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A DFT study of synthesis of acetic acid from methane and carbon dioxide

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Abstract

We have previously reported an experimental investigation on synthesis of acetic acid directly from CH_4 and CO_2 via dielectric-barrier discharge. In this work, a DFT study was conducted using three hybrid DFT methods in order to understand the mechanism of such direct synthesis. It suggests that the synthesis is via two pathways with CO_2^- and CO as key intermediates. The energy requirement with CO_2^- pathway is much less than that with CO. The methyl radical formation and the dissociation of CO_2 are two limiting steps for the synthesis of acetic acid directly from CH_4 and CO_2 . © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Methane is the principal component of natural gas, coalbed methane, associated gas of oil fields and some by-product gases of chemical plants. It can be also produced from some biochemical processes. The utilization of methane will play a vital role in the energy and chemical supplies in this new century thanks to the abundance of the resources. However, methane is the least reactive alkane. An intense investigation has been conducted worldwide to attempt to convert methane directly into more valuable chemicals like ethylene [1,2], methanol [1–4], acetic acid [5–9] and others

* Corresponding author. Fax: +86-22-27890078. *E-mail address:* changliu@public.tpt.tj.cn (C. Liu). [1,2]. But methane utilization still remains as a big challenge to chemists all over the world.

One of the important target molecules of direct methane conversion is acetic acid [5–9]

$$CH_4 + CO_2 \rightarrow CH_3COOH,$$

$$\Delta G^0_{400 \ K} = 80.33 \ kJ/mol$$
(1)

This reaction is not favored thermodynamically. Huang et al. [7] proposed a two-step conversion of methane into acetic acid. With the first step, methane is adsorbed on the catalyst. Then, in the second step, the adsorbed methane reacts with carbon dioxide to produce acetic acid. The main obstacle is presented by thermodynamics rather than kinetics. A periodic operation has been proposed to break the thermodynamic limitations [7]. Regarding this thermodynamic limitation, the gas

discharge plasma can be applied for thermodynamically un-favored reactions. We previously reported a direct synthesis of acetic acid from methane and carbon dioxide using dielectric-barrier discharges (DBDs) [8,9]. A yield of up to 2.7% of acetic acid has been achieved. The discharge plasma has been confirmed to be an effective way to make the reaction (1) become true even at ambient conditions. However, the reaction mechanism for such acetic acid synthesis remains unclear. To improve the synthesis, it is very necessary to investigate the reaction mechanism theoretically. In this work, we use the three hybrid DFT methods to study the reaction mechanism of the formation of acetic acid. Several routes of dissociation of CO₂ have been discussed. The main reaction pathways for acetic acid synthesis have also been analyzed by using the three hybrid DFT methods.

2. Computations

All the calculations have been performed with the GAUSSIAN 98 package [10]. The Becke's three parameters exchange function [11] was used to combine with three different correlation functions: LYP [12,13], Perdew 86 [14] and Perdew and Wang's 1991 gradient-corrected correlation function [15,16]. The structures of all kinds of molecules and radicals were optimized at the B3LYP, B3P86 and B3PW91 level with 6-311G (d, p) basis set. Vibrational frequency calculations were performed for each structure at the same level used for the geometrical optimization. The potential energy surface was obtained by the scan calculation.

When the reactants are fed into the discharge region, they can be dissociated due to the existence of electrons with energies ranged from 96.48 to 964.80 kJ/mol [17,18]. The reaction is thereby initiated from the dissociation reactions of CH_4 and CO_2 :

$$CH_4 \rightarrow CH_3 + H$$
 (2)

$$e^- + CO_2 \to CO_2^- \tag{3}$$

$$e^- + CO_2 \to O^- + CO \tag{4}$$

$$e^- + CO_2 \rightarrow O + CO + e^- \tag{5}$$

The reactions to produce acetic acid via CO_2^- include:

 $\mathrm{CO}_2^- + \mathrm{H} \to \mathrm{COOH}^-$ (6)

$$CH_3 + COOH^- \rightarrow CH_3COOH + e^-$$
 (7)

Acetic acid can also be synthesized via CO:

$$CH_3 + CO \rightarrow CH_3CO$$
 (8)

$$CH_3CO + O \rightarrow CH_3COO$$
 (9)

$$CH_3CO + O^- \to CH_3COO^-$$
(10)

$$CH_3COO + H \rightarrow CH_3COOH$$
 (11)

$$CH_3COO^- + H \rightarrow CH_3COOH + e^-$$
 (12)

or

$$O + H \rightarrow OH$$
 (13)

$$O^- + H \to OH^- \tag{14}$$

$$CH_3CO + OH \rightarrow CH_3COOH$$
 (15)

$$CH_3CO + OH^- \rightarrow CH_3COOH + e^-$$
 (16)

Therefore acetic acid can be formed mainly via these two pathways with CO_2^- and CO as chemical intermediates.

3. Results and discussion

3.1. CO_2 and CO_2^-

Tables 1 and 2 present the calculated structural parameters and frequencies of CO_2 and CO_2^- , obtained from calculations with three hybrid DFT methods. The comparative experimental results shown in Tables 1 and 2 were reported in the literature [19–22]. Like other calculation methods, the three hybrid DFT methods can give reliable geometrical parameters and vibrational frequencies comparing with the experimental results. The B3LYP is better than other two methods for CO_2 molecule. It has also been shown that the three hybrid DFT methods can achieve better results than the CCSD (T) and HTDFT methods reported calculations showed that there existed large deviations

calculated and experimental structural parameters and nequencies for CO_2							
Property	B3LYP	B3P86	B3PW91	Exp ^b			
Re (C–O)	1.160	1.159	1.159	1.162			
$\omega (\pi u)$	666.622	671.555	670.823	667			
$\omega (\sigma g)$	1375.410	1388.719	1386.323	1333			
$\omega (\sigma u)$	2435.684	2467.594	2463.600	2393			
ZPE	30.770	31.099	31.053	29.999			
E	-495246.540	-496246.170	-495043.265				

Table 1 Calculated and experimental structural parameters and frequencies for CO₂^a

^a Bond lengths are in Å, total energies are in kJ/mol, vibration frequencies are in cm⁻¹, and the ZPE are in kJ/mol. ^b See [19].

Table 2 Calculated and experimental structural parameters and frequencies for CO_2^{-a}

Property	B3LYP	B3P86	B3PW91	Exp
Re (C–O) $\angle OCO^{\circ}$ ω (a1) ω (b2) ZPE	1.244 134.127 740.641 1330.506 1689.264 22.492	1.241 134.247 745.004 1348.908 1727.390 22.856	1.242 134.279 744.073 1345.729 1722.368 22.802	$\begin{array}{c} 1.25^{b} \\ 127\pm8^{b},134^{c} \\ 849^{b} \\ 1424^{b} \\ 1671^{b},1658^{d} \end{array}$
E	-495143.045	-496195.871	494939.569	

^a Bond lengths are in Å, total energies are in kJ/mol, vibration frequencies are in cm^{-1} , and the ZPE are in kJ/mol.

^b See [20].

^c See [21].

^d See [22].

between the experimental and calculated geometrical parameters and vibrational frequencies for CO_2^- [19]. But the results calculated in this work using the three hybrid DFT methods are consistent with the experimental values, especially, for the geometrical parameters [19–22].

Figs. 1 and 2 showed the potential energy surface with the B3P86 method. For neutral CO₂ molecule, there is only a single energy minimum, which situated at $\angle OCO = 180^{\circ}$ and R(C-O) = 1.159 Å, while the CO₂ anion presents two equal energy minimums [19]. It clearly shows the stable CO₂ and CO₂⁻ has very different geometrical structure. The CO₂ anion is more active than the neutral CO₂ since the electron attached to carbon dioxide significantly weakens the stretching frequencies of carbon dioxide molecule, as shown in Tables 1 and 2 [23].

3.2. The dissociation of reactants

Table 3 presents enthalpies of dissociation reactions of CH_4 and CO_2 . The dissociation energy of methane calculated with B3LYP, B3P86 and B3PW91 methods is 430.974, 444.120 and 429.092 kJ/mol, respectively, while the experimental result is 434.720 kJ/mol [24]. For the formation of CO_2^- , the enthalpy calculated with B3LYP and B3PW91 methods is slightly higher than the experimental result. But the calculated enthalpy by the B3P86 method is consistent with the experimental value (41.840-62.760 kJ/mol) [25]. The CO₂ molecule can also be dissociated into CO and O radical or O⁻. These conversions need higher energy than the formation of CO_2^- . Upon the calculations with three hybrid DFT methods, about 501.600 kJ/mol is necessary for the dissociation of carbon dioxide to CO. In addition, compared with B3LYP and B3PW91 methods, the reactive enthalpy calculated by B3P86 method is lower for the reaction $e^- + CO_2 \rightarrow O^- + CO,$ but for $e^- + CO_2 \rightarrow O +$ $CO + e^{-}$, the value is higher.

In addition, H, O, O^- and OH^- are also considered to be active species for methyl radical formation after the generation of discharges [26].



Fig. 1. Potential energy surface of CO₂.



Fig. 2. Potential energy surface of CO_2^- .

The enthalpies for these reactions are presented in Table 3.

3.3. The reaction route to produce acetic acid via CO_2^-

Kaneco et al. [27–31] reported a synthesis of formic acid by electrochemical reduction of CO₂.

The group COOH comes from CO_2^- directly. They thought that, through electron transfer, $CO_2^$ could be formed from CO_2 [27–31]. The CO_2^- can also be produced in the discharges via reaction: $CO_2 + e^- \rightarrow CO_2^-$. The CO_2^- can react with H to generate COOH⁻. Acetic acid is thereby synthesized by the reaction between COOH⁻ and methyl radical obtained from the dissociation of methane.

thalpies of dissociation reactions at 298.15 K ^a						
Reaction	B3LYP 6-311G**	B3P86 6-311G**	B3PW91 6-311G**			
$CH_4 \rightarrow CH_3 + H$	434.242	444.545	429.502			
$\rm CO_2 + e^- \rightarrow \rm CO_2^-$	104.151	50.010	104.456			
$e^- + CO_2 \rightarrow O^- + CO$	523.166	494.369	539.202			
$e^- + CO_2 \rightarrow O + CO + e^-$	538.165	567.371	551.482			
$\rm CH_4 + H \rightarrow \rm CH_3 + \rm H_2$	-3.235	-0.449	4.226			
$CH_4 + O \rightarrow CH_3 + OH$	14.216	9.563	13.730			
$\rm CH_4 + O^- \rightarrow \rm CH_3 + OH^-$	275.165	288.790	282.089			

-37.806

Table 3 Enthalpies of dissociation reactions at 298.15 K^a

^a In kJ/mol.

 $CH_4 + OH \rightarrow CH_3 + H_2O$

Table 4

Enthalpies of reactions to produce acetic acid via CO₂⁻ at 298.15 K^a

Reaction	B3LYP 6-311G**	B3P86 6-311G**	B3PW91 6-311G**	
$\begin{array}{l} H+CO_2^- \rightarrow COOH^- \\ CH_3+COOH^- \rightarrow CH_3COOH+e^- \end{array}$	-28.910 -451.850	-28.030 -426.821	-20.213 -464.821	

-44.415

^a In kJ/mol.

Table 4 showed the reaction enthalpy for the formation of acetic acid via CO_2^- route. The reactions to generate $COOH^-$ and acetic acid via CO_2^- are both exothermic reactions. These reactions can easily occur once the formation of CO_2^- , especially, the reaction ($CH_3 + COOH^- \rightarrow CH_3COOH + e^-$). It can be seen that the controlling step is the formation of CO_2^- .

3.4. The reaction route to form acetic acid via CO

Besides the route via CO_2^- , acetic acid can be synthesized via CO too. The methyl radical can react with CO to form CH₃CO. This is a thermodynamically favored reaction. The reaction enthalpy calculated with B3LYP, B3P86 and B3PW31 methods was -54.697, -73.882 and -66.717 kJ/mol, respectively. Table 5 shows the reaction enthalpies to form acetic acid via CO. It can be seen that, the controlling step is the formation of CH₃CO radical. Acetic acid can be formed by several pathways once the generation of CH₃CO radical. CH₃CO can easily react with O or O⁻ and produce CH₃COO or CH₃COO⁻. The hydrogen radical obtained from the dissociation of methane can react with CH₃COO or CH₃COO⁻ to generate acetic acid. Moreover, acetic acid can be synthesized by the reaction of CH₃CO with OH or OH⁻.

-42.073

Comparing with two routes to synthesize acetic acid, it can be seen that the route via the CO_2^- is

Table 5

Entl	nalpies	of	reactions	to	produce	e acetic	acid	via	CO	at	298.	.15	K	Ĺ
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r r				
Reaction	B3LYP 6-311G**	B3P86 6-311G**	B3PW91 6-311G**	
$\rm CH_3 + \rm CO \rightarrow \rm CH_3\rm CO$	-54.750	-73.952	-66.781	
$CH_3CO + O \rightarrow CH_3COO$	-428.391	-453.433	-436.820	
$CH_3CO + O^- \rightarrow CH_3COO^-$	-300.025	-315.864	-306.598	
$CH_3COO + H \rightarrow CH_3COOH$	-431.632	-444.737	-428.460	
$\rm CH_3\rm COO^- + \rm H \rightarrow \rm CH_3\rm COO\rm H + e^-$	-544.999	-509.305	-546.402	
$\mathrm{O} + \mathrm{H} \rightarrow \mathrm{OH}$	-420.026	-434.982	-415.772	
${\rm O}^- + {\rm H} \rightarrow {\rm O}{\rm H}^-$	-159.077	-155.755	-147.413	
$CH_{3}CO+OH \rightarrow CH_{3}COOH$	-439.997	-463.188	-449.508	
$CH_3CO+OH^- \rightarrow CH_3COOH + e^-$	-685.948	-669.414	-705.586	

^a In kJ/mol.

easier than that via CO. The energy requirement to form CO_2^- from CO_2 is much lower than the energy required to generate CO. In addition, the reaction steps are less via CO_2^- than via CO, with which most of CO has become the ultimate product before the formation of acetic acid.

4. Conclusion

In this work, we used three hybrid DFT methods to study the mechanism of the perfect atomic economic reaction: $CH_4 + CO_2 \rightarrow CH_3COOH$. The structural and energy parameters of $CO_2^$ obtained are consistent with the experiments results. Two main routes of the formation of acetic acid directly from CH_4 and CO_2 via CO_2^- and COhave been confirmed by the DFT study. The route via CO_2^- is more thermodynamically favored compared to the route via CO. This study also demonstrates that the DFT study is a powerful tool to understand the mechanism of gas discharge reactions.

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