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SILVER-ION ASSISTED REACTIONS OF CHLOROFORMATE ESTERS IN BENZENE

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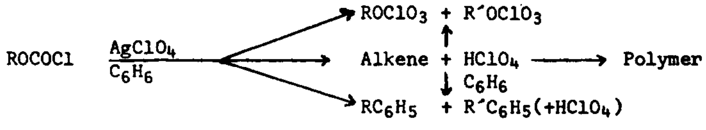
A kinetic investigation of the reactions of silver nitrate with several chloroformate esters in acetonitrile[1,2] indicated that for phenyl, methyl, and primary alkyl chloroformates the rate-limiting factor was attack by dissociated nitrate ion at the acyl carbon and for isopropyl chloroformate the dominant pathway was a silver-ion assisted ionization. Beak and his coworkers have studied several reactions with fluoborate or hexafluoroantimonate as the counterion; these silver-ion assisted reactions can *formally* be considered as proceeding through carboxylium ions ($ROCO^+$)[3]. It was shown that the reactions resemble diazonium ion reactions and, in some instances, Friedel-Crafts reactions. Aryl chloroformates gave products indicative of true carboxylium ion intermediates. However, with alkyl chloroformates, reaction invariably proceeded with loss of carbon dioxide. Two limiting reaction paths are possible for reaction of alkyl chloroformates. In low polarity solvents, these reactions almost certainly involve aggregates and the following schemes are intended only to indicate the basic features. The first scheme involves a silver-ion assisted ionization, to give a carboxylium ion, which can be followed by loss of carbon dioxide:

$$ROCOCl + Ag^+ \xrightarrow{\text{slow}} (ROCO)^+ + Cl^-Ag^+ \xrightarrow{\text{fast}} R^+ + CO_2 + Cl^-Ag^+.$$

The second scheme involves a silver-ion assisted ionization-fragmentation process to yield the carbonium ion directly:

$$ROCOCl + Ag^+ \xrightarrow{\text{slow}} R^+ + CO_2 + Cl^-Ag^+.$$

A kinetic and product study of the reactions of alkyl and arylalkyl chloroformates with silver perchlorate in benzene at 25.0° has been carried out. Phenyl chloroformate was inert under these conditions.



Due to the explosive properties of alkyl perchlorates[4], product isolation was not attempted. The pmr spectra of the aliphatic protons in the product solutions were integrated, after addition of a known concentration of toluene as an internal integration standard. Only alkylbenzenes and alkyl perchlorates were identified and the percentage conversions to these products are indicated in Table I.

TABLE I

Percentages of products identified in the p.m.r. spectra after reaction of 0.16 *M* chloroformate esters (ROCOCl) with 0.20 *M* silver perchlorate in benzene at 25.0°.

R	$ROClO_3$	RC_6H_5	$R'OClO_3$	$R'C_6H_5$
Me	86[a]	14[a]		
Et	47	37		
n-Pr			70[c]	10[c]
iso-Pr	70	10		
iso-Bu	0[b]	0[b]		37[d]

[a] No toluene added, these percentages are ratios. [b] No evidence for methylene doublet of isobutyl group. [c] Isopropyl Derivatives. [d] t-Butylbenzene.

In general, much of the alkylbenzene (and perchlorate ester?) may well be formed *via* an acid promoted alkylation involving initially formed alkene[3]. However, the toluene formation from methyl chloroformate shows that direct alkylation can compete with collapse to perchlorate ester. Reaction of methyl[5] or ethyl[6] iodide with silver perchlorate in benzene leads only to the perchlorate ester, without any benzene alkylation. This difference in behavior is nicely consistent with the diazonium-ion analogy for chloroformate-silver-ion reactions[3]. It is well established that carbonium ions formed from diazonium ions are "hot" and less selective than those formed from alkyl halides[7]. The observation of extensive carbonium-ion type rearrangements with both *n*-propyl and isobutyl chloroformates would appear to rule out either S_N2 attack upon the chloroformate ester or a fast S_N2 attack upon a preformed carboxylium ion.

Initial second-order rate coefficients were found to increase in value with the initial silver perchlorate concentration (0.01 - 0.07 *M*). The kinetic data are reported in Table II.

Rate determining nucleophilic attack at the acyl carbon, followed by fast precipitation of silver chloride and progress to stable products, would give a fast reaction for phenyl chloroformate[2], which is inert under the experimental conditions. Support for the proposed absence of S_N2 attack at the *α*-carbon of the R group, concurrent with a silver-ion assisted reaction, comes from the observation of almost identical rates for ethyl, n-propyl, and isobutyl chloroformates, a series of alkyl derivatives for which steric hindrance to S_N2 attack would increase appreciably.

TABLE II

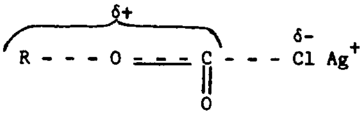
Initial second order rate coefficients[a], k_2, for reaction of 0.1 M chloroformate esters (ROCOCl) with silver perchlorate in benzene at 25.0°.

R	$[AgClO_4]$:	$10^4k_2(l.mole^{-1}sec.^{-1})$ 0.0165	0.035	0.070	Relative Rates[b]
Methyl		0.0101	0.0113	0.0130	0.022
Ethyl		0.42	0.49	0.74	1.00
Allyl		0.65	0.76	1.00	1.48
n-Propyl		0.38	0.48	0.69	0.94
Isopropyl		27	30	37	58
Isobutyl		0.37	0.41	0.60	0.84
Benzyl		2.1	2.5	3.1	4.8
p-Nitrobenzyl		0.052	0.058	0.074	0.114
Cholesteryl		12.2	13.1	15.2	25
Cholestanyl		25	26	32	52

[a] $d[AgCl]/dt = k_2[ROCOCl][AgClO_4]$. [b] Calculated at each of the three $AgClO_4$ concentrations and a mean value then taken.

Along the *α*-methylated series (methyl, ethyl, and isopropyl) the rate differences are quite large. However, in the absence of suitable models, it is not possible to decide whether the magnitudes correlate with inductive stabilization of a proximate or a remote positive charge. Benzyl chloroformate is an important member of the series. The phenyl group would be expected to stabilize positive charge development at the α-carbon by a conjugative mesomeric effect but its effect upon a remote positive charge should be one of destabilization, due to its electron-withdrawing inductive effect; the polar substituent constants (σ^*) are + 0.215 for benzyl, zero for methyl (by definition), and -0.190 for isopropyl[8]. The observation that benzyl chloroformate reacts about 200 times faster than methyl chloroformate suggests, at least for benzyl chloroformate, appreciable charge development at the α-carbon. Consistent with this proposal, a p-nitro-group reduces the rate of reaction of benzyl chloroformate by a fairly large factor. On the other hand, allyl chloroformate, despite the mesomeric stabilization of an incipient carbonium ion, reacts only some 50% faster than *n*-propyl chloroformate. Also, benzyl chloroformate reacts about 12 times slower than isopropyl chloroformate, in contrast to a faster reaction by a factor of about 60 for the corresponding chlorides under the same reaction conditions.

The available evidence can best be accommodated by a transition state of varying structure in which, dependent upon the nature of the R group, both carbon-oxygen and carbon-chlorine heterolyses can have progressed to varying degrees.



$$\overbrace{R - - - O \,=\!-\!-\, \underset{\substack{\| \\ O}}{C}}^{\delta+} - - - \overset{\delta-}{Cl}\ Ag^{+}$$

A possible alternative to this mechanism would involve slow reaction to a $(ROCO)^{+}\ Cl^{-}Ag^{+}$ ion-triplet, and with a fast internal return of chloride occasionally circumvented by loss of carbon dioxide, followed by reaction to products. The overall rate would again be a function of the ease of both carbon-oxygen and carbon-chlorine heterolyses.

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