Acyl-O *versus* Aryl-O Bond Scission in Reactions of Benzenethiolate with Nitrophenyl Esters of Carboxylic Acids

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Summary A number of nitrophenyl esters of carboxylic acids have been found to undergo both carbonyl carbon–oxygen and aryl carbon–oxygen scission in reactions with the benzenethiolate ion in ethanol; the fraction of C_{CO}–O scission increases with increasing polarity of the medium and varies, according to the ester substrate, from 100% with *p*-nitrophenyl acetate to 0% with 2,4,6-trintrophenyl benzoate.

While competition between two electrophilic centres in a single ester substrate is well documented[1] for reactions of nitrophenyl sulphonates, sulphates, and phosphates with nucleophiles, for carboxylic esters mostly acyl–O fission takes place.[1,2] Partial Ar–O fission is reported only for picryl benzoate in neutral methanol[3] and for *p*-nitrophenyl acetate with piperidine in dimethyl sulphoxide.[4]

During research on the reactivity of thiols towards phenyl esters of carboxylic acids,[5] we have surprisingly found that a significant fraction of the reaction between 2,4-dinitrophenyl acetate (2,4-DNPA) and sodium benzenethiolate in ethanol proceeds with attack on C-1 of the phenolic group to give 2,4-dinitrophenyl phenyl sulphide by nucleophilic aromatic substitution. This result is reported in the Table, together with the modes of scission and the rate constants for CO(k_{CO}) and Ar(k_{Ar}) attack in the reactions of sodium benzenethiolate with five other ester substrates, *p*-nitrophenyl acetate (PNPA), *p*-nitrophenyl benzoate (PNPB), 2,4-dinitrophenyl benzoate (2,4-DNPB), 2,6-dinitrophenyl benzoate (2,6-DNPB), and 2,4,6-trinitrophenyl benzoate (2,4,6-TNPB). In two cases (for 2,4-DNPB and 2,4,6-TNPB) the reaction has also been carried out with piperidine; for the reaction of 2,4-DNPB with benzenethiolate the solvent effect on k_{CO} and k_{Ar} has been determined.

TABLE

Ester	Nucleophile	k_{tot}[a]	%C_{CO}–O	k_{CO}[a]	k_{Ar}[a]	Solvent
NPA	PhSNa	0·25[b]	100	0·25	—	Ethanol 95%
PNPB	PhSNa	0·026	100	0·026	—	,, ,,
2,4-DNPA	PhSNa	57·0	48·8	27·8	29·2	,, ,,
2,4-DNPB	PhSNa	8·9	24·3	2·2	6·7	Methanol
2,4-DNPB	PhSNa	64·0	16·7	10·7	53·3	Ethanol 95%
2,4-DNPB	Piperidine	18·5	100	18·5[c]	—	,, ,,
2,6-DNPB	PhSNa	2·61	10·5	0·27	2·34	,, ,,
2,4,6-TNPB	PhSNa[d]	—	0	—	—	,, ,,
2,4,6-TNPB	Piperidine	93	100	93[c]	—	,, ,,

[a] l mol^{-1} s^{-1}; T = 22 °C; [PhS$^-$] = 2 × 10^{-4}—8 × 10^{-3} M; [piperidine] = 4 × 10^{-4} M; [ester] = 10^{-5}—5 × 10^{-4} M. [b] Value taken from ref. 5. [c] Calculated by dividing the observed pseudo-first order rate coefficient by [piperidine]. [d] Reaction too fast to be followed by usual spectrophotometric (u.v.) technique.

The results show that while PNPA undergoes total C_{CO}–O scission by benzenethiolate, 2,4-DNPA is only about 49% cleaved in this manner owing to the strong activation of the 1-position of the phenolic group by the two nitro groups. The percentages of C_{CO}–O cleavage drop to about 17% and 10% with 2,4-DNPB and 2,6-DNPB respectively and 2,4,6-TNPB is totally cleaved by C_{Ar}–O scission. k_{CO} increases in the series PNPB $<$ PNPA $\leqslant$ 2,6-DNPB $<$ 2,4-DNPB $<$ 2,4-DNPA, and k_{Ar} increases in the series 2,6-DNPB $<$ 2,4-DNPA $<$ 2,4-DNPB $<$ 2,4,6-TNPB. The orientation of the attack seems to depend mainly on the relative 'hardness' and 'softness' of the carbonyl carbon and the aryl carbon respectively.[6] This is confirmed by the fact that, while 2,4-DNPB is cleaved by benzenethiolate (a 'soft' base) mainly with aryl–O fission, in the reaction with piperidine (a 'hard' base) 2,4-DNPB undergoes total acyl–O fission. Also, with 2,4,6-TNPB the percentage of attack at the trinitrophenyl carbon varies from 100% with benzenethiolate to 0% with piperidine. It is noteworthy that, conversely from nucleophilic aromatic substitutions[7] where $k_{PhS^-} \gg k_{pip}$, for CO attack in the case of 2,4-DNPB $k_{pip}:k_{PhS^-} > 1{\cdot}0$. This result is in accord with the fact that for CO attack the rates vary fairly regularly with the pK_a of the nucleophile.[2]

In the reaction of 2,4-DNPB with sodium benzenethiolate, the percentage of attack at the carbonyl carbon increases on going from ethanol to methanol. Both k_{Ar} and k_{CO} decrease with increasing polarity of the medium but the solvent effect for Ar attack is larger than for CO attack.

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