

Evidence from Activation Volumes for an Eliminative Mechanism in the Hydrolysis of 2,4-Dinitrophenyl 4-Hydroxybenzoate

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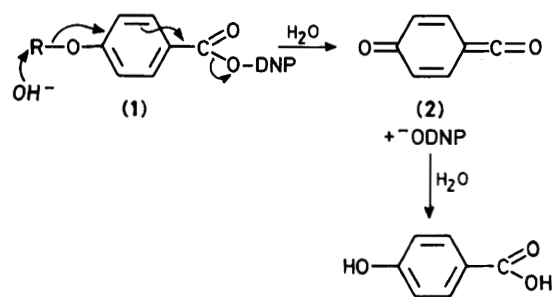
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A positive volume of activation is found for the hydrolysis of 2,4-dinitrophenyl 4-hydroxybenzoate, differentiating its mechanism from the $B_{Ac}2$ route used by other esters, all of which have negative values.

A unique mechanism for the hydrolyses of 4-hydroxybenzoate esters with good leaving groups has been proposed on the basis of non-linear Brønsted-type plots of rates against the pK of the phenol displaced.^{1,2} A mechanistic change is indicated from the $B_{Ac}2$ route, which is presumed to operate when the phenol is of low acidity, to a rate-determining elimination *via*

the oxoketene (**2**) when the phenol is of high acidity, for example, 2,4-dinitrophenol.

We have measured the effect of pressure on the rates of hydrolysis of the 2,4-dinitrophenyl esters of 4-hydroxybenzoic acid and of 4-methoxybenzoic acid. The latter is unable to undergo hydrolysis by the elimination route and so, hydro-



DNP = 2,4-dinitrophenyl.

lyses by the normal $B_{\text{Ac}2}$ mechanism. As with other examples of this type of reaction, the volume of activation is negative, $-14 \text{ cm}^3 \text{ mol}^{-1}$, inferred from the increase in rate with pressure. This is typical of an associative rate-determining step and the value of ΔV^\ddagger is similar to that for the base-promoted hydrolysis of ethyl acetate in aqueous acetone ($-13 \text{ cm}^3 \text{ mol}^{-1}$).³ By contrast, the rates of hydrolysis of the 4-hydroxyester decrease with pressure giving a positive volume of activation, $+12 \text{ cm}^3 \text{ mol}^{-1}$, typical of dissociative reactions, Table 1. This clearly points to a distinctive hydrolytic

Table 1. Rates of hydrolysis ($10^4 k_1/s^{-1}$) of 2,4-dinitrophenyl esters, (1).^a

p/bar	(1, R=H)	$\ln k_{\text{rel.}}$	(1, R=Me)	$\ln k_{\text{rel.}}$
1	7.05	0	8.38	0
300	6.40	-0.148	10.1	+0.199
600	5.17	-0.312	12.0	+0.371
900	4.37	-0.447	13.2	+0.466
$\Delta V^\ddagger \text{ cm}^3 \text{ mol}^{-1} (\pm 1)$	+12		-14	

^a Conditions: solvent, acetone-water (44.5:55.5 v/v); for (1, R=H) pH = 8.00, sodium tetraborate buffer, 28 °C; for (1, R=Me) pH = 10.3, sodium hydrogen carbonate buffer, 29.8 °C.

mechanism for the latter compound and strongly supports the interpretation of the earlier workers.

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References

- 1 S. Thea, G. Guanti, G. Petrillo, A. Hopkins, and A. Williams, *J. Chem. Soc., Chem. Commun.*, 1982, 1977.
- 2 S. Thea, G. Guanti, N. Kashefi-Naini, and A. Williams, *J. Chem. Soc., Chem. Commun.*, 1983, 529.
- 3 M. L. Tonnett and E. Whalley, *Can. J. Chem.*, 1975, **53**, 3414.