Selective Carbonylation of Propane in Superacid Media *via* Hydride Abstraction by the Chlorocarbocations: CCl_3^+ and $CHCl_2^+$

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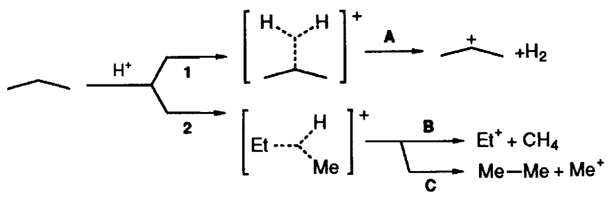
Carbonylation of propane in HF–SbF_5 (5 : 1 molar ratio) superacid in the presence of carbon tetrachloride (or chloroform) at −30 °C yields exclusively the isobutyryl ion (isopropyloxocarbenium ion), analysis of the gaseous fluorocarbons generated as side products showing both hydride abstraction by CCl_3^+ (or $CHCl_2^+$) and Cl/F exchange on the tri- and di-chloromethane formed; in the absence of CCl_4 (or $CHCl_3$) no reaction takes place under the same experimental conditions.

The selective activation and functionalization of saturated alkanes is a major goal in chemistry.[1] Since the pioneering work of Olah *et al.* in the late sixties,[2] developing the concept of σ-bond basicity in relation to the protolytic ionization of alkanes in superacid media, the reactivity of a large number of electrophiles towards C–H and C–C bonds has been tested.[3] Reports of ionic chlorination of alkanes with methylene chloride in SbF_5[4] and the recent observation of the trihalocarbocations as long lived species in SbF_5–SO_2ClF solution[5] prompt us to publish our results on the use of CCl_4 and $CHCl_3$ for the selective, low-temperature ionization of small alkanes, in the HF–SbF_5 superacid system.

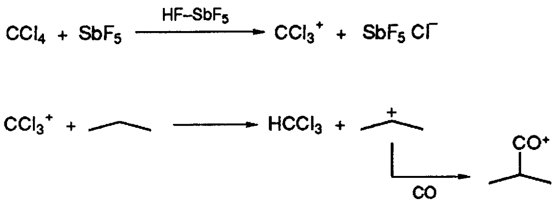
Table 1. Conversion and selectivity of propane carbonylation in HF–SbF_5.

HF–SbF_5 /mol%	CO/C_3 /molar ratio	Temperature /°C	CCl_4/SbF_5 /molar ratio	Propane conversion[a] /mol%	Selectivity in IPOC/IPOC + ETOC /mol%
20	3	−10	no CCl_4	4	41
20	3	−10	0.08	28	100
20	3	−30	no CCl_4	1	40
20	3	−30	0.08	50	100

[a] After 1 h on-stream.



Scheme 1



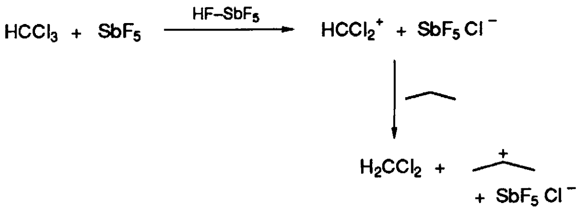
Scheme 2

The carbonylation reaction of alkanes in superacid media has been known since the work of Paatz and Weisgerber[6] in the late sixties. The usual side reactions such as isomerization and cracking of the intermediate carbocations have until recently hindered the development of this method.[7]

The protolytic ionization of propane in 4:1 HF–SbF_5 superacid occurs slowly at −10 °C *via* two competing pathways:[8] cleavage of a secondary C–H bond or cleavage of a C–C bond (Scheme 1). We have shown recently[9] that the trapping of the initial ions by excess carbon monoxide is an efficient method for verifying the bond breaking pattern, as the oxocarbenium ions which are formed can be observed as long lived species in superacid solution.

On the other hand carbonylation of propane provides an alternative route for the preparation of metacrylic esters.[9c] When a propane/carbon monoxide mixture (CO : C_3 molar ratio 3) is bubbled for 1 h at a rate of 220 ml h^{-1} through 1.5 ml of a HF–SbF_5 solution (4 : 1 molar ratio) in a Kel-F reactor at −10 °C, the 400 MHz ^1H NMR spectrum of the resulting solution shows only two ions: the isopropyloxocarbenium ion (IPOC) and the ethyloxocarbenium ion (ETOC) in a relative ratio 2 : 3 (calculated conversion of propane 4%). GC analysis of the gas phase shows the following product distribution $CH_4 >> C_2H_6 >> H_2$ in agreement with the cleavage pattern 2B being prefered over 1A. As no acetyl ion can be detected, pathway 2C can be neglected and the formation of ethane ascribed to selective hydride abstraction on propane by the ethyl cation.[9b] Under the same experimental conditions but at −30 °C negligible conversion of propane is observed.

However, when the reaction takes place in the presence of CCl_4 (CCl_4 : SbF_5, molar ratio 0.08) at −30 °C, a conversion of up to 50% propane with 100% selectivity in the isopropyloxocarbenium ion is determined by both ^1H NMR spectroscopy of the resulting superacid solution in the presence of an internal standard and GC analysis of the esters obtained by quenching the ions in excess methanol. The absence of hydrogen, methane, and ethane in the gas phase indicates the absence of the expected protolytic ionisation steps as indicated in Scheme 1. No SbF_3 can be detected. This is in agreement with a clean hydride abstraction from the alkane by $^+CCl_3$, which was recently observed[5] as a long lived species in SbF_5/SO_2ClF solution (Scheme 2).



Scheme 3

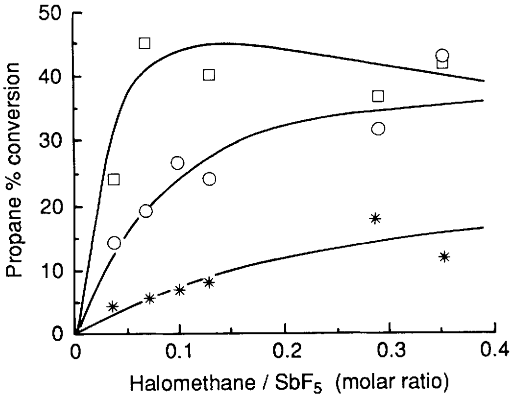


Figure 1. Propane conversion after 1 h reaction *vs.* halomethane/SbF_5 ratios. (□) CCl_4; (○) $HCCl_3$; (*) H_2CCl_2.

The hydride abstraction by the halomethyl cation is further confirmed by GC analysis of the Freons collected in the gas phase. The presence of trifluoromethane and difluoromethane (respectively 17 and 29 mol% based on converted propane) shows clearly that after the initial hydride abstraction the well known chlorine–fluorine exchange reactions[10] occur under these conditions in competition with the generation of $HCCl_2^+$, H_2CCl^+, *etc.* (Scheme 3). The results showing the selectivity and activity of propane carbonylation in the presence of CCl_4 are collected in Table 1. Considering the steric requirements, the selective activation of the C–H bond by the halocations is not surprising. However, the increased reactivity in comparison to the protonic activation is unexpected. When CCl_4 is replaced at the start by chloroform or methylene chloride, the selective C–H bond activation is still observed but the time dependent conversion is lower, as shown in Figure 1. The reactivity seems to be in the decreasing order $CCl_3^+ > HCCl_2^+ > H_2CCl^+$. Whereas alkane oxidation in superacid media may occur directly *via* competitive action of the protons and SbF_5,[11] selective activation can also be performed by a large number of easily generated electrophiles in superacid media.

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