Selective Carbonylation of Propane in HF–SbF₅: The Role of Carbon Monoxide in the Halogen-promoted Activation Step

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The halogen-promoted regioselective carbonylation of propane in HF–SbF₅ shows a strong dependence of the rates on the partial pressure of CO indicating that carbon monoxide is associated with the halogen in the activation step.

Electrophilic reactions at single bonds especially in saturated hydrocarbons are of particular current industrial interest.[1] Since the pioneering work of Olah and his group in the sixties the use of superacidic media[2] has been widely developed for studying the mechanistic aspects of these reactions including the direct observation of many unstable charged intermediates. In the Koch–Haaf synthesis of carboxylic acids, carbon monoxide is used to trap the intermediate carbocations generated from alkenes.[3] In superacid solutions carbocations can be formed directly from alkanes, and the use of CO as

Table 1 Product distribution

|	Gas mixture (mmol) before reaction			Products (mmol) after reaction				
Expt.	C_3H_8	CO	N_2	C_3H_8	C_2H_6	CH_4	Pr^iCO_2Et	$EtCO_2Et$
1	2.65	0.88	6.64	2.07	0.19	0.19	0.23	0.00
2	2.49	1.00	5.89	1.87	0.19	0.18	0.28	0.00
3	2.62	1.50	5.98	2.12	0.18	0.21	0.23	0.02
4	2.50	2.50	4.66	1.99	0.14	0.17	0.15	0.05
5	2.60	2.60	4.76	2.11	0.13	0.20	0.12	0.05
6	2.62	5.24	2.25	2.19	0.07	0.21	0.12	0.21
7	2.48	7.50	0.00	2.14	0.06	0.20	0.08	0.17
	Carbonylation with Br							
8	2.60	0.88	6.53	1.99	0.13	0.13	0.59	0.00
9	2.60	1.02	6.23	1.88	0.12	0.12	0.46	0.00
10	2.43	1.39	5.52	1.58	0.07	0.07	0.65	0.00
11	2.62	2.62	4.76	1.78	0.07	0.08	0.69	0.00
12	2.59	5.14	2.27	1.51	0.03	0.05	1.18	0.01
13[a]	2.43	6.92	0	0.95	0.01	0.01	1.63	0.00
14	2.48	7.55	0	1.28	0.01	0.03	1.31	0.01

[a] 0.58 mmol Br_2, flow rate 0.38 ml min^{-1}
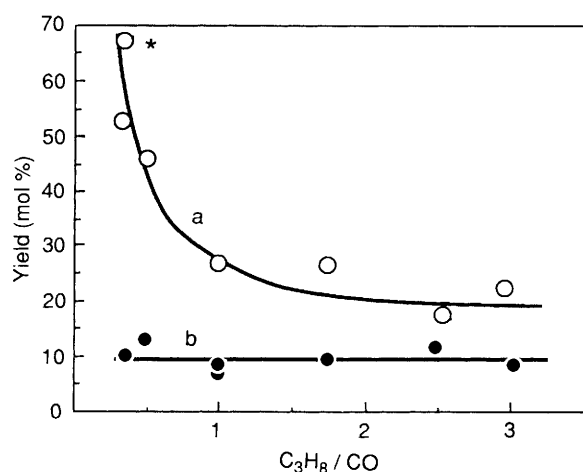
Fig. 1 Dependence of the yield of esters on the propane/carbon monoxide ratio: in the presence (○), and absence (●) of bromine (* see footnote a, Table 1)


Scheme 1

Scheme 2

trapping agent under mild conditions, even at atmospheric pressure, has found new applications recently from both the synthetic and the mechanistic point of view.[4]

The association of CO with the proton is known in the acid-catalysed formylation of aromatic compounds[5] and has also been demonstrated in the formylation of adamantane.[6] Association with Cl^+ has also been suggested in the electrophilic carbonylation of aromatic hydrocarbons;[7] the recently reported direct NMR observation, by Olah and his group, of stable halocarbonyl cations in superacid media[8a] prompts us to present our results on the role of CO in the halogen-promoted C–H bond activation of propane.

When a gaseous mixture of propane, carbon monoxide and nitrogen is bubbled at atmospheric pressure through a $HF–SbF_5$ superacid solution the carbocations formed by ionisation of the alkane are trapped as stable long-lived oxonium ions which can be observed by ^1H and ^{13}C NMR spectroscopy or quenched in excess of ethanolic sodium hydrogencarbonate. GC analysis of the resulting ethyl esters (ethyl propionate and ethyl isobutyrate) combined with the GC analysis of the gaseous products collected at the outlet of the reactor gives a full balance of the products which is essential for determining the mechanistic pathways.

Our results are collected in Table 1.

The experimental conditions are as follows: the gaseous mixture $C_3H_8–CO–N_2$ was bubbled at atmospheric pressure
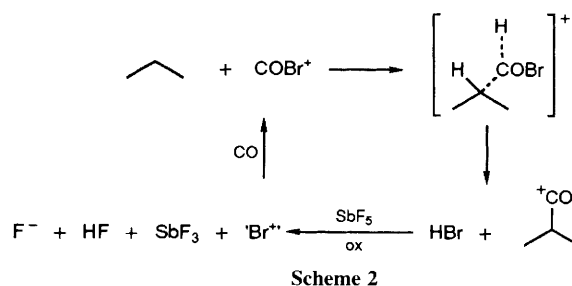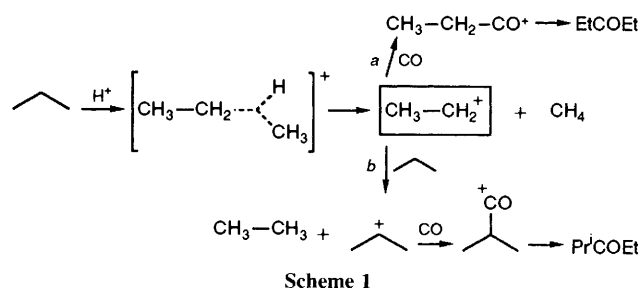
during 1 hour at a rate 4 ml per min through $HF–SbF_5$ (2 ml; 4:1 molar ratio) in a Kel-F reactor at $-10\,^\circ C$. The amount of propane in the starting gas mixture was 2.5 ± 0.1 mmol in all experiments whereas the amount of CO varied in the range 0.9–7.5 mmol, always in excess of the ions produced in the reaction mixture as shown by the negligible amount of side products.

Our results show that in the absence of halogen promoter the complete product distribution can be rationalized by Scheme 1. Under these experimental conditions propane protolysis proceeds *only* by cleavage of the C–C bond yielding quantitatively methane and products resulting from further reaction of the ethyl cation: ethane *via* hydride abstraction and ethyl and isopropyl oxocarbenium ions *via* pathways (*a*) and (*b*). As we have shown earlier[9] the hydride transfer reaction (*b*) is much faster than the carbonylation reaction (*a*). Indeed in experiments 3–7 we note that the amount of ethyl propionate accounts for the difference between methane (always formed) and ethane (only formed *via* pathway *b*).

Nevertheless, since the total balance of carbonylation products is always 5–10% higher than the amount of methane, a competitive means of production of the isopropyl ion has to be ascribed to direct oxidation of the alkane by SbF_5. The existence of this activation process, controversial for a long

time, has been demonstrated recently.[10] As no hydrogen is detected we can neglect the direct formation of the isopropyl cation *via* protolytic cleavage of secondary C–H bonds.

By keeping the amount of propane constant in the gas mixture, variation of the relative amount of carbon monoxide by a factor of 1–8 has no influence on the yield of ester produced *via* the ionisation carbonylation process (Fig. 1, curve *b*) (*ca.* 8–10% based on propane). By running the same set of experiments after addition of a catalytic amount (0.3 mmol) of Br_2 in the HF–SbF_5 solution (respectively 60 and 15 mmol), with all other parameters unchanged (see footnote *a* to Table 1, however), we obtained the results collected in Table 1 (expts. 8–14). In the presence of halogen negligible amounts of protolytic cleavage (0.5–3 mol % based on propane) took place as demonstrated by the absence of ethyl propionate in the products and the small but equivalent amounts of methane and ethane in the resulting gas phase after reaction. The main pathway is the catalytic oxidation of propane to the isopropyl ion by a species which we term 'Br^+' in the absence of other experimental evidence. The polyhalogen cations Br_3^+ and Br_2^+ have been observed experimentally[11] whereas Br^+ has not yet been observed. As we know that the observed selectivity and increase in activity can also be achieved when bromine is replaced by the bromide ion, and considering the high dilution of the halogen at which it is effective in the superacid medium (1 mol% per SbF_5) we doubt very much that the active halogen species is polyatomic. On the other hand, $COBr^+$ was observed by ^{13}C and ^1H NMR spectroscopy as a stable ion, formed from CO and bromine in the presence of SbF_5. In our results in Table 1 (expts. 8–13) the strong influence of the CO/propane ratio on the yield of the carbonylation is noteworthy (Fig. 1, curve *a*). Comparing these results with those obtained in the absence of halogen we are inclined to rationalize the role of CO by the formation *in situ* of the $COBr^+$ cation as the superelectrophilic species causing the reaction to be regioselective (Scheme 2).

In contrast with previous results obtained under pressure no hydrogen could be detected under these experimental conditions, which implies, that, whereas the halogen stays in the catalytic cycle, SbF_5 is concomitantly reduced to SbF_3. Whereas the regioselectivity of the $COBr^+$ reaction is easily ascribed to steric reasons, the absence of C–C bond protolysis in the presence of a large excess of superacidic protons will be due to the large difference in rates. This raises the question as to why such a bulky polarisable electrophile is more reactive in the low nucleophilic superacid solution than the poorly solvated proton present in large excess. The same observation applies also to the CCl_3^+ and $HCCl_2^+$ cations, both of which have also been observed as stable ions by Olah and his group.[8b] The unusual reactivity and regioselectivity of these ions in the presence of excess of superacid have been shown by us[9] as well as by the SbF_5 matrix experiments of Sunko and Vancik.[12]

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