Aspects of tautomerism. 8. Solvolysis of some pseudo and normal acid chlorides*

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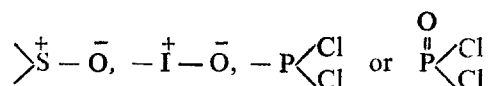† To whom correspondence may be addressed
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Abstract. Pseudo acid chlorides derived from levulinic acid and o-benzoyl-benzoic acid, solvolyse in aqueous acetone, aqueous dioxane and aqueous dimethylformamide by a S_N1 process. Their reaction pattern is distinct from that of typical normal acid chlorides, viz., p-benzoylbenzoyl chloride and fluorene-9-one-1-carboxylic acid chloride, which solvolyse by a S_N2 pathway. No evidence for tautomerism could be obtained either between the normal and pseudo forms of the acid chlorides or the derived ion pairs.

1. Introduction

Acid chlorides derived from γ-keto and δ-keto acids as also from those possessing some functionalities like

$$\overset{+}{\underset{}{>}S - \bar{O}, \quad -\overset{+}{I} - \bar{O}, \quad -P\overset{Cl}{\underset{Cl}{<}} \quad \text{or} \quad \overset{O}{\overset{\|}{P}}\overset{Cl}{\underset{Cl}{<}}$$

in the γ- and δ-position do not always show normal patterns of reactivity. Most of them exist in the pseudo form (Bhatt *et al*   ). Much of the information on these acid chlorides has come from synthetic investigations which took, unexpected turn, because of neighbouring group effects. They highlight the abnormal nature of the product. Considerable obscurity still exists as to the manner in which neighbouring groups influence structure and reactivity of the acid chlorides. We focussed attention on some of these aspects in an earlier paper (Bhatt *et al* 1971). Such basic questions as to whether equilibrium exists between normal and pseudo forms, or whether the derived cationic species exist in equilibrium have not been

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* Aspects of tautomerism 7, Bhatt M V, Rao G V and Rao K S R 1979 *J. Org. Chem.* **44** 984

sufficiently clarified. To the best of our knowledge, no information exists on the solvolysis of pseudo acid chlorides. They possess rather interesting structural features:

(i) They are tertiary or secondary chlorides.

(ii) They possess an a-chlorohydrin system with possibly reduced capacity for lone pair conjugation from the oxygen.

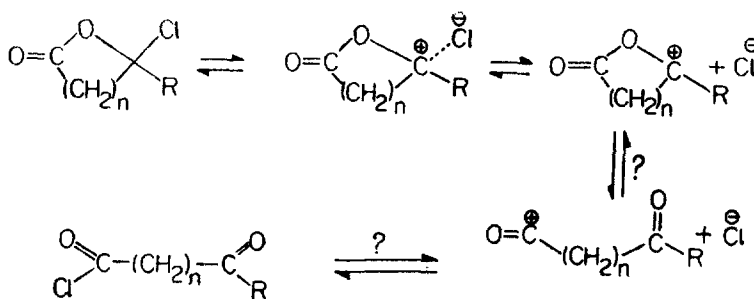(iii) Also, the cationic species, involved in solvolysis, could exist in two tautomeric forms (chart 1).

Chart 1

Esters of both normal and pseudo forms are isolable in the case of many γ-keto acids (Meyer 1904; Newman and Muth 1951; Bhatt and Kamath 1968). Equilibrium of the two forms have been studied in a few cases and generally the open form is the stabler form in the absence of steric or other constraints (Newman and Courduvelis 1965; Bowden and Taylor 1971; Bhatt and Rao) and predominates at equilibrium.

We have undertaken a detailed study of solvolysis of four acid chlorides, I to IV (chart 2) in two solvent systems, viz. aqueous dioxane and aqueous acetone. Additionally, the solvolysis of pseudo acid chlorides I and II have been studied in aqueous dimethylformamide. Fluoren-9-one-1-carboxylic acid chloride IV was included because it is structurally analogous to the open form of the o-benzoylbenzoic acid chloride.
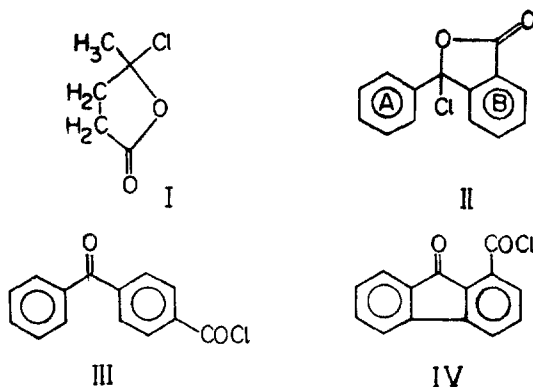

Chart 2

2. Results

2.1. *Does an equilibrium exist between the normal and pseudo acid chlorides?*

There are only a few reports (Newman and Zia Ud Din 1971; Cason and Reist 1958) of normal and pseudo forms existing in equilibrium or identified in both forms. In most cases, only one of the forms, i.e., the pseudo form is favoured. To find out whether this is because of kinetic or thermodynamic considerations, we have treated two acid chlorides I and II with lithium chloride and mercuric chloride in tetrahydrofuran at 50° C for 6 hr. The ir spectra of these acid chlorides remained unaffected. During solvolysis also, when more polar media were used, there was little evidence for isomerisation. This would have been revealed in the reaction pattern. The solvolysis of pseudo acid chlorides and normal acid chlorides follow distinctly different patterns. Barring extreme cases, normal acid chlorides solvolyse by a bimolecular pathway, whereas pseudo acid chlorides do so by a unimolecular route (see below). Also, the pseudo and the normal acid chlorides respond differently to solvent polarity change. The reactions gave good rate plots with no evidence of deviation from steady rate for over 80% of the reaction.

2.2. *Levulinyl chloride*

In table 1, are compared the rates of solvolysis of levulinyl chloride with that of *t*-butyl chloride and acetyl chloride. Levulinyl chloride is far more reactive than the analogous tertiary halide or acetyl chloride. Because of its high reactivity, its hydrolysis could be studied only in a limited range of solvent composition.

In all the solvent systems studied, viz. aq. dioxane, aq. acetone and aq. DMF, solvolysis was suppressed by chloride ions (table 2). The solvent isotope effect (SIE) decreases steadily with increasing solvent polarity. For a change in solvent system from 95% dioxane to 95% DMF it decreases from $1 \cdot 4$ to $1 \cdot 13$ (table 3). All these results point to a unimolecular mechanism of solvolysis.

2.3. *o-Benzoylbenzoic acid chloride*

The influence of increase in water content was studied in three solvent systems, viz. aq. dioxane, aq. acetone and aq. DMF. In dioxane, the *m* parameter (susceptibility of the reaction to the variation of solvent polarity) of Grunwald–Winstein (1948) equation remained steady at $0 \cdot 72$ (table 4). The variation of temperature

Table 1. Comparison of rates of solvolysis of levulinic acid chloride at 25° with two analogous chloride in 95% aq. acetone v/v.

	k. sec^{-1}	Relative rate
t-butyl chloride	$0 \cdot 48 \times 10^{-6}$	1
Acetyl chloride	$6 \cdot 6 \times 10^{-3}$	13, 750
Levulinyl chloride	$14 \cdot 5 \times 10^{-3}$	30, 200

Table 2. Common ion effect for the solvolysis of levulinyl chloride.

Temp.: 25° C.

KCl [Salt] M	Solvent %	$k_1 \times 10^3$ sec^{-1}
No salt	95% Dioxane	8·52
0·002	,,	5·94
0·005	,,	5·41
No salt	95% Acetone	14·56
0·002	,,	13·58
0·005	,,	9·76

Table 3. Solvent isotope effect (SIE) for the solvolysis of levulinyl chloride.

Temp. $t°$ C	Solvent	H_2O or D_2O	$k_1 \times 10^3$ sec^{-1}		k_{H_2O}/k_{D_2O}
			H_2O	D_2O	
30	95% Dioxane	5%	12·16	8·91	1·36
25	,,	5%	8·52	5·87	1·40
25	95% Acetone	5%	14·56	11·94	1·20
20	95% ,,	5%	10·50	8·75	1·20
15	95% ,,	5%	7·25	5·57	1·30
20	95% DMF	5%	23·72	20·95	1·13

Table 4. Variation of % water and Y-values for the solvolysis of o-benzoylbenzoic acid chloride in dioxane–water.

[Substrate] = 0·02 M D = dioxane   W = water

Temp. ° C	% D (v/v)	% W (v/v)	log [H_2O]	Y-value	$k_1 \times 10^3$ sec^{-1}	$3 + \log k_1$	m-value
15	90	10	0·7451	−2·030	1·266	0·1025	0·73
	85	15	0·9212	−1·430	3·789	0·5785	
	80	20	1·0461	−0·833	8·747	0·9418	
25	90	10	0·7451	−2·030	2·64	0·4216	0·70
	88	12	0·8241	−1·795	4·38	0·6415	
	86	14	0·8910	−1·555	6·68	0·8248	
	84	16	0·9489	−1·315	8·29	0·9186	
	80	20	1·0461	−0·833	16·22	1·2100	
30	90	10	0·7451	−2·030	3·92	0·5933	0·72
	85	15	0·9212	−1·430	12·16	1·0849	
	80	20	1·0461	−0·833	28·30	1·4518	
40	95	5	0·4440	..	1·310	0·1173	0·70
	90	10	0·7451	−2·030	9·750	0·9420	
	88	12	0·8241	−1·555	16·92	1·2284	
	85	15	0·9212	−1·430	27·77	1·4436	

did not substantially influence this value (figure 1). The solvolysis takes place clearly by a unimolecular mechanism. The pattern is repeated in the case of aqueous acetone (table 5, figure 2) and aq. DMF (table 6, figure 3), the m values being $0 \cdot 94$ and $2 \cdot 0$ respectively. Most of these values remain steady with increas-
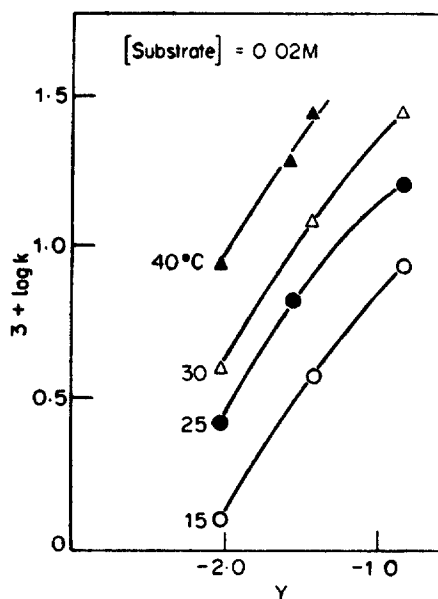

Figure 1. Plot of Y-values vs log k for the solvolysis of o-benzoylbenzoic acid chloride in dioxane–water.

Table 5. Variation of % water and Y-values for the solvolysis of o-benzoylbenzoic acid chloride in acetone–water.

[Substrate] = $0 \cdot 02$ M A = acetone   W = water

| Temp. °C.	% A (v/v)	% W (v/v)	log H_2O	Y-value	$k_1 \times 10^3$ sec^{-1}	$3 + \log k_1$	m-value
15	90	10	0·7451	−1·856	2·303	0·3623	0·94
	85	15	0·9212	−1·270	8·380	0·9232	
	80	20	1·0461	−0·673	33·39	1·5236	
30	95	5	0·4440	−2·71	1·612	0·2074	0·92*
	93	7	0·5899	−2·35	2·726	0·4355	
	90	10	0·7451	−1·865	6·590	0·8189	
	85	15	0·9212	−1·27	21·878	1·3385	
40	95	5	0·4440	−2·71	1·9575	0·2912	0·94
	93	7	0·5899	−2·35	4·1454	0·6175	
	90	10	0·7451	−1·865	12·890	1·1100	
	88	12	0·8241	..	23·830	1·3772	
	85	15	0·9212	−1·27	40·740	1·6100	

* For more than 10% H_2O.
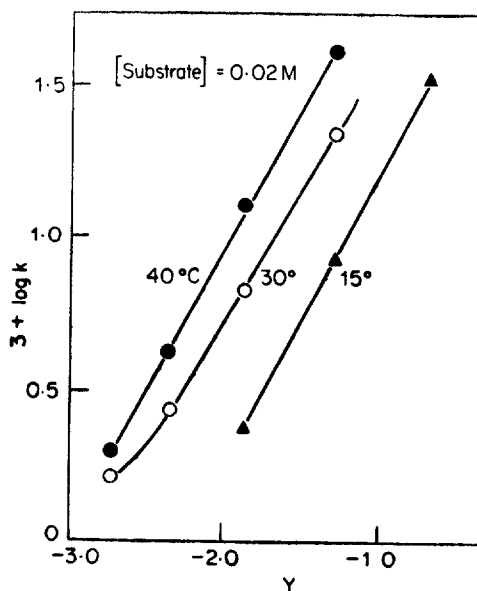
Figure 2. Plot of Y-value vs log k for the solvolysis of o-benzoylbenzoic acid chloride in acetone–water.

Table 6. Variation of % water a41 Y-values in the solvolysis of o-benzoylbenzoic acid chloride in DMF–water.

[Substrate] = 0·02 M DMF = dimethylformamide   W = water

| Temp. °C	% DMF (v/v)	% W (v/v)	log [H₂O]	Y-value	$k_1 \times 10^3$	$3 + \log k_1$	m-value
15	90	10	0·7451	−0·2625	1·99	0·3000	>2
	85	15	0·9212	−0·048	15·57	1·1923	
	80	20	1·0461	+0·1853	44·22	1·6456	
20	90	10	0·7451	−0·2625	3·24	0·5100	>2
	88	12	0·8241	..	8·29	0·9186	
	85	15	0·9212	−0·048	25·56	1·4075	
	80	20	1·0461	+0·1853	58·95	1·7705	
25	90	10	0·7451	..	5·623	0·7500	
	85	15	0·9212	..	42·60	1·6294	
	82	18	10·00	..	59·87	1·7772	
30	90	10	0·7451	..	8·75	0·9420	
	88	12	0·8241	..	29·01	1·4625	
	85	15	0·9212	..	61·95	1·7921	
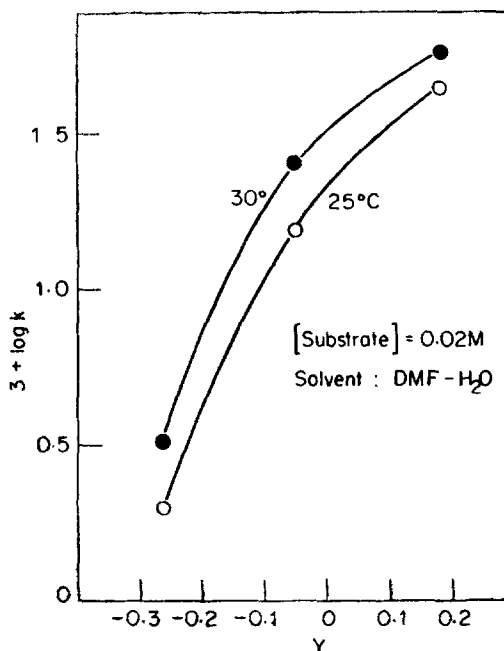
Figure 3. Plot of Y-value vs log k for the solvolysis of *o*-benzoylbenzoic acid chloride.

ing water content of solvent and with temperature variation. The rates of solvolysis in all three solvents are compared in figure 4. The log-log plots of pseudo unimolecular rate constant *versus* water concentrations are steady and linear in keeping with expectations (figure 5).

The rates decrease in the presence of common ions (NaCl and KCl) but increase in the presence of NaN_3, due to the conventional salt effect (table 7). This behaviour is repeated in all the three solvents.

The solvent isotope effects (k_{H_2O}/k_{D_2O}) are 1·15 for aq. dioxane, 1·20 for aq. acetone and aq. DMF mixtures (table 8). These values are lower than those observed for normal acid chlorides III and IV, viz., 1·40 to 1·47 and 1·30 to 1·41 and arise from decreased dependence on hydrogen bonding in the transition state for these compounds. In unimolecular solvolysis similar trend is generally observed.

2.4. *p-Benzoylbenzoic acid chloride*

As a typical normal acid chloride, the solvolysis of the title compound was studied for comparison. Reaction could be followed only in acetone–water, and dioxane–water mixtures. Normal acid chlorides form a strongly polar condensation product instantly with DMF, making this solvent unsuitable for the study. The m value in the two solvent mixtures remained fairly steady. In acetone–water mixture it varied between 0·30 to 0·36 and in dioxane-water mixture the m value was in the range of 0·38 to 0·42 (table 9, figure 6). These values are typical of bimolecular displacement mechanism. The insensitivity to the influence of common ions (table 10) and solvent isotope effect of 1·40 to 1·47 in both acetone-water and
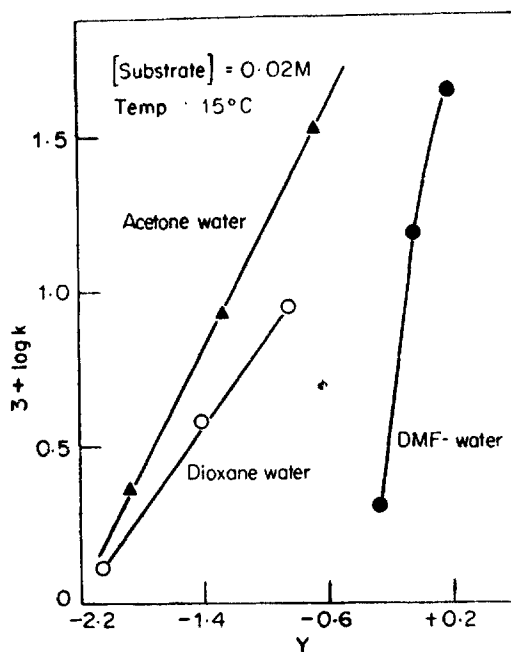
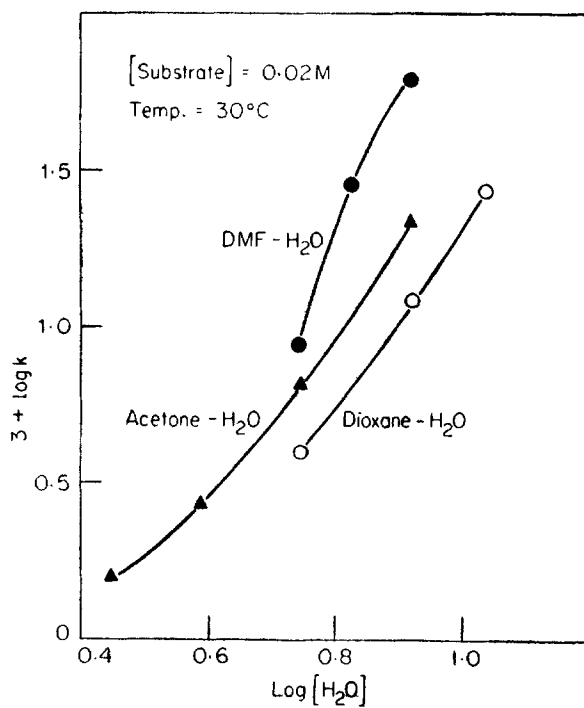**Figure 4.** A comparison of Y-log k graphs of the solvolysis of o-benzoylbenzoic acid chloride.

Figure 5. Plot of log (H_2O) vs log k for the solvolysis of o-benzoylbenzoic acid chloride,

Table 7. Common-ion effect and salt effect for the solvolysis of *o*-benzoylbenzoic acid chloride.

[Substrate] = $0 \cdot 02\,M$. Solvent = 90%.

D = dioxan A = acetone DMF = dimethylformamide

Temp. °C	Solvent	[Salt] M	$k_1 \times 10^3$ sec^{-1}		
			KCl	NaCl	NaN$_3$
25	D–W	No salt	2·64	2·64	2·64
		0·002	2·303	2·21	2·65
		0·004	2·490	2·18	2·64
		0·008	2·52	2·08	3·22
40	D–W	No salt	8·75	..	8·75
		0·002	8·29	..	12·43
		0·005	8·33	..	13·47
30	A–W	No salt	6·49	6·49	6·49
		0·002	5·36	4·01	6·91
		0·005	3·45	2·65	6·99
40	A–W	No salt	12·89	..	12·89
		0·002	11·74	..	15·66
		0·005	10·80	..	16·12
25	DMF–W	No salt	5·62	5·62	5·62
		0·002	4·84	4·61	5·76
		0·004	4·38	4·25	5·90
		0·008	4·38	4·15	6·20
30	DMF–W	No salt	8·75	..	8·75
		0·002	7·19	..	9·44
		0·008	6·30	..	11·51
		0·010	6·80	..	12·01

Table 8. Solvent isotope effect (SIE) for the solvolysis of *o*-benzoylbenzoic acid chloride.

[Substrate] = $0 \cdot 02\,M$.

| Temp. °C	Solvent	%H$_2$O or D$_2$O	$k_1 \times 10^3$ sec^{-1}		k_{H_2O}/k_{D_2O}
			H$_2$O	D$_2$O	
30	90% Dioxane	10	3·92	3·40	1·15
30	85% Acetone	15	21·88	18·23	1·20
30	90% Acetone	10	6·49	5·40	1·20
15	85% DMF	15	15·57	12·89	1·20
20	90% DMF	10	3·23	2·87	1·13
25	90% DMF	10	5·62	4·68	1·20

Table 9. Variation of solvent composition in the solvolysis of *p*-benzoylbenzoyl chloride (III).

Temp. : 30° C.   Substrate = 0·02 M

% Solvent (v/v)	%H_2O (v/v)	Log H_2O	Y Value	$k_1 \times 10^3$ sec^{-1}	$3 + \log k_1$
			Dioxane-water		
90	1C	0·7451	−2·03	1·38	0·1400
80	20	1·0461	−0·83	3·86	0·5866
70	30	1·2219	+0·013	8·75	0·9420
			Acetone-water		
90	10	0·7451	−1·865	1·56	0·1948
80	20	1·0461	−0·673	3·54	0·5487
70	30	1·2219	+0·130	6·75	0·8293

m value : Dioxane-water = 0·38 to 0·42. Acetone-water = 0·30 to 0·36.
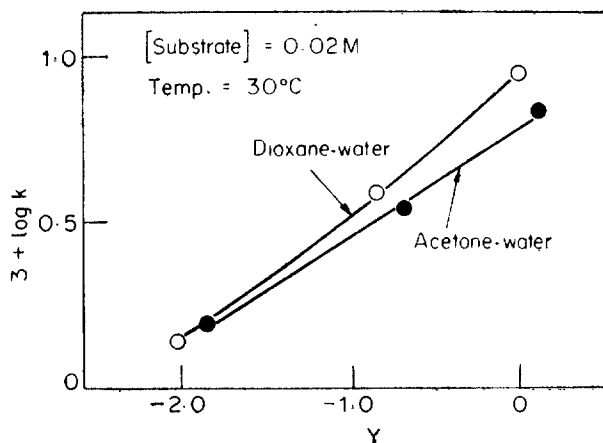
Figure 6. Plot of Y-value vs log k for the solvolysis of *o*-benzoylbenzoic acid chloride.

dioxane–water mixture (table 11) support the bimolecular mechanism. The slight enhancement of the rates due to added salts sodium azide and potassium bromide (tables 9 and 10) could have been caused by the conventional salt effect.

2.5. *Fluoren-9-one-1-carboxylic acid chloride*

Although a γ-keto acid chloride, the title compound exists exclusively in the open form (see experimental). The pseudo derivative is not formed presumably because of angular strain involved. The *m* values both in aq. acetone and aq. dioxane are

Table 10. The common ion effect and salt effect for the solvolysis of the acid chlorides.

Substrate = $0 \cdot 02 \, M$.   W = Water;   D = Dioxane;   A = Acetone;   DMF = Dimethylformamide.

Acid chloride	Temp. °C	Solvent	Salt M	KCl	NaN$_3$	KBr
				$k_1 \times 10^3$ sec^{-1}		
I	25	95% D–W	No salt	8·52		
			0·002	5·94		
			0·005	5·41		
	25	95% A–W	No salt	14·56		
			0·002	13·58		
			0·005	9·76		
II	25	90% D–W	No salt	2·64	2·64	
			0·002	2·30		
			0·004	2·49		
			0·008	2·52	3·22	
	30	90% A–W	No salt	6·49	6·49	
			0·002	5·36	6·91	
			0·005	3·45	6·99	
	30	90% DMF–W	No salt	8·75	8·75	
			0·002	7·19	9·44	
			0·008	6·30	11·51	
			0·010	6·80	12·01	
III	30	90% D–W	No salt	1·38	1·38	1·38
			0·002	1·38	1·49	1·36
			0·005	1·30	1·52	1·51
			0·010	1·38	..	1·50
	30	90% A–W	No salt	1·56	1·56	
			0·002	1·56	..	
			0·005	1·54	..	
			0·010	1·56	1·61	
IV	30	90% D–W	No salt	9·71		
			0·002	9·71		
			0·005	9·70		
	30	90% A–W	No salt	6·07		
			0·002	5·64		
			0·005	4·95		

Table 11. Kinetic solvent isotope effect (SIE) for the solvolysis of acid chlorides.

[Substrate] $= 0 \cdot 02\ M$

Acid chloride	Temp. °C	Solvent	$k_1 \times 10^3$ sec^{-1} for		k_{1H_2O}/k_{1D_2O}
			H_2O	D_2O	
I	25	95% Dioxane	8·52	5·87	1·40
	25	95% Acetone	14·56	11·94	1·20
	20	95% DMF	23·72	20·95	1·13
II	30	90% Dioxane	3·92	3·40	1·15
	30	90% Acetone	6·49	5·40	1·20
	25	90% DMF	5·62	4·68	1·20
III	30	90% Dioxane	1·38	0·935	1·47
	30	90% Acetone	1·56	1·12	1·40
IV	30	90% Dioxane	9·72	6·91	1·41
		90% Acetone	6·07	4·67	1·30

The remaining percentage of the solvent is either H_2O or D_2O as the case may be.

low (table 12, figure 7) viz. 0·18 to 0·23 in dioxane–water and 0·24 in acetone–water. This behaviour is typical of normal acid chlorides. An interesting feature is the observed higher rate of about 6 fold in 90% dioxane at 30° C compared to that of *p*-benzoylbenzoyl chloride (table 13). The carbonyl group in fluoren-9-one 1-carbonyl chloride, being fused to the aromatic ring and planar, possibly has a higher electron withdrawing effect compared to the benzoyl group in *p*-benzoyl-benzoyl chloride in which it may be slightly non-planar. Also, the field effect of the rigid carbonyl group in IV may play a part.

3. Discussion

The activation parameters for the solvolysis of the compounds I to IV are presented in table 14. It is clear that different patterns of reactivity of normal (III and IV) and pseudo acid chlorides (I and II) are reflected in the more negative entropy of activation of the former, conceivably due to more ordered transition state in the case of III and IV.

Our study shows that pseudo acid chlorides solvolyse by a unimolecular mechanism. There is no evidence that equilibrium gets established between the two forms either under normal or solvolytic conditions. This probably is due to preponderant stability of the pseudo form compared to the open form among these acid chlorides.

It is a fact that pseudo acid chlorides are formed because of a favourable kinetic pathway. Our experiments demonstrate that they may also be the stabler isomers in many cases.

Table 12. Variation of solvent composition in the solvolysis of fluorene-9-one-1-carboxylic acid chloride (IV).
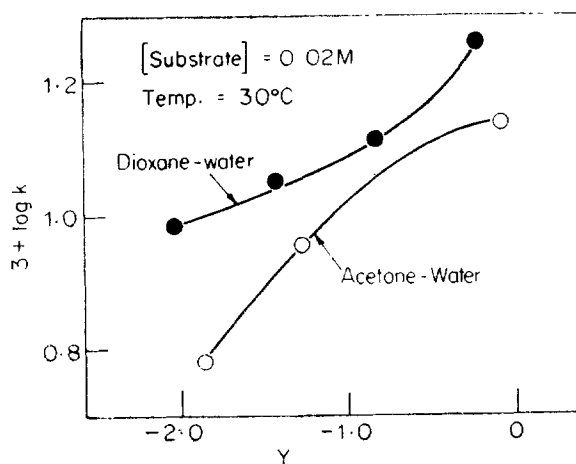
Temp. : 30° C.   [Substrate] $= 0 \cdot 02\ M$.

% Solvent (v/v)	% H_2O (v/v)	Log H_2O	Y-Value	$k_1 \times 10^3$ sec^{-1}	$3 + \log k_1$
		Dioxane-water			
90	10	0·7451	−2·03	9·72	0·9876
85	15	0·9212	−1·43	11·28	1·0522
80	20	1·0461	−0·83	13·36	1·1258
75	25	1·1428	−0·21	18·15	1·2590
		Acetone-water			
90	10	0·7451	−1·865	6·070	0·7832
85	15	0·9212	−1·27	9·027	0·9555
80	20	1·0461	−0·673	13·650	1·1351

Value: Dioxane-water $= 0 \cdot 18$-$0 \cdot 23$.

Acetone-water $= 0 \cdot 24$ (with some deviation on the graph).

Figure 7. Plot of Y-values vs log k for the solvolysis of fluoren-9-one-1-carboxylic acid chloride.

4. Experimental

All the melting points and boiling points reported are uncorrected. Infrared spectra were taken on Perkin–Elmer Model 137 or Model 700 or Carl–Zeiss Jena UR 10 instruments.

Table 13. A comparison of the rate constants (k_1) of the pseudo-first order reactions for the solvolysis of pseudo- and normal acid chlorides.

Temp. : 30° C.   [Substrate] = 0·02 M.

Acid chloride	Solvent	$k_1 \times 10^3$ sec^{-1}
I	95% Dioxane	8·52*
	95% Acetone	14·56*
II	90% Dioxane	3·92
	90% Acetone	6·49
	90% DMF	5·62*
III	90% Dioxane	1·38
	90% Acetone	1·56
IV	90% Dioxane	9·72
	90% Acetone	6·07

* k_1 at 25° C.

Table 14. Activation parameters for the solvolysis of the acid chlorides.

[Substrate] = 0·02 M.

Acid chloride	Solvent	E_a (kcal/mole)	$\triangle S^{\ddagger}$ (eu)	$\triangle H^{\ddagger}$ (kcal/mole)	$\triangle F^{\ddagger}$ (kcal/mole)
I	95% Dioxane	12·6	−25·9	11·98	19·80
	95% Acetone	12·2	−26·1	11·60	19·50
	95% DMF	10·1	−31·7	9·50	19·10
II	90% Dioxane	14·2	−22·9	13·59	20·60
	90% Acetone	12·4	−22·83	11·70	20·20
III	90% Dioxane	7·41	−47·20	6·81	21·11
	90% Acetone	10·46	−38·16	9·47	21·02
IV	90% Dioxane	7·75	−42·22	7·15	19·94

4.1. *Preparation of the acid chlorides*

4.1a. *Levulinyl chloride* (*I*) : Prepared according to literature procedure using thionyl chloride (Cason and Reist 1958); ir 1802 cm^{-1} (lactone).

4.1b. *o-Benzoylbenzoic acid chloride (II)* : Prepared by the standard procedure using thionyl chloride without solvent (Martin 1916). It was purified by distillation, 177–8°/3 mm; ir (neat), 1775 cm⁻¹ (lactone).

4.1c. *p-Benzoylbenzoic acid chloride (III)* : Prepared using thionyl chloride. The acid chloride was purified by recrystallisation from benzene-petrol (40–60°), mp 92–93° (Martin 1916); ir 1695 cm⁻¹ and 1760 cm⁻¹.

4.1d. *Fluoren-9-one-1-carboxylic acid chloride (IV)* : Prepared from the corresponding acid and thionyl chloride. The product is bright yellow solid, mp 132–133° (Sawicki and Chastain 1956); ir 1710 and 1780 cm⁻¹.

4.2. *Kinetic studies of solvolysis of the acid chlorides*

Conductivity water was prepared by triple distillation of distilled water over potassium permanganate. Acetone, dioxane and ethanol were purified by standard methods (Vogel 1975). Dimethylformamide (DMF) was dried over a mixture of potassium hydroxide and barium oxide, filtered and distilled over phosphorus pentoxide, 152°/684 mm.

The kinetics of solvolysis of pseudo acid chlorides was followed conductometrically using a conductivity measuring bridge, a Philips Model PR 9500/90 conductivity meter (Shedlovsky and Shedlovsky 1971).

The pseudo-first order rate constant was calculated assuming the concentration of HCl produced to be proportional to the conductivity. The acid chloride in the solution was allowed to hydrolyse completely and the resistance R of the solution was measured at different intervals of time (Crunden and Hudson 1956). The reciprocal of the resistance was found to be directly proportional to the concentration of the chloride. A typical example, involving determination of pseudo first order rate constant is given in figure 8.
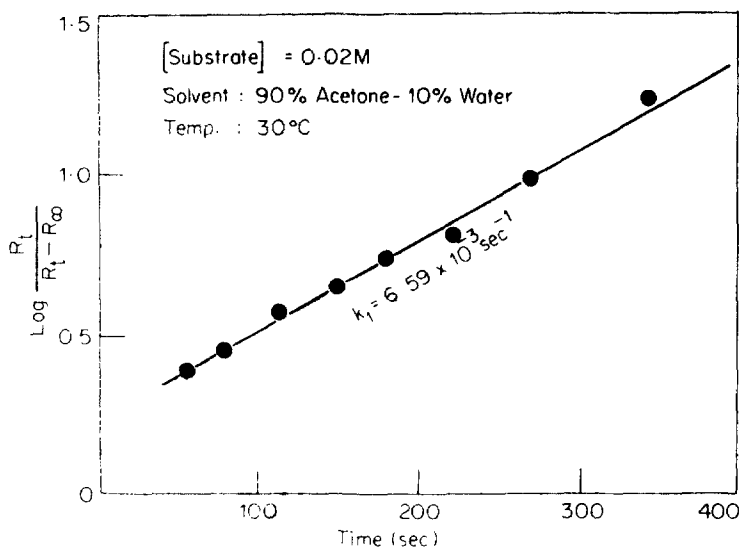

Figure 8. Pseudo-first order plot for the solvolysis of *o*-benzoylbenzoic acid chloride in acetone–water.

4.3. *Variation of solvent composition and determination of m values*

The rate constants were measured at different solvent compositions (increasing water content) and the log of the water concentration was plotted against log k_1. Also the Y-values taken from literature for different solvent compositions were plotted against log k_1. The slopes of these graphs gave the m values. Y-values were available for aq. dioxane and aq. acetone. For DMF–water solution Y-values were experimentally determined.

4.4. *The Y-values of DMF-water mixtures*

The solvolysis of *t*-butyl chloride in DMF–water solutions and in 80% ethanol were studied to determine the Y-scale, applying the Grunwald–Winstein equation:

$$\log \ k/k_0 = mY$$

where k is the rate constant for different DMF–water mixtures and k_0 is the rate constant in 80% ethanol. The kinetic data are presented in table 15.

4.5. *Solvolysis of benzhydryl chloride*

To test the reliability of the conductivity method, and as a check on our determinations, we studied the solvolysis of benzhydryl chloride and compared the rates with literature values (Winstein *et al* 1957).

	$k_1 \times 10^5$	$k_1 \times 10^5$ (lit)
90% Dioxane at 25°	0·169	0·168
80% Dioxane at 25°	2·69	2·67
90% Dioxane at 30°	0·32	..
80% Dioxane at 30°	4·85	..
90% Acetone at 25°	0·495	0·460
80% Acetone at 25°	7·25	7·27
90% Acetone at 30°	0·84	..
80% Acetone at 30°	13·29	..
90% Dimethylformamide at 30°	2·11	..
80% Dimethylformamide at 30°	15·66	..

(The concentration of the substrate in all the cases was 0·02 M).

4.6. *Common ion and salt effects*

To study the common ion effect different concentrations of potassium chloride or sodium chloride were used, and the rate constants were measured as usual.

4.7. *Solvent isotope effects (SIE)*

The solvent isotope effect was studied by determination of conductivity using H_2O or D_2O and the rate constants were measured in the usual manner.

Table 15. Determination of *Y*-values for dimethylformamide-water mixtures using the kinetic data of solvolysis of *t*-butyl chloride.

Temp. : 25°   Solvent : DMF-water

$$k_0 = 9 \cdot 26 \times 10^{-6} \, \text{sec}^{-1}$$

% DMF v/v	% H$_2$O v/v	k sec^{-1} $\times 10^6$	k/k_0	$\log k/k_0$ (Y)
90	10	5·06	0·5464	−0·2625
80	20	14·19	1·532	0·1853
70	30	50·56	5·46	0·7372
60	40	140·41	15·16	1·1807
50	50	497·35	53·71	1·7301
40	60	1471·41	158·90	2·2041

$m = 1$ for *t*-butyl chloride by definition.

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