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. they report pyrolytic and free-radical reactions (such as combustion, hydrogenation, nitration, sulfochlorination).2 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 oxides³ gained significance. Conversion to ethylene and acetylene via high-temperature conversion with chlorine 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.⁵ 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.

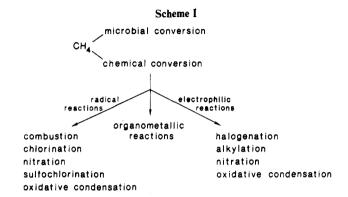
In the present Account an additional alternative, i.e., the electrophilic conversion reactions of methane to condensed and substituted products, will be discussed, a field where the research interest of my group centered in recent years.

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.⁶

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.⁷ 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 ${\rm CH_5}^+$ 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. Methane was found to undergo with deuteriated 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 ${\rm C_2-C_6}$ 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 4199 533, 1980.
 (5) (a) Bergman R. G. Science 1984, 223, 902 at
- (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.

	products normalized, %					label content of C_3 fraction, %	
¹³ CH ₄ :C ₂ H ₄	catalyst	C_2H_6	C_3H_8	i-C4H10	C_2H_5F	$\overline{^{13}\mathrm{CC_2H_8}}$	C_3H_8
98.7:1.3	TaF5:AlF3	51.9	9.9	38.2		31	69
99.1:0.9	TaF_5		15.5	3.0	81.5	91	9
99.1:0.9	SbF ₅ :graphite	64.1	31.5		4.4	96	4

$$\begin{array}{c} \text{CH}_4 \xrightarrow{\text{DSO}_3\text{F}/} \text{[CH}_4\text{D}^+] \xrightarrow{-\text{H}^+} \text{CH}_3\text{D, etc.} \\ \text{SbF}_6 & \text{//CH}_4 \\ \\ \text{HD} + \left[\text{CH}_3\text{--} \checkmark \xrightarrow{\text{CH}_3} \right] \xrightarrow{-\text{H}^+} \text{CH}_3\text{CH}_3 \implies (\text{CH}_3)_3\text{CH, etc.} \end{array}$$

Combining two methane molecules to ethane and hydrogen

$$2CH_4 \rightarrow C_2H_6 + H_2$$

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 SbF₅ or FSO₃H of the used superacid system also acted as oxidants. The oxidative condensation of methane was subsequently further studied in more detail.9 It was found that with added suitable oxidants such as halogens, oxygen, sulfur, or selenium the superacid-catalyzed condensation of methane is feasible.

$$CH_4 \xrightarrow{\text{halogens, O}_2, S_z, Se} \text{hydrocarbons}$$

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, C₃-C₆ products predominate.

A further approach found useful was the use of natural gas instead of pure methane in the condensation reaction.9 When natural gas is dehydrogenated, the C₂-C₄ 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

$$CH_4 + RCH = CH_2 \rightarrow CH_3CHRCH_3$$

That methane under superacid catalysis is capable of electrophilic alkylation by olefins was demonstrated both in solution chemistry under stable ion conditions¹⁰ and in heterogeneous gas-phase alkylations over solid catalysts using a flow system. 11 Not only propylene and

(9) Olah, G. A. U.S. Patents 4443192, 1984; 4513164, 1984; 4465893,

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

butylenes but also ethylene could be used as alkylating agents. When excess ¹³C-labeled methane was reacted with ethylene over solid superacid catalysts, mono-¹³Clabeled propane, ¹³CH₃CH₂CH₃, 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. 12a 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 (CH₃OH₂⁺) and thus is protected from further oxidation. Similarly, we have studied the superacid-catalyzed oxygenation of methane with ozone which gives predominantly formaldehyde. 12b The reaction is best understood as electrophilic insertion of +O₃H 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 O2 elimination, but this reaction is only a relatively minor one.

$$CH_{4} \xrightarrow{H_{2}O_{2} \text{ or } O_{3}} CH_{3}OH$$

$$H_{2}O_{2} \xrightarrow{H^{+}} H \xrightarrow{\downarrow} OH \xrightarrow{CH_{4}} CH_{3} - CH_{3}OH$$

$$O_{3} \xrightarrow{H^{+}} OOOH \xrightarrow{H} CH_{4} \xrightarrow{O_{2}} CH_{3} - OOH \xrightarrow{H_{2}O_{2}} CH_{3} - OOH \xrightarrow{CH_{2}OO} CH_{2}OOH$$

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 4443 192, 1984; 4513 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. Myller, M. Laeli, K. Noun, J. Chim. 1982, 6, 3 J.; Muller, M.; Laali, K. Nouv. J. Chim. 1982, 6, 3

% product

Table II

Chlorination and Bromination of Methane over Supported Acid Catalysts

					% pi	oduct
catalyst	$\mathrm{CH_4/Cl_2}$	react temp, °C	GHSV, $mL g^{-1} h^{-1}$	% convers	CH ₃ Cl	CH ₂ Cl ₂
			A			
10% FeO _x Cl _y /Al ₂ O ₃	1:2	250	100	16	88	12
20% TaOF ₃ /Al ₂ O ₃	1:2	235	50	14	82	6^a
5, 2 5	1:2	235	1400	15	93	7
	2:1	235	1200	13	96	4
20% NbOF ₃ /Al ₂ O ₃	1:3	250	50	10	90	10
10% ZrOF ₂ /Al ₂ O ₃	1:4	270	100	34	96	4
Nafion-H	1:4	185	100	18	88	12
20% GaO _x Cl _y /Al ₂ O ₃	1:2	250	100	26	90	10
20% TaF5-Nafion-H	1:2	200	100	11	97	3
25% SbF ₅ -graphite	1:2	180	100	7	98	2

					,0 Pi	ouucu
catalyst	$\mathrm{CH_4/Br_2}$	react temp, °C	GHSV, $mL g^{-1} h^{-1}$	% convers	$\overline{\mathrm{CH_{3}Br}}$	CH_2Br_2
			В			
20% SbOF ₃ /Al ₂ O ₃	5:1	200	100	20	99	
$20\% \text{ TaOF}_3/\text{Al}_2\text{O}_3$	15:1	250	50	14	99	

Supported Platinum Metal Catalyzed Halogenation of Methane

					% p	roduct
catalyst	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\mathrm{CH_{2}Cl_{2}}$				
			Chlorination			
0.5% Pt/Al ₂ O ₃	1:3	100	600	11ª	~100	
,	1:3	150	600	16^a	92	8
	1:3	200	600	32^a	92	8
	2:1	250	300	23^b	98	<2
	3:1	250	300	36^b	99	1
$5\% \text{ Pd/BaSO}_4$	2:1	200	600	30^{b}	99	1
]	Bromination			
0.5% Pt/Al ₂ O ₃	2:1	200	300	8^b	99	c

^a Based on methane. ^b Based on chlorine (bromine). ^c Trace.

hydrogen peroxide chemistry is limited to the liquid phase, and the desirable goal of achieving selective heterogeneous catalytic oxidation of methane to methyl alcohol remains elusive. Consequently, in our continued studies we concentrated on combining selective halogenation of methane to methyl halides with subsequent hydrolysis to methyl alcohol.

Selective Halogenation to Methyl Halides. In 1972 we first observed that chlorination of methane in low-nucleophilicity, superacidic solutions at low temperature gives methyl chloride in high selectivity. No methylene chloride or chloroform was observed in the reaction. Under the used stable ion conditions dimethylchloronium ion formation also occurs. This is, however, a reversible process and helps to minimize competing alkylation of methane to ethane (and higher homologues) which is becoming more predominant when methyl fluoride is formed via halogen exchange.

$$CH_4 \xrightarrow{SbF_5-Cl_2-SO_2ClF} \begin{bmatrix} H & C \\ -78 & C \end{bmatrix} \xrightarrow{-H^+} CH_3Cl \xrightarrow{CH_3Cl} CH_3ClCH_3$$

In extending the electrophilic halogenation (chlorination and bromination) of methane to catalytic heterogeneous gas-phase reactions, we have recently found^{14a,b} that methane can be chlorinated or brominated over various solid acid or supported platinum group metal catalysts (the latter is the heterogeneous analogue of Shilov's solution chemistry) to methyl

(13) Olah, G. A.; Mo, Y. K. J. Am. Chem. Soc. 1972, 94, 6864. Olah, G. A.; Schilling, P.; Mo, Y. K. J. Am. Chem. Soc. 1973, 95, 7686.

halides with high selectivity under relatively mild conditions. Table II summarizes some of the results.

Both reactions mechanistically are electrophilic insertion reactions into the methane C-H bonds. In the platinum insertion reaction subsequent chlorolysis of the surface-bound methylplatinum chloride complex regenerates the catalyst and gives methyl chloride.

$$\begin{array}{c} X_2 + catalyst & \rightleftharpoons [X^+][catalyst - X^-] & (X = CI, Br) \\ [X^+][catalyst - X^-] + CH_4 & \rightleftharpoons \begin{bmatrix} CH_3 - -\sqrt{H} \\ -\sqrt{H} \end{bmatrix}^+ \\ CH_3 - X + catalyst + HX \\ CH_4 + PtCI_2 & \rightleftharpoons \begin{bmatrix} CH_3 \\ -\sqrt{H} \end{bmatrix} & CH_3 Pt \begin{bmatrix} CI \\ -\sqrt{H} \end{bmatrix} & CH_3$$

Concerning the electrophilic halogenation of methane, it should also be pointed out the singlet-triplet energy difference of positive halogens (as illustrated for the hypothetical X⁺ ions) favors the latter. Electrophilic halogenations thus may be more complex and can involve radical ions even under conditions where con-

(14) (a) Olah, G. A.; Gupta, B.; Farnia, M.; Felberg, J. D.; Ip, W. M.; Husain, A.; Karpeles, R.; Lammertsma, K.; Melhotra, A. K.; Trivedi, N. J. J. Am. Chem. Soc. 1985, 107, 7097. (b) Olah, G. A. U.S. Patent 7523 040, 1985 and corresponding foreign patents. (c) Work carried out in cooperation with Prof. K. N. Houk.

Scheme II

$$CH_{4} \xrightarrow{\text{acid cat.}} HX + CH_{3}X$$

$$Pt \text{ or } Pd \xrightarrow{HX} HX + CH_{3}X$$

$$CH_{3} CH_{3} CH_{$$

ventional radical chain halogenation is basically absent. In the halogenation of methane hydrogen halides are the equimolar byproducts. Hydrogen halides are similarly byproducts in subsequent condensation or sub-

sitution reactions. Their recycling by oxyhalogation is essential to be able to utilize halogen only as catalytic agent in the overall conversion of methane into methyl alcohol, ethylene, or higher hydrocarbon products.

The Deacon process for oxidation of hydrogen chloride to chlorine is technologically difficult, although Kellogg's improved Kel-Chlor process was used in the 1970s industrially. Recently, an improved version of the Deacon process is reported by Mistui Toatsu Chemicals (MT-Chlor process) using a chromium-based catalyst in a gas-phase, fluidized bed reaction at a relatively modest 400 °C. Regardless, technical problems of oxidative chlorine recycling remain formidable.

The oxychlorination of methane with HCl + $\rm O_2$ was also extensively studied and is industrially used. ^{16a} As the direct radical chlorination of methane, this also gives mixtures of all chloromethanes. In contrast, we found that the selective monoxychlorination of methane over supported noble-metal catalyst is possible and gives methyl chloride in good selectivity. ^{16b} Oxybromination of methane with hydrogen bromide is even more effective. As HBr is very readily oxidized to bromine, its direct oxidation and continuous recycling can be more easily and effectively affected. Corrosion problems and the need to continuously oxidatively recycle HX obviously represent substantial, but technically solvable, problems particularly as the reactions are carried out at relatively modest temperatures.

Methyl Alcohol. Combining the halogenation of methane with catalytic gas-phase hydrolysis, methyl alcohol (and dimethyl ether) can be obtained in high selectivity¹⁴ (see Scheme II). The hydrolysis of methyl chloride with caustic was first carried out by Berthelot in the 1830s.¹⁷ He first prepared methyl alcohol by the reaction, which was, however, never utilized in a practical way. Seemingly, no attempt was made until our work to extend the hydrolysis of methyl halides to catalytic gas-phase conditions. In the course of our work we carried out an extensive study of such reactions and found that methyl halides hydrolyze over alumina to methyl alcohol-dimethyl ether in yields up to 25% per pass with gaseous space velocities of up to 1500 mL g⁻¹ h⁻¹ and high turnovers¹⁴ (see Table III). Even better results were obtained over supported metal oxide-hydroxide catalysts (see Table IV).

On the catalyst surface in the course of hydrolysis reactions intermediate complexes are formed which are themselves, however, further hydrolyzed, regenerating

Table III

Hydrolysis of Methyl Halides over γ -Alumina

	react	GHSV.		% p	roduct
H_2O/CH_3Cl				CH ₃ OH	CH ₃ OCH ₃
		Methyl Ch	loride		
5	375	1500	13	45	55
10	375	1500	16	70	30
15	375	1500	18	80	20
		Methyl Bro	omide		
10	375	1000	23	73	27
		Table l	(V		

Hydrolysis of Methyl Chloride over γ -Alumina-Supported Metal Oxide/Metal Hydroxide Catalysts (H₂O/CH₃Cl Ratio 10, 375 °C, GHSV \sim 1200 mL g⁻¹ h⁻¹)

cat. $10\% \text{ M}_{x}\text{O}_{y}/10\%$ $\text{M(OH)}_{x}/80\% \gamma\text{-Al}_{2}\text{O}_{3}$	% convers to CH ₃ OH/CH ₃ OCH ₃
$V_2O_5/Al(OH)_3/\gamma-Al_2O_3$	5
$MnO_2/Al(OH)_3/\gamma$ - Al_2O_3	13
$\text{Cr}_2\text{O}_3/\text{Al}(\text{OH})_3/\gamma\text{-Al}_2\text{O}_3$	14
$MgO/Al(OH)_3/\gamma-Al_2O_3$	17
$ZrO_2/Al(OH)_3/\gamma-Al_2O_3$	14
$BaO/Al(OH)_3/\gamma-Al_2O_3$	9
$TiO_2/Al(OH)_3/\gamma-Al_2O_3$	18
$ZnO/Al(OH)_3/\gamma-Al_2O_3$	25
$\text{Fe}_2\text{O}_3/\text{Al}(\text{OH})_3/\gamma\text{-Al}_2\text{O}_3$	9
$ZnO/(Ni(OH)_2/\gamma-Al_2O_3$	11
$ZnO/Bi(OH)_3/\gamma-Al_2O_3$	7
$\mathrm{ZnO/Mg(OH)_2/\gamma\text{-}Al_2O_3}$	6

Hydrolysis of Methyl Chloride over γ -Alumina-Based Catalysts

cat.	% convers	cat.	% convers
γ -Al ₂ O ₃	16	$Al(OH)_3/\gamma$ - Al_2O_3	15
$ZnO/\gamma-Al_2O_3$	19	$ZnO/Al(OH)_3/\gamma-Al_2O_3$	25

the metal hydroxide (oxide). Eventually, however, metal halide formation on the catalyst surface from the hydrogen halide byproduct of the reaction takes place, and the catalysts must be regenerated by oxidative hydrolysis.

We have also found that solid acid catalysts, such as Nafion-H, are also capable of catalyzing the hydrolysis of methyl halides and yield under the reaction conditions of 150-170 °C dimethyl ether^{16b}

$$2CH_3X \xrightarrow{H_2O} CH_3OCH_3 + 2HX$$

Halogenation of methane followed by hydrolysis consequently is a suitable way to obtain methyl alcohol (and dimethyl ether).

CH₄
$$\frac{x_2}{cat}$$
 CH₃X + HCI
 $\frac{x_2 \cdot H_2O}{cat}$ (X = CI, Br)
CH₃OH [(CH₃)₂O]

It was also possible to prove that halogens together with steam can be reacted with methane over acidic catalysts in a single step, producing methyl alcohol (dimethyl ether), although conversion of methane so far was only modest.^{16b}

$$CH_4 + Br_2 + H_2O \rightarrow CH_3OH + 2HBr$$

Simultaneous oxidation of HBr can make the reaction catalytic in bromine and also minimize reversible formation of methyl bromide.

$$2HBr + {}^{1}/{}_{2}O_{2} \rightarrow H_{2}O + Br_{2}$$

 $CH_{4} + {}^{1}/{}_{2}O_{2} \xrightarrow{Br_{2}} CH_{3}OH$

^{(15) (}a) Weissermel, K.; Arpe, H. J. Industrial Organic Chemistry; Verlag-Chemie: Weinheim, 1978; p 195. (b) Chem. Week 1987, 18. (16) (a) See ref 15a, pp 47-48. (b) Olah, G. A.; et al., unpublished results.

⁽¹⁷⁾ Berthelot, M. Ann. Chim. 1858, 52, 97.

Table V

Conversion of Heterosubstituted Methanes over Bifunctional Acid-Base Catalysts

	CH ₂ OH	CH ₂ OCH ₃	CH ₃ OCH ₃	CH ₃ OCH ₃	CH ₃ SCH ₃	CH ₃ NH ₂	(CH ₂) ₂ NH	(CH ₂) ₂ N	CH ₃ Cl
				011300113				. 0,0	
catalyst	WO ₃ on alumina	WO ₃ on alumina	tantalum oxyfluoride on alumina	zirconium oxyfluoride on alumina	WO ₃ on alumina	WO ₃ on alumina	WO ₃ on alumina	WO ₃ on alumina	WO ₃ on alumina
temp, °C	325	320	250	370	380	360	350	340	327
$GHSV^a$	50	50	50	50	50	900	360	360	50
conversion,	99°	70	25	86	32	15	100	100	36

	product distribution, b mol %								
	CH ₃ OH	CH ₃ OCH ₃	CH ₃ OCH ₃	CH ₃ OCH ₃	CH ₃ SCH ₃	CH ₃ NH ₂	$(CH_3)_2NH$	$(CH_3)_3N$	CH ₃ Cl
CH ₄	46.2	39.8	30.1	46.3	63.8	34.5	29.9	25.1	57.3
C_2H_4	29.8	28.6	26.2	20.6	15.4	10.8	31.5	61.7	15.8
C_2H_6	0.8	1.2	3.7	7.5	1.0	8.9	2.0		2.2
C_3H_6	19.3	20.6	19.9	12.9	18.5	13.0	17.2	0.9	9.3
C_3H_8	d	0.8	1.8	2.4	d	d			2.4
C_4H_8	3.9	7.9	15.2	9.4	1.3	28.4	19.2	12.3	12.0
C_5H_{10}	d	1.1	3.1	0.9		4.3	0.2	d	1.0

^a Gaseous hourly space velocity (mL g⁻¹ h⁻¹). ^b Excluding higher aromatics, such as hexamethylbenzene and eventual coke formation on catalyst, as discussed in text. ^c Including 30% dimethyl ether. ^d 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.¹⁸

$$2CH_3Cl(Br) \xrightarrow{\text{acid cat.}} CH_3OCH_3 + CuCl_2(Br_2)$$

$$CuCl_2(Br_2) \xrightarrow{O_2} CuO + Cl_2(Br_2)$$

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 $C_1 \rightarrow C_2$ 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. ¹⁹ 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).²⁰

$$2CH_3X \rightarrow CH_2 = CH_2 + 2HX$$
 (X = halogen)

or

$$2CH_{2}XH \rightarrow CH_{2}=CH_{2} + 2H_{2}X$$
 (X = 0, S)

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 $C_1 \rightarrow C_2$ conversion step. The ethyloxonium ion formed subsequently readily eliminates ethylene. All other hydrocarbons are derived from ethylene by known oligomerization—fragmenation chemistry. Propylene is formed via cyclopropane (see Scheme III).

The intermolecular nature of the C_1 – C_2 transformation step was proven by experiments using mono- 13 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 4373109, 1983 and corresponding foreign patents.

$$\begin{array}{c} \text{Scheine III} \\ \text{2CH}_3\text{OH} & \frac{\text{cat.}}{-\text{H}_2\text{O}} & \text{CH}_2 = \text{CH}_2 \\ \text{CH}_3\text{OCH}_3 & \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \\ & & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & \\ & & & \\ &$$

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. 20,21a,b

$$(CH_3)_2O + cat.$$
 $CH_3 \rightarrow CH_3 \rightarrow Cat.$ $CH_3 \rightarrow Cat.$ $CH_3 \rightarrow Cat.$ $CH_3 \rightarrow Cat.$ $CH_3OH + CH_2 \rightarrow CH_2 \rightarrow CH_3$ $CH_3 \rightarrow Cat.$ $CH_3CH_2 \rightarrow Cat.$ $CH_3CH_2 \rightarrow Cat.$

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.²²

$$(CH_{3})_{2}O + CH_{2}N_{2} \xrightarrow{h_{\nu}} CH_{3}OCH_{2}CH_{3}$$

$$CH_{3} \xrightarrow{+} CH_{3}$$

$$CH_{3} \xrightarrow{+} CH_{3}$$

$$CH_{3} \xrightarrow{+} CH_{2}$$

$$(CH_{3})_{3}SICH_{2}O$$

$$CH_{3} \xrightarrow{+} CH_{3}$$

(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

$$\exists \text{A1} \xrightarrow{\downarrow 0} \text{S1} \rightleftharpoons \rightarrow \exists \text{A1} \xrightarrow{\downarrow 0} \text{S1} \rightleftharpoons \Rightarrow \text{A1} \xrightarrow{\downarrow 0} \text{S1} \rightleftharpoons \xrightarrow{\downarrow 0} \text{CH}_2 \rightleftharpoons \text{CH}_2$$

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

Scheme IV

$$[CH_{2} + H_{3}O^{+}] \cdot zeolite^{-}$$

$$CH_{3}OH \xrightarrow{H-zeolite} CH_{3}OH_{2} \xrightarrow{zeolite} CH_{3}OH_{2} \xrightarrow{H-zeolite} CH_{3}OH_{2} + H_{2}O] \cdot zeolite^{-}$$

$$CH_{3}OH \xrightarrow{H-zeolite} CH_{2} + H_{2}O \xrightarrow{L_{3}OH_{3}} CH_{3}OH_{2} + H_{2}O \xrightarrow{L_{3}OH_{3}OH_{3}} CH_{2}OH_{3}OH_{3} + H_{2}O \xrightarrow{L_{3}OH_{3}OH_{3}} CH_{2}OH_{2$$

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_1 – C_2 transformation. ^{21a,b} The competing formation of C_1 \rightarrow C_2 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.23 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 β -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 studies²⁴ with the use of dimethysulfonium 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 $^{13}\mathrm{CH_3OCH_3})$ in heterogeneous gas-phase reactions over WO_3/Al_2O_3 catalyst showed that the C_1-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 demontrated. 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 fivecoordinate carbonium ion intermediates of the CH₅⁺ type.²⁵ 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 $\mathrm{CH_5}^+$ 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 synthesis²⁶ (regardless of its economic or its social-political considerations), it is customary to refer to C₁ 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, 19 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, C₁ 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 earth²⁷) 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.