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COMPETING SOLVOLYSIS-DECOMPOSITION OF 1-ADAMANTYL CHLOROFORMATE[1]

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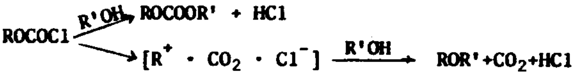
Recently, the preparation of 1-adamantyl chloroformate was reported[2] and the decomposition of this compound to yield 1-adamantyl chloride has been studied[3]. The kinetic procedure was to hydrolyze the unreacted chloroformate ester in aqueous acetone and titrate against methanolic sodium methoxide. The 1-adamantyl halide, produced in the decomposition, was inert under these conditions. We found that the acid present after hydrolysis was only proportional to, and not equivalent to, the concentration of unreacted chloroformate ester. It was apparent that, within the aqueous acetone, decomposition was effectively competing with solvolysis.

The solvolysis of a tertiary chloroformate ester may proceed not only by attack at the acyl carbon but also by ionization to a carbonium ion followed by solvolysis. These routes can readily be distinguished for alcoholysis:



A detailed study has been made of several competing solvolysis-decomposition reactions of 1-adamantyl chloroformate. The kinetic procedure was to withdraw aliquots into neutral acetone, cooled to ice-salt temperature, and titrate against standardized triethylamine in toluene[4]. The infinity titers were also used to determine the product ratio of 1-adamantyl alkyl ether (or 1-adamantanol) relative to 1-adamantyl chloride. The presence of both components in the product was confirmed by evaporation of solvent and comparison of the infrared spectrum of the residue with those for the pure compounds. For solvolysis-decomposition in t-butanol, the infrared spectrum indicated a mixture of 1-adamantanol and 1-adamantyl chloride and it was shown, independently, that 1-adamantyl-t-butyl ether underwent acid catalyzed decomposition in t-butanol to yield 1-adamantanol. The mixed 1-adamantyl alkyl carbonates were synthesized and recovered after submission to the solvolysis-decomposition experimental conditions, showing that the ethers did not arise by formation and subsequent decomposition of these mixed esters. The infinity titers were virtually unchanged by additions of tetra-*n*-butylammonium chloride of up to 0.1M, consistent with a scheme in which there is little, if any, 1-adamantyl chloride formation from dissociated ions.

TABLE I

Specific Reaction Rates at 25.0° and Enthalpies ($\Delta H^{\ddagger}$) and Entropies ($\Delta S^{\ddagger}$) of Activation for the Competing Solvolysis-Decomposition of 1-Adamantyl Chloroformate.

Solvent	k_1(sec^{-1})	$\Delta H^{\ddagger}$ (Kcal/mole)	$\Delta S^{\ddagger}_{298}$(e.u.)
80% Ethanol	$(1.15\pm0.02)\times10^{-2}$	22.30±0.65	+7.58±2.23
Methanol	$(3.36\pm0.03)\times10^{-3}$	21.95±0.20	+3.75±0.69
Ethanol	$(5.53\pm0.01)\times10^{-4}$	23.79±0.12	+6.34±0.41
Isopropanol	$(1.64\pm0.05)\times10^{-4}$	24.42±0.15	+6.02±0.55
t-Butanol	$(9.89\pm0.04)\times10^{-5}$	23.84±0.40	+3.08±1.35

The entropy of activation of +7.6 e.u. for the solvolysis-decomposition in 80% ethanol is some 16-20 e.u. more positive than values which have been reported[5] for solvolyses of 1-adamantyl halides in this solvent. Even for identical ionization processes, the larger leaving group, with the possibility of internal charge disposal, would be expected to lead to a more positive entropy of activation value[6]. However, the bulk of this unusually large difference can best be considered to result from loss of carbon dioxide concurrent with, or subsequent to, the ionization process.

TABLE II

(1-Adamantyl Alkyl Ether)/(1-Adamantyl Chloride) Product Ratios for Reactions in Dry Alcohols.

Temp	:	35.4	24.8	15.1	0.0	25.0	25.0	25.0
Solvent	:	MeOH	MeOH	MeOH	MeOH	EtOH	i-PrOH	t-BuOH
[ROR']/[RCl]	:	3.80	3.60	3.33	2.87	1.51	0.904	0.357

A reaction scheme is suggested in which, after loss of carbon dioxide, an ion-pair is formed which either collapses to 1-adamantyl chloride or separates, with separation followed by solvolysis:

$$\begin{tikzcd}
 & \mathrm{RCl} & \\
\mathrm{R^+Cl^-} \arrow[ur] \arrow[r] & (\mathrm{R^+} + \mathrm{Cl^-}) \arrow[r, "\mathrm{R'OH}"] & \mathrm{ROR'} + \mathrm{HCl}.
\end{tikzcd}$$

In order to carry out a treatment of the solvolysis-decomposition rates in terms of the Grunwald-Winstein equation[7], the reaction kinetics were established at 25.0° in several aqueous-organic mixtures (Table III). By combination with determinations of the percentage of reaction proceeding with hydrogen chloride formation, corresponding to solvolysis, it was possible to carry out equivalent treatments of the solvolysis and decomposition components of the overall specific rates.

TABLE III

Specific Rates and Percentages of Reaction Proceeding with Solvolysis for Solvolysis-Decomposition of 1-Adamantyl Chloroformate at 25.0°.

Solvent[a]	k_1(sec.$^{-1}$)	% Solvolysis	Y[b]
80% Ethanol	$(1.15\pm0.02)\times10^{-2}$	70	0.000
95% Ethanol	$(1.62\pm0.01)\times10^{-3}$	62	-1.287
80% Dioxane	$(4.96\pm0.02)\times10^{-3}$	63.7	-0.833
90% Dioxane	$(8.48\pm0.04)\times10^{-4}$	53.5	-2.030
90% Methanol	$(1.11\pm0.04)\times10^{-2}$	80	-0.301
95% Acetone	$(1.67\pm0.02)\times10^{-3}$	66.3	-2.76
90% Acetone	$(3.99\pm0.06)\times10^{-3}$	68.2	-1.856
80% Acetone	$(1.28\pm0.04)\times10^{-2}$	72.5	-0.673

[a] X% solvent means a binary-aqueous mixture prepared by combining X ml. of solvent with 100-X ml. of water at 25.0. [b] The Y-parameters were from a listing in reference 7.

Using the data of Tables I, II, and III, the Grunwald-Winstein *m*-values reported in Table IV were computed. The quantitative correlation of specific decomposition rates against solvent ionizing power (Y values) is we believe the first to be reported for an S_Ni type decomposition.

TABLE IV

m-Values for Reactions of 1-Adamantyl Chloroformate at 25.0°.

Solvents	No. of Points	Solvolysis-Decomposition	Solvolysis	Decomposition
80-100% Ethanol	3	0.650±0.005	0.684±0.010	0.587±0.003
90-100% Methanol	2	0.658	0.669	0.612
Dry Alcohols	4	0.721±0.042	0.906±0.012	0.537±0.055
80-90% Dioxane	2	0.641	0.704	0.551
80-95% Acetone	3	0.424±0.002	0.442±0.003	0.381±0.003
All but aq. Acetone	9	0.682±0.030	0.795±0.036	0.546±0.032
All Alcoholic	7	0.682±0.028	0.800±0.036	0.543±0.023

A fairly delicate balance between attack at the acyl carbon and ionization is indicated by the introduction of a pronounced second order component on addition of small concentrations of sodium ethoxide to the reaction in ethanol (Table V).

TABLE V

Second-order Rate Coefficients (M^{-1} sec^{-1}) for the reaction of 0.00400M 1-Adamantyl Chloroformate with 0.00597M Ethanolic Sodium Ethoxide[a].

Temp	:	25.0	14.8	6.0	0.0	-10.0
k_2	:	1.63	0.704	0.380	0.226	0.074

a Activation Parameters are $\Delta H^{\ddagger}$ = 12.92±0.39 Kcal/mole and $\Delta S^{\ddagger}_{298}$ = -14.2±1.3 e.u. At 25.0°, calculation shows that 94.6% of initial reaction involves bimolecular attack at acyl carbon and only 5.4% is underlying unimolecular solvolysis-decomposition.

A product study carried out with 0.50 g of 1-adamantyl chloroformate in 5.0 ml of 0.50M methanolic sodium methoxide led to 0.40 g (82%) of 1-adamantyl methyl carbonate: mp 99-100°; ir (KBr) 5.79 (C=O) and 8.02 (C-O) μ. Similarly, replacement of methoxide by azide has been shown[8] to lead to 1-adamantyl azidoformate.

It is predicted that alcoholysis of bridgehead chloroformates which on ionization would lead to carbonium ions of energy appreciably greater than for 1-adamantyl will proceed in a manner analogous to that previously observed for primary and secondary chloroformates, so as to lead quantitatively to disubstituted carbonate esters and not to ether plus chloride.

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