The New Pathway for Methanol Synthesis: Generation of CH$_3$ Radicals from Alkanes

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Abstract—Methanol synthesis was achieved by a free-radical reaction mechanism through reaction of methyl radical with water molecule at a temperature of 100°C, at an atmospheric pressure, in the presence of nitrogen-dioxide radical and under ultra-violet radiation (λ>250 nm). The major product was methanol and nitrous acid. It is expected that only the participation of catalysts and a low-temperature reaction of alkanes would not only control the reaction but also give outstanding results.

Key words – methane activation, hydroxyl radical, methyl radical, methane partial-oxidation, quantum chemical calculations, methanol synthesis.

I. Introduction

Although, methane is perhaps the most attractive substrate for direct oxidation to its alcohol product, its conversion to more energy-dense liquid derivatives, or a value-added product would significantly increase its utilization on a world wide scale. However, the most significant challenge has always been the scientific difficulty associated with upgrading methane, due to its perfect symmetry and poor coordinative ability, thereby making it the least reactive of all hydrocarbons due to large kinetic barrier to cleave the C-H bond at 438 kJ/mol [1].

Conventionally, methanol production requires the steam-methane reforming (SMR) to synthesis gas, then subsequent catalytic conversion to fuels via Fischer-Tropsch or hydrogenation processes[2–4].

CH$_4$ + H$_2$O → CO + 3H$_2$ $\Delta H_{298}^0 = + 206$ kJ/mol \hspace{1cm} (1)

CO + 2H$_2$ → CH$_3$OH $\Delta H_{298}^0 = -90.7$ kJ/mol \hspace{1cm} (2)

A plethora of investigations regarding methane activation/conversion to methanol has been a subject of considerable scrutiny, hence various technological approaches such as catalytic [5–6], chemical [7–9], photochemical [10–14], plasma-based techniques [15–16], and energetic species [17–18] have been extensively-examined and applied, but notwithstanding, most of these studies still suffer low methane conversion, poor methanol yield, and well-articulated mechanistic limitations, even under mild conditions [1–18].

All the same, this process suffers from low energy efficiency and high capital and operating cost of steam reforming. In order to significantly minimize the reforming cost, the conversion of methane into its value-added products via direct oxidation (preferably in one-step), which ideally avoids the current indirect route via synthesis gas, has attracted many researchers interest. The direct partial oxidation of methane to methanol [Eq. (3)] is an exothermal reaction that is energetically more efficient and can give quite good results than the endothermic SMR reaction, nevertheless it is operated by a free radical mechanism, which is hard to control.

CH$_4$ + $\frac{1}{2}$O$_2$ → CH$_3$OH $\Delta H_{298}^0 = -126.4$ kJ/mol \hspace{1cm} (3)

A technical economic assessment showed that the direct process for methanol production could compete with the conventional method (indirect) in terms of production costs if an 80% selectivity of methanol could be achieved at a single pass methane conversion of 10%.

In this present study, to overcome the barrier that has characterized CH$_4$ activation, we developed a new process for methanol synthesis through the interaction CH$_4$ with OH radical to form CH$_3$ radical (highly reactive specie), which is then reacted with water vapor at 100°C and at atmospheric pressure under the auto-catalytic action of NO$_2$ radical (initiator and process-catalyst).

II. Theoretical concept and quantum chemical study of the reaction mechanism for photochemical conversion of methane to methanol

Methane activation with OH radical (generated through water photolysis) was first proposed almost 20 years back. Since methane formation in the martian atmosphere is realized by water photolysis in the presence of CO, the generation of OH radical requires a very hard ultraviolet radiation, hence, result-oriented and efficient scheme was not successfully achieved.

H$_2$O + $\text{h}\nu$ (λ ≤ 180 nm) → OH + •H \hspace{1cm} (4a)

In this paper, the suggested pathway for the photochemical conversion methane to methanol involves the photo-dissociation of nitric acid vapor to generate hydroxyl radical, which is then reacted with a saturated hydrocarbon molecule (methane) to form alkyl radical and water molecule [19].

HNO$_3$ + $\text{h}\nu$ (250<λ<400 nm) → OH + •NO$_2$ \hspace{1cm} (4b)

CH$_4$ + OH → •CH$_3$ + H$_2$O $\Delta G_{298}^0 = -64.3$ kJ \hspace{1cm} (5)

![Fig. 1. Structure of transition state (TS) for the reaction: CH$_4$ + OH ↔ CH$_3$ + H$_2$O, B3LYP/6-311++G(3df) calculation. Equilibrium distances in angstroms (Å).](image)

The calculated activation energy ($E_a$ = 8.2 kJ/mol) for Eq. (5) quite agrees well with the experimental value ($E_a$ = 15–23 kJ/mol).

•CH$_3$ + H$_2$O → CH$_3$OH + •H \hspace{1cm} (6)

The calculated value for the Gibbs free energy of [Eq. (6)] ($\Delta G_{298}^0 = + 121.6$ kJ) is broadly consistent with the experimental value $\Delta G_{298}^0 = + 130.5$ kJ, however, the
reaction is characterized by a very high activation energy \( E_a = 182.4 \text{kJ/mol} \), thus, it could be assumed that [Eq. (6)] is clearly unreal and thermodynamically forbidden. Furthermore, to overcome the reaction barrier from [Eq. (6)], the reaction of two methyl radicals with water-dimer to enhance a better cleavage and formation of molecular hydrogen is shown in [Eq. (7)]

\[
2 \cdot \text{CH}_3 + 2 \cdot \text{H}_2 \cdot \text{O} \rightarrow 2 \cdot \text{CH}_3 \cdot \text{OH} + \text{H}_2
\]  

This is consistent with the \( \Delta G^0_{298} = -158.7 \text{kJ (Cal.)} \) is quite consistent with the \( \Delta G^{0}_{298} = -163.4 \text{kJ (Exp.)} \). Also, from the optimized structure of the transition state for [Eq. (7)], calculated value of activation energy was 145.9 kJ/mol. Thereby, it is evident that the rate limiting step for methanol formation is the reaction between methyl radical and water molecule.

In the vapor-phase nitration of methane, methane is the most difficult to be nitrated and even at high temperature \( T > 700 \text{K} \), the reaction rate and yields are still low. However, the gas-phase nitration of alkane was further developed for the conversion of \( \text{CH}_4 \cdot \text{O}_2 \rightarrow \text{NO}_x \) to \( \text{C}_1 \)-oxygenerates [20].

Recently, Teng et al. found that: (i) when NO or \( \text{NO}_2 \) was introduced into methane-oxygen system as initiator, methane was able to be oxidized to methanol and formaldehyde even under ambient pressure, (ii) the nitrogen atom in \( \text{NO}_x \) showed higher activity for cleavage of the C-H bond than oxygen atom, so as to initiate methane oxidation at ambient condition [21].

\[
\text{•CH}_3 + \text{H}_2 \cdot \text{O} + \text{•NO}_2 \rightarrow \text{CH}_3 \text{NO}_2 + \text{H}_2 \cdot \text{O}
\]  

The absorption spectrum of nitro-methane in the gas-phase is observed under soft ultraviolet light \( 250 \text{nm} < \lambda < 340 \text{nm} \) but its photolysis products are mainly radicals [22].

\[
\text{CH}_3 \text{NO}_2 + h \nu \rightarrow \text{CH}_3 + \text{•NO}_2
\]  

It should be noted that under the experimental conditions, nitro-methane was not detected in the reaction product probably due to: (i) the possibility of its photodissociation under the experimental conditions (peak of absorption spectrum is located at 300 nm), (ii) the subsequent involvement of \( \text{CH}_3 \) and \( \text{NO}_2 \) radicals in the catalytic process of \( \text{CH}_3 \cdot \text{OH} \) formation, (iii) nitro-methane is very labile and characterized also with a small binding energy \( E_{C-N} = -260 \text{kJ/mol} \), which is susceptible to cracking in gas-phase oxidation at high temperature \( T \sim 800 \text{K} \). Therefore, based on the author’s assumption, nitro-methane is an unstable intermediate compound in the gas-phase oxidation of alkane molecules to \( \text{C}_1 \)-oxygenerates.

\[
\text{•CH}_3 + \text{H}_2 \cdot \text{O} + \text{•NO}_2 \rightarrow \text{CH}_3 \cdot \text{OH} + \text{HNO}_2
\]  

The calculated energy barrier for splitting water molecule by methyl radical in the presence of \( \text{•NO}_2 \) is \( E_a = +16.4 \text{kJ/mol} \) [Eq. (10)]. From Fig. 3b, it is apparent that \( \text{NO}_2 \) abstracts atomic hydrogen to itself to form nitrous acid, which also, above room temperature, is unstable and decay as shown by [Eq. (11)].

\[
\text{2HNO}_2 \rightarrow \text{NO}_2 + \text{NO} + \text{H}_2 \cdot \text{O}
\]  

The decomposition product \( \text{NO} \) is quickly oxidized to \( \text{NO}_2 \) by molecular oxygen, even under normal condition, which can be returned to the oxidation cycle, hence [Eq. (12)] shows that the oxidation of nitrous acid to nitric acid completes a cycle for the catalytic conversion of methane to methanol.

\[
\text{2NO} + \text{O}_2 \rightarrow 2\text{NO}_2
\]  

\[
\text{HNO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{HNO}_3
\]  

Quantum chemical calculations [19] have substantiated the mechanism for methanol formation through the reaction of methyl radical with water molecule under the catalytic influence of \( \text{•NO}_2 \) radical. The theoretical value of the calculated Gibbs free energy \( \Delta G^0_{298} = -163.3 \text{kJ} \) for [Eq. (12)] is in excellent agreement with the experimental value of the \( \Delta G^0_{298} = -175.9 \text{kJ} \).
Results of quantum chemical calculation for total energy ($E_{\text{total}}$), zero vibrational energy ($E_0$), and absolute entropy $S^0_{298}$ for ground and excited-state molecule and the thermodynamic parameters ($\Delta G^0_{298}, \Delta H^0_{298}, \Delta S^0_{298}$) for: $\text{CH}_2 + \cdot \text{OH} \rightarrow \text{H}_2\text{C} - \cdot \text{OH} \rightarrow \cdot \text{CH}_3 + \cdot \text{H}_2\text{O}$

<table>
<thead>
<tr>
<th>Molecular system (electronic State)</th>
<th>B3LYP/6-311++G(3df,3pd)</th>
<th>Experimental Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total Energy $E_{\text{total}}$, au</td>
<td>ZeroVibrational Energy $E_0$, kJ/mol</td>
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<tr>
<td>------------------------------------</td>
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</tr>
<tr>
<td>$\text{CH}_2 \left( ^1A_1 \right)$ + $\cdot \text{OH} \left( ^1\Pi \right)$</td>
<td>$- 40.537394$</td>
<td>$117.0 \left( 0 \right)$</td>
</tr>
<tr>
<td>TS ($^4A'$) \text{Fig. 1} \downarrow</td>
<td>$- 75.766245$</td>
<td>$22.2 \left( 0 \right)$</td>
</tr>
<tr>
<td>$\Delta E_p = 8.2$ kJ/mol</td>
<td>$- 116.300514$</td>
<td>$133.6 \left( 1 \right)$</td>
</tr>
<tr>
<td>$\cdot \text{OH} \rightarrow \text{H}_2\text{C} - \cdot \text{OH}$</td>
<td>$- 39.858357$</td>
<td>$78.0 \left( 0 \right)$</td>
</tr>
<tr>
<td>$\cdot \text{CH}_2 \left( ^4A'' \right)$ + $\cdot \text{H}_2\text{O} \left( ^1A_1 \right)$</td>
<td>$- 76.464512$</td>
<td>$55.9 \left( 0 \right)$</td>
</tr>
<tr>
<td>$\Delta G^0_{298} = - 52.0$ kJ</td>
<td>$\Delta S^0_{298} = + 7.2$ J/k</td>
<td>$\Delta S^0_{298} = + 12.9$ J/k</td>
</tr>
</tbody>
</table>

Results of quantum chemical calculation for total energy ($E_{\text{total}}$), zero vibrational energy ($E_0$), and absolute entropy $S^0_{298}$ for ground and excited-state molecule and the thermodynamic parameters ($\Delta G^0_{298}, \Delta H^0_{298}, \Delta S^0_{298}$) for: $2 \cdot \text{CH}_3 + 2 \cdot \text{H}_2\text{O} \rightarrow 2 \cdot \text{CH}_2\text{OH} + \cdot \text{H}_2$

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<td>------------------------------------</td>
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<tr>
<td>$2 \cdot \text{CH}_3 \left( ^1A'' \right)$ + $2 \cdot \text{H}_2\text{O} \left( ^1A' \right)$</td>
<td>$2 \cdot (-39.85836)$</td>
<td>$2 \cdot 78.0 \left( 0 \right)$</td>
</tr>
<tr>
<td>TS ($^1A$) \text{Fig. 2b} \downarrow</td>
<td>$- 152.936710$</td>
<td>$121.0 \left( 0 \right)$</td>
</tr>
<tr>
<td>$\Delta E_p = 145.9$ kJ/mol</td>
<td>$- 234.522882$</td>
<td>$278.7 \left( 1 \right)$</td>
</tr>
<tr>
<td>$\cdot \text{CH}_2\text{OH} \left( ^1A' \right)$ + $\cdot \text{H}_2 \left( ^1\Sigma_g^+ \right)$</td>
<td>$2 \cdot (-115.77432)$</td>
<td>$2 \cdot (134.1) \left( 0 \right)$</td>
</tr>
<tr>
<td>$\Delta G^0_{298} = - 158.7$ kJ</td>
<td>$\Delta S^0_{298} = - 71.4$ J/k</td>
<td>$\Delta S^0_{298} = - 155.7$ J/k</td>
</tr>
</tbody>
</table>
calculation of energy for the reaction was made on assumption of primary formation of molecular adduct (Fig. 3a)

\[ \text{•NO}_2 + \text{H}_2\text{O} \rightarrow \text{•NO}_2\text{H}_2\text{O} \]  \hspace{1cm} (14)

III. Experiment

Prior to conducting the experimental procedure, it was affirmed that total content of methane gas was \( 94.5 \pm 99.3\% \), and the gas pressure did not exceed 0.03 MPa.

The experimental set up consists of a reactor (3L volume) made of stainless steel and equipped with gas inlet fittings and a water output. The vapor-gas mixture is fed into the reactor, heated at 100°C, and on the upper lid encased in a 4mm thick quartz glass, it is irradiated at a UV range between 240 – 450 nm by a high pressure mercury lamp DRT – 100 (12mm diameter, 60mm length and with a 100 watt power consumption), and at a transmittance coefficient not less than 92%. The reaction mixture was delivered in the trap (to prevent partial ablation of nitric acid in the reaction zone), where the condensation of acidic solution occurred.

The reaction mixture was cooled by circulating water in the refrigeration condenser, separated in the condensate collector where the non-reactive gas is discharged as flare.

The gas composition was determined by gas chromatography using: (i) CLARUS 500 GC with a 1m long activated carbon and (ii) LKhM-8 GC with a 3m polysorb.

To ascertain the catalytic ability of nitric acid, three series of experiments were carried out at a gas : vapor ratio = 1 : 10, at a temperature of 100°C and at atmospheric pressure.

In the 1\textsuperscript{st} experiment when the gas-vapor mixture was just blown through the reactor, no methanol sample was detected, thus implying that the reactor material does not have any catalytic effect. In the 2\textsuperscript{nd} experiment when the gas-vapor mixture was exposed to photo-irradiation, methanol content in the condensate was about 0.05 %,

which is typical for water photolysis under a soft ultraviolet radiation. In the 3\textsuperscript{rd} experiment when the gas-vapor mixture was exposed to photo-irradiation in the presence of nitric acid vapor, the average concentration of methanol in the condensate was about 1.6 %. Moreover, regardless of the sampling time, methanol concentration was always the same, thereby, suggesting a very high rate of reaction.

The flow of bulk gas through the reactor was \( 1.0 \) L/min., the maximum evaporation rate was \( 10 \) L/min., the average residence time of gas-vapor mixture in the reactor was about 10 seconds, the analysis of condensate sample was at 5 – 30 min. intervals, the calculated degree of conversion of methane was \( 10 \% \) and conclusively, from the analysis of the reaction products performed using liquid chromatography crystal 2000 M with a 3m long polysorb, traces of the reaction by-products such as other alcohols, aldehydes, ethers, nitro-methane and e.t.c
in the condensate were not detected in all the experimental series.

**TABLE IV**

<table>
<thead>
<tr>
<th>Sampling Time (Min.)</th>
<th>Series of Experimental Conditions</th>
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<tr>
<td></td>
<td>I</td>
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<tr>
<td></td>
<td>Gas + Vapor (%)</td>
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<tr>
<td>5</td>
<td>0</td>
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<tr>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>0</td>
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<tr>
<td>60</td>
<td>0</td>
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<tr>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>120</td>
<td>0</td>
</tr>
</tbody>
</table>

**Conclusion**

This paper describes the concept and theoretical basis for methanol formation in a vapor-gas system by the summarized equation below:

\[ \text{CH}_4 + \text{H}_2\text{O} + \text{O}_2 + \text{hv}/\text{HNO}_3 \rightarrow \text{CH}_3\text{OH} + \text{HNO}_2 \]

From the detailed studies on CH4 activation at the B3LYP/6-311++G(3df,3pd) level [19], it can be concluded that:

[i] With the activation of methane by hydroxyl radical, methanol synthesis is effectively realized.

[ii] NO2 radical significantly spurred the limiting stage of the reaction between the CH3 radical and H2O molecule.

[iii] Abundant availability of reagents.

[iv] A high reaction rate, high degree of conversion per pass (~10%), as well as, methanol formation under mild condition (T = 100°C, P = 1 atm.) in a single reactor.

Based on the results obtained in this work, CH4 activation with photo-dissociation products of HNO3 for methanol synthesis, apparently finds quantum chemical justification.

Thereby, a novel, simple (single-step process), efficient, and cost-effective model for methanol production, which is considered environmentally benign, and that could serve as a useful guidance to design an industrial plan for the direct oxidation of methane to methanol has been presented.

**Acknowledgement**

The author is grateful to the Ukrainian–American Laboratory of Computational Chemistry at the Scientific-Technical Complex, “Institute of Single Crystals for the assistance rendered to perform the quantum chemical calculations.

**References**


