Evidence from Activation Volumes for an Eliminative Mechanism in the Hydrolysis of 2,4-Dinitrophenyl 4-Hydroxybenzoate
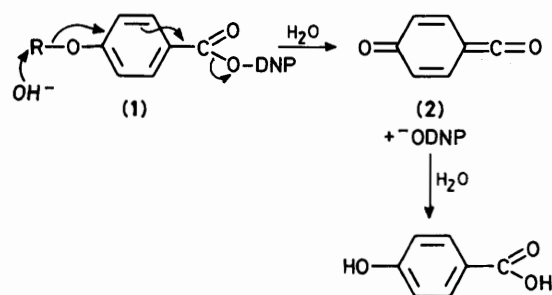
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A positive volume of activation is found for the hydrolysis of 2,4-dinitrophenyl 4-hydroxybenzoate, differentiating its mechanism from the $B_{Ac}2$ route used by other esters, all of which have negative values.

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.

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

p/bar	(**1**, R=H)	ln $k_{rel.}$	(**1**, R=Me)	ln $k_{rel.}$
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
$\Delta V^{\ddagger}$ cm^3 mol^{-1} (±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.

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

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.