

THE USE OF METHANE AS SOURCE OF HIGHER HYDROCARBONS AND HYDROGEN FOR UPGRADING HEAVY OILS AND BITUMEN

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ABSTRACT

Both the production of synthetic crude from the oil sands in Alberta and the upgrading of heavy oils to lighter products require hydrogen. The production of hydrogen by the steam reforming of methane is not only expensive but also contributes significantly to the production of greenhouse gases. Therefore, in bitumen and heavy oil upgrading, there is a major incentive to use methane directly. This paper describes the reactions of hydrogen and of methane plasma with olefin and aromatic model compounds and presents possible reaction mechanisms.

INTRODUCTION

Because of economic and environmental impacts, the direct use of methane or natural gas which contains 90 mole % methane in place of hydrogen has attracted considerable attention in recent years. It has been shown that different ranks of coal under coal liquefaction conditions and presence of methane produce more volatile products than under nitrogen.¹⁻³ Using model compounds such as benzene, naphthalene, toluene, bibenzyl and phenol, it has been demonstrated that a moderate degree of methylation can be achieved under certain conditions.⁴⁻⁶ Recently, Pang et al.⁷ concluded that, in the reaction of methane with petroleum and coal model compounds and the presence of catalyst, methylation yields are low because of the thermodynamics of the reaction is unfavorable. Ovalles et al.⁸⁻⁹ reported the use of methane as a source of hydrogen for the upgrading of heavy oils. These authors reported a significant decrease in the viscosity of the crude and conversion of 540° C⁺ with methane. Ilton and Maron have also demonstrated that the activity of methane can be enhanced in the presence of certain catalysts and their enhancement results in a high conversion of methane into higher hydrocarbons.¹⁰

Using microwave discharge, Mazur et al.¹¹ reported that atomic hydrogen can be generated from hydrogen gas and this atomic hydrogen can be reacted with olefins to form saturated and dimeric products. Tanner et al.¹² subsequently showed that the addition of hydrogen to olefins can be regiospecific.

The available data in the literature regarding the use of methane as a source of hydrogen indicate that methane is not useful for upgrading heavy hydrocarbons to lighter products because the use of methane results in low or no conversion. Other efficient methods for methane activation must be discovered in order to be able to use more or all of the available hydrogen in this molecule.

For the data reported in this paper, the use of methane as a source of hydrogen and higher hydrocarbons was investigated using microwave discharge. The objective was to follow the fate of methyl radicals and hydrogen atoms formed from methane under microwave discharge and reacted with model compounds containing double bonds. Furthermore, to shed light on the mechanism of dealkylation or cleavage of strong C-C bonds, the reaction of hydrogen atoms generated from hydrogen/helium plasma was investigated using toluene.

EXPERIMENTAL

General method for CH₃ radicals and H atoms reaction

Experimental details for H atom reactions with model compounds can be found elsewhere.¹² Similar Pyrex reactor and experimental conditions were used for the reaction of CH₄ with the model compounds. Briefly, the reactions with substrates (model compounds) were carried out in a Pyrex reactor neat or in acetone solution at -78°C. Helium-hydrogen or helium-methane was

introduced into the reactor system at the desired flow rate. The pressure of the reactor was maintained at 3-4 Torr. H_2 -He or H_2 - CH_4 plasma was generated in the microwave cavity. Hydrogen atoms or methyl radicals were swept into the stirred solution. The reaction products were analysed and identified using GC/FTIR and GC/MS and quantified using a Varian Vista 6000, equipped with FID detector and a glass capillary column (PONA, 30 mx0.25mm, HP).

RESULTS AND DISCUSSION

Reaction of CH_4 with model compounds

In a previous study, the results of hydrogen radical addition to model compounds indicated that these molecules can be saturated at very low temperatures.¹² In the present study, the reaction of methane as a source of hydrogen with 1-octene and cyclohexane was investigated. The product distributions from He/ CH_4 plasma are shown in Table 1 and Table 2. For comparison, the products from the reaction of He/ H_2 plasma with these model compounds are also shown in these tables. No attempts were made to optimize the product yields. The results show that the products in the reaction of He/ CH_4 plasma with both olefins are identical to those of the reaction of H_2 /He plasma with the olefins. However, in the reaction with CH_4 , a number of higher alkanes which were assumed to be resulting from the polymerization of methane could be identified (not quantified) in the reaction mixtures. Formation of higher hydrocarbons in these experiments was not quantified but their production signifies the possibility of the formation of higher hydrocarbons from methane. Although there was no evidence of the reaction of methyl radicals with the olefinic substrates, methyl radicals could be trapped by a spin trap such as tert-butylphenylnitron. This material was added to the reaction mixture before the plasma was activated; upon treatment with methane plasma the stable EPR spectra of the methyl radical spin adduct was observed.

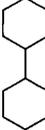
The product distribution in the reaction of He/ CH_4 plasma with toluene at $-78^\circ C$ is shown in Table 3. Beside hydrogenation products, addition of, methyl radicals to toluene produced substituted toluene and combination reactions of benzyl and methyl radicals produced ethyl benzene. Formation of benzene in this reaction mixture has mechanistic significance since it indicates that hydrogen atoms had displaced methyl radical via ipso attack.

The mechanistic investigation of hydrogen addition to substituted aromatics was further continued by the reaction of H_2 /He plasma with model compounds such as bibenzyl, 9-dodecylanthracene, dodecylbenzene, dibenzothiophene and 2-naphthalene thiol, but this investigation will be the subject of a later publication.

REFERENCES

1. Yang, K., Batts, B.D., Wilson, M.A., Gorbaty, M. L., Maa, P.S., Attalla, M.I., Long, M.A., and He, S.J.X., *Fuel*, 76, 1105 (1997).
2. Sundaram, M. S. and Steinberg, M., US Patent No. 4,687,570, 1987.
3. Egiebor, N.O. and Gray, M.R., *Fuel*, 69, 1276 (1990).
4. Wilson, M.A., Attalla, M.I., Yang, K., He, S.J.X., Long, M.A., Batts, B.D., Smith, J.W., Voigtmann, M.F. and Smith, D.R., *Synthetic Fuels from Coal and Natural Gas, NERDPP End of Grant Report Project No. 1613, Canberra, Australia, 1993.*
5. Scott, D.w., *Bulletin* 666, US Bureau of Mines, 1974.
6. He, S. X. J., Long, M.A., Wilson, M.A., Gorbaty, M. L., and Maa, P.S., *Energy and Fuels*, 9, 616 (1995).
7. Yang, K., Wilson, M.A., Quezada, R.A., Prochazka, J.L., Long, M.A., He, S.J.X., Gorbaty, M. L., and Maa, P.S., *Fuel*, 76, 1091 (1997).
8. Ovalles, C., Hamana, A., Rojas, I., and Bolivar, R., *Proceedings of Eastern Oil Shel Symposium*, 161, 1993.
9. Ovalles, C., Arias, E.S., Hamana, A., Badell, C.B., and Gonzalez, G., *Fuel Chemistry preprints*, 39, 973 (1994).
10. Iton, L.E. and Maron, V.A., US Patent No. 5,068,485, 1991.
11. Berri, A., Berman, E., Vishkautsan, R., and Mazur, Y., *J. Am. Chem. Soc.*, 108, 6413 (1986)
12. Tanner, D.D and Zhang, L. *J. Am. Chem. Soc.*, 116, 6683 (1994)

Table 2. A comparison of the product distribution of the addition of atomic hydrogen (generated by microwave discharge of methane or H₂) to cyclohexene at -78°C.

Reaction %	CH ₄ or H ₂ Flow Rate (mL/min)	Time (min)			
0.90	4	15	79.6	15.8	4.7
0.80	6	30	73.6	17.3	9.0
0.80	1	30	55.3	29.4	15.3
1.4 ^a	4	20	91.8	5.9	2.3
2.1 ^a	4	30	86.0	11.3	2.7

^a Reaction with H₂.

Table 3. The Reaction of a CH₄ Plasma with Toluene (-78°C).

CH ₄ (mole) Passed into The System	Reaction Time (min)	C ₂ H ₆									Dimer	% CH ₄ Consumed
0.008	65	NQ	98.2	0.04	1.07	0.08	0.08	0.08	0.08	0.18	0.29	26
0.007	40		99.2	0.02	0.20	0.05	0.05	0.05	0.06	0.06	0.44	16.1
0.016	90		98.7	0.02	0.32	0.13	0.06	0.06	0.07	0.07	0.50	8.8
0.0018	10		99.4	0.03	0.10	0.04	0.05	0.05	0.05	0.05	0.13	37.9

NQ - not quantitated.