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ScienceDirect
Catalysis Today 119 (2007) 209–212
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Insight into the chemical reaction of CH_2OH with NO: Formation of *N*-hydroxy formamide as an isocyanic acid precursor

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Available online 7 September 2006

Abstract

This study has explored the potential energy surface on the chemical reaction of CH_2OH with NO by using ab initio calculation. We have found the new reaction pathway producing *N*-hydroxy formamide, which can further decompose to generate isocyanic acid as a reducing agent of hydrocarbons selective catalytic reduction.

Keywords: *N*-Hydroxy formamide; Isocyanic acid; Selective catalytic reduction (SCR)

1. Introduction

Detailed understanding on the chemical reaction mechanisms behind the abatement of nitrogen oxides ($DeNO_x$) emitted from various anthropogenic sources, i.e., coal-burning power station and diesel engine, is of prime scientific concern because of their detrimental influence on the formation of ozone, air toxics and secondary organic aerosol [1–3]. There are several established techniques for $DeNO_x$ such as selective catalytic reduction (SCR) [4–6], selective non-catalytic reduction (SNCR) [7–9] and non-thermal plasma (NTP) [10–12]. Interestingly, methanol is found commonly to be very effective for reduction in SCR as well as oxidation of NO in SNCR and NTP [13–19]. In SNCR and NTP, the crucial step is to produce hydroxymethyl radical (CH_2OH) through the reaction of methanol with radicals, i.e., OH, H and O. Then the CH_2OH radical contributes to the propagation steps producing active species responsible for the conversion of NO to NO_2. Despite its importance, however, there has been no thorough examination on the chemical reaction of CH_2OH with NO [20,21]. Furthermore, very little is known about the chemistry of SCR by which CH_3OH also achieves such an impressive reduction of NO like conventional hydrocarbons such as CH_4, C_2H_4, C_3H_6 and so on [4–6].

Given its chemical importance, we have set out to explore the potential energy surface on the chemical reaction of CH_2OH with NO by using ab initio calculation since methanol will favor producing CH_2OH predominantly in many processes of SCR, SNCR and NTP. Here, we have found a new reaction pathway producing *N*-hydroxy formamide (HFA). It is worthy to note that HFA can decompose to produce isocyanic acid (HNCO) and water. To the best of our knowledge, this type of new reaction channel has not been characterized before. In this study, we have also discussed possible implication of this observation for the formation of HFA and subsequent release of HNCO toward chemical processes concerning the removal of NO_x.

2. Computational methods

Standard ab initio calculations are carried out with Gaussian 98 suite of programs [22]. The fully optimized geometries are obtained by using MP2(full)/6-31G(d,p) level of theory. The optimized structures are characterized by harmonic frequency analysis. The MP2 frequencies are corrected by 0.931 and used to calculate zero-point vibrational energy (ZPVE). Intrinsic reaction coordinate (IRC) analysis is performed for each transition state to make sure that the transition structure connects two structures. The single point energy calculations at MP4SDTQ/6-311+G(d,p) level are also performed based on geometries optimized at MP2(full)/6-31G(d,p) level.

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doi:10.1016/j.cattod.2006.08.044

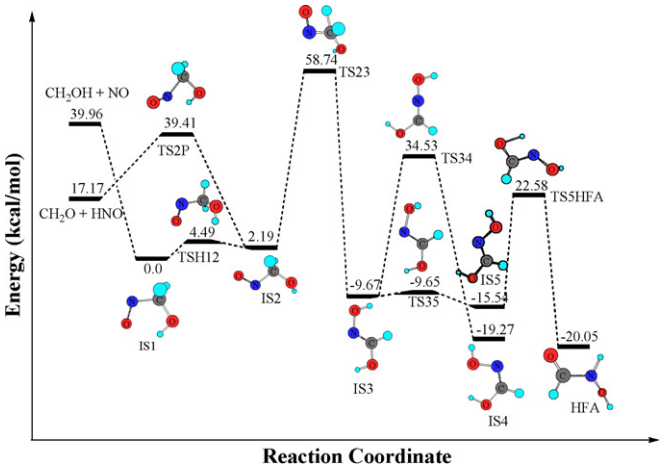

Fig. 1. Potential energy surface diagram on the chemical reaction of CH_2OH with NO. The energy values are in units of kcal/mol and have been calculated by performing single-point calculations with the MP4SDTQ/6-311+G(d,p) method and the use of the optimized geometries obtained from the MP2(full)/6-31G(d,p) calculation. The energy values are corrected for ZPVE obtained from the MP2(full)/6-31G(d,p) calculations.

3. Results and discussion

It is well known that CH_2OH, together with CH_3O radical, is central reaction intermediate in the atmospheric oxidation of volatile organic compounds (VOC) as well as in hydrocarbon combustion processes [23]. Combustion of methanol favors pyrolytic formation of CH_2OH because the C–H bond in CH_3OH is about 10 kcal/mol weaker than the O–H bond [24] and CH_2OH has a relative energy of about 6.2 kcal/mol below CH_3O [25]. Therefore, this study has been confined to the investigation on the chemical reaction of CH_2OH with NO.

The calculated energetics of the reaction intermediates and several key transition states are given in Fig. 1, along with a schematic potential surface. Only the global minimum energy structure (optimized at the MP2 level) and its corresponding energy (calculated at the MP4 level) are reported in this study.

The reaction of CH_2OH with NO leads to the formation of the stable adduct, $HOCH_2NO$ (IS1), which lies 39.96 kcal/mol lower in energy. The relative energies in Fig. 1 and Table 1 are given with respect to IS1. Initially produced $HOCH_2NO^{\dagger}$ either decomposes or loses its excess energy in collision with the bath gas (M) [20,21];

$$HOCH_2NO^{\dagger} \rightarrow CH_2O + HNO \quad (1)$$

$$HOCH_2NO^{\dagger} \xrightarrow{M} HOCH_2NO \quad (2)$$

As for the reaction of CH_2OH with NO, we note that $HOCH_2ON$, together with $HOCH_2NO$, is also possible. Investigating the detailed potential energy surface for the formation of $HOCH_2ON$ and its subsequent decomposition is the subject of next ongoing work.

Formation of IS1 has been inferred from ultraviolet absorption spectroscopy [19]. The dissociation of IS1 into CH_2O plus HNO proceeds through the conformational isomerization of IS1 into $ONCH_2OH$ (IS2) with an energy barrier of 4.49 kcal/mol, where the ONCO dihedral angles of IS1 and IS2 are 0 and 180°, respectively. On the dissociation pathway from IS2 to CH_2O and HNO products, the transition state (TS2P) with a relative energy of 37.22 kcal/mol and a backward barrier of 22.24 kcal/mol is located. The low relative energy of IS1 as compared to IS2 can be attributed to the hydrogen bonding between H atom of –OH and O atom of –NO in IS1.

Previous studies [20,21] for the chemical reaction of CH_2OH with NO have indicated that the reaction may proceed by addition or abstraction in order to form $HOCH_2NO$ or HNO plus CH_2O, respectively. Besides, we have found the previously unknown reaction pathway producing HFA in this study. In the first step, the migration of a hydrogen atom from $–CH_2–$ group to the oxygen atom of –NO group in IS2 leads to the formation of hydroxy formaldoxime HOCH=NOH (IS3) via a four-centered transition state (TS23) with an energy barrier of 56.55 kcal/mol. After that, HOCH=NOH (IS3) undergoes

Table 1
Calculated energetics of reactants, intermediates, transition states and products in the chemical reaction of CH_2OH with NO

Species[a]	MP2 (ZPVE)[b]	MP4[c]	ΔE (MP2)[d]	ΔE (MP4)[d]
CH_2OH + NO	−244.3022227 (0.0444152)	−244.465922	40.44	39.96
IS1	−244.3684423 (0.0461916)	−244.5313724	0.0	0.0
TS12	−244.3597227 (0.0464858)	−244.5245070	5.66	4.49
IS2	−244.3624932 (0.0460156)	−244.5277082	3.62	2.19
TS2P	−244.3007519 (0.0423949)	−244.4647775	40.09	39.41
CH_2O + HNO	−244.3302839 (0.025.5336)	−244.4963579	19.14	17.17
TS23	−244.2675864 (0.0409323)	−244.4325064	59.99	58.74
IS3	−244.3866965 (0.0466031)	−244.5471985	−11.20	−9.67
TS34	−244.3156737 (0.0455799)	−244.4757291	32.73	34.53
IS4	−244.4020690 (0.0475099)	−244.563401	−20.27	−19.27
TS35	−244.3853594 (0.0461618)	−244.5467164	−10.63	−9.65
IS5	−244.3953386 (0.0469904)	−244.5569395	−16.38	−15.54
TS5HFA	−244.3308577 (0.0424136)	−244.4916037	21.21	22.58
HFA	−244.4036248 (0.0475871)	−244.5647183	−21.20	−20.05

[a] See Fig. 1 for notation.
[b] MP2(full)/6-31G(d,p)//MP2(full)/6-31G(d,p) (with the zero-point vibrational energy corrected by 0.931 in parentheses).
[c] MP4SDTQ/6-311+G(d,p)//MP2(full)/6-31G(d,p).
[d] Relative energies in kcal/mol are with respect to the IS1.

subsequent isomerization to either HOCH=NOH (IS4) or HOCH=NOH (IS5). The energy barriers involved in these isomerizations are 44.2 and 0.02 kcal/mol, respectively. Conformers IS3, IS4 and IS5 differ only in the placement of the OH bond relative to the CN double bond as displayed in Fig. 1. Examining Table 1 and Fig. 1 shows that IS4 is favored by 4 and 10 kcal/mol over IS3 and IS5 conformers, respectively. The considerable stability of IS4 conformer originates from the hydrogen bonding through the five-membered ring structure as shown in Fig. 1, while one and two four-membered hydrogen bonds exist in IS3 and IS5, respectively.

As shown in Fig. 1, IS5 can undergo further hydrogen atom migration to N atom via a four-centered transition state (TS5HFA) with an energy barrier of 38.12 kcal/mol, resulting in the formation of HFA. Then HFA decompose to produce HNCO plus H_2O via reaction (3) [26]. HNCO acid is very stable in the gas phase, but hydrolyzes readily on many solid surfaces with water vapor originating from the combustion process via reaction (4) [27]:

$$HC(O)NHOH \rightarrow HNCO + H_2O \quad (3)$$

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \quad (4)$$

HNCO has been suggested as an additive for selective NO reduction according to RAPIDNOx process [8] because of the release of NH_i (for $i = 1$, 2 and 3) through the chemical reactions with radicals and water. This result leads us to expect that there may be possible reaction channels generating HNCO or NH_3 species through the reaction of CH_2OH with NO in SCR, SNCR and NTP processes.

Based on our result, the activation energy leading to IS3 from IS2 is just about 19 kcal/mol higher than that of the reaction channel leading to CH_2O plus HNO. As the temperature is increased, therefore, the reaction channel producing IS3 (eventually leading to the formation of HFA through successive isomerizations) may become significant. This suggests that it is necessary to reappraise whether the chemistry occurring in SNCR and NTP is influenced on the addition of the reaction channel leading to HFA or HNCO plus water.

As mentioned above, the responsible mechanism behind SCR process of NO reduction still remains unanswered [4–6]. The reactions in SCR which have been postulated include intermediates, i.e., nitroalkane, alkyl nitrate, alkyl isocyanate, alkyamine, etc., formed in the course of heterogeneous as well as homogenous chemical reactions of NO_x with hydrocarbons in the presence of excess O_2. These nitrogen-containing intermediates may be deposited on the catalyst in small amounts or decomposed to form amines including NH_3 as reducing agents [4–6,28,29]. They in turn react with NO_x to form the N–N bond through a combination of heterogeneous surface reactions and homogeneous gas phase reactions [30–32]. Nearly every oxygenated hydrocarbons (i.e., methanol and dimethyl ether) and hydrocarbons significantly produce CH_2OH radical during the SCR for NO_x reduction. The catalyst in SCR may facilitate the formation of HFA (or further subsequent decomposition) through reducing an activation energy barrier. This seems that the reaction of CH_2OH with NO may be also a singular important position in SCR processes. The main role of the reaction of CH_2OH with NO in SCR will be to produce carbonaceous nitrogen-containing species such as HOC(H)NOH and HFA, including the formation of HNCO or NH_3 as mentioned above.

4. Conclusions

The present study reports the formation of HOC(H)NOH and HFA through the chemical reaction of CH_2OH with NO. The structural and energetic data on the reaction of CH_2OH with NO have an important ramification for the combustion and catalytic field. We hope that looking at the chemical reaction of CH_2OH with NO from this different perspective will be helpful to better understanding on the chemical systems in which both CH_2OH and NO involve simultaneously.

Acknowledgements

This work was supported by the Korea Ministry of Environment under ‘‘The Eco-Technopia 21 program’’. I.P. Hamilton thanks the Natural Sciences and Engineering Research Council (Canada) for financial support.

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