Experimental Section

Chemicals. Ketones either were obtained from commerical sources and purified or were synthesized by well-established methods. A complete description will appear in a separate paper.[27] Both 4,4′-dicyanobenzophenone and 4-cyano-4′-methoxybenzophenone were obtained from Professor Donald Arnold. Two varieties of cyclopentane were used. All product studies were done with Mallinckrodt reagent grade which had been washed with sulfuric acid, neutralized, dried, and distilled. This material was shown by GC analysis to contain $<10^{-4}$ M cyclopentente; the only volatile impurities were traces of other saturated alkanes. The solvent used for most laser kinetics measurements was Aldrich Gold Label spectrophotometric grade cyclopentane, and it was used as received. Several kinetics runs were done with the carefully purified cyclopentane as well. Identical triplet lifetimes were obtained in both solvents for all ketones with lifetimes less than 150 ns. Longer lifetimes were obtained in the *unpurified* solvent for the longest lived triplets, and, therefore, the reported lifetimes are those measured in this solvent. We assume that a small amount of a triplet quencher was present in the "purified" material.

Product studies were conducted as usual[4] by gas chromatographic analysis of irradiated solutions. Product concentrations were determined by comparison to known concentrations (~0.003 M) of inert internal standards: dodecane and hexadecane for the products from cyclopentane; chlorobenzene for chlorocyclopentane. Actinometry was provided by parallel irradiation of valerophenone samples.[29]

Flash kinetics was conducted as described in the literature.[8] Samples were contained in 7 × 7 mm quartz cells fitted at the top with septa to allow nitrogen purging. Proper deaerating times were determined by measuring lifetimes until further purging produced no change.

Acknowledgment. The research was supported by the National Science Foundation. P.J.W. thanks the John Simon Guggenheim Foundation for a fellowship and the National Research Council of Canada for its hospitality.

Registry No. $(CH_3)_2CHCH(CH_3)_2$, 79-29-8; $(4\text{-}MeOC_6H_4)_2CO$, 90-96-0; $(4\text{-}MeC_6H_4)_2CO$, 611-97-2; $(C_6H_5)_2CO$, 119-61-9; $(4\text{-}ClC_6H_4)_2CO$, 90-98-2; $(4\text{-}FC_6H_4)_2CO$, 345-92-6; $4\text{-}NCC_6H_4COC_6H_5$, 1503-49-7; $PhCOCH_3$, 98-86-2; $PhCOCF_3$, 434-45-7; $4\text{-}MeOC_6H_4COC_6H_5$, 611-94-9; $(4\text{-}t\text{-}BuC_6H_4)_2CO$, 15796-82-4; $(3\text{-}MeC_6H_4)_2CO$, 2852-68-8; $3\text{-}MeC_6H_4COC_6H_5$, 643-65-2; $4\text{-}FC_6H_4COC_6H_5$, 345-83-5; $(4\text{-}FC_6H_4)_2CO$, 345-92-6; $4\text{-}ClC_6H_4COC_6H_5$, 134-85-0; $3\text{-}ClC_6H_4COC_6H_5$, 1016-78-0; $4\text{-}MeOC_6H_4COC_6H_4CN\text{-}4$, 27645-60-9; $4\text{-}MeOCOC_6H_4COC_6H_5$, 6158-54-9; $(4\text{-}ClC_6H_4)_2CO$, 90-98-2; $3,4(Cl)_2C_6H_3COC_6H_5$, 6284-79-3; $3\text{-}F_3CC_6H_4COC_6H_5$, 728-81-4; $4\text{-}F_3CC_6H_4COC_6H_5$, 728-86-9; $3\text{-}NCC_6H_4COC_6H_5$, 6136-62-5; $(4\text{-}NCC_6H_4)_2CO$, 32446-66-5; $2\text{-}MeOCOC_6H_4COC_6H_5$, 606-28-0; $C_6F_5COC_6H_5$, 1536-23-8; $(C_6F_5)_2CO$, 853-39-4; $4\text{-}MeOC_6H_4COCH_3$, 100-06-1; $3\text{-}MeOC_6H_4COCH_3$, 586-37-8; $4\text{-}CH_3COC_6H_4COCH_3$, 1009-61-6; $4\text{-}t\text{-}BuC_6H_4COCH_3$, 943-27-1; $4\text{-}MeC_6H_4COCH_3$, 122-00-9; $4\text{-}ClC_6H_4COCH_3$, 99-91-2; $4\text{-}NCC_6H_4COCH_3$, 1443-80-7; $3\text{-}ClC_6H_4COCH_3$, 99-02-5; $3\text{-}F_3CC_6H_4COCH_3$, 349-76-8; $4\text{-}F_3CC_6H_4COCH_3$, 709-63-7; $4\text{-}MeOC_6H_4COCF_3$, 711-38-6; $3,4\text{-}(Me)_2C_6H_3COCF_3$, 75833-26-0; $4\text{-}CH_3COC_6H_4COCF_3$, 86988-49-0; $4\text{-}t\text{-}BuC_6H_4COCF_3$, 73471-97-3; $3\text{-}MeC_6H_4COCF_3$, 1736-06-7; $4\text{-}ClC_6H_4COCF_3$, 321-37-9; $3\text{-}ClC_6H_4COCF_3$, 321-31-3; $4\text{-}FC_6H_4COCF_3$, 655-32-3; $4\text{-}F_3CC_6H_4COCF_3$, 74853-66-0; $3\text{-}F_3CC_6H_4COCF_3$, 721-37-9; $c\text{-}C_6H_{12}$, 110-82-7; $c\text{-}C_5H_{10}$, 287-92-3; D_2, 7782-39-0.

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Selective Monohalogenation of Methane over Supported Acid or Platinum Metal Catalysts and Hydrolysis of Methyl Halides over γ-Alumina-Supported Metal Oxide/Hydroxide Catalysts. A Feasible Path for the Oxidative Conversion of Methane into Methyl Alcohol/Dimethyl Ether[1]

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Abstract: The catalytic monohalogenation (chlorination and bromination) of methane was achieved over either supported solid acid (such as FeO_xCl_y/Al_2O_3, $TaOF_3/Al_2O_3$, $NbOF_3/Al_2O_3$, $ZrOF_2/Al_2O_3$, $SbOF_3/Al_2O_3$, SbF_5/graphite, and Nafion-H/TaF_5) or platinum metal (Pt/Al_2O_3 and $Pd/BaSO_4$) catalysts. The reactions were carried out at temperatures between 180 and 250 °C, with GHSV of 50–1400 giving 8–58% conversions with selectivity in methyl chloride (bromide) generally exceeding 90%. Limited methylene halide formation accompanies the reactions, but no formation of haloforms or carbon tetrahalides was observed. The mechanism of the halogenations is considered to involve insertion of a surface-coordinated electrophilic halogen species or electron-deficient metal site into a methane C–H bond involving five-coordinate intermediate carbonium ion formation, with subsequent cleavage–halogenolysis giving the monohalogenated methane. Catalytic hydrolysis of methyl halides was also studied over γ-alumina-supported metal oxide/hydroxide catalysts, giving mixtures of methyl alcohol and dimethyl ether. Combining the selective monohalogenation of methane with subsequent hydrolysis and oxyhalogenative recycling of byproduct HX allows conversion of methane to methyl alcohol/dimethyl ether, a route which offers an alternative to the presently exclusively used preparation of methyl alcohol via syngas. The preparation of methyl halides and/or methyl alcohol/dimethyl ether directly from methane also offers a way to convert methane via previously described bifunctional acid–base-catalyzed condensation into ethylene and subsequently into homogeneous lower olefins and/or higher hydrocarbons.

Recently there has been a revival of interest in "C_1 chemistry"[2] mostly utilizing syngas (i.e., mixtures of CO and H_2 produced from coal or natural gas) aiming at devising economical processes to manufacture hydrocarbons. An innovative new process for the

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manufacture of gasoline from methanol was developed by the Mobil Corp.[3] In the Mobil process, coal (or methane) is first converted to synthesis gas, which then is converted to methanol in a conventional processes and subsequently to hydrocarbons using shape-selective Zeolite catalysts (ZSM-5).

A possible alternative to syngas chemistry is the direct oxidative conversion of methane to higher hydrocarbons[4a] or through its monosubstituted derivatives, such as methyl halide or methyl alcohol.[4b] As methane has the highest possible H/C ratio of any hydrocarbon, i.e., 4, no additional hydrogen is needed. To the contrary hydrogen must be oxidatively removed to allow methane molecules to combine to higher hydrocarbons. This approach would eliminate the costly, energetic step of production of syngas and subsequently turning it back into hydrocarbons (Fischer–Tropsch) or to methyl alcohol, followed by its condensation to hydrocarbons.

Besides its major use as an energy source, methane is an important raw material for the chemical industry. Methane is for example used in the production of acetylene, ammonia, and methyl alcohol.[5] For the synthesis of methyl alcohol, the first step is the reforming of methane in the presence of steam over a nickel catalyst, resulting in synthesis gas with a ratio of H_2 to CO of 3:1 based on the reaction

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

To adjust the CO/H_2 ratio in the subsequent methyl alcohol forming step, a source of CO_2 is added over zinc chromite or more recently $Cu/ZnO/Al_2O_3$ catalyst according to

$$3CO + 9H_2 + CO_2 \rightarrow 4CH_3OH + H_2O$$

Methyl alcohol production from coal is also gaining importance in view of the decreasing world reserves of oil and natural gas, but it accounted for under 2% of the worldwide capacity in 1980.[2a] The development of coal conversion technology is, however, the key for the success of the coal to gasoline conversion process via methyl alcohol.

Natural gas is found associated with crude oil (associated gas) or in gas reservoirs in which no oil is present (nonassociated gas). Methane can also be produced by bacterial decomposition of biomass and is for example a byproduct of some sewage treatment plants. A recent interesting, although not yet proven, theory considers abiological sources of methane (and hydrocarbons) deep in the earth's crust.[6]

The chlorination of paraffins, discovered by Dumas in 1840,[7] is the oldest substitution reaction. Photochemical or thermal chlorination as we understand it today is a radical process which lacks selectivity and generally yields mixtures of chloroparaffins. In the chlorination of methane, all four chloromethanes are obtained.

$$CH_4 \xrightarrow{Cl_2} CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$

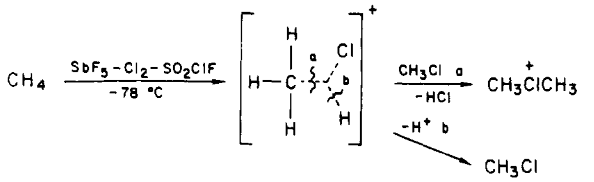
Methyl chloride is chlorinated more rapidly than methane itself; so if methyl chloride is the desired product, a ratio of methane to chlorine of at least 10:1 is required.[8] Consequently, the preferred route to methyl chloride has been the reaction of methanol with HCl.

$$CH_3OH + HCl \rightarrow CH_3Cl + H_2O$$

Chlorination of methane has been reported over catalysts such as active carbon,[9] Kieselguhr, pumice,[10] alumina, kaoline, silica gel, and bauxite (either alone or impregnated with metal salt, especially copper salt[11]) but showed limited selectivity. These reactions can be considered consequently as only promoted thermal reactions proceeding through free-radical chlorination.

Whereas the electrophilic chlorination of π-donor hydrocarbons (aromatics and olefins) is well-known and industrially utilized on a large scale, similar electrophilic chlorination of σ-donor alkanes, including the parent methane, was only recently achieved.

Olah et al. reported[12] that methane reacted with excess SbF_5–Cl_2 in SO_2ClF solution at −78 °C to give dimethylchloronium ion. On the other hand, when the reaction was carried out with excess methane in an autoclave at room temperature, the gaseous product was methyl chloride with only traces of methylene chloride formed during the reaction. The conversion was only about 1% and, therefore, no attempt was made to adapt the reaction for preparative use.



In continuation of our work, we now report to have developed supported solid acid-catalyzed selective electrophilic monochlorination (bromination) of methane under heterogeneous catalytic gas phase conditions as a practical preparative method.

We have also studied the related supported platinum metal-catalyzed selective monochlorination (bromination) of methane.

Alkanes were long considered to be less susceptible to transition-metal complex catalysis due to the absence of any accessible nonbonding electrons which might serve to bind the molecule to the metal complex to facilitate bond cleavage.

The activation of the C–H bonds of paraffins is somewhat similar to the activation of the H_2 molecule where a strong σ bond has to be broken. The intermediate formation of a M–H hydride bond[13] is commonly observed when H_2 is activated by metal complexes. Since M–C bonds are only slightly weaker than M–H bonds,[14] the activation of alkanes by metal complexes can be explained by the formation of C–M bonds.

Recently, Bergmann[15] and Schwarz[16] developed interesting new chemistry of the activation of methane via iridium or rhodium complexes, respectively. These systems activate the methane C–H bond via intermediate insertion involving two-electron three-center interaction, not dissimilar from the electrophilic attack responsible in acid-catalyzed reactions. The chemistry, however, involves

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molar equivalents of the metal complexes and therefore at this stage is not adapatble for practical preparative conversions.

The activation of C–H bonds in alkanes by transition-metal complexes usually occurs via formation of a labile C–M bond which can subsequently readily undergo reaction with an added reagent. Two major activation mechanisms have been suggested.[17] One involves attack on the C–H bond by an electrophilic metal ion

$$\mathrm{C{-}H + M^+ \rightleftharpoons C{-}M + H^+}$$

The other entails oxidative addition of a C–H bond to a low-valent metal center (i.e., metal insertion into the C–H bond)

$$\mathrm{C{-}H + M \rightleftharpoons C{-}M{-}H}$$

Both processes provide low-energy pathways for substitution reactions.

Only a few platinum metal complexes are known to interact with alkanes. The best studied catalyst for solution reactions of alkanes is $[\mathrm{PtCl_4}]^{2-}$,[18] but $\mathrm{RhCl_3}$[19] and $\mathrm{Na_3IrCl_6}$[20] have been reported to have similar activity for exchange between methane and $\mathrm{D_2O}$.

In addition to HD exchange, the $[\mathrm{PtCl_4}]^{2-}$ system catalyzes chlorination of alkanes in solution.[21] In this system, the Pt(II) complex with a $\mathrm{Cl^-}$ ligand deficiency activates the C–H bond via formation of an alkylplatinum intermediate. Subsequent oxidative chlorination by the Pt(VI) complex yields the chloroalkane. On the basis of the kinetic studies, the following mechanism was proposed:

$$\mathrm{PtCl_4^{2-} \rightleftharpoons PtCl_3^- + Cl^-}$$

$$\mathrm{PtCl_3^- \rightleftharpoons PtCl_2 + Cl^-}$$

$$\mathrm{PtCl_2 + RH \rightarrow RPtCl + H^+ + Cl^-}$$

$$\mathrm{RPtCl + PtCl_6^{2-} \rightarrow RCl + 2PtCl_3^-}$$

Tretyakov et al.[22] carried out experiments under heterogeneous solution conditions by supporting $\mathrm{K_2PtCl_4{\cdot}H_2PtCl_2}$ and $\mathrm{HgSO_4}$ on $\mathrm{SiO_2}$. Mercury(II) functioned as a $\mathrm{Cl^-}$ acceptor to obtain $\mathrm{Cl^-}$ ligand deficiency in Pt(II). Oxidative chlorination of methane gave $\mathrm{CH_3Cl}$ in 6.5% yield (relative to initial methane) in 5 h at a temperature of 100 °C. On prolonged reaction time, $\mathrm{CH_2Cl_2}$, $\mathrm{CHCl_3}$, and $\mathrm{CCl_4}$ were also formed.

No attempt was made so far to explore the heterogeneous catalytic gas-phase chlorination (bromination) of methane over platinum metal catalysts, such as Pt or Pd. In view of the expected similarity of these reactions with supported solid acid-catalyzed halogenations, such investigations seemed of interest and we report our results.

The selective catalytic monochlorination (monobromination) of methane has also allowed us to subsequently study the catalytic hydrolysis of methyl halides to methyl alcohol/dimethyl ether, opening up an alternative way to produce methyl alcohol/dimethyl ether directly from methane instead of going through the presently used industrial process via synthesis gas.

Methyl alcohol was first isolated and identified in a pure form in 1835 by Peligot and Dumas.[23] It was synthesized 23 years later by Berthelot[24] via the saponification of methyl chloride.

Interest in the saponification of methyl chloride was renewed in 1916 when Szarvasy,[25] and somewhat later Lacy,[26] described the pressure reaction of calcium hydroxide with methyl chloride and water for the formation of methyl alcohol. Lacy reported in an additional patent[27] the use under pressure of an acid-binding medium for the hydrolysis reaction. The evolution of calcium hydroxide technology was advanced further by McKee's introduction of an atmospheric pressure saponification process.[28] In his patent, barium, magnesium, and aluminum hydroxide were claimed to be inferior catalyst systems to calcium hydroxide. Higher proportions of dimethyl ether were formed when the process was run with aluminum hydroxide, but overall yields were much lower. In all cases, dimethyl ether was reported as a side product of methyl alcohol production. The hydrolysis reaction was reported to be inhibited by the use of copper or iron reactor vessels. Glass and porcelain do not interfere or assist in the hydrolysis reaction, while alloys of aluminum or aluminum itself gave enhanced results when the process was run between 350 and 375 °C. At lower temperatures (e.g., 300 °C) the reaction proceeds extremely slowly. Petrenko-Kritschenke and Opotzky[29] expanded the study of alkyl halide hydrolysis and described the reactions of potassium, thalium, barium(II), and ammonium hydroxides with chloromethanes and ethanes in solution. The utilization of calcium hydroxide for the hydrolysis reaction was extended by Nekrasov and Karicheva[30] to include ethyl halides for obtaining ethyl alcohol.

Kinetic studies of the hydrolysis of methyl halides under neutral conditions in solution have been reported by Moelwyn-Hughes,[31] Fells,[32] and Heppolette and Robertson.[33] The rate of reaction for methyl chloride was found to be $1.99 \times 10^{-8}\ \mathrm{s^{-1}}$ at 298.1 K, with an activation energy of 27, 7 kcal/mol. Increasing the temperature decreases E_A (e.g., at 373.1 K, E_A = 22, 7 kcal/mol) and increases the reaction rate k ($k_{373.1} = 1.08 \times 10^{-4}\ \mathrm{s^{-1}}$). The influence of temperature on the rate does not conform to the predictions made by the Arrhenius equation.

Thermodynamic parameters were calculated by Heppolette and Robertson[33] for methyl chloride hydrolysis and were also given by Stull, Westrum, and Sinke.[34]

No studies seem to have been carried out on the gas-phase hydrolysis reaction.

In addition to the studies described under neutral conditions, the reaction of the hydroxyl ion and methyl chloride was studied by Moelwyn-Hughes.[35] It was found that methyl halides react with the hydroxyl ion *and* water simultaneously in aqueous alkaline solution to give a more complicated kinetic expression. In this reaction, in contrast to the neutral hydrolysis, the rate constant k_2 follows the Arrhenius equation.

The activation energy for reaction of hydroxide ion with methyl chloride is 24.3 kcal/mol at 298.1 K, which in comparison is 3.4 kcal/mol less than the neutral hydrolysis reaction. A corresponding rate increase of approximately 3×10^2 is observed.

Past studies on the hydrolysis of methyl chloride to methyl alcohol involved only noncatalytic methods such as the well-studied hydrolysis with metal hydroxides. It is interesting to note that whereas the conversion of methyl alcohol to methyl chloride by reacting with hydrogen chloride is industrially used and was much

$$\mathrm{CH_3OH + HCl \rightarrow CH_3Cl + H_2O}$$

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Table I. Halogenation (A) and Bromination (B) of Methane over Supported Acid Catalysts

catalyst	CH_4/Cl_2	react temp, °C	GHSV, mL g^{-1} h^{-1}	convers, %	% product CH_3Cl	% product CH_2Cl_2
			A			
10% FeO_xCl_y/Al_2O_3	1:2	250	100	16	88	12
20% $TaOF_3/Al_2O_3$	1:2	235	50	14	82	6[a]
	1:2	235	1400	15	93	7
	2:1	235	1200	13	96	4
20% $NbOF_3/Al_2O_3$	1:3	250	50	10	90	10
10% $ZrOF_2/Al_2O_3$	1:4	270	100	34	96	4
Nafion-H	1:4	185	100	18	88	12
20% GaO_xCl_y/Al_2O_3	1:2	250	100	26	90	10
20% TaF_5–Nafion H	1:2	200	100	11	97	3
25% SbF_5–graphite	1:2	180	100	7	98	2

catalyst	CH_4/Br_2	react temp, °C	GHSV, mL g^{-1} h^{-1}	convers, %	% product CH_3Br	% product CH_2Br_2
			B			
20% $SbOF_3/Al_2O_3$	5:1	200	100	20	99	
20% $TaOF_3/Al_2O_3$	15:1	250	50	14	99	

[a] 12% ethane (with some ethyl chloride) was also obtained.

studied, the hydrolysis of methyl chloride to methyl alcohol (i.e., the reverse reaction) was never considered as a path for practical synthesis of methyl alcohol. Thus, our investigations seemed to fill a significant void, and we report our results centered on catalytic gas-phase hydrolysis of methyl halides over γ-alumina-supported metal oxide/hydroxide catalysts.

By combining selective catalytic monohalogenation of methane to methyl halides with subsequent catalytic hydrolysis opens up the possibility to convert methane to methyl alcohol without going through the presently used synthesis gas route. As hydrogen halide (HX) is formed as a byproduct of the reactions, it must be recycled via oxyhalogenation to make the conversion of methane to methyl alcohol a catalytic oxidative conversion. This is readily achieved in the case of hydrogen bromide, but in subsequent work, we will also report new selective catalytic oxymonochlorination of methane. The high selectivity of obtaining methyl alcohol/dimethyl ether from methane free of the further oxidation products (formaldehyde, CO, and CO_2) makes this approach not only feasible, but attractive. In contrast to syngas-based methyl alcohol plants which by necessity are extensive capital demanding large installations, the present route could also be applied economically to much smaller installations, as well as allowing conversion of methane (natural gas) to easily transported methyl alcohol, when this is necessary.

Results and Discussions

Chlorination (Bromination) of Methane over Solid Acid Catalysts. Supported Lewis acid halide–oxyhalide catalysts such as $FeOCl/Al_2O_3$, $TaOF_3/Al_2O_3$, $NbOF_3/Al_2O_3$, $ZrOF_2/Al_2O_3$, $SbOF_3/Al_2O_3$, SbF_5/graphite, and Nafion-H/TaF_5 have been investigated as catalysts for chlorination (bromination) of methane under heterogeneous gas-phase conditions. The composition of supported metal oxyhalides is not stochiometric. Ferric oxychloride for example should be denoted more properly as FeO_xCl_y, etc., but for simplicity "stochiometric" formulas for oxychlorides will be used, denoting the supported catalysts.

Chlorination of methane over supported catalysts such as FeO_xCl_y/Al_2O_3 or $TaOF_3/Al_2O_3$ was generally carried out in the temperature range of 180–250 °C at atmospheric pressure in a flow system with GHSV of 50 to 1400 (gaseous hourly space velocity, mL g^{-1} h^{-1}). As shown in Table I, it was found that the CH_4/Cl_2 ratio had little effect on the observed methyl chloride selectivity, which generally was in excess of 90%, the balance being methylene chloride, with no chloroform or carbon tetrachloride formed. Significantly, even when using an excess of chlorine in the reaction, the high selectivity of monochlorination was maintained with no chloroform or carbon tetrachloride formed (Table I). It is also seen from Table I that flow rates had little effect on the selectivity of the reactions.

$NbOF_3/Al_2O_3$- and $ZrOF_3$-catalyzed chlorination of methane shows similar selectivity of methyl chloride. Unsupported Nafion-H catalyst gave 88% CH_3Cl and 12% CH_2Cl_2. When enhancing the Nafion-H acidity by complexing with 25% TaF_5, 97% methyl chloride and 3% methylene chloride were obtained.

Table II. Effect of the CH_4/Cl_2 Ratios in the $TaOF_3/Al_2O_3$-Catalyzed Chlorination of Methane

CH_4/Cl_2 ratio	1:4	1:2	2:1	4:1	8:1
% convers	27[a]	13[a]	80[b]	83[b]	85[b]
prod composit					
% CH_3Cl	90	92	99	99	99
% CH_2Cl_2	10	8	trace	trace	trace

[a] Based on methane. [b] Based on chlorine.

Similar results were obtained with other solid acid catalysts such as antimony pentafluoride intercalated into graphite and gallium oxychloride supported on alumina.

The methane-to-chlorine mole ratios used in the chlorination reactions generally were kept low (1:2 or 1:4) in part to prove the selectivity of the reactions under the catalytic reaction conditions even in the presence of excess chlorine, in part, however, also to allow ease of analysis by determining (by GLC) the amount of methyl (and methylene) chloride in relationship to unreacted methane. With higher methane-to-chlorine ratios, the selectivity increases further and reaches nearly 100%.

In $TaOF_3/Al_2O_3$-catalyzed chlorination, we carried out a study of varying the CH_4/Cl_2 ratio from 1:4 to 8:1 on selectivity (and conversion). The results are shown in Table II. The chlorinations were carried out at 240 °C with GHSV of 100 mL g^{-1} h^{-1}. Results show that the catalytic selective monochlorination reaction operates in a wide range of CH_4/Cl_2 ratios, and statistical factors dominant in free-radical chlorinations are substantially absent.

Catalytic bromination of methane over 20% $SbOF_3/Al_2O_3$ or $TaOF_3/Al_2O_3$ catalysts at 200–250 °C with CH_4/Br_2 mole ratios of 5:1 and 15:1, respectively, gave 14–20% conversions to methyl bromide, with practcially 100% selectivity.

Mechanistically, the heterogeneous catalytic surfaces with their acidic sites act to polarize the chlorine (bromine) molecules. Subsequent halogenation of methane takes place under electrophilic (ionic) conditions. In other words, chlorine (bromine) complexed to the catalyst surface acts as an electrophilic reagent reacting with methane in a typical electrophilic insertion reaction.

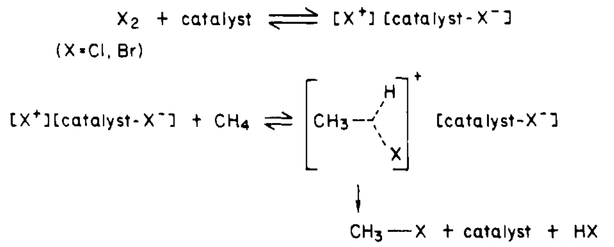
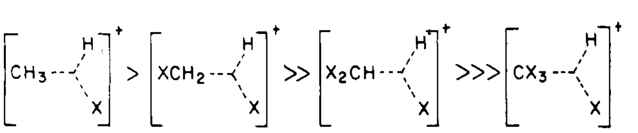


Table III. Supported Platinum Metal Catalyzed Halogenation of Methane

catalyst	CH_4/X_2 (X = Cl, Br)	reaction temp, °C	GHSV, mL g^{-1} h^{-1}	convers, %	% prod CH_3Cl	% prod CH_2Cl_2
			Chlorination			
0.5% Pt/Al_2O_3	1:3	100	600	11[a]	~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% $Pd/BaSO_4$	2:1	200	600	30[b]	99	1
			Bromination			
0.5% Pt/Al_2O_3	2:1	200	300	8[b]	99	trace

[a] Based on methane. [b] Based on chlorine (bromine).

The heterogeneous catalytic halogenations depend on the extent of complexing ability of the catalyst with the halogen and the polarizability of the catalytic surface. The halogenations take place with high selectivity due to the ionic conditions involved in the formation of the intermediate five-coordinate carbonium ions. Monohalogenated methane is favored due to the preference of formation of the monohalomethonium ion as compared to dihalogenated or higher halogenated ions where the halogen atoms increasingly dominate the donor ability of the σ C–H bonds. The nearly 100% selectivity observed in monobromination of methane also seems to reflect the additional effect of the increased size of bromine.



It is interesting to note that in the $TaOF_3/Al_2O_3$-catalyzed reaction with a 1:2 CH_4/Cl_2 ratio, 12% of ethane was also formed as a byproduct. Its formation is considered to be due to secondary methylation of methane. Initially formed methyl chloride can complex with the catalyst to give a methylating agent which can further react with excess methane to give ethane. On the other hand, with a high concentration of chlorine, chlorinolysis of ethane can take place, forming methyl chloride and methane.

$$CH_3Cl + \text{catalyst} \rightleftharpoons [\overset{\delta+}{CH_3Cl} \rightarrow \overset{\delta-}{\text{catalyst}}]^- \xrightarrow{CH_4} C_2H_6 + HCl + \text{catalyst}$$

The supported acid catalysts found most effective for the selective halogenation reactions are specific in regard to allowing ionic activation of chlorine (bromine) but at the same time they generally do not promote, as stronger superacidic catalysts tend to, condensation of formed methyl halides with excess methane, or self-condensation of methyl halides to higher hydrocarbons.

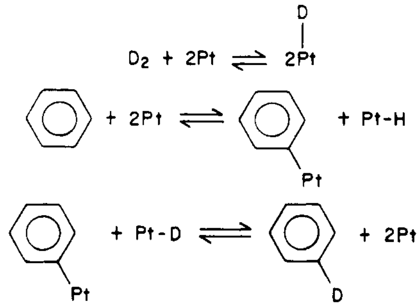
Supported Platinum Metal Catalyzed Halogenation of Methane. The supported solid acid-catalyzed halogenations of methane involve insertion of electrophilic halogen, formed by coordination to an acidic site, into a C–H bond of methane via two-electron three-center bond formation. The realization that certain metal complexes are capable of similar insertion reactions offered the possibility to study the catalytic halogenation of methane over supported platinum metal catalysts.

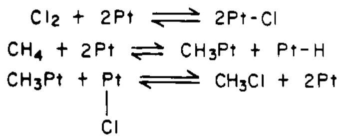
A. Pt/Al_2O_3-Catalyzed Halogenation of Methane. The chlorination of methane was investigated over 0.5% Pt supported on an alumina catalyst. Methane and chlorine in varying molar ratios were reacted in a flow reactor packed with the catalyst at temperatures ranging from 100 to 250 °C (see Table III). Methyl chloride was obtained with 92–100% selectivity. Conversions ranged from 11% to 36%. Besides small amounts of methylene chloride, no chloroform or carbon tetrachloride was formed. This is in sharp contrast to the purely thermal (or photo induced) chlorination of methane, typically giving about 11% CH_3Cl, 35% CH_2Cl_2, 45% $CHCl_3$, and 9% CCl_4.[36]

The effect of different molar ratios of CH_4/Cl_2 on conversion and methyl chloride selectivity was also investigated. Catalysts used in the experiments were reused after regeneration and found unchanged in activity. The methane–chlorine system is known to be explosive within the range from about 62% to 6% by volume methane and 38% to 94% by volume chlorine. Thus, working outside these limits is advisable or care must be exercized to avoid explosive danger. In the studied flow system, no explosions were observed. Changing the molar ratio of CH_4/Cl_2 has little effect on the methyl chloride selectivity. This again is different from thermal chlorination which by its statistical nature is sensitive to changes in the CH_4/Cl_2 molar ratio.

The related bromination of methane over 0.5% Pt/Al_2O_3 catalyst using a 2:1 molar mixture of methane and bromine at 200 °C gave in 8% conversion nearly 100% selectivity in methyl bromide.

The mechanism for the heterogeneous exchange of aromatic and unsaturated compounds over metal catalyst with isotopic hydrogen was originally suggested by Farkas and Farkas.[37] They proposed a dissociative mechanism in which benzene was chemisorbed through C–H bond rupture and then exchanged with a deuteron from dissociatively absorbed deuterium gas. Although this mechanism was later superceded by a π-complex mechanism,[38a] it is generally accepted that saturated hydrocarbons exchange by a dissociative mechanism. Taylor et al. first found related Ni-catalyzed isotopic exchange between methane and deuterium.[38b] By analogy with the D_2/benzene system, one can suggest a similar mechanism for the gas-phase chlorination of methane over the Pt/Al_2O_3 catalyst. Supported platinum catalysts





$$Cl_2 + 2Pt \rightleftharpoons 2Pt\text{-}Cl$$
$$CH_4 + 2Pt \rightleftharpoons CH_3Pt + Pt\text{-}H$$
$$CH_3Pt + \underset{\displaystyle Cl}{\underset{|}{Pt}} \rightleftharpoons CH_3Cl + 2Pt$$

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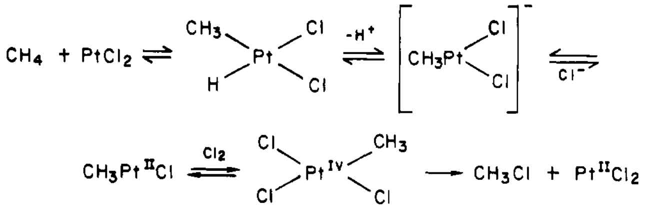
(36) (a) Asinger, F. "Paraffins—Chemistry and Technology"; Pergamon Press: Oxford, 1968; p 229. (b) Poutsma "Methods in Free Radical Chemistry"; Huyser, E., S., Ed.; Marcel Dekker: New York, 1969; Vol. II. (c) Weissermel, R.; Arpe, H. J. "Industrial Organic Chemistry"; Verlag Chimie: New York, 1978.

(37) Farkas, A.; Farkas, L. *Proc. R. Soc. London, A* **1934**, *A144*, 467.

(38) (a) Garnett, J. L. *Proc. R. Aust. Chem. Inst.* **1961**, *28*, No. 8, 328. (b) Morikawa, K.; Benedict, W. S.; Taylor, H. S. *J. Am. Chem. Soc.* **1935**, *57*, 592.

such as Pt/Al_2O_3 upon chlorination, however, are also known to form both Pt(II) and Pt(IV) complex sites.[39] Sivasankar et al.[40] reported the observation (by electron spin resonance spectroscopy) of a chloroplatinum species on the Pt/Al_2O_3 catalyst, and $[PtCl_2]^-$ was identified to be the active platinum species. The platinum atoms are anchored through chlorine atoms in the alumina structure, rendering them less susceptible to sintering compared to those Pt atoms in metal clusters. The realization that the Pt(II)(catalyst)–Pt(IV)(oxidant) system is active in the oxidative chlorination of alkanes both in aqueous solutions and in SiO_2-supported systems further indicates similar interaction mechanisms for dissolved and suppoted platinum. In the present case, Cl_2 itself can be the oxidant instead of Pt(IV). Hence, as alternative mechanism is possible in which platinum(II) chloride complexes activate the C–H bond of methane via formation of intermediate methylplatinum compounds, thus lowering the energy barrier for subsequent chlorolysis:



The formation of smaller amounts of CH_2Cl_2 in the studied systems indicates that methyl chloride itself can react further, albeit slower. The possibility that a radical process initiated by hydrogen-atom abstraction is competing with the carbene-like metal insertion into the C–H bonds can be substantially excluded as no chloroform or carbon tetrachloride was formed in the reactions.

In conclusion, both platinum metal and platinum(II) chloride complexes (with a Cl-ligand deficiency) could be responsible for the C–H bond activation observed with Pt/Al_2O_3 catalyst. Typical soluble catalysts generally require ligand dissociation to free a catalyst "site". For example,[41] photolysis of $TaH_3(C_5H_5)_2$ liberates H_2 and generates the active species $TaH(C_5H_5)_2$ which reacts with C–H bonds. The active site for C–H cleavage has two orbitals containing two electrons. This situation is very similar to H–H and C–H bond activation by clean platinum surfaces[42] where "step" (or "edge") atoms with more exposed orbitals are the active sites. Thus, it seems that C–H bonds interacting with a platinum metal center capable of forming a two-electron, two-orbital interaction can be activated and subsequently chlorolyzed. The related bromination reaction is considered to proceed in a similar fashion. The nearly 100% selectivity observed in methyl bromide may also reflect the increased size of bromine which tends to further decrease disubstitution.

B. $Pd/BaSO_4$-Catalyzed Chlorination of Methane. Palladium(II) salts catalyze a variety of practically important aromatic substitution reactions. Examples are the oxidative coupling of benzene and ethylene to produce styrene[43] and the oxidation of propionic acid and benzene to produce cinnamic acid.[44] Activation of the arene C–H bonds appears to occur by the attack of an electrophilic Pd^{2+} ion to generate a C–Pd bond which then undergoes substitution under mild conditions. However, activation of alkane C–H bonds by palladium(II) salts has not yet been observed. In contrast to platinum, the d^6 Pd(IV) state is of lower stability and the Pd–C bond is of lower strength. It is probably for this reason that the activation of alkanes by complexes of d^8 Pd(II) has not been successful.

Nonetheless, Pd $(OOCCF_3)_2$–CF_3COOK in anhydrous trifluoroacetic acid[45] at 90 °C and sulfate complexes of palladium[46] in concentrated sulfuric acid bring about oxidative dehydrogenation, e.g., that of cyclohexane to benzene. Unlike the complex palladium sulfate system, the $Pd(OOCCF_3)_2$ system is insensitive to changes in the acidity of the medium. The absence of hydrogen–deuterium exchange of alkanes was explained by the lower stability of alkylpalladiums compared to alkylplatinums.

In our present study, selective monochlorination of methane was observed over 5% palladium supported on barium sulfate catalyst. When chlorine and methane in a molar ratio of 2:1 were passed over the catalyst at 200 °C, a product composition of 99% methyl chloride and 1% methylene chloride was obtained with 36% conversion based on methane. Concerning the mechanism since no comparison with homogeneous catalysis can be made to assess the role of Pd(II) complexes in the catalyst, the activation is attributed to the palladium metal surface. Adsorption and chemical reaction would occur predominantly on active centers on the palladium metal surface, identified as certain types of lattice defects.

$$Cl_2 + 2Pd \rightleftharpoons 2Pd\text{–}Cl$$

$$CH_4 + 2Pd \rightleftharpoons CH_3Pd + PdH$$

$$CH_3Pd + PdCl \rightleftharpoons CH_3Cl + 2Pd$$

Over the supported Pd catalyst, methane chlorination is considered to proceed only in this fashion as activation of alkane C–H bonds by d^8 Pd(II) is not known.

From the studied systems for the selective monochlorination of methane (from a practical point of view) the supported Pt catalyst looks most suitable, having high catalytic stability and easy regeneration.

Concerning the studied chlorination of methane, we also carried out control experiments in which methane and chlorine in various mole ratios were reacted in the absence of any catalyst under the experimental conditions. It was of interest to note that some chlorination of methane took place under these conditions, showing, however, limited selectivity; i.e., besides methyl chloride, not only methylene chloride but also chloroform and carbon tetrachloride were obtained. These "uncatalyzed" chlorinations were mainly observed with high chlorine-to-methane ratios (CH_4/Cl_2 1:2 and 1:4), indicating that excess chlorine in the system tends to promote the reaction probably through some self-association of chlorine and surface effects of the glass reaction tube (or glass beads used to enlarge the surface). This was substantiated when carrying out the reaction in an all-Teflon apparatus where the degree of chlorination sharply decreased, as did selectivity.

No attempt was made to eliminate diffuse room light during the experiments, but this effected only the premixing chamber of methane and chlorine. The reactor tube itself was enclosed in a tube furnace which is not exposed to any direct light. These considerations emphasize that the observed supported acid and platinum metal catalyzed reactions are indeed predominantly catalytic reactions. The stability and life time of the supported platinum metal catalysts are considered to be good, although generally only 8-h runs were studied and no longer time range continuous experiments were performed. However, catalyst activities were found to be unchanged upon use of regenerated catalyst in repeated runs. The lifetime of the supported metal oxyhalide–halide catalysts is by necessity shorter, but they can also be regenerated.

Catalytic Hydrolysis of Methyl Halides over γ-Alumina and γ-Alumina-Supported Metal Oxide/Hydroxide Catalysts. To develop an alternative to the syngas-based methyl alcohol synthesis led us to explore the catalytic conversion of methane via methyl chloride to methyl alcohol. In the course of this investigation,

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[43] Shue, R. S. *J. Catal.* **1972**, *26*, 112.

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Table IV. Hydrolysis of Methyl Halides over γ-Alumina

H_2O/CH_3Cl	react temp, °C	GHSV	convers, %	% prod CH_3OH	% prod CH_3OCH_3
		Methyl Chloride			
5	375	1500	13	45	55
10	375	1500	16	70	30
15	375	1500	18	80	20
		Methyl Bromide			
10	375	1000	23	73	27

Table V. Hydrolysis of Methyl Chloride over γ-Alumina-Supported Metal Oxide/Metal Hydroxide Catalysts (H_2O/CH_3Cl Ratio 10, 375 °C, GHSV ~1200)

catal 10% M_xO_y/ 10% $M(OH)_x$/ 80% γ-Al_2O_3	% convers to CH_3OH/CH_3OCH_3
$V_2O_5/Al(OH)_3/\gamma$-Al_2O_3	5
$MnO_2/Al(OH)_3/\gamma$-Al_2O_3	13
$Cr_2O_3/Al(OH)_3/\gamma$-Al_2O_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
$ZnO/Al(OH)_{33}/\gamma$-Al_2O_3	25
$Fe_2O_3/Al(OH)_3$-$/\gamma$-Al_2O_3	9
$ZnO/Ni(OH)_2/\gamma$-Al_2O_3	11
$ZnO/Bi(OH)_3/\gamma$-Al_2O_3	7
$ZnO/Mg(OH)_2/\gamma$-Al_2O_3	6

Table VI. Hydrolysis of Methyl Chloride over γ-Alumina-Based Catalysts

catal	% convers	catal	% convers
γ-Al_2O_3	16	$Al(OH)_3/\gamma$-Al_2O_3	15
ZnO/γ-Al_2O_3	19	$ZnO/Al(OH)_3/\gamma$-Al_2O_3	25

we studied and report the results of the gas-phase hydrolysis of methyl halides over γ-alumina and related supported heterogeneous catalysts to methyl alcohol/dimethyl ether.

The hydrolysis of methyl chloride over alumina catalysts was studied in the range of 200–400 °C while the CH_3Cl-to-H_2O ratio was varied from 1:5 to 1:20. α-Alumina was only of low activity, whereas γ-alumina with a surface area of 200 m^2/g was found to be active. At 375 °C with a H_2O/CH_3Cl ratio of 10 and at GHSV of ~1500–1800 mL g^{-1} h^{-1}, the per pass average conversion of methyl chloride was 16%, with the product containing about 70% methyl alcohol and 30% dimethyl ether. This represents close to the equilibrium composition calculated from thermodynamic data for these conditions.[34] Products were analyzed by gas–liquid chromatography, and the HCl formed was titrated in the usual way. When the ratio of H_2O/CH_3Cl was decreased to 5, the coversion decreased to 13% and the dimethyl ether content increased to over 50%. Lower GHSV also increased the amount of dimethyl ether content relative to methyl alcohol. Dimethyl ether thus seems to be formed as a secondary product from the bimolecular dehydration of methyl alcohol and not from the reaction of methyl alcohol with excess methyl chloride. On the other hand, increasing the H_2O/CH_3 ratio to 15 increased the conversion to 18%. Methyl bromide gave comparable results with a conversion of 23% using a H_2O/CH_3Br ratio of 10 at 375 °C with GHSV of 1000 mL g^{-1} h^{-1} (Table IV).

There is an apparent initial uptake of HCl (HBr) on the catalyst which is more predominant at lower $H_2O/CH_3Cl(Br)$ ratios and GHSV. It can shift the equilibrium composition to some degree and increase conversion at the early stages of the reaction. The catalyst, however, stabilizes under the reaction conditions found preferential in our studies, and consistent results were obtained in runs of 12–18-h duration. Catalysts could also be reused in subsequent runs with no apparent change in activity. When methyl halides were reacted with the same mole ratio of water in the absence of alumina, hydrolysis observed under the reaction condition was limited (2–5%).

In order to improve catalyst activity, we subsequently attempted to combine the known activity of metal hydroxides with dehalogenation catalysts, while supporting them on γ-alumina. In preparing such catalysts, we eliminated thermally unstable dehalogenation systems such as magnesium iodide, copper(II) chloride, copper nitrate, and copper and zinc chromite and studied a series of thermally stable metal oxides ranging from highly acidic to basic in nature which were combined with aluminum(III) hydroxide on γ-alumina support for the hydrolysis of methyl halides to methyl alcohol.

Tanabe and Yamamaka established the relative acid–base properties of some of the metal oxides incorporated into the catalyst systems used in our investigations.[47] The basic strengths were determined by titration of the solid metal oxide, suspended in benzene, with trichloroacetic acid and the relative order was reported to be

$$ZnO > TiO_2 > BaO > ZrO_2 > MoO_3$$

In contrast, Kireev[48] reported the higher basicity of ZrO_2 relative to BaO in their reaction with SO_3, while Kireev[48] and Flood et al.[49] reported the basicity order of oxides of nickel, zinc, and copper to be

$$CuO > ZnO > NiO$$

Similarly, Halgeri and Walvekar[50] determined the relative order for the more acidic metal oxides. These are reported in order of increasing acidity:

$$MgO < V_2O_5 < WO_3 < MoO_3$$

Manganese(IV) oxide is reported[51] to be neutral in character, while chromium(III) oxide is amphoteric and niobium(V) oxide is highly acidic. The overall decreasing sequence of acidity of used metal oxides is thus the following:

$$V_2O_5 > MnO_2 > Cr_2O_3 > BaO > MgO > TiO_2 > NiO > ZnO > CuO > Fe_2O_3$$

The hydrolysis reactions were carried out over catalysts comprised of 10% (weight) metal oxide, 10% aluminum hydroxide, and 80% γ-alumina support prepared by a water slurring procedure described in the Experimental Section followed by calcination.

Results of the hydrolysis of methyl chloride over different metal oxide/hydroxide catalysts supported on γ-alumina are summarized in Table V.

The most effective catalyst was the $ZnO/Al(OH_3)/\gamma$-Al_2O_3 system which gave 25% conversion. Nickel, bismuth, and magnesium hydroxides gave lower reactivity, as did other metal oxides when replacing zinc oxide. The composition of metal hydroxides such as aluminum hydroxide (used from commercial source) is not necessarily stoichiometric and can involve mixed oxides–hydrates, but for simplicity "stoichiometric" formulas are used. Activated γ-alumina is itself an active catalyst and not just a support. In test runs with zinc oxide and aluminum hydroxide on silica–alumina support, only low (2–5%) conversions were observed. Further evidence for the participation of the γ-alumina support was shown by the much lower activity of the catalyst when substituting α-alumina.

Hydrogen chloride formed during the reactions tends to cause some catalyst deactivation by leaching out aluminum and zinc chloride, respectively. Similar observations were reported during reactions involving acidic zeolite catalysts with high alumina-to-silica ratios.[52] Excess steam (preferentially in a ratio of 10:1)

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(47) Tanabe, K.; Yamanaka, T. *J. Phys. Chem.* **1975**, *79*, 2409.
(48) Kireev, V. A. *Zh. Fiz. Khim.* **1964**, *38*, 1027.
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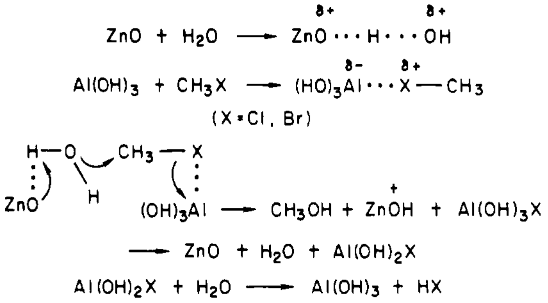
(51) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Wiley: New York, 1972.

thus is essential in purging the system of HCl and hydrolyzing surface-bound halide sites, thus restoring catalytic activity.

Unsupported aluminum hydroxide itself brings about the hydrolysis of alkyl halides, albeit generally in low yields. The reactivity of supported aluminum hydroxide on γ-alumina without zinc oxide was found to be somewhat lower than when zinc oxide is incorporated into the catalyst system as shown in Table VI. In addition, the reactivity of supported zinc oxide without aluminum hydroxide in catalyzing the hydrolysis of methyl chloride was also studied and was found to be less than the combined zinc oxide, aluminum hydroxide, γ-alumina system. It was, however, slightly more active than aluminum hydroxide supported on γ-alumina. γ-Alumina alone, as discussed previously, shows catalytic activity in the hydrolysis of methyl halides, but again it is less active than the tertiary catalyst (see Table VI).

The improved conversions observed can be best explained by partial retention of hydrogen chloride on the catalyst to form Zn–Cl and Al–Cl bonded sites. Leaching of zinc chloride (or aluminum chloride), however, was found to be slow. It is suggested that the mechanism of the catalyzed hydrolysis involves interaction of the hydrated metal oxide or hydroxide with methyl halide coordinated to an electron-deficient aluminum site to form a polarized intermediate which then readily cleaves to give methyl alcohol. The intermediate metal hydroxide halides themselves readily hydrolyze, allowing a catalytic process with only slow formation of any metal chlorides. Eventually deactivated catalyst can be readily regenerated.



A Feasibile Path for the Oxidative Conversion of Methane into Methyl Alcohol/Dimethyl Ether. The selective monohalogenation of methane reported in our present study together with the described catalytic gas-phase hydrolysis of methyl halides to methyl alcohol/dimethyl ether represent a feasible approach to convert methane into methyl alcohol without going through the syngas route. It also avoids the inevitable difficulties involved in the direct oxidation of methane where further oxidation to formaldehyde and CO is unavoidable. The two steps

$$CH_4 + X_2 \xrightarrow{\text{catalyst}} CH_3X + HX$$

$$CH_3X + H_2O \rightarrow CH_3OH + HX$$

give the overall reaction

$$CH_4 + X_2 + H_2O \rightarrow CH_3OH + 2HX$$

In order to make the reaction overall a catalytic process HX must be oxidatively recycled.

In the case of chlorinative conversion Deacon type of oxychlorination, methane is unselective and the associated corrosion problems are substantial. However, selective catalytic oxidative chlorination of methane with HCl and oxygen is a possible way to achieve the recycling of HCl, and we will report in a subsequent paper our studies in this regard.

In the brominative conversion of methane, hydrogen bromide is the byproduct of the reactions. In contrast to hydrogen chloride, its redox potential is much lower, and it is oxidized with ease with oxygen or air to bromine

$$2HBr + {}^1/_2O_2 = H_2O + Br_2$$

The ease of oxidation of HBr thus allows its easy recycling and thus the overall reaction where bromine is only a catalyst

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

$$2HBr + {}^1/_2O_2 = H_2O + Br_2$$

$$CH_4 + {}^1/_2O_2 = CH_3OH$$

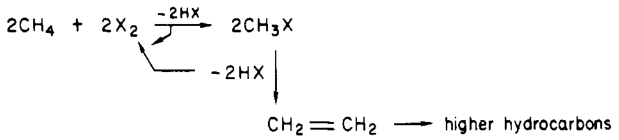
In some cases, the separate steps can be combined. Indeed, we were able to show that when methane was reacted with bromine in the presence of steam and oxygen over 0.5 Pt/Al_2O_3 catalyst at 250 °C, besides methyl bromide, about 6% methyl alcohol and dimethyl ether were the observed products. Further, when methane, HBr, and oxygen were reacted, methyl bromide was obtained in about 8–12% conversion.

When bromine and steam were passed at 260 °C over 20% $TaOF_3/Al_2O_3$ catalyst with excess methane, a 12–18% conversion was obtained (initial conversion higher, but after 3 h it settles at this level). The product is composed of 90% methyl bromide and 10% methyl alcohol/dimethyl ether. This shows that methane under oxidative halogenation conditions can be converted even in a single-step operation into methyl alcohol/dimethyl ether, although for practical reasons it is more advantageous to operate the steps separately.

Summary

In summary, the catalytic monohalogenation of methane was achieved over either supported acid or platinum metal catalysts. The reactions show high selectivity in methyl halide (chloride or bromide) generally exceeding 90%, accompanied by up to 10% methylene halide formation, but in the absence of haloform or carbon tetrahalide. The mechanism of the halogenations is considered to involve insertion of a surface-coordinated electrophilic halogen species or electron-deficient metal site into a methane C–H bond involving five-coordinate intermediate carbonium ion formation, with subsequent cleavage–halogenolysis giving the monohalogenated methane.

Catalytic hydrolysis of methyl halides was also studied over γ-alumina-supported metal oxide/hydroxide catalysts, giving mixtures of methyl alcohol and dimethyl ether. Combining the selective monohalogenation of methane with subsequent catalytic gas-phase hydrolysis allows conversion of methane to methyl alcohol/dimethyl ether, a route which offers an alternative to the presently exclusively used synthesis from syngas. The ready preparation of methyl halides and/or methyl alcohol/dimethyl ether directly from methane also offers a convenient way to subsequent conversion to ethylene (and through ethylene to homologous lower olefins and higher hydrocarbons) via the previously described bifunctional acid–base-catalyzed condensation[4b]



The use of methane (natural gas) as a direct building block for higher hydrocarbons without its prior conversion to synthesis gas is an interesting and potentially useful alternative to the Fischer–Tropsch synthesis.

Experimental Section

Materials and Chemicals. Catalyst supports were obtained from Strem Chemicals. The γ-alumina used was high activity with a composition of 96% Al_2O_3 and a surface area of 200 m^2/g. α-Alumina, a highly inert low surface area material, was 99.5% Al_2O_3 in $^1/_4$-in. granules. High surface area silica–alumina (425–500 m^2/g) was of the composition 87% SiO_2/12% Al_2O_3. Metal oxides, halides, and hydroxides were obtained from Pfaltz and Bauer [$Bi(OH)_3$], Aldrich [Cr_2O_3, Fe_2O_3, LiOH, MgO, MnO_2, $MgCl_2$, $FeCl_3$, Nb_2O_5, TiO_2, ZnO, and ZrO_2], and Alfa [BaO, $Al(OH)_3$, $Mg(OH)_2$, and $Ni(OH)_2$]. Methane (99.5%), chlorine

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(99.5%), hydrogen chloride (99.0%), and hydrogen bromide (99.8%) were purchased from Matheson. Bromine (99%) was obtained from the Dow Chemical Co.

Catalysts. Ferric oxychloride, FeO_xCl_y (10%), on alumina catalyst was prepared by impregnating Al_2O_3 (~200 m^2/g) with an aqueous solution of ferric chloride. After evaporation of water, the catalyst was dried in air at 105–115 °C and calcined at 350–450 °C for 5 h. Ferric oxybromide, FeO_xBr_y (10%), on alumina and gallium oxychloride GaO_xCl_y, on alumina (20%) were prepared similarly.

Tantalum oxyfluoride (20%) on alumina was prepared by slowly dissolving tantalum pentafluoride into cold methyl alcohol (−78 to −10 °C) with evolution of some hydrogen fluoride. The support was then treated with the solution as before and heated to 250–300 °C to obtain 20% tantalum oxyfluoride deposited on the alumina. Niobium oxyfluoride on alumina was prepared similarly.

Zirconium oxyfluoride (10%) on alumina was prepared as above by treating alumina with zirconium tetrafluoride dissolved in methyl alcohol.

SbF_5/Graphite (20%) (Alfa Inorganics) was used as obtained and Nafion-H was prepared from Du Pont Nafion-501 resin as previously reported and Nafion-H/TaF_5 by complexing Nafion-H with TaF_5.

Platinum (0.5%) on alumina was obtained from Air Products Co. with a surface area of ~100 m^2/g and 0.5% palladium on barium sulfate obtained from Strem Chemicals with a surface area specified only as "high".

Supported metal oxide catalysts were generally prepared as described previously for WO_3 on Al_2O_3.[4b] ZnO on alumina catalyst was prepared by using an aqueous slurry of ZnO (20 g in 100 mL of water); 80 g of alumina was then stirred into it with continuous stirring for 24 h. Water was thereafter removed in vacuum; the catalyst was dried at 150 °C and calcinated at ~450 °C for 4 h.

γ-Alumina supported metal oxide/hydroxide catalysts were prepared by placing γ-alumina (20 g), metal oxide (2.5 g), and metal hydroxide (2.5 g) in a 1-L round-bottom flask. Five hundred milliliters of water was added and the mixture stirred for 2 h. The water is then removed under reduced pressure and the resulting catalyst dried in a vacuum oven at 110 °C. Prior to use, the catalyst is loaded into a glass reactor tube with glass wool packed on both ends and calcined at 400 °C overnight in a Lindberg SB heavy duty tube furnace under nitrogen flow.

Regeneration of Deactivated Catalysts. Pt/Al_2O_3 and Pd/$BuSO_4$ catalysts are regenerated by heating at 380 °C overnight under a flow of N_2.

γ-Alumina-based hydrolysis catalysts are reactivated by steam treatment and subsequent calcination at ~450 °C.

General Procedure for the Catalytic Halogenation of Methane over Supported Acid or Platinum Metal Catalysts. All reactions were carried out at atmospheric pressure in a fixed-bed, continuous-flow, electrically heated (with a Lindberg furnace) 550 × 10 mm Pyrex glass tube reactor, similar to that described in our previous work.[4b,53] Generally 10 g of supported catalyst, previously calcinated, was placed in a stream of dry nitrogen into the reactor, and mixtures of methane and chloride or bromine (the latter introduced via a metered pump) in the ratios stated were passed through with a gaseous space velocity (volume of gas passed over volume of catalyst per hour) of between 50 and 1500 under conditions shown in the tables. Samples were taken at the outlet of the reactor and analyzed by GC and GC/MS. Hydrogen halides were determined by titration.

General Procedure for the Gas-Phase Heterogeneous Hydrolysis of Methyl Halide with Steam over Supported γ-Alumina-Based Catalysts. The Lindberg oven is set to the desired reaction temperature, and 10 g of precalcinated catalyst is placed into the reactor tube supported between glass wool plunges. Gaseous methyl chloride (bromide) is passed into the reaction chamber simultaneously with water, being introduced in ratios indicated into the heated chamber via a metered Sage Model 355 syringe pump. The eluent reaction mixture is monitored by analyzing both gaseous products and products collected in cold traps by GC and GC–MS.

Analyses. GC analyses of the reaction mixtures were conducted on the following instruments: (a) Hewlett-Packard 5130 A with a Poropak Q column (12 ft, $^1/_8$ in.); (b) Varian 3700 with an OV 101 glass capillary column (50 m). All percentage numbers are corrected for FID response factors and are given in mole percent.

MS analyses were carried out on a Hewlett-Packard 5985 A GC/MS spectrograph equipped with a Poropak column.

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Registry No. Methane, 74-82-8; CH_3Cl, 74-87-3; CH_2Cl_2, 75-09-2; CH_3Br, 74-83-9; FeOCl, 13870-10-5; $TaOF_3$, 20263-47-2; $NbOF_3$, 15195-33-2; $ZrOF_2$, 14984-80-6; GaOCl, 15588-51-9; TaF_5, 7783-71-3; SbF_5, 7783-70-2; $SbOF_3$, 15195-35-4; Pt, 7440-06-4; Pd, 7440-05-3; alumina, 1344-28-1; CH_3OH, 67-56-1; CH_3OCH_3, 115-10-6; V, 7440-62-2; Mn, 7439-96-5; Cr, 7440-47-3; Mg, 7439-95-4; Zr, 7440-67-7; Ba, 7440-39-3; Ti, 7440-32-6; Zn, 7440-66-6; Fe, 7439-89-6; Ni, 7440-02-0; Bi, 7440-69-9; Al, 7429-90-5.

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Conversion of Serine to Stereochemically Pure β-Substituted α-Amino Acids via β-Lactones

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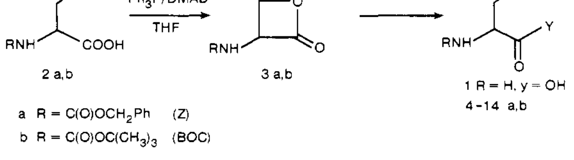
Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2. *Received April 26, 1985*

Abstract: Pure enantiomers of *N*-(benzyloxycarbonyl)serine (**2a**) or *N*-(*tert*-butoxycarbonyl)serine (**2b**) are cyclized without racemization to N-protected α-amino β-lactones **3a** and **3b** in 60–72% yield by using modified Mitsunobu conditions (Ph_3P, dimethyl azodicarboxylate). Treatment of the β-lactones with a variety of halogen, oxygen, sulfur, or nitrogen nucleophiles gives pure enantiomers of N-protected β-substituted alanines **4–14a** and **4b** in high yield. Only hard nucleophiles (e.g., methoxide) attack these lactones at the carbonyl.

A variety of β-substituted alanines **1** having a 2*S* configuration occur in higher plants,[1] whereas the 2*R* isomers are frequently constituents of microbial peptides with antibiotic or antitumor activity.[1,2] The ability of some of these compounds to act as enzyme inactivators[3] or as potential intermediates[4] in enantioselective synthesis of other amino acids[5] makes an efficient route

Scheme I



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