

Direct Carbonylation of Polychloroalkanes into Acid Chlorides Using Metallic Salts Ternary Systems: an Example of Multistep Catalysis

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A catalytic cycle for the direct carbonylation of CCl₄ into CCl₃COCl, catalysed by metallic salts mixtures, *e.g.* AlCl₃/MCl_n/CuCl, under unexpectedly mild conditions, is proposed on the basis of FTIR, ¹⁷O and ²⁷Al NMR spectroscopic studies.¹

Polychloroalkanes are of interest as industrial intermediates but suffer from relative chemical inertness. Direct carbonylation of polychloroalkanes into acid chlorides has previously been reported and this reaction requires harsh conditions: a high pressure of carbon monoxide (900 bar)² or medium pressure (300 bar) using metal carbonyls such as Fe(CO)₅.³ Consequently, direct carbonylation still remains a real challenge.

We report here that the carbonylation of polychloroalkanes, especially carbon tetrachloride, can be performed under milder conditions by using a ternary catalytic system, to produce the corresponding acid chlorides. The results are presented in Table 1.

The catalytic efficiency decreases in the order: AlCl₃/FeCl₂/CuCl > AlCl₃/CuCl ≫ AlCl₃ (runs 1–8). In the ternary system, the use of other Lewis acids instead of FeCl₂ also makes it possible to obtain better yields than with a AlCl₃/CuCl mixture (runs 9–11).

Recently, Olah and coworkers⁴ have observed, by

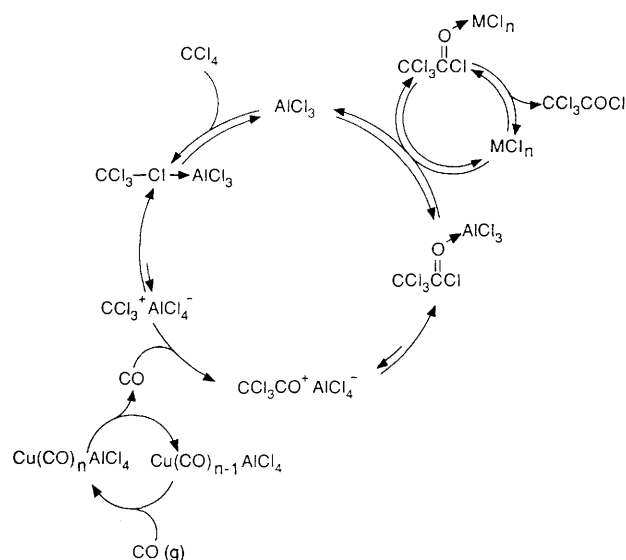
¹³C NMR in SO₂ClF at –78 °C, that the trichloromethyl cation is generated *in situ* from a mixture of CCl₄/SbF₅. This data and run 1 suggest that aluminium trichloride, through its strong acid character, can activate the C–Cl bond of CCl₄ to generate a catalytic amount of trichloromethyl cation. Carbonylation of this species gives the intermediate trichloroacetyl cation (CCl₃CO⁺) which is rapidly converted to trichloroacetyl chloride.

We have examined spectroscopically the behaviour of an AlCl₃/CCl₃COCl/CCl₄ mixture: a CCl₄/CCl₃COCl solution, initially colourless, rapidly became dark brown in the presence of AlCl₃. ¹⁷O and ²⁷Al NMR spectra showed signals, respectively at δ 507.6 and 102.5 (W_{1/2} = 2000 Hz) which were different from signals of pure samples (CCl₃COCl ¹⁷O: δ 510.9 and AlCl₃ ²⁷Al: δ 93.0) (Figs. 1 and 2). The major species, detected by ¹⁷O and ²⁷Al NMR, is assumed to be the addition compound CCl₃COCl/AlCl₃ resulting from the interaction between an aluminium atom and the carbonyl moiety. This hypothesis is in agreement with other compounds described in

Table 1 Carbonylation of polychloroalkanes with metallic salts mixtures.^a

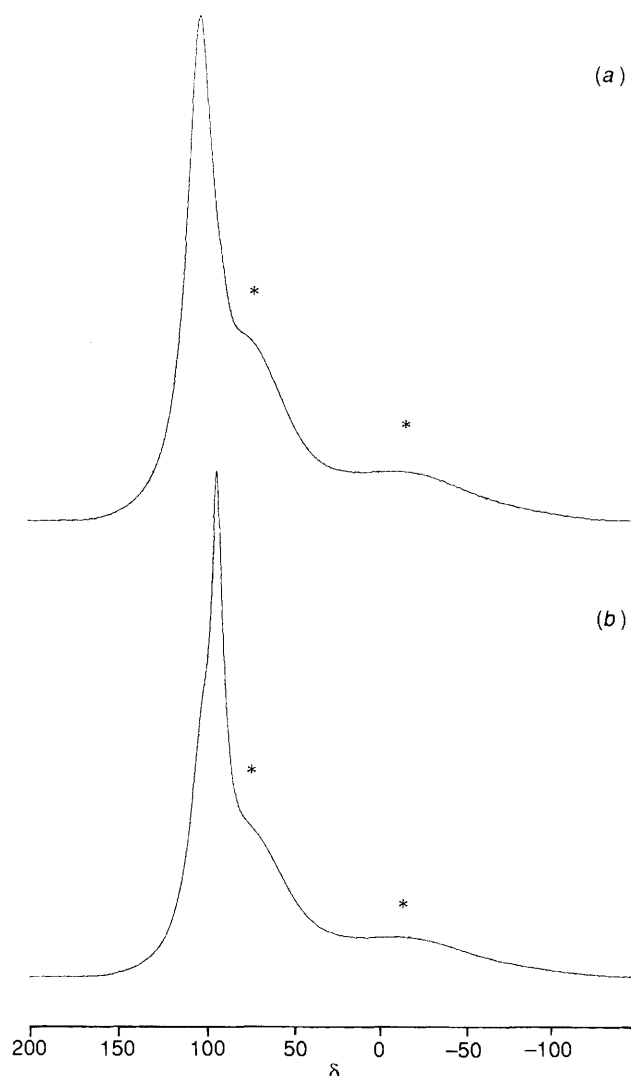
Run	Substrate	Catalytic system	Catalyst(s) amount/mol% ^b	Yield/mol% ^b
1	CCl ₄	AlCl ₃	26	6
2	CCl ₄	CuCl	5	0
3	CCl ₄	AlCl ₃ /FeCl ₂	26/7	6
4	CCl ₄	AlCl ₃ /FeCl ₂	26/12	7
5	CCl ₄	AlCl ₃ /CuCl	26/5	26
6	CCl ₄	AlCl ₃ /CuCl	11/3	18
7	CCl ₄	AlCl ₃ /FeCl ₂ /CuCl	26/7/5	43 ^c
8	CCl ₄	AlCl ₃ /FeCl ₂ /CuCl	11/3/3	33
9	CCl ₄	AlCl ₃ /NdCl ₃ /CuCl	11/3/3	35
10	CCl ₄	AlCl ₃ /CdCl ₂ /CuCl	11/3/3	28
11	CCl ₄	AlCl ₃ /ZnCl ₂ /CuCl	11/3/3	27
12 ^{d,e}	CCl ₃ Br	AlCl ₃ /FeCl ₃ /CuCl	12/3/3	8
13 ^{f,g}	CCl ₃ H	AlCl ₃ /FeCl ₃ /CuCl	10/5/4	10

^a The catalyst(s) and the polychloroalkane (0.207 mol) were loaded under nitrogen in an autoclave which was pressurised at 100 bar and heated at 120 °C under stirring for 5 h. At the end of the reaction, the reaction crude was esterified by butan-1-ol in a three necked flask and analysed by GPC. ^b Related to initial polychloroalkane compound. ^c This run stopped after 20 h gave the same yield. After evaporation of the volatiles from the mixture, the catalysts could be recovered and reused several times without loss of activity. These results suggest that the carbonylation reaction under these conditions is in a state of equilibrium. ^d *t* = 19 h. ^{e,f} The respective acid halides are CCl₃COBr and CCl₂HCOCl. No attempts at optimisation were made. ^g *t* = 19 h; CO (115 bar); *T* = 90 °C.

**Scheme 1** Catalytic cycle proposed for CCl₄ carbonylation into CCl₃COCl

the literature.⁵ So, the addition compound is formed easily and mainly from AlCl₃ and CCl₃COCl. Thus, the catalyst AlCl₃ could be trapped by CCl₃COCl and, therefore, gradually becomes less available for the reaction.

Upon addition of a second Lewis acid such as FeCl₂, ZnCl₂, CdCl₂, NdCl₃, the dark brown solution of AlCl₃/CCl₃COCl in CCl₄ became partially or totally colourless, indicating that the addition compound AlCl₃/CCl₃COCl has split. Indeed, the ²⁷Al NMR spectrum of the final solution displayed two signals at δ 102.5 and 92.9, the relative intensity of which depended on Lewis acid added (Figs. 1 and 2). The signal at δ 92.9 was assigned to free AlCl₃. The driving force for decomplexation of compound CCl₃COCl/AlCl₃ could be the oxophilic character of the second Lewis acid, which can form the addition compound (CCl₃COCl)_n/MCl_n.

**Fig. 1** ²⁷Al NMR (104 MHz, 25 °C, chemical shifts relative to external aqueous acidic Al(H₂O)₆³⁺): (a) CCl₄/CCl₃COCl/AlCl₃ solution, (b) CCl₄/CCl₃COCl/AlCl₃/CdCl₂ solution—the shoulder at δ 102.5 has been confirmed by high temperature NMR. * background signals due to the multinuclear probe head

The role of CuCl can be deduced from FTIR and NMR studies: the FTIR spectra of a CCl₄/AlCl₃/CuCl solution under carbon monoxide (Fig. 3) changed with time and exhibited three bands at 2128, 2152 and 2179 cm⁻¹, which were, respectively assigned, according to literature data,⁶ to ν(CO) vibrations of the following species: Cu(CO)Cl, Cu(CO)⁺ and Cu(CO)_m⁺. The latter can be seen as a CO reserve, which increases the carbon monoxide availability in solution. Subsequently, the same solution has been analysed by ²⁷Al NMR spectroscopy. The spectrum (*t* = 60 min) showed a signal at δ 101.4 with *W*_{1/2} = 650 Hz; this chemical shift is typical of a tetrahedral AlCl₄ complex⁷ and the *W*_{1/2} suggests that one Al-Cl bond is probably elongated towards the copper(I) to form the following species: (CO)_nCu···Cl···AlCl₃. These results suggest that Cu(CO)_nAlCl₄ complexes can be formed, unexpectedly in a noncoordinating solvent; they improve the CO availability in solution and, therefore, favour the carbonylation step (compare run 1 and runs 5–6).

Whether this complex contributes to the catalytic cycle by CO activation or only by enhancing the CO concentration is still an open question. Whatever the situation, this reaction is at least catalysed *via* two consecutive catalytic pathways (Scheme 1) or perhaps provides a new example of triple catalysis⁸ if we consider the third cycle involving carbon monoxide as an activation reaction.

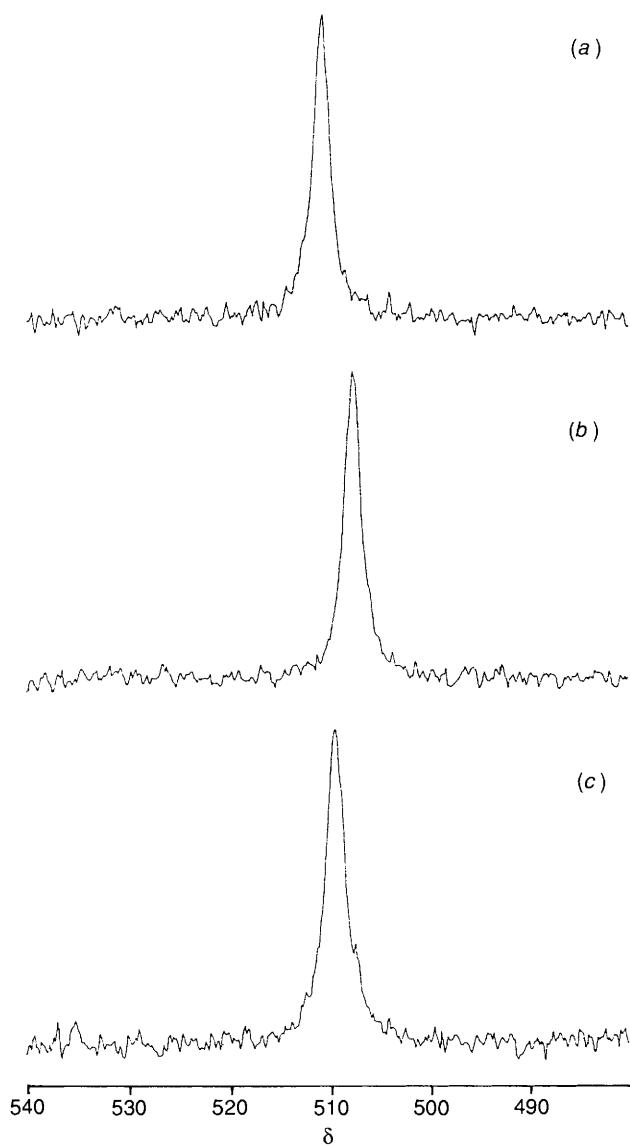


Fig. 2 ^{17}O NMR (54 MHz, 25°C, chemical shifts relative to external D_2O): (a) $\text{CCl}_4/\text{CCl}_3\text{COCl}$ solution, (b) $\text{CCl}_4/\text{CCl}_3\text{COCl}/\text{AlCl}_3$ solution, (c) $\text{CCl}_4/\text{CCl}_3\text{COCl}/\text{AlCl}_3/\text{CdCl}_2$ solution

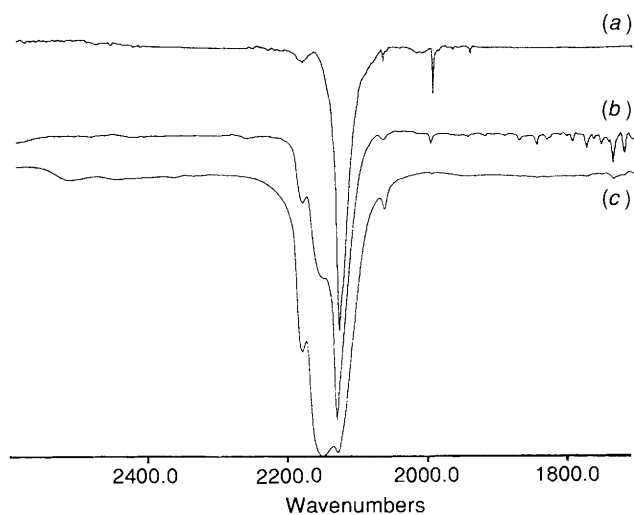


Fig. 3 FTIR spectra of $\text{AlCl}_3/\text{CuCl}/\text{CCl}_4$ solution under carbon monoxide, $\text{AlCl}_3 = \text{CuCl} = 3$ mmol, $\text{CCl}_4 = 0.207$ mol, $P_{\text{CO}} = 1$ bar, $T = 25^\circ\text{C}$: (a) $t = 10$ min, (b) $t = 30$ min, (c) $t = 60$ min

We thank the National Society for Powders and Explosives for financial support of this work and B. Mouchel of Lille University for skilful assistance in NMR spectroscopy.

Received, 10th December 1991; Com. 1/06196H

References

- 1 This work was patented in 1991 by SNPE Company; Fr Pat 9107359, June 1991.
- 2 C. E. Frank, A. T. Hallowel, C. W. Theobald and G. T. Vaala, *Ind. Eng. Chem.*, 1949, **41**, No. 9, 2061; US Pat. 2378048 (April 1944); US Pat. 2411982 (November 1944).
- 3 D. Pat. 2648134 (April 1978).
- 4 G. A. Olah, L. Heiliger and G. K. Surya Prakash, *J. Am. Chem. Soc.*, 1989, **111**, 8020.
- 5 F. A. Cotton and G. Wilkinson, *Adv. Inorg. Chem.*, Wiley, New York, 5th edn., 1988, p. 219.
- 6 Y. Souma, J. Iyoda and H. Sano, *Inorg. Chem.*, 1975, **15**, 197.
- 7 R. K. Harris and B. E. Mann, *NMR and Periodic Table*, Academic Press, New York, 1978, p. 279 and references cited therein.
- 8 J. E. Bäckvall, A. K. Awashi and Z. D. Rindo, *J. Am. Chem. Soc.*, 1987, **109**, 4750.