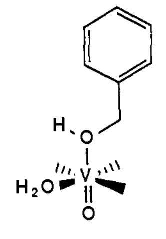
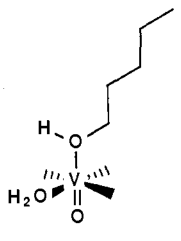
layer must interpenetrate those of the adjacent layer. Furthermore, the chains must not be perpendicular to the layer but must be slanted at an angle equal to $\sin^{-1} 1.05/1.27$ or 56°. This is the angle expected for a P–C bond that is perpendicular to the inorganic layers. A schematic representation of the packing of the alkyl chains and the alcohol molecules in the interlayer region is given in Scheme I.

Alcohol molecules are readily reabsorbed into the interlayer region of $VO(C_nH_{2n+1}PO_3)\cdot H_2O$ by contacting the dried precursor with alcohol at room temperature. Not only can benzyl alcohol be reabsorbed to regenerate the initial compounds, but a variety of other alcohols can intercalate as well. When treated with *n*-pentanol, the $VO(C_nH_{2n+1}PO_3)\cdot H_2O$ compounds expand to give a series $VO(C_nH_{2n+1}PO_3)\cdot H_2O\cdot C_5H_{11}OH$ (**2**) that has layer spacings very similar[13] to those of the $VO(C_nH_{2n+1}PO_3)\cdot H_2O\cdot C_6H_5CH_2OH$ (**1**) series. The length of a benzyl alcohol and an *n*-pentanol molecule are similar as depicted in the conformations of the line drawings.



1



2

Vanadyl hexylphosphonate hydrate, $VO(C_6H_{13}PO_3)\cdot H_2O$, was treated with a series of linear 1-alkanols with carbon number from 2–10. The layer spacings of the resulting $VO(C_6H_{13}PO_3)\cdot H_2O\cdot C_nH_{2n+1}OH$ compounds are plotted in line c of Figure 1. In this case the layer separation is controlled by the length of the alcohol chain not by the length of the alkyl group on the phosphonate which is held constant at C_6. The slope of the line is 1.1 Å/CH_2 unit, very similar to that of the lines generated by varying the length of the alkylphosphonate chains, reinforcing the structural model suggested by Scheme I.

In their alcohol intercalation reactions, vanadyl organophosphonates can distinguish between groups of alcohol molecules. This selectivity can be controlled by the steric constraint around the absorption site, which in turn is determined by the nature of the organic group bound to phosphorus. For example, vanadyl phenylphosphonate absorbed primary *n*-alkanols over a period of hours at elevated temperature. The same alcohols are intercalated rapidly at room temperature into vanadyl alkylphosphonates, because the more flexible alkyl groups surround the coordination site. Vanadyl hexylphosphonate hydrate, $VO(C_6H_{13}PO_3)\cdot H_2O$, intercalates the primary alcohols *n*-butanol and isobutyl alcohol but does not react with *sec*-butanol or *tert*-butyl alcohol. In general, primary alcohols can be separated from secondary and tertiary alcohols with high selectivity by using vanadyl alkylphosphonates as sorbents. However, sufficiently bulky primary alcohols like neopentanol do not intercalate into $VO(C_6H_{13}PO_3)\cdot H_2O$.

We have shown that the alternating inorganic/organic layer compounds $VORPO_3\cdot H_2O$ can discriminate among isomeric alcohols. This discrimination arises because the vanadium coordination site on the intralayer surface is sterically restricted by the organic groups which surround it. In addition, reaction rates are also controlled by varying the organic group bound to phosphorus. Thus vanadyl *p*-biphenylphosphonate does not react with alcohols at all,[10] whereas the vanadyl alkylphosphonates rapidly intercalate primary alcohols at room temperature. Further work extending the synthetic and intercalation chemistry of vanadyl organophosphonates by exploring the effects of steric constraints in the organic layer will be reported in future publications.

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(13) Layer spacings of $VO(C_nH_{2n+1}PO_3)\cdot H_2O\cdot C_5H_{11}OH$ for n = 2, 4, 6, 8: slope = 1.18 Å/CH_2; intercept = 10.85 Å.

Halogen Promoted Selective Carbonylation of Propane in Superacid Media

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Since the pioneering work of Olah and his group in the late sixties it is known that small alkanes do react with a large variety of electrophiles in superacid media under mild temperature and pressure conditions.[2] For industrial applications a major problem to solve is the lack of selectivity due to side reactions such as cracking and isomerization. We report here our results on selective carbonylation of propane in $HF\text{-}SbF_5$, the first step of an alternative method for preparing methacrylates via isobutyric acid derivatives.[3]

Earlier reports of direct carbonylation of saturated alkanes in superacid media include the reactions of C_6 cycloalkanes[4] and C_5–C_8 alkanes[5] as well as adamantane,[6] whereas in the classical Koch–Haaf synthesis[7] the intermediate carbocation is obtained by protonation of an alkene; in the superacid media it is generated directly from the alkane via the protolytic ionization process.

Two main pathways must be considered: cleavage of a secondary C–H bond or cleavage of a C–C bond. In the presence of excess carbon monoxide the initial cations are trapped giving the much more stable oxocarbenium ions[8] which can then be observed as long living species by NMR. Further titration can also be made by quenching the oxo ions in excess methanol and GC analysis of the resulting methyl esters. Our results show that the selectivity of propane carbonylation can be remarkably modified by adding catalytic amounts of halide ions. When a propane–carbon monoxide mixture ($CO{:}C_3$ molar ratio = 3) was bubbled during 1 h at a rate of 220 mL per hour 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 proton NMR spectrum of the resulting solution showed only two ions: the isopropyloxocarbenium ion (IPOC) and the ethyloxocarbenium ion (ETOC) in a relative ratio of 2:3 (calcd conversion of propane: 4%).

All our experiments carried out with an excess of carbon monoxide showed the predominant formation of the propionyl ion resulting from the preferential C–C bond cleavage in the initial attack. This is in agreement with the observation made by Olah

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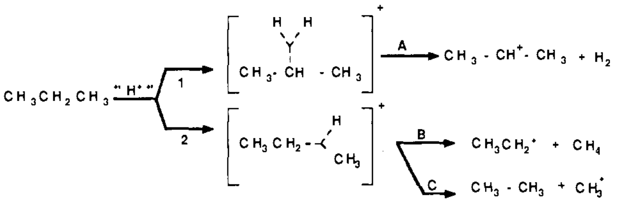
Scheme I



and his group[9] on the relative reactivity of the σ bonds toward the electrophilic proton:

primary C–H ≪ secondary C–H < C–C < tertiary C–H

When the propane-carbon monoxide mixture (CO:C_3 molar ratio = 3) was bubbled through HF-SbF_5 under the same conditions as above but after addition of a small amount of sodium bromide (Br^-/Sb:0.5 mol %), the NMR spectrum of the resulting solution showed a selectivity of 95% in IPOC formation with a total conversion of 9% of the propane. The influence of the bromide ion on the selectivity of propane is shown in Figure 1. When the same reaction was carried out on a 20 times larger scale under a pressure of 6 atm in a Hastelloy Autoclave (reaction time: 5 h), the GC analysis of the products obtained by quenching the reaction mixture in ice–water shows a selectivity of 98% in isobutyric acid with a conversion of 80% of the propane. Analysis of the gas phase shows the following product distribution

$$H_2 \gg CH_4 \gg C_2H_6 \ (90:10:0)$$

in agreement with the hydride-abstracting ability of the ethyl cation generated via pathway 2B.

The nature of the bromide salt has little effect on the product distribution as shown by replacing NaBr by tetramethylammonium bromide. The presence of iodide ions shows also an increase in selectivity, whereas the chloride ions have little effect.

The results can be rationalized as follows: When the bromide ion is dissolved in the superacid medium, it is oxidized via protonation of the hydrogen halide. The second step, key step for the observed selectivity, is the electrophilic attack of the secondary C–H bond, as preferred for steric reasons; and in this way HBr is regenerated. The better selectivity observed with the bromide ion seems to be due to the fact that the chloride ion is too difficult to oxidize under the present conditions, whereas the "I^+" ion is less electrophilic.

In contrast to many well defined polyatomic halogen cations[10] such as I_2^+ and Br_2^+ no experimental evidence has been brought for the existence of the monoatomic ions. The Lewis acid assisted generation of "Cl^+" and "Br^+" from chlorine and bromine has been suggested by Olah on the basis of electrophilic chlorination and bromination of alkanes.[11] Bromine itself is easily oxidized in HF-SbF_5 via the Br_2H^+ ions[12] and has been used in selective aromatic bromination.[13] It can also replace the bromide ion in the experiments described above with the same selectivity.

On the other hand, we cannot exclude that CO itself may participate in the key step as [$COBr^+$] analogous to the formyl cation [HCO^+] which has recently been identified in the carbonylation reaction of adamantane or [$COCl^+$] reported as an intermediate in the electrophilic carbonylation of benzene in the liquid SO_2–Br_2–$SbCl_5$–CO system.[14]

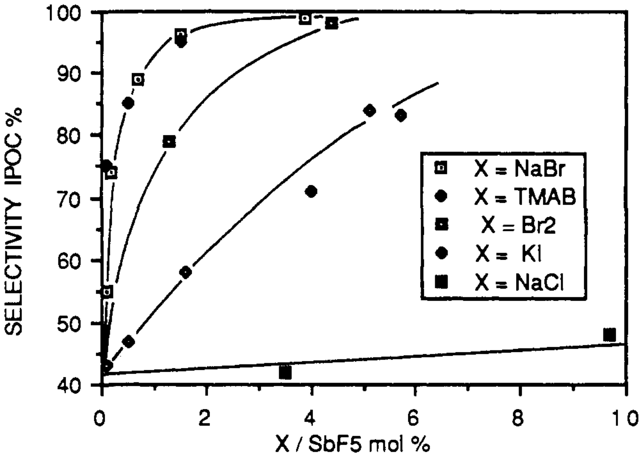
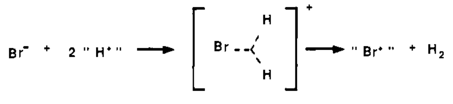
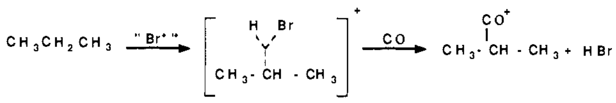


Figure 1. Selectivity in the carbonylation of propane as a function of halide ion concentration in HF-SbF_5.

Scheme II



Scheme III



The intriguing point in these results is the high selectivity observed with catalytic amounts of bromide ion in a large excess of protonic superacid. This can only be explained by the large rate enhancement as observed. The addition of excess HF leads to the formation of isobutyryl fluoride. In this way the total reaction of carbonylation of propane in HF-SbF_5 can be written as

$$C_3H_8 + HF + CO \rightarrow C_3H_7COF + H_2$$

Acknowledgment. We would like to thank NORSOLOR (subsidiary company of ORKEM) for financial support.

Registry No. C_3, 74-98-6; TMAB, 64-20-0; Br, 24959-67-9; I, 20461-54-5; NaBr, 7647-15-6; Br_2, 7726-95-6; KI, 7681-11-0; isobutyric acid, 79-31-2.

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Convenient Conversion of Aldehydes and Ketones into the Corresponding Alkenes via Hydroboration of Their Enamines. A Remarkably Simple Synthesis of Either [*Z*]- or [*E*]-Alkenes[1a]

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Aldehydes and ketones are converted into the corresponding alkenes via hydroboration of their enamines. The synthesis of pure [*Z*]- or [*E*]-alkenes is readily achieved from the same acyclic ketone enamine by modification of the hydroboration–elimination procedure: (A) hydroboration of the enamine by 9-borabicyclo[3.3.1]nonane (9-BBN) followed by methanolysis or (B) hy-

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