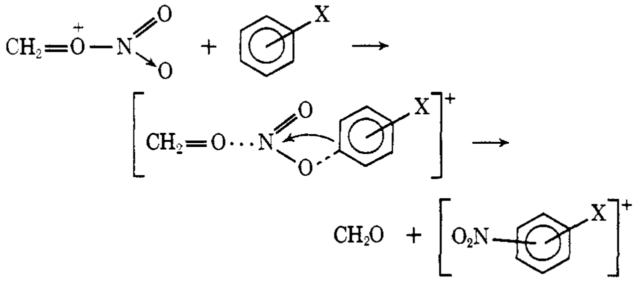
bly lower due to the high reactivity of the gaseous cations.

Reaction 1, by contrast, shows an inverted order of relative rates. Thus, for instance, fluorobenzene and α,α,α-trifluorotoluene react as fast or faster than toluene and aniline. There is qualitatively an inverse correlation between the gas-phase relative rates of reaction 1 and the relative rates of solution-phase electrophilic reactions, and this strongly suggests that reaction 1 in the gas phase is nucleophilic in character, and thus does not correspond at all to solution-phase electrophilic nitration by the NO_2^+ ion. We tentatively suggest as a possible rationalization of this unexpected result that reaction 1 involves primary electrostatic interaction of the aromatic substrate with the nucleophilic terminal oxygen of the $CH_2ONO_2^+$ cation, followed by displacement by the aromatic ring on nitrogen, with simultaneous elimination of formaldehyde.



We believe this to be the first clearcut case in which two gas-phase cation–molecule reactions with aromatic substrates have been observed with one reaction showing nucleophilic, the other electrophilic substituent effects on the reaction rates.

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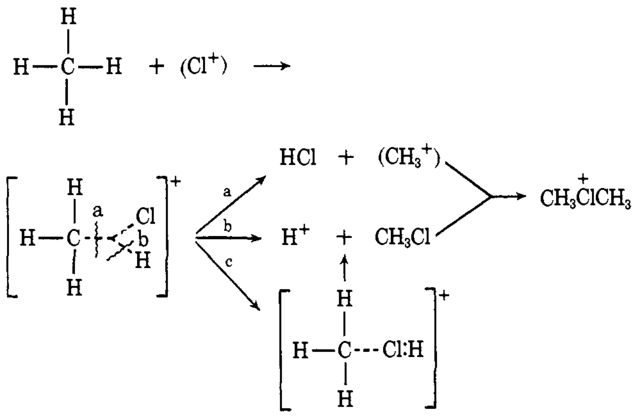
Electrophilic Reaction at Single Bonds. XIII.[1] Chlorination and Chlorolysis of Alkanes in $SbF_5{-}Cl_2{-}SO_2ClF$ Solution at Low Temperature

Sir:

In preceding studies, we have shown the reactivity of alkanes in typical electrophilic reactions such as protolytic processes (isomerization, hydrogen–deuterium exchange, protolysis),[2] alkylation,[3] and nitration.[4] We presently would like to report the chlorination and chlorolysis[5] of alkanes in $SbF_5{-}Cl_2{-}SO_2ClF$ solution,[6] a powerful new electrophilic chlorinating system.[7]

Methane reacts in $SbF_5{-}Cl_2{-}SO_2ClF$ solution at −78° to give dimethylchloronium ion exclusively. As a small amount of HF can always be present in the $SbF_5{-}SO_2ClF$ solution, a protolytic process of methane leading to the formation of CH_3^+ and H_2 would also seem possible. The formed methyl cation then could react with chlorine to give methyl chloride. However, methane as well as ethane, to be discussed subsequently, do not react with $SbF_5{-}SO_2ClF$ at −78°. In fact, protolytic cleavage of methane can be achieved only above room temperature in $FSO_3H{-}SbF_5$ solution to give trimethylcarbenium ion as a main product. Furthermore, both methane and ethane do not react with $Cl_2{-}SO_2ClF$ in the absence of SbF_5 under the same reaction conditions. Consequently, the formation of dimethylchloronium ion from methane in $SbF_5{-}Cl_2{-}SO_2ClF$ can be rationalized as depicted in Scheme I.

Scheme I



The electrophile ("Cl^+")[8] attacks the C–H bond through a two-electron three-center bound transition state to give either (CH_3^+) and HCl (a route) or H^+ and CH_3Cl (b route). Under the stable ion conditions, dimethylchloronium ion is formed. It is also possible that the hydrogen involved in the three-center bond may intramolecularly shift to the *n*-donor chlorine site ($CH_3Cl{:}H)^+$ (c route), which subsequently deprotonates to methyl chloride.

Alternatively, the $Cl\cdot^+$ (or $Cl_2\cdot^+$) radical cation (*i.e*, the triplet state) could also be involved in the reaction. If this is the case, the transition state would involve three-center three-electron bond formation cleaving to HCl and $CH_3\cdot$, the latter initiating radical chain chlorination of methane. Methyl chloride subsequently would form with SbF_5 the dimethylchloronium ion. That no radical chain chlorination is probable in the system is demonstrated when toluene is treated under identical conditions and only electrophilic (mostly ortho–para) ring-chlorinated products are obtained. When excess methane was treated with $SbF_5{-}Cl_2{-}SO_2ClF$ in a bomb at room temperature for 24 hr, it gave besides dimethylchloronium ion (in solution), methyl chloride (in gas phase). No methylene chloride is formed, indicating the absence of less selective radical chlorination.

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[1] Part XII: G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, *J. Amer. Chem. Soc.*, submitted for publication.

[2] G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, *ibid.*, **93**, 1251 (1971).

[3] (a) G. A. Olah and J. A. Olah, *ibid.*, **93**, 1256 (1971); (b) G. A. Olah, Y. K. Mo, and J. A. Olah, *ibid.*, submitted for publication.

[4] G. A. Olah and H. C. Lin, *ibid.*, **93**, 1259 (1971).

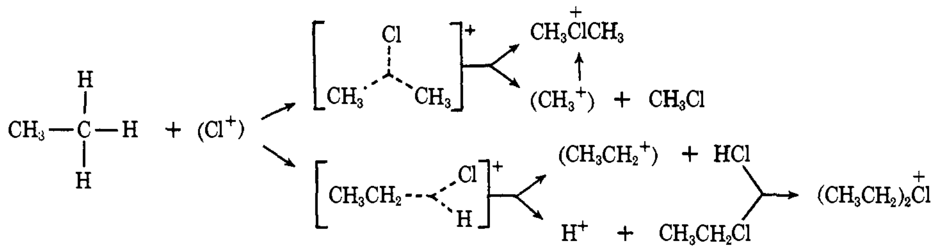
[5] The terms are defined as substitution (of hydrogen for a chlorine atom) and chlorolytic cleavage (of C–C bonds), respectively.

[6] The solution was prepared by condensed excess Cl_2 in $SbF_5{-}SO_2ClF$ solution at −78°.

[7] The electrophilic chlorination of aromatic systems with this reagent was reported: G. A. Olah, H. C. Lin, and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 3667 (1972).

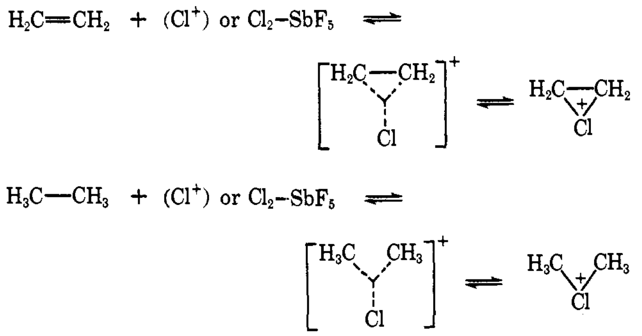
[8] For simplicity, we are depicting the electrophile as "Cl^+" although there is presently no evidence for the existence of the chlorinium ion, $Cl_2{-}SbF_6$, or any well-defined species in the system. Studies relating to the nature of the active chlorinating agent will be reported separately.

Scheme II



When ethane reacted with SbF_5–Cl_2–SO_2ClF solution at −78°, dimethyl- and diethylchloronium ions (as well as some methylethylchloronium ion) were formed in a ratio of 7:3. Identification of the dialkylchloronium ions is based on the increase of the pmr absorption intensities by adding an authentic solution of dialkylchloronium ions. Methyl and ethyl chloride were obtained also in a ratio of 7:3 when the reaction was carried out in a bomb at room temperature for 24 hr. Chlorination and chlorolysis of ethane in SbF_5–Cl_2–SO_2ClF solution may involve electrophilic (Cl^+) attack at C–H and C–C bonds as shown in Scheme II. It should be noted that chlorolytic C–C bond reactivity is higher than that of the primary C–H bonds (as also found in protolytic[1] and nitrolytic[4] cleavage processes of ethane).

It is further rather interesting to point out the obvious similarity of C=C and C—C bonds in alkenes and alkanes, respectively, in their ability to form halonium ions. In both cases interaction with (Cl^+) initially involves an electron pair (π or σ) of the carbon–carbon bonds, followed by halonium ion formation with participation of the nonbonded halogen electron pairs



The significant difference is that alkenes, in which the C—C σ bond is not involved in the process, form three-membered ring cyclic chloronium ions, whereas alkanes form open-chain dialkylchloronium ions.

Propane treated with SbF_5–Cl_2–SO_2ClF solution at −78° gave diisopropylchloronium ion as the major product. Higher homolog alkylcarbenium ions such as t-$C_4H_9^+$, t-$C_5H_{11}^+$, and t-$C_6H_{13}^+$ were also observed as minor products (<10%). Chlorination of isomeric butanes, pentanes, hexanes, heptanes, and octanes was also studied in SbF_5–Cl_2–SO_2ClF solution at −78°. In all cases, stable tertiary alkylcarbenium ions such as $C_4H_9^+$, $C_5H_{11}^+$, $C_6H_{13}^+$, and $C_7H_{15}^+$ and dialkylchloronium ions were formed as the products, depending on the reaction conditions and nature of alkanes. These results indicate the formed alkyl chlorides are further reacting in the system to give stable alkylcarbenium ions and dialkylchloronium ions.

Chlorination of C–H bonds forms the corresponding alkyl chloride and generates an equimolar amount of acid. Protolysis of alkanes to alkylcarbenium ions by the formed acid is also possible. However, the acid formed under the reaction conditions (−78°) is not used

$$R\text{–}H + (Cl^+)SbF_5Cl^- \longrightarrow RCl + H^+SbF_5Cl^-$$

$$R\text{–}H + H^+SbF_5Cl^- \longrightarrow R^+ + SbF_5Cl^- + H_2$$

up, as it shows a pmr absorption at δ 14.0–15.0. Since Cl_2 is always present in large excess, chlorolysis and chlorination compete effectively with protolytic processes. Consequently, comparison of product ions formed can be made in SbF_5–FSO_3H–SO_2ClF and in SbF_5–Cl_2–SO_2ClF solutions. For example, neopentane reacted with SbF_5–FSO_3H–SO_2ClF (or SbF_5–SO_2ClF) solution at −78° gave trimethylcarbenium ion as major product and a small amount of dimethylethylcarbenium ion. On the other hand, it reacts with SbF_5–Cl_2–SO_2ClF solution at −78° to give dimethylethylcarbenium ion as the major product. In addition 2,2,3,3-tetramethylbutane with superacids at −78° gives trimethylcarbenium ion exclusively. It reacts with SbF_5–Cl_2–SO_2ClF solution at −78° to give 27% dimethyl-*tert*-butylcarbenium ion and 73% trimethylcarbenium ion, and some dimethylchloronium ion. These results show that the smaller proton preferentially attacks the sterically crowded but more nucleophilic C–C bonds in neopentane and 2,2,3,3-tetramethylbutane while ("Cl^+") being larger and sterically unfavorable for such attack, will preferentially interact with the more accessible C–H bonds.

Our studies were primarily directed toward establishing that electrophilic chlorination (chlorolysis) of alkanes, including methane, can be carried out in solution at low temperature under typical electrophilic conditions, excluding radical processes. These chlorinations show high selectivity and reactivity of not only C–H but also C–C bonds (chlorolysis) not found in radical chlorinations.

It can be concluded that electrophilic chlorination and chlorolysis of alkanes is a general reaction and represents a significant example of electrophilic reactions at single bonds. Preparative applications of such chlorination will be reported in our forthcoming publications.

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