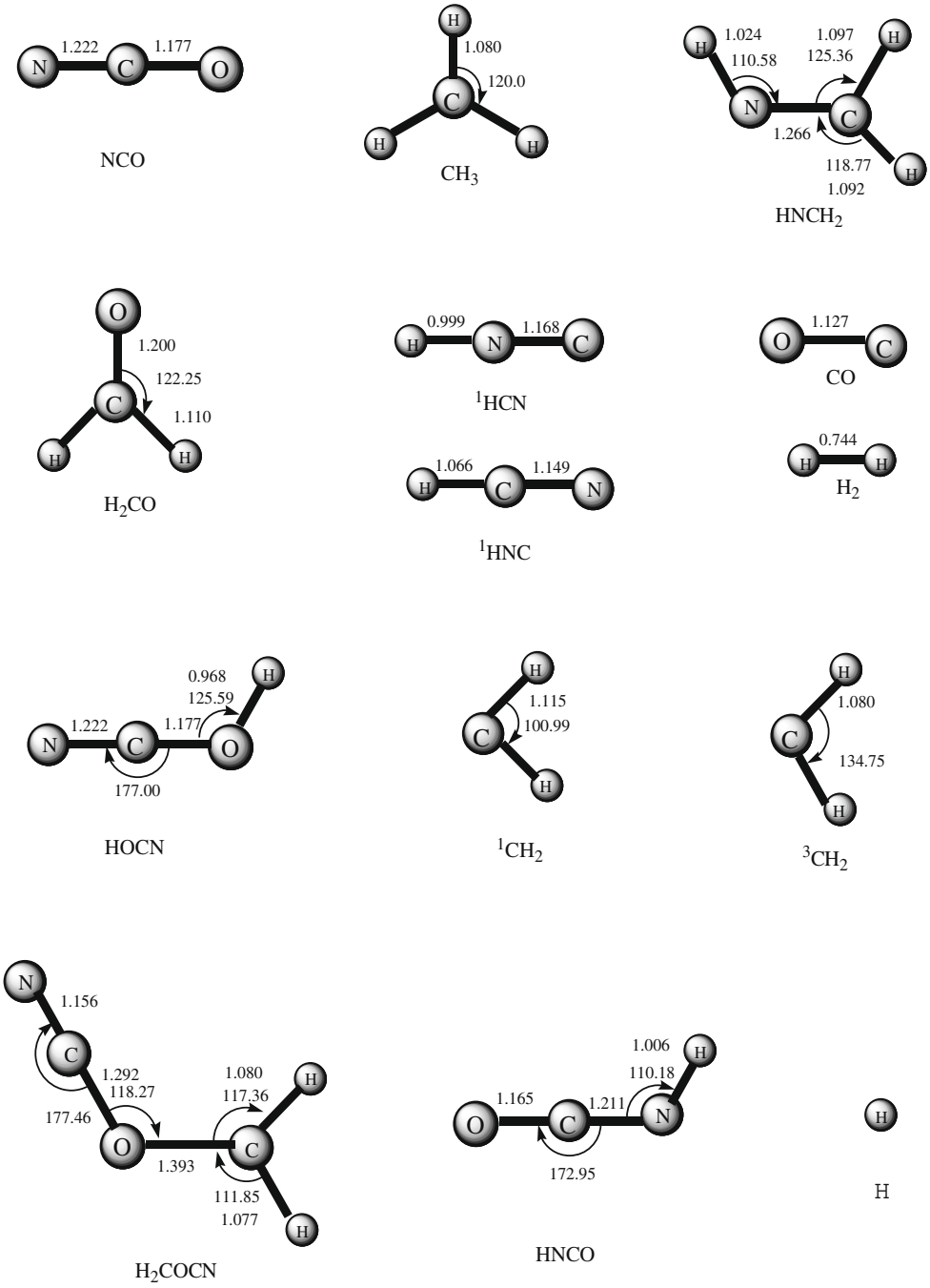

Fig. 1. The optimized structures of the reactant and products at the B3LYP/6-311G(d,p) level. Distances are given in angstroms and angles in degrees.

the relative energies mentioned here after refer to the CCSD(T)/6-311++G(3df,2pd)//B3LYP/6-311G(d,p)+ZPVE (zero point vibrational energy) level.

3.1. Singlet PES

For the singlet reaction of NCO + CH_3, two initial adducts are obtained without any encounter barrier, that is, $OCNCH_3$ ^{1}**1** (−87.6)(−88.3) and $NCOCH_3$ ^{1}**2** (−61.3)(*−61.9*). The italic value in parentheses is at G3B3 level. Obviously, formation of ^{1}**1** is favorable over ^{1}**2**. This is understandable, because the spin density is mainly located on terminal N for NCO (0.714334e, −0.08026e, and 0.365925e for N, C, and O, respectively). In the following discussion, we will discuss the reaction pathways proceeding via ^{1}**1** and ^{1}**2**.

Starting from $OCNCH_3$ ^{1}**1**, four possibilities are opened, that is, (i) isomerizes into $NCOCH_3$ ^{1}**2** through methyl radical migration from N- to O-terminal, the evolution of ^{1}**2** will be discussed later (ii) 1,4-H shift to form isomer $HOCNCH_2$ ^{1}**3**. Subsequently, ^{1}**3** can either take 1,3-H shift along with C–N bond rupture give rise to CO + $HNCH_2$ (**P$_1$**) or undergo H_2 extrusion accompanied by C–N bond rupture to form CO + H_2 + HCN (**P$_2$**) (iii) concerted 1,2-H shift and C–N bond cleavage to generate CO + $HNCH_2$ (**P$_1$**). (iv) 1,2-H shift along with C–N bond rupture to form the weakly complex OC. . .N(H)CH_2 ^{1}**4**, then ^{1}**4** will dissociate to CO + $HNCH_2$ (**P$_1$**).

Starting form $NCOCH_3$ ^{1}**2**, three kinds of pathways are identified: (i) 1,4-H shift along with C–O bond rupture to form H_2CO + HNC (**P$_3$**) (ii) 1,4-H shift accompanied by C–C bond formation to form the three-membered ring isomer HN-c-$COCH_2$ ^{1}**5**.