

## The new pathway for methanol synthesis: Generation of methyl radicals from alkanes



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### ARTICLE INFO

#### Article history:

Received 8 May 2014

Received in revised form 13 July 2014

Accepted 2 August 2014

Available online 8 August 2014

#### Keywords:

Methane activation

Hydroxyl radical

Methyl radical

Quantum chemical calculations

Density functional theory (DFT)

Photochemical alkane conversion

Methanol synthesis

### ABSTRACT

The proposed scheme for methane oxidation to methanol in a vapor–gas system:  $\text{CH}_4 + \frac{1}{2}\text{O}_2 + (h\nu/\text{HNO}_3) \rightarrow \text{CH}_3\text{OH}$  under mild conditions: at a temperature ( $T = 100^\circ\text{C}$ ), atmospheric pressure ( $P = 1\text{ atm}$ ), ultraviolet radiation of  $\text{HNO}_3$  ( $\lambda > 230\text{ nm}$ ), and autocatalytic influence of nitric acid was investigated. In this way, methanol with 90% selectivity can be achieved at a methane conversion level of 10%. Quantum chemical calculations for the activation reaction of methane by hydroxyl radical (via  $\text{HNO}_3$  photo-dissociation) were performed using the density functional theory (DFT) method at the B3LYP/6-311++G(3df,3pd) level. Results of the DFT calculations which are broadly consistent with the experimental data, clearly find physicochemical justification. By and large, a possible extension of the technique here in, for the oxidation of higher alkanes (instead of methane) to methanol, in principle, also enhances the opportunity to recycle nitric acid, and the valuable semi-products (alkene and/or oxide of alkene).

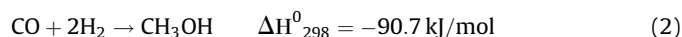
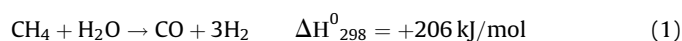
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### Introduction

Natural gas (mainly composed of methane), is an abundant energy resource predicted not only to outlast the oil reserves by a significant margin, but also, is more uniformly distributed than oil reserves [1]. However, given its abundance and versatility (theoretically, a large number of important species may be produced via the careful construction of the  $\text{C}_1$  units), it is still, greatly under-utilized due to: (i) its high transportation costs; since a substantial amount of natural gas is inconveniently located, and there is currently no safe and economically viable method in place for its transportation, and (ii) more significantly: the scientific and technical challenges of its activation; owing to factors such as the incredibly high energies required for both heterolytic and homolytic cleavage of C–H bond, negligibly small electron affinities, large ionization energies, huge HOMO/LUMO gaps, and the extremely high  $\text{pK}_a$  values of the organic substrates, and as a consequence; it the most stable (least reactive) of all hydrocarbon molecules [2].

Methane, being part of green-house gases (GHG), also contributes to global warming. However, owing to its low C–H ratio and high calorific value, it has an enormous potential as an ideal fuel in the continuing efforts to minimize the local and global environmental impact from energy use [3], and as a feedstock for chemical synthesis. Therefore, it is desirable to convert methane into liquid transportable fuels such as methanol, as it retains most of methane energy, for safe transportation and clean environment using economically-viable and easily-accessible resources.

Conventional technologies for the conversion of methane into alternative fuels such as the initial conversion of methane to syn-gas (Eq. (1)), followed by the high-pressure catalytic conversion of syn-gas to methanol (Eq. (2)), are energy-intensive, less-efficient and not cost-effective mainly due to the limitations imposed by the reaction equilibrium and low heat efficiency [4].

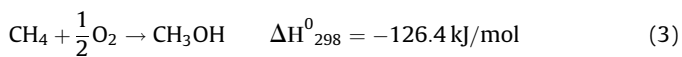


Moreover, the direct partial oxidation of methane (POM) to methanol (Eq. (3)) is an exothermal reaction which is: energetically more-efficient, tends to minimize temperature-and-pressure fluctuations, decreases the second-law efficiency losses, and can give quite good results than the endothermic steam-methane

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reforming (SMR) reaction. Nevertheless, it is operated by a free radical mechanism which is hard to control.



Although least explored, a more energetically-efficient conversion of methane into methanol, is photocatalysis (using abundant and inexpensive reactants such as water, photo-energy and/or photo-catalyst), with a tremendous potential to make thermodynamically-difficult reactions proceed at lower temperature, has been considered by many researchers, as an attractive option [5–10].

It has been reported that methane may be converted to methanol, in a strictly photochemical reaction by first sparging it through a heated (90 °C) water-bath in order to saturate it with water vapor, which is then exposed to ultraviolet (UV) light at a wavelength ( $\lambda = 185 \text{ nm}$ ) in a photochemical reactor [7,8].

Based on a technical-economic analysis of methanol production from methane, it was found that, the direct method 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% [11].

In this present study, we have reported that, methanol with 90% selectivity can be achieved at a methane conversion level of 10% by soft UV radiation at a wavelength ( $\lambda > 230 \text{ nm}$ ) in the presence of water ( $\text{H}_2\text{O}$ ), air, nitric acid vapor, and under mild reaction conditions at low temperature ( $T = 100 \text{ }^\circ\text{C}$ ), atmospheric pressure ( $P = 1 \text{ atm}$ ), in a photochemical reactor.

## Theory and calculation

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

All quantum chemical calculations were performed by molecular orbital (MO) method at the density functional theory (DFT) level: Becke's three-parameter hybrid functional with Lee–Yang–Par exchange-correlation functional B3LYP [12,13] were applied in a very systematic way using the valence-split basis set 6-311++G (3df,3pd) with the help of GAUSSIAN 92 software [14].

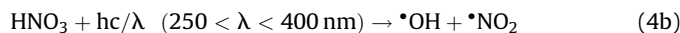
The photolysis of water molecules is an important source of hydroxyl radical ( $\bullet\text{OH}$ ) in the upper atmosphere. However, this splitting of water to generate hydroxyl radical and hydrogen atom (Eq. (4a)) is an uphill process, which requires  $\sim 235 \text{ kJ}$  energy or photons of energy  $\leq 6.7 \text{ eV}$  corresponding to a hard UV radiation ( $\lambda \leq 180 \text{ nm}$ ).



Methane activation with photo-generated hydroxyl ( $\bullet\text{OH}$ ) radical (via water photolysis) was first proposed almost 26 years back [6].

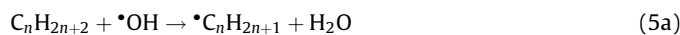
Since, methane formation in the martian atmosphere is realized by water photolysis (in the presence of CO), the energy threshold of photochemical decay of water vapor corresponds to hard UV radiation. Moreover, the photo-generated hydroxyl radical (via water photolysis) initiates a variety of complex side reactions and electron donating behavior of the product molecules, limits the yield and selectivity of desired product, hence  $\bullet\text{OH}$  radical (via water photolysis), is non-selective, and consequently, impressive results were not obtained.

In this paper, the suggested pathway for the photochemical conversion of methane to methanol involves the photo-dissociation of nitric acid vapor to generate hydroxyl radical (Eq. (4b)), which is then reacted with a saturated hydrocarbon molecule (methane) to form alkyl radical and water molecule [14,15].

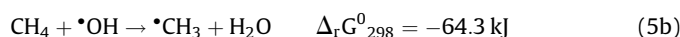


The importance of atmospheric reactions is supported by the high reactivity of the hydroxyl radical, which provides activation of such inert molecules like methane. The sink of methane in the upper troposphere is realized by reaction with the hydroxyl radical [16].

From a number of studies devoted to methane oxidation by hydroxyl radical, it has been demonstrated that hydroxyl radical is a key reactive intermediate in both combustion [17–19] and tropospheric free-radical chemistry [20–22] of hydrocarbons and carbon monoxide. Upon the interaction of the generated hydroxyl radical with a saturated hydrocarbon molecule (Eq. (5a)), an alkyl radical and water molecule are formed.

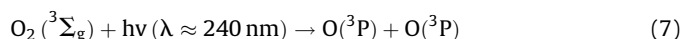


The hydroxyl radical reaction with alkane proceeds by H-atom abstraction from the C–H bond (Eq. (5b)) to form a methyl radical and a water molecule.

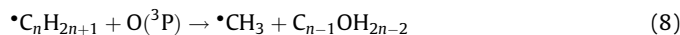


whereas, the subsequent homolytic decomposition of C–C alkyl radical (Eq. (6)) connected with the formation of new alkyl radical and alkene molecule ( $\text{C}_{n-1}\text{H}_{2n-2}$ ) is a well-known radical-chain process in thermal cracking. In terms of this process, the selectivity of formation of  $\bullet\text{CH}_3$  is close to 100%:

Under the condition of ultraviolet (UV) radiation of atmospheric oxygen (Eq. (7)):



the following process (Eq. (8)) is also possible:



Upon the reaction of methyl radical with water molecule, methanol and a hydrogen atom (Eq. (9)) are formed.



The calculated value of the Gibbs free energy ( $\Delta_r G^0_{298} = +121.6 \text{ kJ}$ ) (Eq. (9)), is though, broadly consistent with the experimental value  $\Delta_r G^0_{298} = +130.5 \text{ kJ}$ . However, the reaction is characterized by a very high activation energy ( $E_a = 182.4 \text{ kJ/mol}$ ), and it can therefore be assumed that (Eq. (9)) clearly, is thermodynamically forbidden: needless to say, it is an unreal reaction.

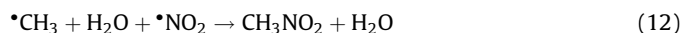
Furthermore, to overcome the reaction barrier from (Eq. (9)), the reaction of two methyl radicals and a water-dimer (Fig. 2(a)) to enhance a better cleavage and formation of molecular hydrogen is shown in (Eq. (10)).



The preliminary attempt to nitrate methane in the laboratory met with failure via the formation of nitromethane (Eq. (11)) because the exposure time was too short for the temperature used.



The vapor-phase nitration of methane (Eq. (11)) is the most difficult and even at high temperature  $T > 700 \text{ K}$ , the reaction rate and yields are low, still. Nonetheless, the experimentally-determined value of the activation energy ( $E_a = 217 \text{ kJ/mol}$ ) [23] for the nitration of methane is virtually identical to that obtained by quantum chemical DFT calculation ( $E_a = 157\text{--}192 \text{ kJ/mol}$ ) [24].



The absorption spectrum of nitro-methane in the gas-phase is observed under soft ultraviolet light ( $230 < \lambda < 340 \text{ nm}$ ), and the

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