

Aspects of tautomerism 9-solvolysis of normal and pseudo phthaloyl chlorides*

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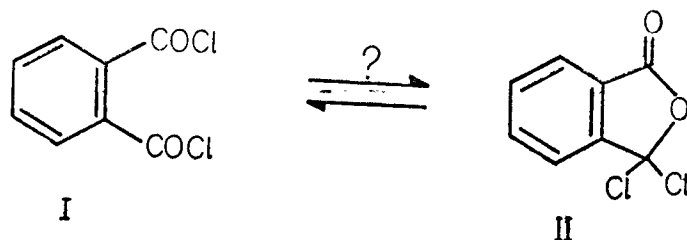
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Abstract. Solvolysis of normal and pseudo phthaloyl chlorides in aqueous acetone and in aqueous dioxane has revealed that the former solvolyses about hundred-fold faster than the latter. Contrary to the accepted belief, there is no evidence for equilibrium between the normal and the pseudo forms of phthaloyl chloride, under a variety of conditions.

Keywords. Phthaloyl chloride isomerism ; tautomerism ; solvolysis.

1. Introduction

The isomerism of normal and pseudo phthaloyl chlorides has been designated as tautomerism in text books (Fieser and Fieser 1961), treatises (Rodd 1956) and scientific literature (Chase and Hey 1952, Csányi 1919 and Ott 1943).



Both forms have been isolated and are well characterised. In connection with an extended study of 'abnormal' features of structure and reactivity patterns of γ - and δ -keto-substituted derivatives of carboxylic acids, we had occasion to study these compounds.

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The pseudo acid chloride is prepared by heating the normal acid chloride with anhydrous aluminium chloride (Ott 1943). It has been reported that the pseudo tautomer slowly reverts to the normal form on slow distillation at atmospheric pressure and on melting (Ott 1943).

We have studied the solvolysis of I and II in two solvent systems *viz.* aqueous acetone and aqueous dioxane and in addition that of II in aqueous dimethylformamide.

2. Results and discussion

The solvolytic patterns of normal and pseudo acid chlorides are ordinarily quite different (Bhatt *et al* 1979). The former by and large hydrolyses by a bimolecular pathway whereas the latter follows a unimolecular route. In the case of phthaloyl chloride, the normal acid chloride solvolyses about a hundred-fold faster than the pseudo isomer (table 1). A number of probes could be used to delineate the mechanisms of solvolysis of I and II *viz.* common ion effect, salt effect, susceptibility of the reaction rate to increase in the polarity of the medium, etc. The observed *m* value of I—the susceptibility of the substrate to solvent polarity, of Grunwald and Winstein (1948; also Winstein *et al* 1957)—in dioxane-water is 0.33 and for acetone-water it is 0.34 (table 1, figure 1). For a typical normal acid chloride like *p*-benzoylbenzoyl chloride, the *m* value is 0.38 to 0.42 for dioxane-water and 0.31 to 0.36 for acetone-water mixtures (Bhatt *et al* 1979). There is little effect on the rate by added sodium chloride (no common ion effect) and only slight rate enhancement by added sodium azide due to the conventional salt effect. The solvent isotope effect (SIE) is 1.50 for aqueous dioxane and 1.47 for aqueous acetone. These values are similar to those found for normal acid chlorides. From all these experiments we conclude that solvolysis of normal phthaloylchloride proceeds by a bimolecular mechanism, similar to that of other acid chlorides.

Surprisingly, the rate of hydrolysis of I is only $2.07 \times 10^{-3} \text{ sec}^{-1}$ which when compensated for the statistical factor, becomes $1.035 \times 10^{-3} \text{ sec}^{-1}$ as against

Table 1. Solvolysis data for normal phthaloyl chloride (I) Temp : 30° C;
Substrate = 0.02 M)

Solvent	Y value	$k_1 \times 10^3 \text{ sec}^{-1}$	$3 + \log k_1$	<i>m</i>
90% Dioxane	-2.03	2.07	0.3160	..
85% ..	-1.43	3.68	0.5658	..
80% ..	-0.83	5.76	0.7604	0.33*
75% ..	-0.21	7.37	0.8675	..
90% Acetone	-1.856	2.37	0.3774	..
85% ..	-1.270	3.57	0.5740	0.34
80% ..	-0.673	5.98	0.7767	..

* There is a deviation for above 20% water (v/v).

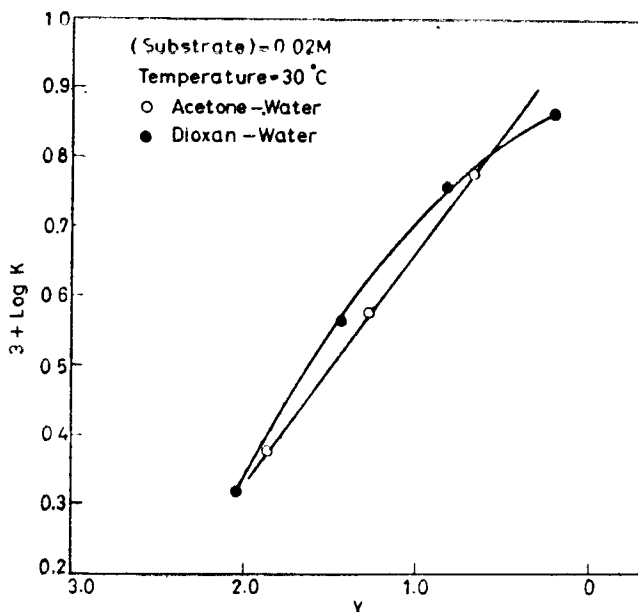


Figure 1. y values vs. $\log k$ for the solvolysis of phthaloyl chloride.

$1.38 \times 10^{-3} \text{ sec}^{-1}$ for *p*-benzoylbenzoyl chloride (both at 30° C in 90% dioxane-water mixture). Any neighbouring group participation in the hydrolysis of I should have enhanced the rate significantly. Participation can therefore be ruled out. The hydrolysis of the second acid chloride group takes place, apparently, in a fast step, and as such does not contribute to the overall rate. The initial product of solvolysis of I is phthalic anhydride. A plausible scheme for its formation could be written as shown in scheme I. The mono acid chloride could be expected to be converted by a fast step into the pseudo derivative IV. Ortho-substituted carboxylic acids like phthalaldehydic acid VI, *o*-acetylbenzoic acid VII and *o*-carboxybenzoylformic acid VIII exist predominantly in the pseudo form (Jones 1963; Bowden and Taylor 1971). It would not be unreasonable to assume that III gets converted to IV by a fast step. Being an α -halohydrin IV could form V either by elimination of hydrogen chloride or by solvolysis.

The solvolysis of pseudo phthaloyl chloride II has been studied in dioxane-water, acetone-water and dimethylformamide-water mixtures. The influence of solvent polarity change on the rate of hydrolysis of II is significantly different from that of I. The m value for a typical pseudo acid chloride like *o*-benzoylbenzoic acid chloride (IX) is in the range of 0.70 to 0.73.

In the case of II, however, the behaviour is untypical of either a normal or a pseudo acid chloride: The m value changes from 0.3 to 0.7 and then again to 0.9 for dioxane-water and acetone-water systems. In dimethylformamide-water it is more or less steady around 0.90 (table 2, figure 2). The common ion effect and salt effects also show ambivalence and depend on the solvent system. In aqueous dimethylformamide (table 3), it corresponds to a unimolecular mechanism. The solvent isotope effect is 1.13 in 90% aqueous dimethylformamide and is typical of unimolecular mechanism. On the other hand solvent isotope effect

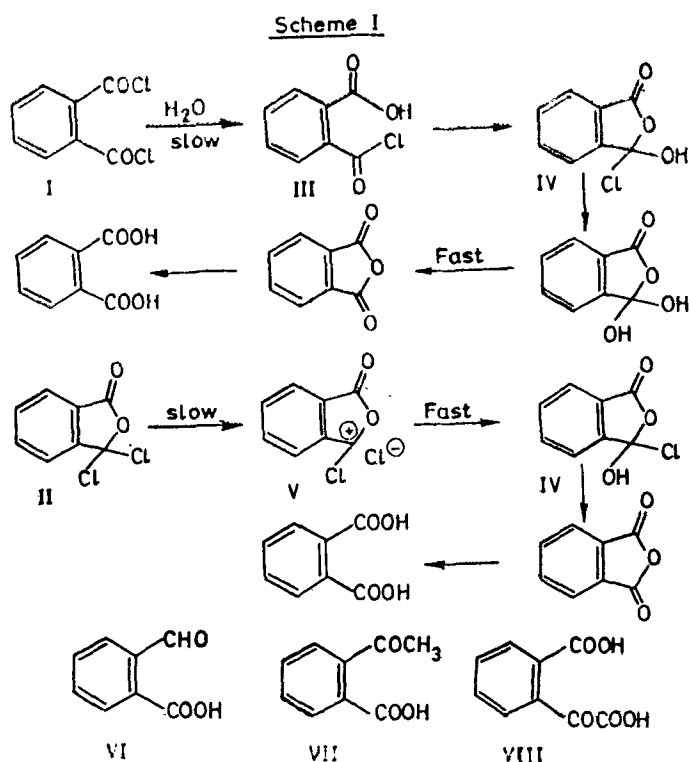


Table 2. Solvolysis data for pseudo phthaloyl chloride(II) Temp.: 30°C;
Substrate = 0.02 M

Solvent	Y value	$k_1 \times 10^5 \text{sec}^{-1}$	$5 + \log k_1$	m
90% Dioxane	-2.030	1.75	0.2430	..
80% ..	-0.833	2.80	0.4472	0.3 to 0.7*
70% ..	0.013	11.51	1.0610	..
60% ..	0.715	27.11	1.4332	..
90% Acetone	-1.856	2.40	0.3802	..
80% ..	-0.673	3.93	0.5944	..
				0.26 to 0.90
70% ..	0.130	9.90	0.9956	..
60% ..	0.797	31.89	1.5036	..
90% DMF	-0.263	5.38	0.7308	..
80% ..	0.185	12.43	1.0944	..
				0.90*
70% ..	0.737	34.19	1.5339	..
60% ..	1.181	95.57	1.9803	..

* See also figure 2.

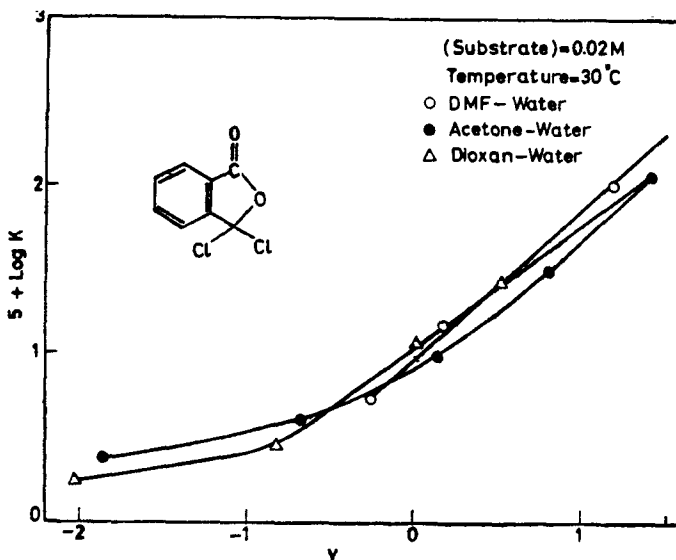


Figure 2. y values vs. $\log k$ for the solvolysis of 3,3 dichloro-phthalide at 30° C .

Table 3. Common ion effect and salt effect for the solvolysis of normal and pseudo phthaloyl chlorides.

Temp : 30° C; Solvent = 90%; water = 10%; [Substrate] = 0.02M

Acid chloride	Solvent	[Salt] M	KCl	NaN ₃
$k_1 \times 10^3 \text{ sec}^{-1}$				
Normal phthaloyl chloride	D-W	No salt	2.07	2.07
		0.002	2.04	2.09
		0.01	2.07	2.14
	A-W	No salt	2.37	2.37
		0.002	2.303	2.94
		0.01	2.303	3.84
$k_1 \times 10^5 \text{ sec}^{-1}$				
Pseudo phthaloyl chloride	D-W	No salt	1.75	1.75
		0.002	0.525	fast
		0.01	0.460	fast
	A-W	No salt	2.40	2.40
		0.01	2.19	fast
	DMF-W	No salt	5.38	5.38
		0.002	5.09	fast
		0.005	3.22	fast

W = water; D = dioxane; A = acetone; DMF = dimethylformamide.

in 90% acetone is 1.4, and common ion effect is very small indicating that the reaction is bimolecular in this solvent mixture (table 4). Evidently, the hydrolysis of II takes place by two parallel pathways, S_N2 and S_N1 , the share of each being determined by solvent polarity.

The thermodynamic parameters for the solvolysis of I and II are compared in table 5. As expected, the entropy of activation for I is more negative than that of II and similar to that of other normal acid chlorides. The values for II could reflect partial involvement of a S_N1 pathway.

The rate-determining step in the case of I is the formation of IV, the subsequent hydrolysis being fast. In figure 3 are compared the rates of solvolysis of normal and pseudo phthaloyl chlorides (cf. also tables 1 and 2). The rate plots were steady in all the determinations (figure 3). These findings definitely rule out the existence of equilibrium or tautomerism between the two isomers in solution or in the solid state at ambient and temperatures up to 40° C.

On slow distillation at 265–67° C/684 mm, the pseudo acid chloride is converted almost completely into the normal form. The ^{13}C NMR spectrum of the distillate is identical to that of pure normal acid chloride and does not show evidence of being a mixture of the two forms. Apparently this transformation takes place by a thermal reaction, whereas the reverse change takes place in the presence of a Lewis acid like aluminium chloride. These different types of chemical reactions require sufficient activation energy for transformation from one species to the other. This system is an example of isomerisation rather than tautomerism. The important difference is in that the equilibrium mixture is not formed from either isomer under a variety of conditions. The essential precondition for tautomerism, viz. low enough activation energies to make interchange of the different forms facile under different conditions is not realised in the present case. The thermal conversion of pseudo acid chloride to the normal isomer, if takes place by a con-

Table 4. Kinetic solvent isotope effects for the solvolysis of normal and pseudo phthaloyl chlorides(I) and (II)

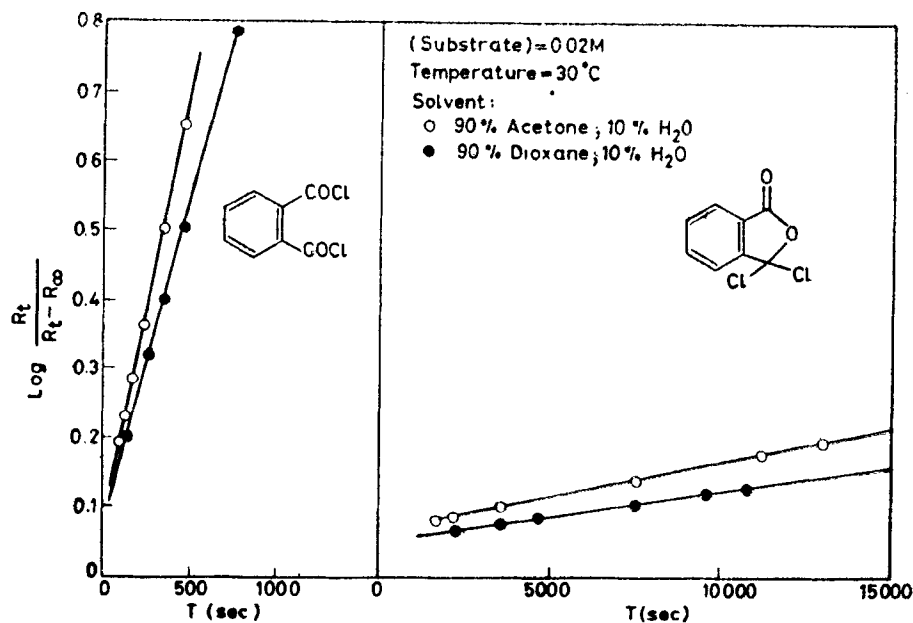
Temp : 30° C; Solvent = 90%_v; H₂O or D₂O = 10%_v; [substrate] = 0.02 M]

Acid chloride	Solvent	$k_{\text{H}_2\text{O}}$	$k_{\text{D}_2\text{O}}$	$k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$
		($\times 10^3 \text{ sec}^{-1}$)	($\times 10^3 \text{ sec}^{-1}$)	
Normal phthaloyl chloride				
	Dioxane	2.07	1.38	1.50
	Acetone	2.37	1.61	1.47
($\times 10^3 \text{ sec}^{-1}$) (% 10^3 sec^{-1})				
Pseudo phthaloyl chloride				
	Dioxane	1.75	1.31	1.43
	Acetone	2.40	1.72	1.40
	DMF	5.38	4.83	1.13

Table 5. Activation parameters calculated from Arrhenius equation for the solvolysis of normal and pseudo phthaloyl chlorides(I) and (II).

(Substrate) = 0.02M; Solvent = 90%; Water = 10%.

Acid chloride	Solvent	t (°C)	k_1 (sec ⁻¹)	E_a Kcal/ mole	ΔS^\ddagger (e.u.)	ΔH^\ddagger Kcal/mole	ΔF^\ddagger (Kcal/ mole)	
Normal phthaloyl chloride	Dioxane		($\times 10^3$)					
		25	1.61	9.12	-40.78	8.52	20.87	
		30	2.07					
	35	2.67						
	Acetone	25	1.68					
		30	2.37	12.45	-29.53	11.88	20.83	
35		3.31						
Pseudo phthaloyl chloride	Dioxane		($\times 10^3$)					
		30	1.75					
		35	2.70	17.02	-24.21	26.42	23.76	
		40	4.28					
		Acetone	30	2.40				
			35	4.60	16.47	-25.40	15.87	23.57
	40		5.78					
	DMF	30	5.38					
		35	8.28	16.47	-23.79	15.87	23.08	
		40	12.75					

**Figure 3.** Pseudo first-order reaction rate for solvolysis of phthaloyl chloride and its cyclic isomer.

certed process, would involve a forbidden type of electrocyclic reaction of four electrons and a non-planar transition state. Possibly, the reaction may be taking place through diradical involvement. A more detailed study of this transformation is planned.

3. Experimental

Acid chlorides were prepared by literature methods (Ott 1943) and conformed to the literature physical constants. IR spectra were consistent with the structures.

Normal phthaloyl chloride had bp 131–3°C/10 mm; IR (neat) 1725 and 1790 cm^{-1} and pseudo phthaloyl chloride mp 86–88°C (lit mp 87–8°C) (Csanyi 1919); IR (nujol) 1795 and 1825 cm^{-1} (possibly due to Fermi resonance). The solvolysis experiments were carried out conductometrically using a conductivity measuring bridge—a Philips Model PR 9500/90 Conductivity meter. Experimental procedure for measuring the rate of solvolysis was similar to that reported earlier (Bhatt *et al* 1979).

3.1. Hydrolysis experiments

Normal phthaloyl chloride I (2.0 g) was dissolved in 2% aqueous acetone (25 ml) and kept at room temperature for 6 hr. The solvent was removed under suction and residue worked with petrol (40–60°C) to remove unreacted acid chloride. Phthalic anhydride (1.4 g) mp 131°C was obtained.

Pseudo phthaloyl chloride II (2.0 g) was dissolved in 10% aqueous acetone (25 ml) and kept at room temperature for 8 hr. On removing the solvent under vacuum, the residue was worked with petrol to yield phthalic anhydride (1.3 g) mp 129°C.

3.2. Conversion of II to I

About 50 g of II was distilled at atmospheric pressure (684 mm) and the clear water-white distillate collected. The liquid distilled at 265–7°C. There was no evidence of any solid subliming over.

^{13}C NMR (ppm δ): C_1' , C_2' —167.6; C_1 , C_2 —134.4; C_4 , C_5 —133.5; C_3 , C_6 —130.0 (for pure I), C_1' —164.0; C_3' —104.6; C_1 —136.0; C_2 —150; C_4 —136.6; C_5 —125.7; C_3 —123.0; C_6 —132.0 (for pure II) and 167.3; 134.4; 133.2 and 130.1 for the sample obtained by distillation of II.

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