Synchronous Displacement *versus* an Addition–Elimination Mechanism in the Nucleophilic Displacement Reaction of Acyl Halides

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Summary Evidence is presented which suggests that the reaction of acyl halides with base proceeds *via* a concerted S_N2-like displacement, which may have a geometry analogous to that of alkyl S_N2 displacement

THE base-catalysed hydrolysis or alcoholysis of acyl halides in non-polar solvents may proceed *via* a one-step, synchronous S_N2-like process or *via* an addition–elimination mechanism analogous to that found in the saponification of esters[1] The bulk of the evidence appears to favour the latter mechanism although a clear distinction has not been made because of the inapplicability of some of the approaches which have solved this problem in the case of ester and amide hydrolysis[2] We report a novel method for distinguishing between these two mechanistic possibilities by the use of the reaction of an acyl halide with an ambident[3] nucleophile

The reaction of a number of benzoyl chlorides with sodium and lithium 2-naphthoxide in several non-polar solvents was found to yield 1-benzoyl-2-naphthol and 1-benzoyl-2-naphthyl benzoate as well as the expected product, 2-naphthyl benzoate   The ratio of carbon to oxygen acylation (C/O was found to depend on the nature of the metal ion, the nature of the substituent in the benzoyl moiety, and the nature of the solvent

The reactions of alkyl halides with a variety of ambident nucleophiles, including 2-naphthoxide, has been the subject of exhaustive study[4]   The generalizations which have arisen from these studies include the following (i) In non-polar solvents, as the cation is changed from K^+ to Na^+ to Li^+, carbon alkylation is favoured over oxygen alkylation   (Because Li^+ being the smallest and the best complexing ion will tend to "solvate" the more electronegative atom of the ambident nucleophile, thus directing attack to the less electronegative atom)[4b] (ii) Electron-withdrawing groups on the alkyl halide increase the electro-

philicity and therefore the reactivity of the carbon undergoing substitution, making it less selective   This favours the less reactive site of the ambident nucleophile[4b]   (iii) Carbon alkylation is favoured over oxygen alkylation as one goes to less polar solvents[4b]   (Because this strengthens the ionic bond between the cation and the oxygen on the ambident anion, blocking reaction on O and thus favouring C)

The ratio of carbon to oxygen acylation (C/O) in the reaction of benzoyl chlorides (0 61M) with sodium and lithium 2-naphthoxide[a] in hexane at 25°

Chloride	2-Naphthoxide	C/O[b] $\times 10^2$
p-Methoxybenzoyl chloride	Na	0 55
p-Methoxybenzoyl chloride	Li	3 6
Benzoyl chloride	Na	0 74
Benzoyl chloride	Li	4 8
p-Nitrobenzoyl chloride	Na	2 8
p-Nitrobenzoyl chloride	Li	17

[a] An equivalent amount of solid 2-naphthoxide was used   The solubility of these two salts in hexane is practically nil

[b] (The yield of 1-benzoyl-2-naphthol plus the yield of 1-benzoyl 2 naphthyl benzoate)/ (the yield of 2-naphthyl benzoate)   The total yields ranged from 85 to 98%   Synthetic mixtures of the three sets of products were separated in the same manner as the reaction product and gave more than 99% recovery   Control experiments showed that no isomerization of products took place, all products being stable under the reaction conditions

Viewing our results (Table) in the light of these considerations we see that the predictions of rules (i) and (ii) are fully borne out by the results obtained in our *acylation* reactions   Results similar to these obtained in hexane solvent were also obtained by us in benzene and in CCl_4 However in the more polar solvents, tetrahydrofuran and 2,2'-dimethoxydiethyl ether a dramatic decrease in the C/O ratio was observed   All but one reaction (lithium 2-naphthoxide with *p*-nitrobenzoyl chloride) in fact gave

exclusively O-acylation $(C/O < 10^{-4})$ in the more polar solvents. This observation is predicted by rule (iii) above.

The fact that rules derived from alkylation reactions of ambident nucleophiles apply so well to acylation reactions must give one pause, as it suggests a similarity in mechanism. This similarity is not likely to consist of the mere fact that both reactions are indeed nucleophilic displacements. Recently, we were able to show that there is very little electronic similarity between the transition state of an S_N2 reaction and the transition state leading to the tetrahedral intermediate in an ester saponification.[5] The former has a great deal of charge delocalization, whereas the latter does not. Thus we regard the similarity in ambident anion behaviour toward alkyl halides and acyl halides to be a strong argument for a synchronous S_N2-like mechanism for the reaction of bases with acyl halides.

The geometries of the transition states leading to carbon and to oxygen acylation assuming sp hybridization are depicted in Figure 1. It is evident that the transition state
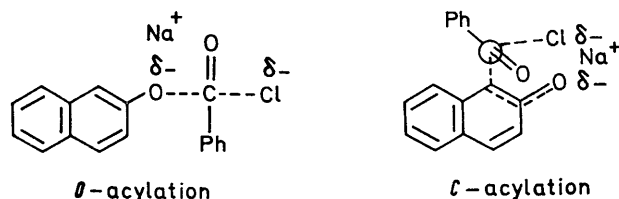

O-acylation C-acylation

FIGURE 1. *Transition states having* sp *geometry*

leading to O-acylation involves considerable charge separation due to the formation of a chloride ion remote from the sodium ion. The transition state leading to C-acylation,

on the other hand, involves no charge separation due to the proximity of the sodium ion and the leaving chloride ion. If this mechanism is operative, then carbon acylation should be favoured by any factor that increases the energy difference between a sodium chloride ion-pair and separated sodium and chloride ions.

The geometries of the transition states leading to carbon and oxygen acylation assuming a tetrahedral transition state are shown in Figure 2. In this case negative charge
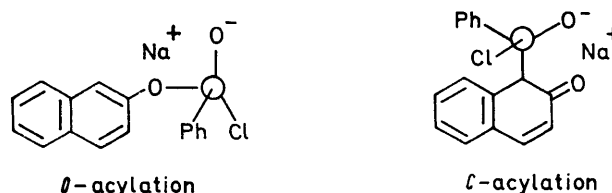

O-acylation C-acylation

FIGURE 2. *Transition states having* sp³ *geometry*.

is being transferred from the naphthoxide oxygen to the acyl oxygen and to the halide ion. It is evident that there is no difference in the degree of charge separation in the transition state leading to O-acylation and in that leading to C-acylation. If this mechanism is operative then no effects on the C/O ratio are predicted by factors that involve the energy differences between ion-pairs and separated ions,

Thus the sp geometry for a displacement reaction on acyl carbon which has not received serious consideration, probably because it is not plausible in terms of bond energies, does seem to fit our ambident nucleophile acylation results.

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