

A mechanistic approach to solvolysis of n-caproyl chloride ($n\text{-CH}_3(\text{CH}_2)_4\text{COCl}$) in solutions of acetone and acetonitrile with nucleophilic solvents

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ABSTRACT

The study of the rate and rate constants in the alcoholysis of n-caproyl chloride in acetone and acetonitrile, reveals that S_N2 mechanism is more favourable than S_N1 . A plot of logarithm of rate constant against the logarithm of molar concentration of alcohol gives a straight line with a slope close to 1.1 and that with respect to water is 1.5 both in acetone and acetonitrile. This shows that in addition to S_N2 mechanism, Addition-ionization mechanism is simultaneously operating. Moderately high enthalpy of activation favours an Addition-ionisation pathway. A large negative entropy of activation favours an S_N2 mechanism. Studies on the effect of methanol, phenol and mercuric chloride on the hydrolysis also gave evidence for simultaneous involvement of S_N2 and Addition-ionization mechanism. However addition-ionisation mechanism is having greater contribution in aqueous acetonitrile than in aqueous acetone.

Key words: n-Caproyl chloride, Addition-Ionisation, Hydrolysis, Alcoholysis, S_N2 , S_N1 , Acylium ion, Enthalpy and Entropy of Activation, Phenol, Mercuric chloride.

INTRODUCTION

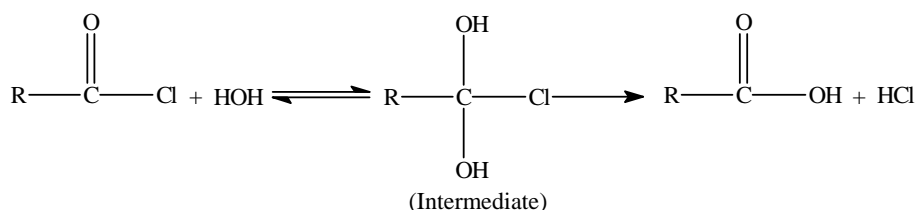
The solvolytic reactions of organic acid chlorides can be divided from mechanistic point of view into two main types, unimolecular (S_N1 type of Ingold)¹ and Bimolecular. In the case of bimolecular mechanism, two different points of view prevail. They are either an S_N2 mechanism or an Addition-Elimination mechanism (A.E).

In the S_N1 mechanism the acyl chloride ionizes into an acylium ion ($R\text{-CO}^+$) and a chloride ion, which is the slow rate determining step, while

the combination of the acylium ion with a hydroxylic solvent is a fast step of the reaction.

The bimolecular S_N2 reaction is a one step conversion of the reactant to product by way of a transition state.

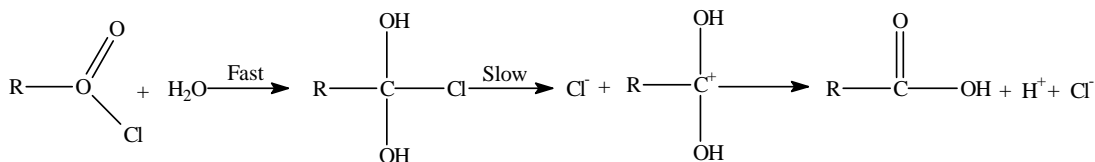
In order to explain the oxygen exchange observed in solvolytic reactions, the bimolecular reaction has been proposed as taking place not in a synchronous substitution reaction, but via a tetrahedral intermediate²



The intermediate formed is so long lived that it may not only change back into the reactants or decomposes to the product but also participate in other reactions. Both these S_N2 and addition-elimination reactions are concurrent and their contribution to overall reaction would vary greatly with the experimental conditions.

If the energy barrier between addition compounds and the products is high, the reaction will proceed by an S_N2 mechanism but still then the equilibrium between addition compound and the reactants will be present.

Order with respect to hydroxylic solvent



Koskikallo⁶ has also claimed the hydrolysis of acetyl chloride in small quantities of water proceed by a bimolecular mechanism.

Formation of acylium ion intermediate can be confirmed by electrophilic catalysis by reagents like mercuric chloride or perchlorates or by trapping the unstable intermediate⁷.

The rate sequence for hydrolysis of different acid chlorides is



Hydrolysis of acetyl chloride takes place much more rapidly than benzoyl chloride

Study of the hydrolysis of benzoyl chloride in aqueous acetone, by Berger and Oliver⁸ leads to the conclusion that in solvent rich in acetone hydrolysis proceeds by S_N2 mechanism, while in water rich solvent a change to an S_N1 mechanism is observed.

and the mechanistic path can be predicted to a large extent by plotting the logarithm of the first order rate constant as a function of the logarithm of the molar concentration of the hydroxylic solvent component. The magnitude of the slope between 6 & 7 favours an S_N1 mechanism and a much lower value of 2 to 3 favours S_N2 ^{3,4}.

For the hydrolysis of acetyl chloride in aqueous acetone or dioxane at low water content, below 4%, the slope is found to be 1.9 while at a higher concentration range of 20 to 75.6 % (v/v) it is approximately found to be 5. To account these facts Hudson and Moss⁵ proposed an ionization mechanism which is possibly preceded by hydration of the reactants. The mechanism is as follows:

The decline in rate from acetyl chloride to ethyl chloroformate followed by a sharp increase suggests a change in mechanism. In dimethyl carbamyl chloride presence of highly electron donating dimethyl amino group favours an S_N1 mechanism. While in the other three cases S_N2 mechanism operates.⁹

Work of C.G.Swain and Scott^{9a,b} shows that acetyl chloride and benzoyl chloride are having high enthalpy of activation (54.4kJ/m and +78.7kJ/m) compared to dimethyl carbamyl chloride. Similarly large -ve entropy of activations of acetyl chloride (-58.6J) and benzoyl chloride (-29.7J) compared to +ve entropy of activation of dimethyl carbamyl chloride (+23.45J) and tert-butyl chloride (+33.5J)¹⁰ clearly favours an S_N2 mechanism in acetyl and benzoyl chloride while an S_N1 mechanism in dimethyl carbamyl chloride. Reactivity of acetyl chloride and benzoyl chloride in presence of OH^- ion is found to increase sharply. ($K_{\text{OH}^-}/K_{\text{H}_2\text{O}}$) is of the order of 10^4 which favours an addition step preceding the bond breaking step.

All these observations lead to the conclusion that hydrolysis in benzoyl chloride and to a larger extent in acetyl chloride proceeds largely by S_N2 mechanism with simultaneous involvement of addition-ionization mechanism proposed by Gold.^{11,12}

In the present work alcoholysis of *n*-caproyl chloride using primary alcohols such as methanol, ethanol, *n*-propanol and *n*-butanol in acetone and acetonitrile was studied in the temperature range of 5°C to 20°C. In addition to this the hydrolysis of caproyl chloride was also studied in 99% to 97% aqueous acetone and aqueous acetonitrile in the same temperature range. The effect of solvolysis using methanol, phenol in 98 % acetone and the effect of added mercuric chloride in the hydrolysis were also carried out.¹³

EXPERIMENTAL

The acid chloride used was Aldrich reagent, and used without distillation or

recrystallisation. All solvents used for the kinetics in this work were dried and distilled by the method given in the literature.¹⁴

The rates in aqueous solvents (99% to 97%, v/v) and solvents containing (0.11m to 0.54 m) of alcohol were measured by following the variation of the conductance of the solution. Titrimetric method is also determine the rates using lacmoid as indicator.

RESULTS AND DISCUSSION

Earlier work on the hydrolysis of acetyl chloride (in general aliphatic acid chloride) shows that the reaction proceeds mainly by an S_N2 mechanism along with slight simultaneous involvement of addition-ionization mechanism¹⁵⁻²⁰ in polar solvents. However in solvents containing larger composition of water, the mechanism of the reaction is found to shifts towards S_N1 . In the case of caproyl chloride in aqueous acetone and acetonitrile as well

Table 1a : Comparison of Rate constants in Acetone and Acetonitrile

Temperature : 5°C
[Substrate] : 0.005 mol/dm³

	Concentration (mol/dm ³)		Rate constant (10 ⁴ K sec ⁻¹)		M	
	Methanol	H ₂ O	Methanol	H ₂ O	Methanol	H ₂ O
Acetone	0.25	0.5555	1.43	0.576	1.12	1.53
	0.50	1.111	3.10	1.67		
Acetonitrile	0.25	0.5555	4.14	0.507	1.04	1.56
	0.5	1.111	8.49	1.5		

Table 1b : Rate constants and m values in Acetone

Temperature : 5°C
[Substrate] : 0.005 mol/dm³

Alcohol (Acetone)	Concentration (mol/dm ³)		Rate constant (10 ⁴ K sec ⁻¹)		m
Methanol	0.25	0.5	1.43	3.1	1.12
Ethanol	0.17	0.52	0.783	2.74	1.1
<i>n</i> -Propanol	0.14	0.27	0.384	0.754	1.02
<i>n</i> -Butanol	0.11	0.33	0.228	0.71	1.03

Table 2 : Rate and activation parameters of the hydrolysis of n-caproyl chloride

Medium	Rate 10 ⁴ 298 K sec-1	$\Delta H^{\ddagger}_{298K}$ kJ/mol	$\Delta S^{\ddagger}_{298K}$ J/mol	$\Delta G^{\ddagger}_{298K}$ kJ/mol
99% Acetone	1.65	34	-202.8	94.5
99% Acetonitrile	1.6	37.7	-191	94.6

Table 3 : Rate and activation parameters of the reaction of n-caproyl chloride with Primary alcohols. [Alcohol] 0.25 mol dm³

Alcohol	Rate 10 ⁴ 298 K sec-1	$\Delta H^{\ddagger}_{298K}$ kJ/mol	$\Delta S^{\ddagger}_{298K}$ J/mol	$\Delta G^{\ddagger}_{298K}$ kJ/mol
Methanol	2.92	22	-239	93
Ethanol	1.75	25	-233	94
n-propanol	1.03	32	-214	96
n-butanol	0.947	42	-173	96

Table 4 : Effect of nucleophiles on the hydrolysis of 98% acetone

Temperature 5°C; [Nucleophile] – 1.111 mol/dm³ [Substrate] – 0.005 mol/dm³

Nucleophile	Rate constant (10 ⁴ k ₁ Sec ⁻¹)	Percentage increase
Water	2.2	
Methanol	6.99	215
Ethanol	6.48	192
Isopropanol	3.8	71
Benzyl alcohol	2.4	8
Phenol	1.11	-50
Sodium hydroxide (0.0185M)	2.51	13

Table 5 : Effect of mercuric chloride

Temperature 5°C [Substrate] – 0.005 mol/dm³

Solvent	[Mercuric chloride]mol/dm ³	Rate constant(10 ⁵ k ₁ Sec ⁻¹)	Percentage increase
98 % Acetone	Nil	5.76	—
	0.001	12	108
98 % Acetonitrile	Nil	5.07	—
	0.001	2.00	295

as in solutions of acetone and acetonitrile containing alcohol like methanol, ethanol, n-propanol and n-butanol the results of solvolysis is in par with the above conclusion

The rate constant for the hydrolysis of caproyl chloride in aqueous acetone and acetonitrile of similar concentrations are found to be same at same temperature. However the rate constant for methanolysis is found to be greater in acetonitrile than in acetone. The order with respect to the nucleophilic solvent (*m* value) is found to be 1.5 for water both in acetone and acetonitrile and between 1 and 1.1 for alcohols (Table 1). Thus the reaction is unimolecular in acid chloride with overall molecularity of 2 to 3 in presence of the nucleophilic solvent. The value close to 2 in the case of alcohols reveals that the reaction proceeds purely by an S_N2 mechanism.²¹

For an S_N1 reaction the value of '*m*' must be in the range of 5 to 6. In the case of methanol the increase in rate in acetonitrile compared to acetone can be accounted in terms of transition state stabilization in solvents having greater dielectric constant.

Slightly greater '*m*' value for water (1.5) compared to that of alcohols reveals that in addition to S_N2 mechanism there is involvement of addition-ionisation mechanism operating simultaneously even though its contribution will be low.

The stabilization of acylium ion intermediate is enhanced by the nucleophilic solvent molecules accounts for the increase in '*m*' value.

The enthalpy of activation will be in the range of 42 to 52 kJ in aqueous acetone while in aqueous aceto nitrile it will be in the range of 37.7 to 46 kJ. The enthalpy of activation of methanolysis is 22 kJ in acetone. Similarly enthalpy of activation of ethanolysis, propanolysis and butanolysis in acetone are 25, 32 and 42 kJ respectively. Low enthalpy of activation favours S_N2 mechanism. Comparatively high enthalpy of activation in hydrolysis reaction compared to alcoholysis reveals that there is greater involvement of addition ionization mechanism in hydrolysis (Table 2 & 3).

There is a gradual increase in the enthalpy of activation with increase in bulkness of the alkyl group, which may be due to steric factor. However low enthalpy of activation in all cases disfavours S_N1 mechanism. Involvement of addition ionization mechanism along with S_N2 may be another factor which increases the enthalpy of activation.

The entropy of activation is found to have a large -ve value both for hydrolysis and alcoholysis reaction which favours S_N2 mechanism. With increase in bulkness of alkyl group the magnitude of the enthalpy of activation decreases. Similarly hydrolysis will also have relatively lower magnitude for entropy of activation. This shows that in methanolysis and ethanolysis reaction take places solely by S_N2 mechanism while in hydrolysis, propanolysis and butanolysis reaction a small extent of addition-ionization mechanism is also operating. Alcoholysis using 2% phenol shows a decrease in rate compared to water which may be due to lower nucleophilicity of phenol compared to water.^{22, 23, 24} Presence of 0.0185M OH⁻ concentrations in 98% aqueous acetone is found to increase the rate of the reaction only to small extent (13%). This accounts for the small contribution of addition ionization mechanism for the overall rate of hydrolysis (Table 4).

In 99% aqueous acetone presence of .001M mercuric chloride is found to double the rate while in aqueous acetonitrile the increase is about 4 fold (Table 5). The acylium carbonium ion formed as intermediate in addition-ionisation mechanism is stabilized by mercuric chloride which behaves as electrophilic catalyst. Larger increase of rate in aqueous acetonitrile shows that there is a greater contribution of addition ionization mechanism in aqueous acetonitrile than in aqueous acetone. The low entropy of activation in acetonitrile compared to that in acetone also favours the above concept.

CONCLUSION

The hydrolysis of caproyl chloride in aqueous acetone and aqueous acetonitrile (99-97%) and alcoholysis with methanol, ethanol, n-propanol and n-butanol are studied at a temperature range of 5°C to 20°C. The enthalpy values (22 kJ to 42 kJ) and the large negative entropy values (-172

to -212) confirm the involvement of addition ionization mechanism for the solvolysis of n-caproyl chloroide. More over the 'm' values between 1 and 1.5 (<2) clearly indicates the presence of addition ionization pathway for the solvolytic reactions of calproyl chloroide. Hence it can be concluded that Alcoholysis as well as hydrolysis of caproyl chloroide take place by the combined mechanisms of S_N2

and addition ionization. The contribution of addition ionization pathway is greater in acetonitrile than in acetone. The involvement of addition ionization mechanism increases as the length of carbon chain increases from ethanol to n-butanol. For methanolysis the mechanism is found to be purely S_N2.

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