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Strong Acid Chemistry. 4.[1] Direct Reduction of Alkyl Chlorides

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Abstract: The interaction of haloalkanes with such superacids as HF-TaF_5, HCl-$AlCl_3$, and HBr-$AlBr_3$ has been investigated. The outstanding feature of these reactions is the initial rapid conversion of the alkyl halide to the corresponding alkane in good yields via a hydride transfer mechanism. The impact of our results on interpretation of carbocation formation is discussed.

Almost a century ago, Friedel and Crafts[2] reported that "when a small amount of anhydrous aluminum chloride was added to amyl chloride an immediate vigorous evolution of gas was observed in the cold. The gas was composed of hydrogen chloride accompanied by gaseous hydrocarbons not absorbed by bromine." The precise nature of these saturated hydrocarbons has not been well understood. In the course of our continuing studies of hydrocarbon chemistry in strong acids we now report the observation of the direct reduction products of several alkyl chlorides.

Results and Discussion

While there exists an extensive literature on the behavior of alkyl halides in acidic and superacidic media, we believe this paper reports the first conversion of C_1–C_3 alkyl halides to the corresponding alkane. We have looked at the following systems in HF–TaF_5 at 40 °C: CH_3Cl, C_2H_5Cl, and i-C_3H_7Cl. The latter systems and n-C_3H_7Cl were also studied in HCl:$AlCl_3$ at 140 °C. In all cases the gas phase was analyzed and, where reaction occurred, the corresponding alkane was found to be the major product. Thus, for example, after 5 min at 140 °C in a 45-cm^3 Hastelloy C reactor charged with aluminum chloride and 2-chloropropane, the pressure was 500 psig of which 70.7% was propane by mass spectroscopic analysis. In other words, of the initial charge of isopropyl chloride, 34.2% of the carbon is converted to propane under these conditions. A comparable sample of 1-chloropropane under identical reaction conditions, of excess alkyl halide vs. Lewis acid, was converted after 5 min to the extent of 18% to propane. The results of these studies are summarized in Table I. In both of these cases the other major component in the gas phase was hydrogen chloride. After 15 min the relative amount of propane had decreased as a result of further acid-catalyzed polycondensation reactions of the propane itself.[3]

With 10:1 HF–TaF_5 at high Lewis acid:alkyl halide ratios, selectivity to the alkane is significantly lower, with hydrogen the only other major product in the gas phase. This indicates that, in this more acidic system, a major competing reaction is polycondensation of the alkyl halide similar to that previously described by Olah.[4]

Since the ratio of HX:MX_n to alkyl halide could conceivably affect the effective acidity of the medium and, hence, the reaction mechanism, these reactions were also carried out under widely varying ratios. The results indicate that in AlX_3 systems the stoichiometry does not alter the primary pathway. In the more acidic 10:1 HF–TaF_5 system, however, the isopropyl cation in 2-chloropropane undergoes a shift in reaction mechanism at low acid:alkyl halide ratio to form the direct reduction product, propane. The more acidic methyl cation, on the other hand, undergoes only slow polycondensation (~25% in 1 h) reaction and no direct reduction at the low acid:alkyl halide ratio.

The major finding is the direct reduction of the haloalkane to the hydrocarbon. Equations 1, 2, and 3 present three alternatives which explain the observed results: i.e., alkane formation via dialkylhalonium ions, via haloalkyl carbenium ions, or via propyl carbenium ions (applies only to C_3 and larger systems).

via dialkylhalonium ions:

$$2R_2CHCl + MX_n \rightleftharpoons (R_2CH)_2Cl^+(MX_nCl)^-$$

$$(R_2CH)_2Cl^+(MX_nCl)^- + R_2CHCl \rightarrow R_2CH_2 + (R_2CHCl^+CR_2Cl)(MX_nCl)^- \tag{1}$$

via haloalkyl carbenium ions:

$$R_2CHCl + MX_n \rightleftharpoons R_2{}^+CH(MX_nCl)^-$$

$$R_2{}^+CH(MX_nCl)^- + R_2CHCl \rightarrow R_2CH_2 + R_2{}^+CCl(MX_nCl)^- \tag{2}$$

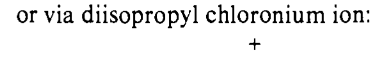
Table I. Summary of Results of the Reactions of Alkyl Chlorides with Strong Acids

Alkyl chloride (R-Cl)	MXn/RCl (mole ratio)	Acid	t, °C	T, min	% RH in gas phase	% RH in total HC gases
CH_3Cl	4.0	10:1 $HF\text{-}TaF_5$[a]	40	30	6.6	21.5[d]
				60	7.5	42.3
				120	8.9	57.0
CH_3Cl	0.2	10:1 $HF\text{-}TaF_5$	40	60	0.0	0.0
CH_3CH_2Cl	4.0	10:1 $HF\text{-}TaF_5$	40	30	9.7	25.7
				60	10.0	32.2
				120	8.6	49.3
$CH_3CH_2CH_2Cl$	0.2	1:1 $HCl\text{-}AlCl_3$	140	5	45.0[b]	97.2
				15	47.0[b]	93.0
$(CH_3)_2CHCl$	0.2	1:1 $HCl\text{-}AlCl_3$	140	5	70.7[c]	97.1
				15	56.8[c]	92.8
	4.0	1:1 $HCl\text{-}AlCl_3$	140	5	>90	96.8
	2.5	10:1 $HF\text{-}TaF_5$	40	30	30.1	43.0
				60	32.5	46.0
				120	33.4	47.8
	0.2	10:1 $HF\text{-}TaF_5$	40	5	55.5	97.0
				60	61.8	96.7
	0.2	1:1 $HBr\text{-}AlBr_3$	20	2	~100	~100[e]
				18	~90	~90

[a] $HF\text{-}TaF_5$ (2.0 mol:0.2 mol) + RCl (0.05 mol) in a 300-cm^3 Hastelloy C Autoclave Engineers autoclave stirred at 1000 rpm. [b] Yields: 9.5 and 9.0% in 5 and 15 min, respectively. [c] Yields: 34.2 and 23.6% in 5 and 15 min, respectively. [d] 21.5% of the hydrocarbons in the gas phase is methane. [e] Analysis via gas chromatography.

The possibility of dehydrohalogenation followed by hydride abstraction to produce saturated hydrocarbons, while remote, cannot be discounted.

via propenyl cation formation:



$$CH_3\underset{\displaystyle Cl}{C}HCH_3 + MX_n \rightarrow \underset{+}{(CH_3CHCH_3)}\,(MX_nCl)^-$$

$$\underset{+}{(CH_3CHCH_3)}\,(MX_nCl)^- \rightarrow H^+(MX_nCl)^- + CH_3CH{=}CH_2$$

$$CH_3CH{=}CH_2 + \underset{+}{(CH_3\dot{C}HCH_3)}\,MX_nCl^- \rightarrow CH_3CH_2CH_3 + (CH_2\overset{+}{\cdots}CH\cdots CH_2) \quad (3)$$

or via diisopropyl chloronium ion:

$$CH_3CH{=}CH_2 + (CH_3CHCH_3)_2\,\overset{+}{Cl}(MX_nCl)^- \rightarrow CH_3CH_2CH_3 + (C_3H_5){-}\overset{+}{Cl}{-}(C_3H_7)(MX_nCl)^- \quad (3a)$$

We believe, however, that olefin formation would produce oligomerization and polymerization products and thus is not consistent with fully one-third of the product going to propane.

In any case, the conversion of methyl or ethyl halides to methane and ethane, respectively, precludes the allylic hydrogen donation pathway for these systems and lends support to a mechanism such as outlined in eq 1 or 2.

Evidence for the presence of dialkylhalonium ions and, hence, support for the possibility of the occurrence of, e.g., eq 1, etc. has come from low-temperature 60-MHz ^1H NMR spectra of the acid layer which slows a sharp singlet at −35 °C at δ 4.1 in HF solution relative to Me_4Si in an external capillary tube. This peak is ~50% of unreacted CH_3Cl remaining in the acid layer. The existence of halogen-substituted cations[6] is well documented in the literature as is the existence of dialkylhalonium ions.[7] The existence of simple halomethyl cations has to date only been the subject of speculation and discussion.[8,9] The stability of such species should become increasingly favorable as the size of the alkyl group and number of such groups is increased.

Recent energy calculations by Hehre favor the 1-haloethyl form of the cation.[10] Based upon the temperature dependence of the observed NMR spectrum, Olah[11,12] has postulated the formation of the 1-fluoroethyl cation by the reaction of SbF_5 with 1,1-difluoroethane. He also observed the 1-chloroethyl and chlorine-bridged ethyl cation in the NMR by reaction of SbF_5 in sulfuryl chloride and from ^{13}C NMR results predicts a significant contribution by the $CH_3\text{-}CH{=}Cl^+$ resonance form. We have not yet been successful, however, in identifying by NMR experiments or quenching the intermediate ions in solution and thus are unable to select between eq 1 and 2 at this time.[14]

In a related experiment we looked at the chemistry of methanol in $HCl\text{-}AlCl_3$. We were interested in determining whether a reduction reaction of methanol to methane could be competitive with conversion to methyl chloride.

$$2CH_3OH + AlCl_3 \overset{H^+}{\rightleftharpoons} (CH_3)_2\overset{+}{O}H\,(AlCl_3OH)^-$$

$$(CH_3)_2\overset{+}{O}H(AlCl_3OH)^- + CH_3OH \rightarrow CH_4 + (HOCH_2{-}\overset{+}{O}{-}CH_3)(AlCl_3OH^-) \quad (4)$$

vs.

$$CH_3OH + AlCl_3 \overset{H^+}{\rightleftharpoons} CH_3Cl + AlCl_2OH \quad (5)$$

Mass spectroscopic results show copious amounts of methyl chloride in the gas phase with little or no methane thus arguing that (4) if occurring does not kinetically compete with (5) under our conditions.

Summary

The results shown here indicate that with very strong acids, simple alkyl halides undergo direct reduction in high yields to the corresponding alkane. As the reaction is permitted to continue, further reaction occurs leading to heavier hydrocarbon products. The complexity of the chemistry involved is apparent from the variety of plausible pathways which can be invoked to explain that part of the reaction we can measure.

The work to date clearly indicates that differences in the chemistry should be expected in comparing the behavior of carbocations generated from the alkane[1,13] vs. the complex mixture of cationic species generated from the alkyl halide in superacid media. We believe much more work is needed before the true nature of species obtained via the acid-catalyzed treatment of haloalkanes is well understood, and we are loathe to extrapolate from alkane paraffin/acid systems to those involving carbon–halogen bonds.

The further elucidation of the intriguing chemistry of simple alkyl halides in strong acids is presently under investigation.

Experimental Section

Mass spectra were obtained on an MS-9 mass spectrometer.

Gas chromatographic analyses were carried out using a Perkin-Elmer Model 900 gas chromatograph using a 50 ft × 0.02 in. 40% squalane column.

Reduction of 2-Chloropropane. A 45-cm^3 Parr autoclave (Hastelloy C) was cooled to 0 °C and charged with 2-chloropropane (Aldrich) (6.0 g, 0.076 mol) and aluminum chloride (2.0 g, 0.015 mol). The system was flushed with nitrogen, closed, and heated in an oil bath to 140 °C. The pressure rose to 500 psig, and a gas sample was taken for mass spectroscopic analysis. The major components in the mass spectrum were: ethane (0.1%), propane (70%, 0.026 mol), isobutane (1.8%), isopentane (0.4%), 2-chloropropane (2.1%), and HCl (17%). Fifteen minutes later a second gas sample showed a decrease in the propane content to (62%) and increased in the heavier hydrocarbons; isobutane (2.3%), *n*-butane (0.8%), and isopentane (1.2%). These materials account for 40% of the carbon charged. Another 20% of the carbon winds up in a heavy hydrocarbon mixture obtained from *n*-C_5 extracts after an aqueous quench.

Reduction of 1-Chloropropane. Reaction was identical with that described above. The building of heavier hydrocarbons in the gas phase with time shown for the 2-chloropropane above was duplicated in this case. It is interesting to note that after 5 min there was ten times as much *2-chloropropane* as *1-chloropropane* in the gas phase, while 10 min later the total amount of chloropropane was decreased by two-thirds with the *1-chloropropane* tripled and the amount of *2-chloropropane* decreased by >90%.

Reaction of CH_3Cl (or CH_3CH_2Cl) with HF/TaF_5. A typical experiment is as follows: A 300-cm^3 Autoclave Engineers reactor (Hastelloy C) was charged with tantalum pentafluoride (55 g, 0.20 mol) and sealed. Hydrogen fluoride (39 g, 2.0 mol) was added and the reactor heated to 40 °C. Into a tared 10-cm^3 316 stainless steel vessel cooled to <0 °C, methyl chloride (3.9 g, 0.08 mol) was condensed; the 10 cm^3 vessel was connected to the reactor and warmed, and the reactor was stirred at 1000 rpm for 2 h at 40 °C. Gas samples were taken and sent for mass spectroscopic analysis which showed CH_4, C_2H_6, C_3H_6, etc. An acid sample was quenched in water, and the organics were extracted with pentane. The pentane extract contained small but measurable (by gas chromatography) quantities of *i*-C_4, *i*-C_5, and C_6 materials.

Reaction of 2-Chloropropane with $AlBr_3$. This reaction was carried out at room temperature and followed by sampling the product gases via gas chromatography. 2-Chloropropane (6.0 g, 0.076 mol) and aluminum bromide (4.0 g, 0.015 mol) were placed together in autoclave at −10 °C. Upon sealing and warming to room temperature a gas pressure developed. Gas chromatographic analyses were obtained after 2, 4, 18, and 45 min. In the 2-min sample, only propane was observed whereas the later samples showed the buildup of higher molecular weight hydrocarbons (mostly C_6's in the gas phase).

Reaction of Methanol with $AlCl_3$. In a 45-cm^3 autoclave, methanol (2.0 g, 0.063 mol) and aluminum chloride (10.0 g, 0.075 mol) were heated to 150 °C. Gas samples were taken after 5 min (P = 50 psig) and 30 min (P = 120 psig). More than 99% of the gas-phase material was CH_3Cl and HCl.

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$$2R_2CHCl + MX_n \overset{a}{\rightleftharpoons} (R_2CH)_2\overset{+}{Cl}(MX_nCl)^-$$

$$(R_2CH)_2\overset{+}{Cl}(MX_nCl)^- + R_2CHCl \overset{b}{\rightleftharpoons} R_2CHCl + (R_2CH)_2\overset{+}{Cl}(MX_nCl)^-$$

$$(R_2CH)_2\overset{+}{Cl}(MX_nCl^-) + R_2CHCl \xrightarrow{c} R_2CH_2\,(g) + (R_2CHCl\overset{+}{C}R_2Cl)\,(MX_nCl)^-$$

Both eq 1 and 2 involve a hydride transfer from a molecule of alkyl halide to a cationic species to form alkane and a chlorine assisted cation. Even quenching experiments could not unambiguously distinguish between these mechanisms. Only direct observation of the ions in solution [i.e., $(CH_3)_2C^+Cl$ vs. $(CH_3)_2CH^+Cl\ C(CH_3)_2Cl$ for the isopropyl case] will allow us to choose the appropriate intermediate(s).