

## Selective Carbonylation of Propane in HF-SbF<sub>5</sub>: Control of the Activation Step via the Hydrocarbon/Carbon Monoxide Ratio

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The selectivity of propane carbonylation in HF-SbF<sub>5</sub> is found to depend on the propane/CO ratio, and is rationalized in terms of two competing activation processes for the alkane.

The activation of alkanes under mild temperature and pressure conditions is an important goal for industrial organic chemistry. Supercacid media are known, since the pioneering work of Olah and his group,<sup>1</sup> to favour the generation of strong electrophiles able to react with saturated hydrocarbons.<sup>2</sup> The selectivity of these reactions is often limited by side reactions such as cracking and isomerization. In this paper we show how the hydrocarbon/CO ratio influences the selectivity of propane carbonylation in a superacid medium, thus providing an alternative method for preparing isobutyric acid, the starting material for methacrylic ester synthesis (Scheme 1).<sup>3</sup>

The protolytic attack on propane in HF-SbF<sub>5</sub> is postulated to take place either on the secondary C-H bond or on the C-C bond resulting in two competitive pathways (1) and (2) (Scheme 2). From the early studies by Olah and his group on alkane reactivity in superacids<sup>4</sup> it is known that, with the exception of the tertiary C-H bond, the proton prefers to attack the more nucleophilic C-C σ bond, the experimental data indicating the following order of reactivity for single bonds in alkanes: tertiary C-H ≫ C-C > secondary C-H ≫ primary C-H.

Reacting propane with the superacid in the presence of carbon monoxide is a good method to verify the bond breaking pattern. Indeed the primary and secondary cations which are formed in the ionization step react rapidly with CO and yield the much more stable primary and secondary oxocarbenium ions which can be quantitatively analysed by <sup>1</sup>H n.m.r. in the superacid solution<sup>5,6</sup> as long-living species. Quenching these ions in excess ethanol- or water-sodium hydrogen carbonate, followed by g.c. analysis of the resulting esters or acids is a reliable complementary method for quantitative analysis.

When a propane-carbon monoxide mixture (CO : C<sub>3</sub> molar ratio = 3) was bubbled during 1 h at a rate of 220 ml per hour through a solution of HF-SbF<sub>5</sub> (1.5 ml) (4 : 1 molar ratio) in a Kel-F reactor at -10 °C, the 400 MHz proton n.m.r. spectrum of the resulting solution showed only two ions: the isopropyl-oxocarbenium ion (IPOC) and the ethyloxocarbenium ion (ETOC) in a relative ratio of 2 : 3 (calc. conversion of propane 4%). When the reaction was carried out on a 20 times larger scale in a Hastelloy Autoclave under a pressure of 62 atm (CO/C<sub>3</sub> ratio of 16) and the resulting solution quenched in water-sodium hydrogen carbonate, the g.c. analysis of the products showed a ratio of 1 : 6 for isobutyric acid to propionic acid. Small amounts of acetic acid and methanol were detected and the overall conversion of propane was as high as 94%. All our experiments carried out with an excess of carbon monoxide showed the predominant formation of ETOC resulting from the preferential C-C bond cleavage in the initial attack.

The analysis of the gas phase gives H<sub>2</sub> : methane : ethane in a ratio 4 : 89 : 7 which is in good accord with the cleavage scheme. The large excess of methane over ethane and the

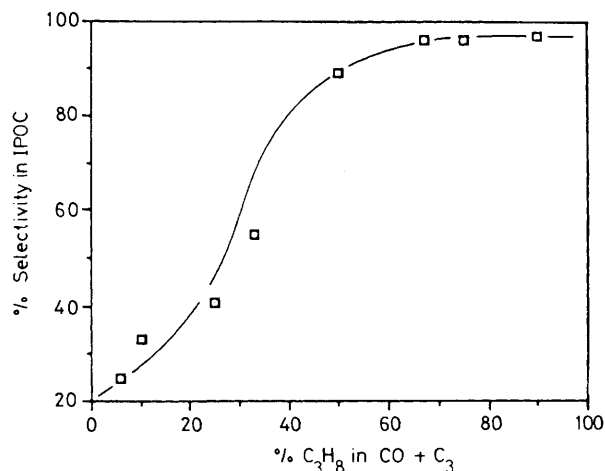
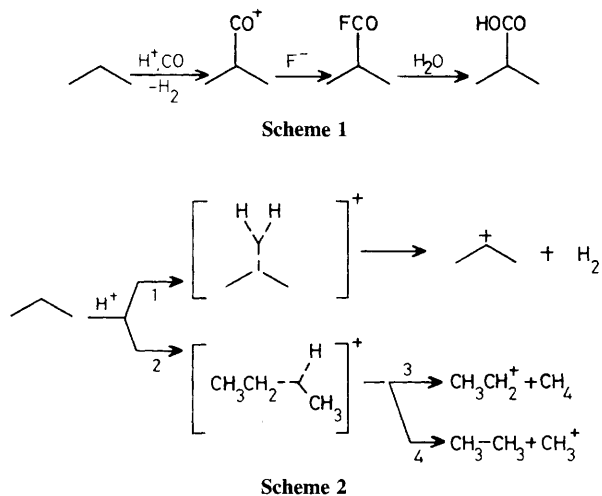
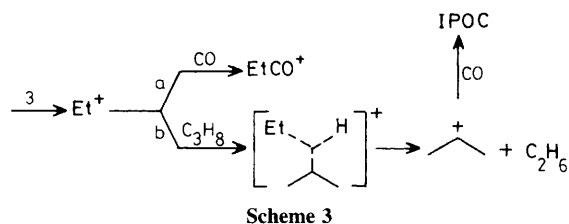


Figure 1. Dependence of the selectivity [IPOC/(IPOC + ETOC)] on the C<sub>3</sub>/CO ratio.

absence of the very stable acetyl ion shows clearly that pathway (4) can be neglected in agreement with the relative stability of the methyl and ethyl cations. As confirmed in Scheme 3, ethane originates indirectly *via* hydride abstraction from propane by the ethyl cations produced *via* (3). However, when a reaction mixture with a large excess of propane was used (CO:C<sub>3</sub> molar ratio = 0.1), under the same reaction conditions as above, isopropylloxocarbenium ion was produced with a remarkable selectivity: IPOC > 97%; ETOC < 2%; t-butyl ion < 1%. The overall conversion to oxocarbenium ions was 2.5%, based on the amount of propane which was bubbled through the superacid. The dependence of the yield of IPOC on the propane/CO ratio is illustrated in Figure 1. At high CO/C<sub>3</sub> ratios the product distribution is in agreement with preferential C–C bond cleavage [pathway (3)] followed by carbonylation of the ethyl cation. However, already at a molar ratio of CO/C<sub>3</sub> = 3:1, hydride abstraction (3b) competes with carbonylation (3a). When the ratio is below unity we can say that the direct protolysis of the C–H bond by the superacid proton (pathway 1) can be neglected in comparison to the activation of propane *via* the ethyl cation. In excellent agreement with this reaction scheme, the analysis of the gas phase then shows negligible amounts of hydrogen but methane and ethane in approximately equivalent amounts. This distribution should be expected when pathway (3b) becomes predominant. The presence of small amounts of t-butyl cation in the superacid phase is in accord with the well-known competitive alkane alkylation<sup>7</sup> and oligocondensation reactions.<sup>8</sup>

Our results illustrate well the early conclusions by Olah and his group: the initial protolysis of the C–C bond in the C<sub>4</sub>–C<sub>8</sub> alkanes, forming lower alkanes and carbocations, is followed by hydride abstraction by these ions from the starting alkanes. Due to the relative bulkiness of the ions, the less hindered C–H bond is then preferred.

We show here that the presence of CO can be very useful in the study of the initial cleavage processes as the initial unstable carbocations react rapidly to form the stable oxo ions.

An increase in pressure of CO will increase the rates of carbonylation of the carbocations without changing the rates of hydride transfer. This is clearly demonstrated by the change

in selectivity, when the reaction was performed with an excess of propane (CO:C<sub>3</sub> molar ratio = 0.1), at a total pressure of 6 atm. The initial distribution: ETOC/IPOC 60/40 was again observed.

For practical applications we must however underline two points at this stage. First, the high selectivity in IPOC which could be reached at low CO/C<sub>3</sub> ratios is obtained at the sacrificial cost of one mole of propane per mole of IPOC produced. At high CO/C<sub>3</sub> ratios and with the help of pressure the selectivity can be orientated towards the production of propionic acid (80%).<sup>3a</sup>

On the other hand, the conversion is limited by the SbF<sub>5</sub> content of the HF solution, as for each oxo-ion, the counterion SbF<sub>6</sub><sup>-</sup> is produced. At the same time the acidity of the superacid which is directly related with concentration of SbF<sub>5</sub> is decreasing.<sup>9</sup>

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