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Catalytic Decomposition of Alkyl Chloroformates by Hexabutylguanidinium Chloride

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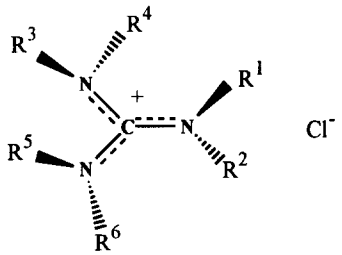
Abstract: *Hexabutylguanidinium chloride (0.5 molar %) efficiently decomposes alkyl chloroformates into chlorides, with low alkenes formation, via a S_N2 mechanism as demonstrated from substituents effects and asymmetric chloride synthesis.* © 1997 Elsevier Science Ltd.

Surfactants, drugs and herbicides are produced from alkyl halides, starting from haloformates.[1,2] Furthermore, recent patents[2,3] and publications[4,5] on syntheses of alkyl halides have appeared, with a particular interest focused on synthesis of optically active products. This prompt us to study in more details the chloroformates decomposition in presence or in absence[6] of hexabutylguanidinium chloride (GCl).

Recent studies performed in our laboratory pointed out the catalytic activity of hexaalkylguanidinium chlorides.[7,8] The efficient nucleophilicity of the chloride anion when associated with the quite planar delocalized guanidinium cation[9] have been reported (Scheme 1).[7]



Scheme 1

The relative rate constants of methyl chloroformate decomposition into methyl chloride were determined in presence of hexaalkylguanidinium or tetraalkylammonium chloride (Scheme 2) which demonstrate GCl to be the most active one.[7]

$$GCl + CH_3OCOCl \longrightarrow CH_3Cl + CO_2 + GCl$$

Scheme 2

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The efficiency of GCl as a catalyst for such a reaction is presented in comparison to other catalysts bearing the same n-butyl groups. This parameter is important since the nature of the alkyl groups may influence the nucleophilic character of the chloride anion.[7] For comparison, tetrabutylammonium (NCl) and tetrabutylphosphonium (PCl) chlorides were chosen. Pyridine is another compound known for its efficiency to perform decarboxylation of haloformates;[6] however in this case, a pyridinium salt is first produced, followed by a nucleophilic attack of the chloride anion. Results obtained for the catalytic decomposition of n-octyl chloroformate are given on the following figure.

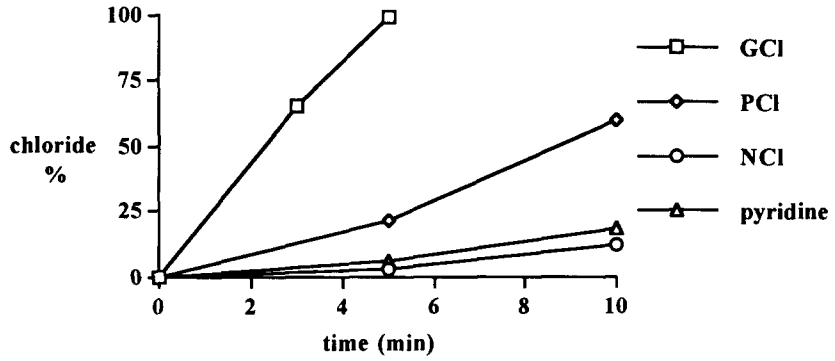

Figure : Catalytic conversion of n-octyl chloroformate into chloride: effect of some catalytic reagents. (0.5 molar % of chloride anion, 100 °C, chlorobenzene)

As shown on the figure, GCl appears as an effective catalyst in conditions where no thermal decomposition occurs; n-octyl chloroformate indeed affords the corresponding chloroalkane only above 150 °C.[6] The superiority of GCl (100% of 1-chlorooctane in less than 5 minutes) is evidenced over the other catalysts demonstrating the high nucleophilicity of the chloride counter-anion associated with the guanidinium cation. Therefore, a nucleophilicity scale is demonstrated by the figure.

As a matter of fact, such a reactivity of GCl is presumed to ensure a S_N2 pathway for the decarboxylation. GCl has also been proved to have a "Lewis acid character" allowing an S_N1 reaction to occur. This was demonstrated in the case of unsymetrical ring opening of epoxides by acid halides.[8]

In order to obtain a mechanistic insight into the assisted decomposition of chloroformates with GCl, we have undertaken to study primary and secondary chloroformates and to determine the balance between S_Ni, S_N1 and S_N2 mechanisms of reaction.

General Procedure: The chloroformate (1mmole) is heated in chlorobenzene at 100°C with 0.5 molar % of GCl in a plugged tube. The reaction is followed by GLC with a Hewlett Packard 5890 II (25 m wide-bore 0.22 mm CPSIL 5 column from 40 to 250°C; injector temperature: 150°C).

Table 1: Decomposition of Chloroformates in Presence of GCl (0.5 molar %) in Chlorobenzene.

	ROCOCl	T °C	Time [a]	Products [b]
R =	n-butyl	100	3 min	1-chlorobutane
	n-octyl	100	5 min	1-chlorooctane
	i-butyl	100	40 min	1-choro-isobutane
	2,2,2-trichloroethyl	100	7 d	carbonate (99%), chloride (1%)
	2-octyl	100	5 h	2-chlorooctane (97%), octenes (3%)[c]

[a]: 100% of conversion; [b]: determined by GLC and NMR; [c]: mixture of 1 and 2-octenes

The results on Table 1 seem to confirm that only an S_N2 process occurs, in agreement with the literature;[10,11] therefore the "Lewis acid character" is apparently not observable in these reactions. Primary chloroformates give easily the chloro compounds in conditions where no thermal decomposition occurs. 2,2,2-trichloroethyl chloroformate is a special case, since no chloro compound is formed but only the 2,2,2-trichloroethyl carbonate obtained at a very slow rate of reaction. This occurs from phosgene elimination as described earlier for the aryl chloroformates (scheme 3).[6] It is noteworthy that, without catalyst, no reaction was observed. The thermal formation of the carbonate was recently reported, but at a higher temperature (6% in 24 h at 170 °C).[12]

$$GCl + ROCOCl \longrightarrow RO^-G^+ + COCl_2$$

$$ROCOCl + RO^-G^+ \longrightarrow ROCOOR + GCl$$

scheme 3

Table 1 also presents the catalytic decomposition of 2-octyl chloroformate by GCl. After 5 hours at 100°C, 2-chlorooctane is obtained in good yield along with 3% of octenes. Without catalyst during the same time, the thermal conversion was low (20%) with simultaneous production of 2-chlorooctane and octenes in a 2:1 ratio. These results were in accordance, both for the conversion and the product ratio, with those reported by Clinch and coll.[11] for the thermal decomposition of 2-pentyl chloroformate.

In order to study in more detail the mechanism of the assisted decomposition toward the true thermal decarboxylation, the optically active 2-octyl chloroformate was submitted to the same conditions of reaction. This is a typical procedure to ascertain the reaction mechanism in S_N reactions. It has been earlier established that a thermal decarboxylation of (S)-2-octyl chloroformate affords the (S)-2-chlorooctane from an S_Ni process.[13] To obtain the (R) enantiomer, a pure S_N2 reaction is needed as demonstrated previously in the presence of pyridine as solvent.[14] Table 2 shows results for the decomposition of (S)-2-octyl chloroformate with GCl.

Table 2: Decomposition of (S) 2-Octyl Chloroformate in the Presence of GCl

Solvent	Time [a]	$[\alpha]_D^{20}$ [b]	ee %
none	10 h	-30.3°	96 %
NMP	5 h	-12.2°	39 %

Conditions: 80°C; 0,5 molar % of GCl; [a] : 100% of conversion; [b]: measured in $CHCl_3$, c=1;
(R)-2-chlorooctane: $[\alpha]_D^{20}$ = -31.5° ($CHCl_3$, c=4.5) [4]

An excellent enantiomeric excess is obtained with GCl, indicating a S_N2 mechanism. In contrast, a run performed in a polar solvent gives quite a low enantiomeric excess, showing a partial ionic process as previouly described for the reaction of butenyl chloroformate with dioxane or nitrobenzene as solvent.[15] Thus, optically active chloro compounds can be easily obtained; however experimental conditions must be carefully controlled. Further studies are in progress to develop the applications of such a catalyst.

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