

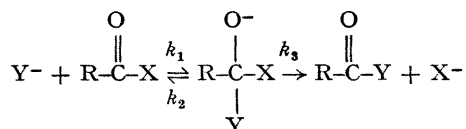
Role of the Leaving Group in the Base-catalysed Hydrolysis of Pseudo-esters

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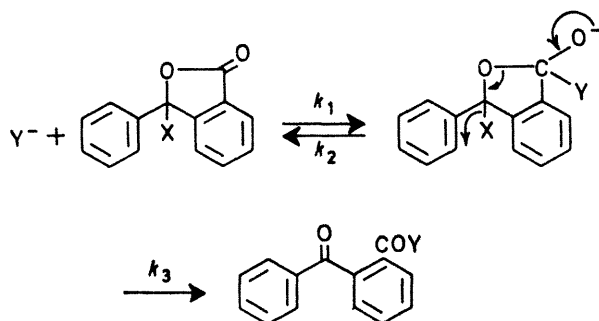
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Summary The relative insensitivity of the rate of hydrolysis of γ -pseudo-esters to the leaving group compared to that of the normal esters emphasises that the conjugative ability is an important factor in determining the rate of hydrolysis of esters.

THE rate constant for the base-catalysed hydrolysis of esters is a function of two parameters, namely, the rate of formation of the tetrahedral intermediate (k_1) and the dominance of forward and backward reactions (α or k_2/k_3).¹



It is not normally possible to assess the relative importance of the two factors k_1 and α since structural changes



† Field effects of the groups, however, may be present; cf. M. V. Bhatt, K. M. Kamath, and M. Ravindranathan, *J. Chem. Soc. (C)*, in the press.

¹ M. L. Bender, *Chem. Rev.*, 1960, **60**, 54.

² E. Tommila, *Ann. Acad. Sci. Fennicae*, 1942, **A59**, 3.

affect both similarly. The pseudo-derivatives of γ - and δ -keto-acids are unique in that the conjugative ability of the leaving group does not influence the carbonyl group of the ester.† We report the rate of base-catalysed hydrolysis of eight pseudo-carboxylic acid derivatives of *o*-benzoylbenzoic acid in 70% aqueous dioxan.

The rates were determined titrimetrically with a screened indicator composed of Neutral Red and Methylene Blue. The kinetic data are presented in the Table.

Effect of the leaving group in basic hydrolysis of pseudo-esters of o-benzoylbenzoic acid in 70% dioxan at 30 °C

Leaving group	$10k_2/l \text{ mol}^{-1}\text{s}^{-1}$	Relative rate	Relative rate for benzoic esters ²
OMe	1.77	6.3	6.8×10^2
OEt	1.12	4.0	2.2×10^2
OBu ^t	0.282	1.0	1.0
OPh	0.602	2.1	2.8×10^3
$\text{O}-\text{CH}(\text{C}_6\text{H}_5)-[\text{CH}_2]_3-\text{CH}_2$	0.614	2.2	3.0×10
$\text{O}-\text{CH}(\text{C}_6\text{H}_5)-[\text{CH}_2]_4-\text{CH}_2$	0.466	1.7	2.0×10
N ₃	3.36	1.1×10	
Cl	35.0	1.2×10^2	

The contrast between the pseudo-acid and normal acid derivatives is striking. Clearly, the conjugative ability of a group is the major factor that determines the rate of base-catalysed hydrolysis. We are exploring the consequences of these observations in the carbonyl-assisted basic hydrolysis of esters and amides.

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