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A CHLORIDE ION CATALYZED DECOMPOSITION OF ALKYL CHLOROFORMATES IN ACETONITRILE

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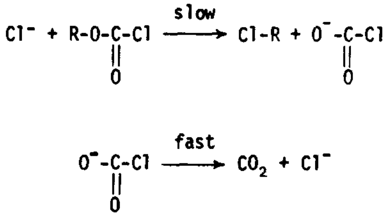
Reaction of tetraethylammonium chloride with acetonitrile solutions of alkyl chloroformates is such that a facile chloride exchange reaction at the carbonyl carbon merely regenerates substrate and, with this nucleophile, a study can be made of a slower S_N2 reaction:



$$\mathrm{Cl^- + R\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}Cl \xrightarrow{slow} Cl\text{-}R + O^-\text{-}\underset{\underset{O}{\|}}{C}\text{-}Cl}$$

$$\mathrm{O^-\text{-}\underset{\underset{O}{\|}}{C}\text{-}Cl \xrightarrow{fast} CO_2 + Cl^-}$$

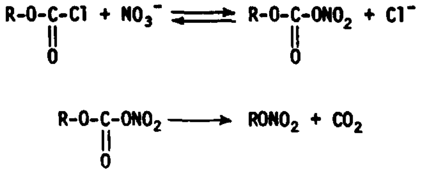
For suitable alkyl groups, E2 reaction can also occur and, in terms of the overall reaction, this was found to be less than 1% for R=ethyl or *n*-propyl, 13% for R=isobutyl and 17% for R=isopropyl; the reported second order rate coefficients are corrected for any elimination contribution to the overall second order rate coefficient. Due to regeneration of chloride ion from the displaced chloroformate anion, the reaction follows pseudo-first order kinetics; the first order rate coefficient is proportional to the chloride ion concentration. Consistent with the above formulation, phenyl chloroformate is stable towards chloride ion.

The reaction sequence not only outlines a new path for the decomposition of alkyl chloroformates but, provided the mechanism is defined as applying to any type of base, it can also be considered as an example of the rather rare $B_{AL}2$ mechanism.

The second order rate coefficients, k_2^{AL} ($1.\ mole^{-1}\ sec^{-1}$), for the substitution reaction of alkyl chloroformates with chloride ion, in acetonitrile at 25.0°, are as follows:

R :	Me	Et	*n*-Pr	isoPr	isoBu
$10^5k_2^{AL}$:	164	6.2	5.8	0.75	0.26
Relative k_2^{AL} :	26	1.0	0.94	0.12	0.042

The reactions of alkyl and phenyl chloroformates with tetraethylammonium nitrate have also been studied. Except for phenyl chloroformate, which yields as the final product a mixture of *ortho-* and *para*-nitrophenols and not the unknown phenyl nitrate,[2,3] and ignoring complications during later stages of reaction due to S_N2 attack by the developing chloride ion, the reaction has been considered to follow the sequence:[4]



$$R\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}Cl + NO_3^- \rightleftharpoons R\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}ONO_2 + Cl^-$$

$$R\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}ONO_2 \longrightarrow RONO_2 + CO_2$$

The second order rate coefficients for chloride ion production, k_2^{AC} (l. mole^{-1} sec^{-1}), during the initial stages of the reaction of chloroformate esters (ROCOCl) with nitrate ion, in acetonitrile at 25.0°, are as follows:

R :	Ph	Me[4]	Et	isoBu	isoPr[5]
$10^5 k_2^{AC}$:	670	20.0	10.6	11.7	3.5
Relative k_2^{AC} :	63	1.89	1.00	1.10	0.33

The two relative rate sequences are fully consistent with the bimolecular reaction of an alkyl chloroformate with chloride ion, to give the alkyl chloride, proceeding *via* a S_N2 process and the bimolecular reaction with nitrate ion, to give as the final product the alkyl nitrate, proceeding *via* an acylation-decomposition mechanism. The observation of S_N2 attack by chloride ion is consistent with the previously expressed interpretation of the tertiary amine catalysis to the decomposition of alkyl chloroformates;[6,7] in this interpretation a replacement by tertiary amine at the carbonyl carbon is followed by an analogous inverting attack at the alkyl group by the displaced chloride ion.

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