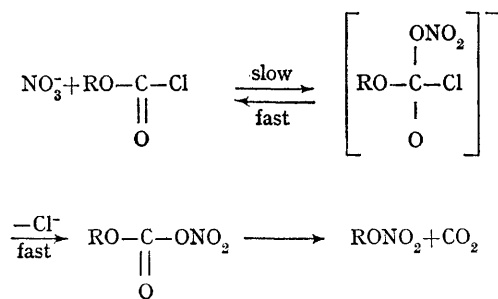


Kinetics and Mechanism of the Reaction of Isopropyl Chloroformate with Silver Nitrate and Perchlorate in Acetonitrile

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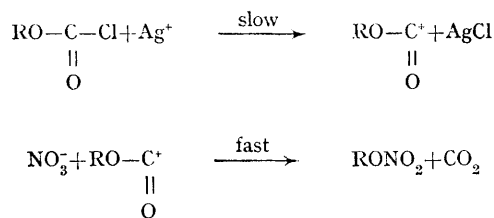
ACETONITRILE solutions of methyl chloroformate have previously been shown to be unreactive towards silver perchlorate but to react with silver nitrate at a rate indicating attack by dissociated nitrate ions, accompanied in some (but not all) instances by silver ion assistance to chloride loss from the intermediate.¹ In Scheme A (R = ethyl, isobutyl, or phenyl) leads to similar kinetic characteristics.



Scheme A

An alternative mechanism, B, originally proposed by Boschan² for n-hexyl chloroformate, apparently does not operate for primary alkyl or phenyl chloroformate esters. However, B (or one of several possible variations of B) has been found to be the dominant mechanism when isopropyl chloroformate reacts with an acetonitrile solution

of silver nitrate; silver perchlorate also reacts, in the rate-determining step of scheme B.



Scheme B

Unlike primary alkyl and phenyl chloroformates, isopropyl chloroformate (~ 0.2 M) is not quite inert in acetonitrile; at 25.0° it slowly produces chloride ion with a first-order rate coefficient of 2.0×10^{-7} sec.⁻¹, increasing to 2.3×10^{-7} sec.⁻¹ when 0.080 M-tetraethylammonium perchlorate is added. Addition of tetraethylammonium nitrate introduces a second-order component with a rate coefficient [$k_2(\text{NO}_3^-)$] of 0.35×10^{-4} l. mole⁻¹ sec.⁻¹. Isopropyl chloroformate reacts readily with silver perchlorate and, after correction for the superimposed first-order component, the second order rate coefficients (k_2'') increase slightly but steadily with silver perchlorate concentration. The experimental second-order rate coefficients for reaction with silver nitrate (k_2^0) are virtually identical to

those arrived at by taking the sum of contributions estimated from measurements upon the reactions with silver perchlorate and tetraethylammonium nitrate (k_2').

S_N2 type reaction. By contrast, we find that the reaction of silver nitrate with acyl halides, compounds which do not normally react by S_N2 -type mechanisms, involves in each individual act of

TABLE^a

[AgNO ₃]	$10^4 k_2^0$	$10^4 k_2(\text{AgClO}_4)^b$	$10^4 k_2''$	$10^4 k_2 \alpha (\text{NO}_3)^{-c}$	$10^4 k_2'^d$
0.00500	1.49	(1.24) ^e	(0.84) ^e	0.28	1.52
0.0100	1.27	1.04	0.84	0.24	1.28
0.0200	1.12 ^f	0.95 ^g	0.85	0.20	1.15
0.0400	1.02	0.95	0.90	0.16	1.11
0.0800	1.10	0.95	0.93	0.12	1.07
0.160	1.09	1.01	1.00	0.09	1.10

^a With the exception of $k_2(\text{AgClO}_4)$ the assignments of the second-order rate coefficients are indicated in the text.

^b Experimental second-order rate coefficients for reaction with identical concentration of silver perchlorate.

^c Product of the second-order rate coefficient for reaction with NET_4NO_3 and the appropriate degree of dissociation of silver nitrate, α (see ref. 1).

^d $k_2' = k_2(\text{AgClO}_4) + k_2(\text{NO}_3^-)\alpha$.

^e Estimated.

^f Added 0.0400 M- NET_4NO_3 raises initial value to 1.80.

^g Added 0.0400 M- NET_4ClO_4 raises value to 1.03.

Acetonitrile solutions of primary and secondary alkyl halides have been shown to react considerably faster with silver nitrate than with an equimolar concentration of either tetraethylammonium nitrate or silver perchlorate^{3,4} and the rate-determining step of the silver nitrate reaction has been considered to involve electrophilic assistance to

substitution either a rate-limiting nucleophilic attack (the rate also being influenced by the partitioning of the intermediate to reactants or products) or a rate-determining electrophilic assistance but not both simultaneously.

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