

# Electrophilic Methane Conversion

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## Introduction

Conversion of methane into substituted derivatives and higher hydrocarbons is a most desirable goal. If we survey the literature and current textbooks of organic chemistry,<sup>1</sup> they report pyrolytic and free-radical reactions (such as combustion, hydrogenation, nitration, sulfochlorination).<sup>2</sup> These reactions show little selectivity, characteristic of radical reactions. The chlorination of methane, for example, gives all four possible chloromethanes. Recently, catalytic oxidative condensation of methane to ethane with metal oxides<sup>3</sup> gained significance. Conversion to ethylene and acetylene via high-temperature conversion with chlorine<sup>4</sup> was also explored. It should be noted that the long-known high-temperature production of acetylene from methane is a related radical process. In many of these processes, however, a significant portion of methane is lost to further oxidation and soot formation.

A new approach to the possible chemical conversion of methane involves organometallic insertion reactions.<sup>5</sup> Pioneering work with iridium complexes and other transition-metal systems (rhodium, osmium, rhenium, etc.) was carried out. However, until now these were noncatalytic, stoichiometric reactions taking place in the coordination sphere of the metal complexes and therefore limited in their practical application.

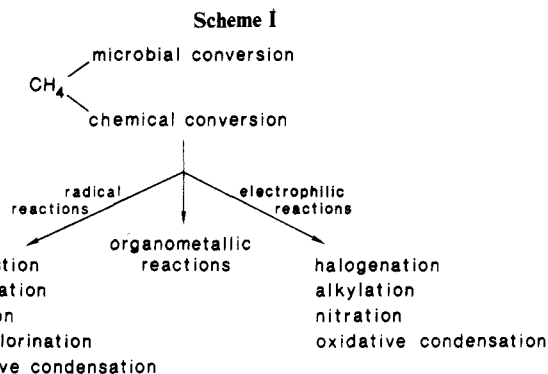
In the present Account an additional alternative, i.e., the electrophilic conversion reactions of methane to condensed and substituted products, will be discussed, a field where the research interest of my group centered in recent years.

Scheme I summarizes the presently existing alternative possibilities of methane conversion. Biological conversion of methane to higher hydrocarbons or to methyl alcohol may also be significant for the future.<sup>6</sup>

## Study of the Electrophilic Conversion of Methane

**Oxidative Condensation.** Our studies of the conversion of methane are based on the feasibility of electrophilic reactions of single bonds and thus saturated hydrocarbons.<sup>7</sup> C-H and C-C bonds can act as electron donors against strongly electrophilic reagents

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in low-nucleophilicity media forming two-electron, three-center (2e-3c) bound five-coordinate carbocations (of which  $\text{CH}_5^+$  is the parent). In the course of our studies on stable carbocations in superacidic systems, we as well as independently Hogeveen discovered in the late 1960s that saturated hydrocarbons, including methane, are readily protonated by these extreme acidic systems.<sup>8</sup> Methane was found to undergo with deuterated superacids rapid hydrogen-deuterium exchange under mild conditions even at room temperature. We have also found in the course of reactions with antimony pentafluoride based superacids that methane at moderate temperatures of 50-60 °C undergoes condensation to homologous  $\text{C}_2$ - $\text{C}_6$  hydrocarbons.

(1) For representative recent textbooks, see: (a) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 5th ed.; Allyn and Bacon: Boston, 1987. (b) Streitwieser, A., Jr.; Heathcock, C. H. *Introduction to Organic Chemistry*; McMillan: New York, 1976. (c) Solomon, T. W. *Organic Chemistry*, 3rd ed.; Wiley: New York, 1984. (d) Vollhart, K. P. C. *Organic Chemistry*; Freeman: New York, 1987. (e) Wade, L. G., Jr. *Organic Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1987.

(2) Asinger, F. *Paraffins, Chemistry and Technology*; Pergamon: Oxford, 1968.

(3) (a) Keller, G. E.; Bhasin, M. M. *J. Catal.* **1982**, *73*, 9. (b) Jones, C. A.; Leonard, J. J.; Saferanko, J. A. U.S. Patents 4 523 050, 1985; 4 499 322, 1985; 4 495 374, 1985; 4 560 821, 1985; 4 443 644, 1984; 4 442 645, 1984; 4 443 646, 1984; 4 443 647, 1984 assigned to Atlantic Richfield Co. (c) Hinsen, W.; Baerns, M. *Chem.-Ztg.* **1983**, *107*, 223.

(4) Benson, S. W. U.S. Patent 4 199 533, 1980.

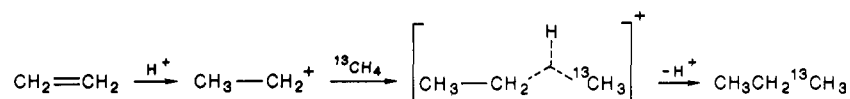
(5) (a) Bergman, R. G. *Science* **1984**, *223*, 902 and references therein. (b) Desrosiers, P. J.; Shinomoto, R. S.; Flood, T. *J. Am. Chem. Soc.* **1986**, *108*, 7964. (c) Schwartz, J. *Acc. Chem. Res.* **1985**, *18*, 302. (d) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1985**, *107*, 620; **1984**, *106*, 1650; **1982**, *104*, 4240; *Organometallics* **1983**, *2*, 562; **1986**, *5*, 590. (e) Crabtree, R. H., et al. *CHEMTECH* **1982**, 506; *Organometallics* **1985**, *4*, 519; **1984**, *3*, 1727; *J. Am. Chem. Soc.* **1984**, *106*, 2913; **1981**, *103*, 1217; **1982**, *104*, 107, 6994. (f) Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1982**, *104*, 2319; *Organomet. Chem.* **1983**, *243*, C78; **1981**, *218*, C39.

(6) Tedder, J. M.; Nechvatal, A.; Jubb, A. H. *Industrial Products. Basic Organic Chemistry*; Wiley: New York, 1975; Part 5.

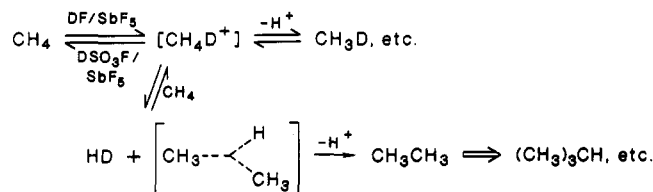
(7) Olah, G. A. *Carbocations and Electrophilic Reactions*; Verlag-Chemie: Weinheim, 1973; *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 173 and references therein.

(8) Olah, G. A.; Schlosberg, R. H. *J. Am. Chem. Soc.* **1968**, *90*, 2726. Olah, G. A.; Kloman, G.; Schlosberg, R. H. *J. Am. Chem. Soc.* **1969**, *91*, 3261. Hogeveen, H.; Gassbeck, C. J. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 319. Olah, G. A.; Halpern, Y.; Shen, J.; Mo, Y. K. *J. Am. Chem. Soc.* **1971**, *93*, 1251. Olah, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 808.

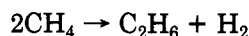
Table I



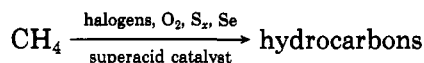
$^{13}\text{CH}_4:\text{C}_2\text{H}_4$	catalyst	products normalized, %				label content of $\text{C}_3$ fraction, %	
		$\text{C}_2\text{H}_6$	$\text{C}_3\text{H}_8$	<i>i</i> - $\text{C}_4\text{H}_{10}$	$\text{C}_2\text{H}_5\text{F}$	$^{13}\text{CC}_2\text{H}_8$	$\text{C}_3\text{H}_8$
98.7:1.3	$\text{TaF}_5:\text{AlF}_3$	51.9	9.9	38.2		31	69
99.1:0.9	$\text{TaF}_5$		15.5	3.0	81.5	91	9
99.1:0.9	$\text{SbF}_5$ :graphite	64.1	31.5		4.4	96	4



Combining two methane molecules to ethane and hydrogen

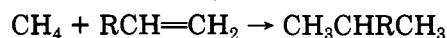


is endothermic by some 16 kcal/mol. Any condensation of methane to ethane and subsequently to higher hydrocarbons must thus overcome unfavorable thermodynamics. This can be achieved in condensation processes of oxidative nature, where hydrogen is removed by the oxidant. It is thus clear that in our original studies  $\text{SbF}_5$  or  $\text{FSO}_3\text{H}$  of the used superacid system also acted as oxidants. The oxidative condensation of methane was subsequently further studied in more detail.<sup>9</sup> It was found that with added suitable oxidants such as halogens, oxygen, sulfur, or selenium the superacid-catalyzed condensation of methane is feasible.



Significant practical problems, however, remain to carry out the condensation effectively. Conversion was so far achieved only in low yields. Due to the easy cleavage of longer chain alkanes by the same superacids,  $\text{C}_3$ - $\text{C}_6$  products predominate.

A further approach found useful was the use of natural gas instead of pure methane in the condensation reaction.<sup>9</sup> When natural gas is dehydrogenated, the  $\text{C}_2$ - $\text{C}_4$  alkanes it contain are converted into olefins. The resulting methane-olefin mixture can then without separation be passed through a superacid catalyst, resulting in exothermic alkylative condensation

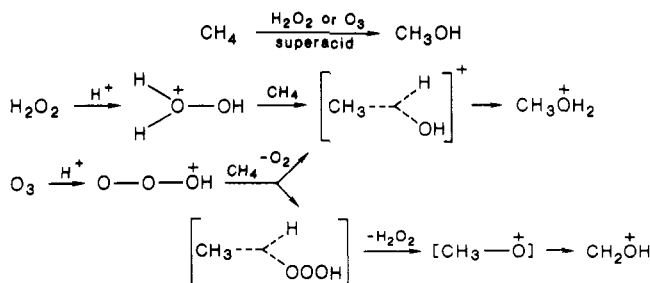


That methane under superacid catalysis is capable of electrophilic alkylation by olefins was demonstrated both in solution chemistry under stable ion conditions<sup>10</sup> and in heterogeneous gas-phase alkylations over solid catalysts using a flow system.<sup>11</sup> Not only propylene and

butylenes but also ethylene could be used as alkylating agents. When excess  $^{13}\text{C}$ -labeled methane was reacted with ethylene over solid superacid catalysts, mono- $^{13}\text{C}$ -labeled propane,  $^{13}\text{CH}_3\text{CH}_2\text{CH}_3$ , was obtained. As the acid catalysts also tend to oligomerize olefins, including ethylene, to minimize oligomerization, a substantial excess of methane was used in a flow system (Table I).

Superacid-catalyzed oxidative condensation of methane shows higher selectivity and can be carried out under milder conditions than radical reactions. A further challenge lies in finding conditions to carry out the condensation more effectively with suitable dehydrogenating agents (oxidants) such as oxygen, sulfur, selenium, etc. Combining superacidic activation with radical or radical cation oxidative processes is also pursued in our laboratory.

**Selective Oxygenation.** In our studies on superacid-catalyzed oxyfunctionalization of methane some time ago, we found that hydrogen peroxide in superacidic media gives methyl alcohol with very high (>95%) selectivity.<sup>12a</sup> Electrophilic OH insertion by protonated hydrogen peroxide in the C-H bonds of methane is the indicated reaction path. The reaction is limited, however, by the use of hydrogen peroxide to the liquid phase. In the superacidic medium methyl alcohol formed is immediately protonated to methyloxonium ion ( $\text{CH}_3\text{OH}_2^+$ ) and thus is protected from further oxidation. Similarly, we have studied the superacid-catalyzed oxygenation of methane with ozone which gives predominantly formaldehyde.<sup>12b</sup> The reaction is best understood as electrophilic insertion of  $^+\text{O}_3\text{H}$  into the methane C-H bonds, leading to a hydrotrioxide which then eliminates hydrogen peroxide giving protonated formaldehyde. The competing pathway forms protonated methyl alcohol with  $\text{O}_2$  elimination, but this reaction is only a relatively minor one.



Electrophilic oxygenation of methane to methyl alcohol under superacidic conditions proves the high selectivity of electrophilic substitution contrasted with nonselective radical oxidation. However, as indicated,

(12) (a) Olah, G. A.; Yoneda, N.; Parker, D. G. *J. Am. Chem. Soc.* 1976, 98, 483. (b) Olah, G. A.; Yoneda, N.; Parker, D. G. *J. Am. Chem. Soc.* 1976, 98, 5261.

(9) Olah, G. A. U.S. Patents 4 443 192, 1984; 4 513 164, 1984; 4 465 893, 1984; 4 467 130, 1984; 4 513 164, 1985.

(10) Olah, G. A.; Olah, J. A. *J. Am. Chem. Soc.* 1971, 93, 1256. Roberts, D. T., Jr.; Calihan, L. E. *J. Macromol. Sci., Chem.* 1973, A7(8), 1629, 1641. Siskin, M. *J. Am. Chem. Soc.* 1976, 98, 5413. Siskin, M.; Schlosberg, R. H.; Kocsis, W. P. In *New Strong Acid Catalyzed Alkylation and Reduction Reactions*; Albright, L. F., Goldsly, A. R., Eds.; ACS Monograph 55; American Chemical Society: Washington, DC, 1977. Sommer, J.; Muller, M.; Laali, K. *Nouv. J. Chim.* 1982, 6, 3.

(11) Olah, G. A.; Felberg, J. D.; Lammertsma, K. *J. Am. Chem. Soc.* 1983, 105, 6529.



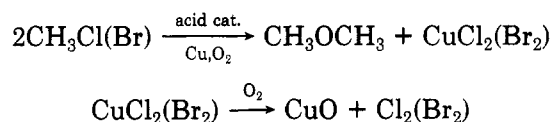


Table V

Conversion of Heterosubstituted Methanes over Bifunctional Acid-Base Catalysts									
	CH <sub>3</sub> OH	CH <sub>3</sub> OCH <sub>3</sub>	CH <sub>3</sub> OCH <sub>3</sub>	CH <sub>3</sub> OCH <sub>3</sub>	CH <sub>3</sub> SCH <sub>3</sub>	CH <sub>3</sub> NH <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> NH	(CH <sub>3</sub> ) <sub>3</sub> N	CH <sub>3</sub> Cl
catalyst	WO <sub>3</sub> on alumina	WO <sub>3</sub> on alumina	tantalum oxyfluoride on alumina	zirconium oxyfluoride on alumina	WO <sub>3</sub> on alumina	WO <sub>3</sub> on alumina	WO <sub>3</sub> on alumina	WO <sub>3</sub> on alumina	WO <sub>3</sub> on alumina
temp, °C	325	320	250	370	380	360	350	340	327
GHSV <sup>a</sup>	50	50	50	50	50	900	360	360	50
conversion, %	99 <sup>c</sup>	70	25	86	32	15	100	100	36
product distribution, <sup>b</sup> mol %									
	CH <sub>3</sub> OH	CH <sub>3</sub> OCH <sub>3</sub>	CH <sub>3</sub> OCH <sub>3</sub>	CH <sub>3</sub> OCH <sub>3</sub>	CH <sub>3</sub> SCH <sub>3</sub>	CH <sub>3</sub> NH <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> NH	(CH <sub>3</sub> ) <sub>3</sub> N	CH <sub>3</sub> Cl
CH <sub>4</sub>	46.2	39.8	30.1	46.3	63.8	34.5	29.9	25.1	57.3
C <sub>2</sub> H <sub>4</sub>	29.8	28.6	26.2	20.6	15.4	10.8	31.5	61.7	15.8
C <sub>2</sub> H <sub>6</sub>	0.8	1.2	3.7	7.5	1.0	8.9	2.0		2.2
C <sub>3</sub> H <sub>6</sub>	19.3	20.6	19.9	12.9	18.5	13.0	17.2	0.9	9.3
C <sub>3</sub> H <sub>8</sub>	<i>d</i>	0.8	1.8	2.4	<i>d</i>	<i>d</i>			2.4
C <sub>4</sub> H <sub>8</sub>	3.9	7.9	15.2	9.4	1.3	28.4	19.2	12.3	12.0
C <sub>5</sub> H <sub>10</sub>	<i>d</i>	1.1	3.1	0.9		4.3	0.2	<i>d</i>	1.0

<sup>a</sup> Gaseous hourly space velocity (mL g<sup>-1</sup> h<sup>-1</sup>). <sup>b</sup> Excluding higher aromatics, such as hexamethylbenzene and eventual coke formation on catalyst, as discussed in text. <sup>c</sup> Including 30% dimethyl ether. <sup>d</sup> Traces.

Since hydrolytic reactions inevitably raise problems of corrosion (although compared to the complexity and expense of syngas operations this seems to be well manageable), we have also studied the oxidative conversion of methyl halides with copper oxides (or copper and oxygen) into dimethyl ether under superacid-catalyzed nonaqueous conditions.<sup>18</sup>



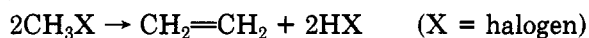
Since halogens can be used overall in a catalytic way (involving oxyhalogenative recycling of hydrogen halides) in the oxidative conversion of methane to methyl alcohol (dimethyl ether) via halogenation-hydrolysis, it is possible to convert methane to methyl alcohol without going through synthesis gas (the only commercial process used today). Syngas-based commercial methyl alcohol plants by economic necessity are of very large scale and involve huge capital investments. There seem to be advantages in the possibility of low-cost, smaller scale conversion facilities of methane to methyl alcohol, which also could provide a liquid product for transportation from remote locations where piping or cryoscopic transportation is not feasible (or may represent safety hazards).

**Condensation of Monosubstituted Methanes to Ethylene and Higher Hydrocarbons.** The feasible selective catalytic preparation of methyl halides and methyl alcohol from methane also allows subsequent condensation to ethylene and higher hydrocarbons.

Our studies centered primarily on the condensation of heterosubstituted methanes to ethylene and investigation of the mechanism of the essential initial C<sub>1</sub> → C<sub>2</sub> conversion step fundamental to all further transformations.

The Mobil Oil Corp. was first to develop a methyl alcohol to hydrocarbons process using an intermediate pore size zeolite (ZSM-5) catalyst.<sup>19</sup> In contrast to the

Mobil process which starts with syngas-based methyl alcohol, our studies were an extension of the previously discussed electrophilic functionalization of methane and have not involved any zeolites as catalysts. We have found that bifunctional acidic-basic catalysts such as tungsten oxide on alumina or related supported transition metal oxides or oxyfluorides such as tantalum or zirconium oxyfluoride are capable of condensing methyl chloride, methyl alcohol (dimethyl ether), methyl mercaptan (dimethyl sulfide), or methylamines primarily to ethylene (and propylene).<sup>20</sup>



or

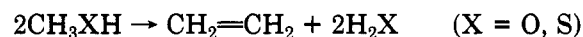


Table V summarizes typical results.

In the reactions methane is the major byproduct formed probably by competing radical reactions. However, since the overall starting material is methane, this represents only the need for recycling.

According to our studies the conversion of methyl alcohol over bifunctional acidic-basic catalyst after initial acid-catalyzed dehydration to dimethyl ether involves oxonium ion formation catalyzed also by the acid functionality of the catalyst. This is followed by basic site catalyzed deprotonation to a reactive surface-bound oxonium ylide, which is then immediately methylated by excess methyl alcohol or dimethyl ether leading to the crucial C<sub>1</sub> → C<sub>2</sub> conversion step. The ethyloxonium ion formed subsequently readily eliminates ethylene. All other hydrocarbons are derived from ethylene by known oligomerization-fragmentation chemistry. Propylene is formed via cyclopropane (see Scheme III).

The intermolecular nature of the C<sub>1</sub>-C<sub>2</sub> transformation step was proven by experiments using mono-<sup>13</sup>C-labeled dimethyl ether and determining the isotopic composition of product ethylene. This ruled out an intramolecular Stevens type rearrangement under the reaction conditions.

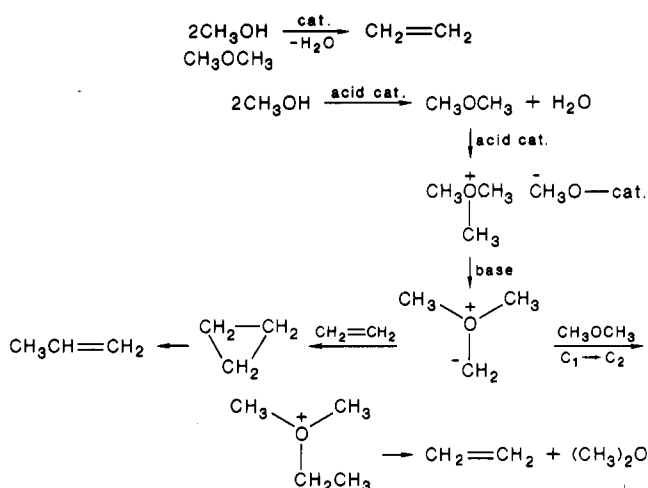
It is not necessary to involve the formation of a free

(18) Bukala, J.; Olah, G. A. *Abstracts of Papers*, 192nd National Meeting of the American Chemical Society, Anaheim, CA; American Chemical Society: Washington, DC, 1986; ORGN 328.

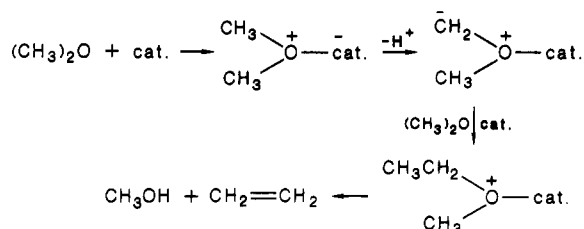
(19) For a review, see: Chang, C. D. *Catal. Rev.—Sci. Eng.* 1983, 25, 1 and references therein.

(20) Olah, G. A.; Doggweiler, H.; Felberg, J. D.; Frohlich, S.; Grdina, M. J.; Karpeles, R.; Keumi, T.; Inaba, S.; Ip, W. M.; Lammertsma, K.; Salem, G.; Tabor, D. C. *J. Am. Chem. Soc.* 1984, 106, 2143. Olah, G. A. U.S. Patent 4373 109, 1983 and corresponding foreign patents.

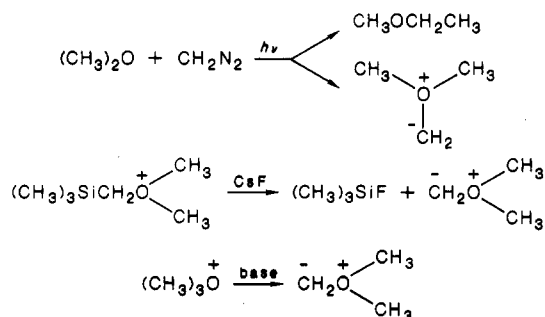
Scheme III



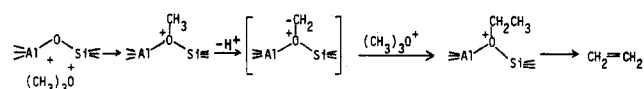
Meerwein type trimethyloxonium ion in the heterogeneous catalytic reaction. Lewis type coordination complexes of dimethyl ether with the acidic catalyst sites having oxonium ion character can be involved, giving subsequently via deprotonation surface-bound oxonium ylides followed by methylation and elimination of ethylene.<sup>20,21a,b</sup>



In our work dealing with the reaction mechanism, we carried out model studies of the generation of the interesting novel oxonium ylides by the reaction of dimethyl ether with methylene generated by photolysis of diazomethane, by fluorinative cleavage of silylated oxonium ions, and even by strong base induced deprotonation of trimethyloxonium ion salts.<sup>22</sup>

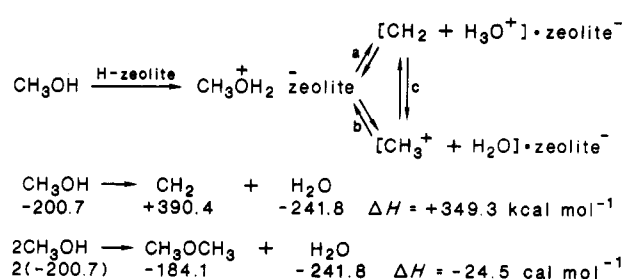


(21) (a) Olah, G. A.; Prakash, G. K. S.; Ellis, R. W.; Olah, J. A. *J. Chem. Soc., Chem. Commun.* 1986, 9. (b) Note Added in Proof. The just published communication by Hellring et al. (Hellring, S. D.; Schmitt, K. D.; Chang, C. D. *J. Chem. Soc., Chem. Commun.* 1987, 1320) on the decomposition of trimethyloxonium ion in zeolite ZSM-5 reports initial O-transmethylation of the aluminosilicate site followed by deprotonation to a surface-stabilized ylide which then undergoes subsequent methylation to give ethyl-ZSM-5 and through it ethylene

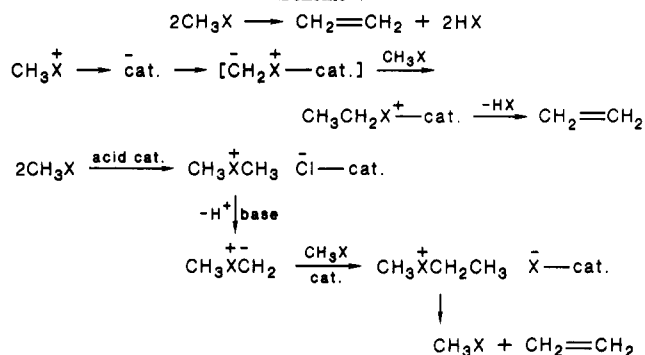


This mechanism clearly is an interesting variation of our original oxonium ylide mechanism.

Scheme IV



Scheme V



Whereas our studies did not involve zeolite catalysts, it is probable that in the ZSM-5-catalyzed Mobil process too no direct monomolecular dehydration of methyl alcohol to methylene is involved. This is thermodynamically not feasible even when considering that surface complexation could somewhat affect the otherwise very endothermic thermodynamics (see Scheme IV).

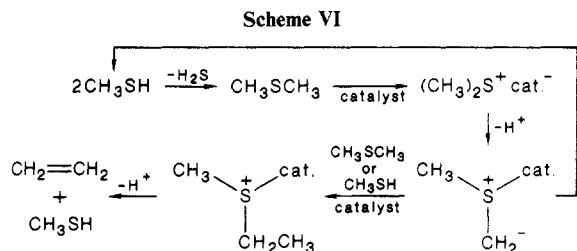
It is, therefore, reasonable to suggest that in the zeolite-catalyzed process, too, condensation proceeds via bimolecular dehydration of methyl alcohol to dimethyl ether, which subsequently is transformed via the oxonium ylide pathway and intermolecular methylation responsible for the crucial C<sub>1</sub>-C<sub>2</sub> transformation.<sup>21a,b</sup> The competing formation of C<sub>1</sub> → C<sub>2</sub> conversion products via free radical (homolytic) or radical cation processes (involving one-electron transfer) cannot be completely excluded in heterogeneous catalytic reactions at higher temperatures. Observed methane formation is indicative for possible radical reactions, but the amount of ethane observed is generally low. A radical or radical ion type condensation mechanism inevitably should also give related coupling products which are, however, not observed. Once ethylene is formed in the reactions, it can undergo acid-catalyzed oligomerization-cleavage reactions, undergo methylene insertion, or react further with methyl alcohol giving higher hydrocarbons.

When the acidity of the catalyst is increased, condensation of methyl alcohol or dimethyl ether leads to saturated hydrocarbons and aromatics, with no olefins found in the products. With tantalum or niobium pentafluoride based catalysts our studies at 300 °C resulted in conversion to gasoline range branched hydrocarbons and some (30%) aromatics.<sup>23</sup> This composition is similar to that reported with H-ZSM-5 zeolite catalyst.

The condensation of methyl chloride or bromide to ethylene proceeds by a related mechanistic path in-

(22) Olah, G. A.; Doggweiler, H.; Felberg, J. D. *J. Org. Chem.* 1984, 49, 2112, 2116; *J. Am. Chem. Soc.* 1985, 107, 4975.

(23) Salem, G. Ph.D. Thesis, University of Southern California, 1980.



volving initial acid catalyzed dimethylhalonium ion (or related catalyst complex) formation with subsequent proton elimination to a reactive methylhalonium methylide which then is readily methylated by excess methyl halide. The ethylhalonium ion intermediate gives ethylene by  $\beta$ -elimination (see Scheme V).

Similar reaction paths can be visualized for condensation of methyl mercaptan or methylamines. It is interesting to note that Corey's well-known synthetic studies<sup>24</sup> with the use of dimethylsulfonium methylide mentioned the need to generate the ylide at low temperatures; otherwise, decomposition to ethylene takes place. Indeed, this is a similar reaction to that involved in the higher temperature acid-base-catalyzed condensation reaction (see Scheme VI).

Labeling experiments using mono C-13 label dimethyl sulfide (similar to experiments using  $^{13}\text{CH}_3\text{OCH}_3$ ) in heterogeneous gas-phase reactions over  $\text{WO}_3/\text{Al}_2\text{O}_3$  catalyst showed that the  $\text{C}_1$ - $\text{C}_2$  formation step under these conditions is intermolecular in nature, involving transmethylation of the ylide, and not a Stevens type intramolecular rearrangement.

## Conclusions

The feasibility of superacid-catalyzed oxidative condensation of methane as well as its electrophilic selective conversion to monofunctionalized derivatives including methyl halides and methyl alcohol was demonstrated. Subsequent conversion to ethylene and through it to higher hydrocarbons is also readily carried out over bifunctional acid-base catalysts. The underlying chemistry of electrophilic methane functionalization is based on the ability of carbon to form five-coordinate carbonium ion intermediates of the  $\text{CH}_5^+$  type.<sup>25</sup> These do not violate the octet rule as they involve only eight electrons in the carbon valence shell with one electron pair, however, forming a two-electron, three-center bond. Further condensation of substituted methanes to ethylene (propylene) and derived hydrocarbons proceeds through an onium-ylide pathway. It is not intended to suggest that the electrophilic path is at the present time the most feasible or promising in

(24) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353.

(25) For a review of the chemistry of  $\text{CH}_5^+$  and related systems, see: Olah, G. A.; Prakash, G. K. S.; William, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley-Interscience: New York, 1987.

methane conversion chemistry. Metal oxide catalyzed oxidative condensation to ethane, for example, recently made much progress. At the same time discussed superacid catalyzed electrophilic activation combined with oxidative processes could provide significant advantages and certainly represent a new alternative worthy of further studies.

During the short-lived alternate fuel research boom of the 1970s and early 1980s (following the oil crises), extensive research on Fischer-Tropsch chemistry was carried out in the U.S. Western Europe, and Japan. On the basis of the proven commercial feasibility of the Fischer-Tropsch hydrocarbon synthesis<sup>26</sup> (regardless of its economic or its social-political considerations), it is customary to refer to  $\text{C}_1$  chemistry (i.e., the chemistry of one-carbon entities) as the conversion of syngas into higher hydrocarbons. This generalization includes Mobile Oil's ZSM-5-catalyzed methyl alcohol to gasoline conversion process,<sup>19</sup> as the starting methyl alcohol itself is manufactured from syngas. Based on ongoing research studies on oxidative radical condensation of methane and its organometallic insertion reactions, as well as the electrophilic chemistry discussed in this Account,  $\text{C}_1$  chemistry can hardly be equated anymore only with syngas chemistry. Direct conversion to methane represents a possible attractive alternative to Fischer-Tropsch chemistry to produce synthetic hydrocarbons from a still abundant natural source. Even after our presently known natural gas reserves are exhausted, new drilling technology exploring increasingly greater depths (including the possibility of finding a biological deep methane in the mantle of the earth<sup>27</sup>) and use of the biomass may substantially extend the availability of natural gas. Its use as raw material and building block for our future hydrocarbon needs is a promising one. Our presently still quite abundant oil reserves give us time to develop through basic research new approaches for the future. Chemistry should welcome the chance and take on the challenge.

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**Registry No.** Methane, 74-82-8.

(26) (a) Fischer, F.; Tropsch, H. Ger. Patent 411 216, 1925; Ger. Patent 484 337, 1929. (b) Asinger, F. *Paraffins*; Pergamon: Oxford, 1968; Chapter 2 and references therein.

(27) For a review, see: Frohning, C. D.; Kolbel, H.; Ralek, M.; Rottig, W. In *Chemierohstoffe aus Kohle*; Farbe, J., Ed.; Thieme: Stuttgart, 1977; Chapter 8, pp 219-299.