SHORT COMMUNICATION

## SOLVOLYSIS OF SOME BENZYLIC AND NON-BENZYLIC TERTIARY p-NITROBENZOATES. A NEW Y_{BnOPNB} SCALE

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A new Y scale for the correlation of solvolytic reactivities for benzylic p-nitrobenzoates was established based on rate data for 2-phenyl-2-adamantyl p-nitrobenzoate, and from which the solvent assistance in the solvolysis of tert-cumyl p-nitrobenzoate is suggested.

It has been generally considered that different Y scales based on 1- or 2-adamantyl derivatives should be used for substrates with different leaving groups in the correlation analysis of solvolytic reactivities.[1] However, no Y scale for p-nitrobenzoate esters has ever been developed, presumably owing to the very low reactivity of 1-adamantyl p-nitrobenzoate. Although an excellent correlation with Y_{OTs} was found in the solvolysis of diarylmethyl p-nitrobenzoates in aqueous trifluoroethanol and aqueous ethanol ($R = 0.998$),[2] the correlation in the case of 1-(1-methyl-2-pyrrolyl)-2,2,2-trifluoroethyl p-nitrobenzoate was not as good ($R = 0.986$).[3] Recently we demonstrated the necessity of using a new Y scale, Y_{BnCl}, based on 2-aryl-2-chloroadamantanes, for benzylic chlorides, in which the delocalization of the cationic transition state was significant.[4] A search for an appropriate reference standard for p-nitrobenzoate esters is then also desirable. We now report the development of a new Y scale based on 2-phenyl-2-adamantyl p-nitrobenzoate (1) for benzylic p-nitrobenzoates. Moreover, it suggests the possibility of solvent assistance in the solvolysis of tert-cumyl p-nitrobenzoate (2).

To avoid the possible intervention of a nucleophilic solvent in the case of a secondary substrate, representative tertiary derivatives 1, 2, 2,2-dimethyl-1-(4′-methyl)phenyl-1-phenyl-2-propyl p-nitrobenzoate (3)[5] and 1-methyl-1-cyclopentyl p-nitrobenzoate (4)[6] were studied. They were solvolyzed in a variety of solvents and the rates were monitored conductimetrically
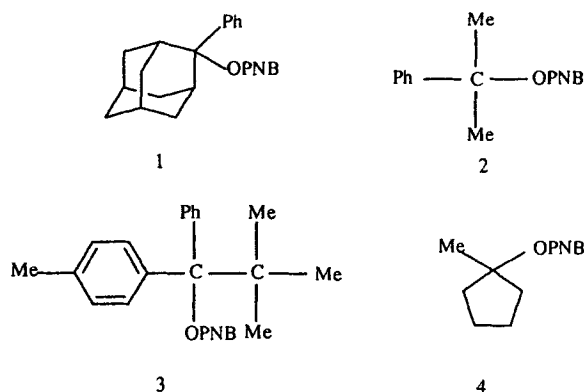
or, in a few cases, titrimetrically. Solvents of high acidity or of high water content were not used because of the experimental difficulty, such as low acidity of p-nitrobenzoic acid and low solubility of 1. Pertinent data are given in Table 1.

Correlation analyses with Y_{OTs}[1b] using the Grunwald–Winstein equation,[7] $\log k = mY$, showed dispersions (Figures 1 and 2) in the plots for 1 ($R = 0.931$), 2 ($R = 0.973$) and 3 ($R = 0.954$), the same as those observed for benzylic chlorides.[4] Only the non-benzylic substrate 4 gave a better linear relationship ($R = 0.988$). A new Y scale was therefore likely to be necessary for correlating the solvolytic reactivities of benzylic p-nitrobenzoates. Similarly to the case with Y_{BnCl},[4] a series of Y_{BnOPNB} values were calculated from the log k values for 1 and are listed in Table 1. Log k vs Y_{BnOPNB} plots for 2–4 are given in Figure 3.

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Table 1. Y_{BnOPNB} values and pertinent rate constants for 1–4[a]

Solvent[b]	$k(25\,^\circ C)^c\,(s^{-1})$				Y_{BnOPNB}
	1	2	3	4	
100E	$1\cdot63\times10^{-7}$	$1\cdot73\times10^{-8}$		$5\cdot87\times10^{-10}$	$-1\cdot36$
90E	$9\cdot96\times10^{-7}$	$1\cdot53\times10^{-7}$	$3\cdot48\times10^{-6}$	$2\cdot66\times10^{-9}$	$-0\cdot57$
80E	$3\cdot73\times10^{-6}$	$6\cdot38\times10^{-7}$	$1\cdot02\times10^{-5\,d}$	$9\cdot38\times10^{-9}$	$0\cdot00$
70E	$9\cdot66\times10^{-6}$	$1\cdot72\times10^{-6}$	$2\cdot48\times10^{-5\,d}$	$3\cdot11\times10^{-8}$	$0\cdot41$
80A	$3\cdot05\times10^{-7}$	$7\cdot20\times10^{-8}$	$9\cdot81\times10^{-7}$	$2\cdot11\times10^{-9}$	$-1\cdot09$
70A	$1\cdot74\times10^{-6}$	$3\cdot01\times10^{-7}$	$3\cdot03\times10^{-6}$	$7\cdot48\times10^{-9}$	$-0\cdot33$
60A	$8\cdot56\times10^{-6}$	$1\cdot22\times10^{-6}$		$2\cdot74\times10^{-8}$	$0\cdot36$
100M	$1\cdot51\times10^{-6}$	$1\cdot92\times10^{-7}$		$1\cdot54\times10^{-9}$	$-0\cdot39$
90M	$6\cdot69\times10^{-6}$	$7\cdot14\times10^{-7}$		$6\cdot63\times10^{-9}$	$0\cdot25$
80M	$2\cdot02\times10^{-5}$	$2\cdot63\times10^{-6}$	$3\cdot69\times10^{-5\,d}$	$2\cdot32\times10^{-8}$	$0\cdot73$
100T	$1\cdot35\times10^{-3\,d}$	$1\cdot27\times10^{-5\,d}$	$1\cdot04\times10^{-3\,d}$	$1\cdot44\times10^{-7}$	$2\cdot56$
80T–20E	$1\cdot77\times10^{-4\,d}$	$2\cdot54\times10^{-6\,d}$	$2\cdot81\times10^{-4\,d}$	$3\cdot50\times10^{-8}$	$1\cdot68$
40T–60E	$4\cdot74\times10^{-6}$	$2\cdot33\times10^{-7\,d}$			$0\cdot10$
50H–50T	$1\cdot36\times10^{-2\,d}$				$3\cdot56$

[a] Average of at least two independent runs, with error within 2%.

[b] Abbreviations: A, acetone; E, ethanol; M, methanol; H, hexafluoroisopropanol; T, trifluoroethanol. The numbers denote volume percentage in the mixtures (mixtures with water except for the last three entries).

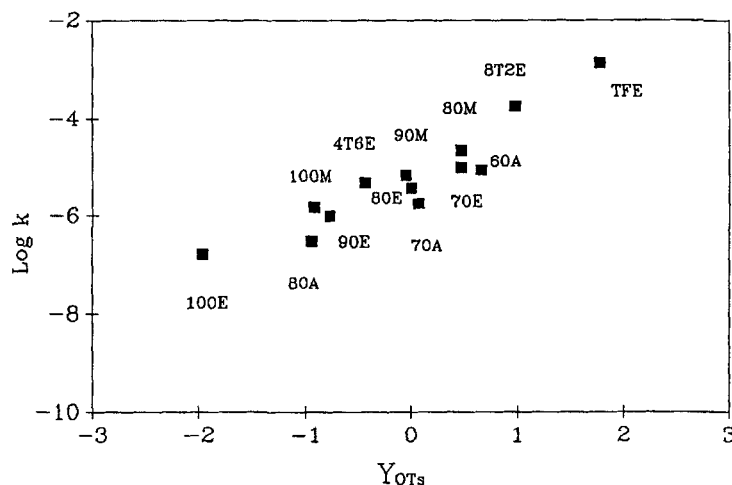[c] Extrapolated from other temperatures unless indicated otherwise.

[d] Measured at $25\,^\circ C$.

Figure 1. Plot of logarithms of rate constants for 1 versus Y_{OTs}. For abbreviations, see Table 1

The excellent linear log k vs Y_{BnOPNB} relationship ($R = 0\cdot995$) and the high m value ($0\cdot865$) observed for 3 support the validity of using this new Y scale in the study of solvolytic mechanisms for benzylic p-nitrobenzoates, because the involvement of solvent assistance is unlikely in the solvolysis of this bulky ester. With 2 the significant deviation from linearity ($R = 0\cdot940$) was obviously due to the depression of log $k(2)$ in ethanol–trifluoroethanol mixtures (closed circles in Figure 3), which might be interpreted by nucleophilic solvent assistance,[8] as has been observed in

the solvolysis of substituted $tert$-cumyl chloride.[4] The non-linear correlation ($R = 0\cdot918$) for 4 (closed triangles in Figure 3) indicates that this Y_{BnOPNB} scale is not suitable for non-benzylic p-nitrobenzoates.

For the non-benzylic p-nitrobenzoate 4, Y_{OTs} can be employed to display a linear correlation (Figure 2), although the leaving groups are different. It is probably due to the similarity of the two anions, p-nitrobenzoate and tosylate, in solvation. The general application of Y_{OTs} to non-benzylic p-nitrobenzoates is likely, but awaiting for further confirmation. The observed linear

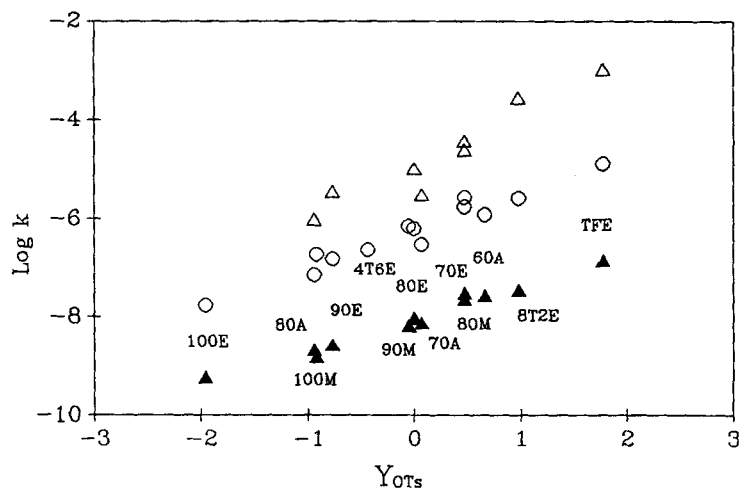Figure 2. Plot of logarithms of rate constants for ($\circ$) 2, ($\triangle$) 3 and ($\blacktriangle$) 4 versus Y_{OTs}. For abbreviations, see Table 1
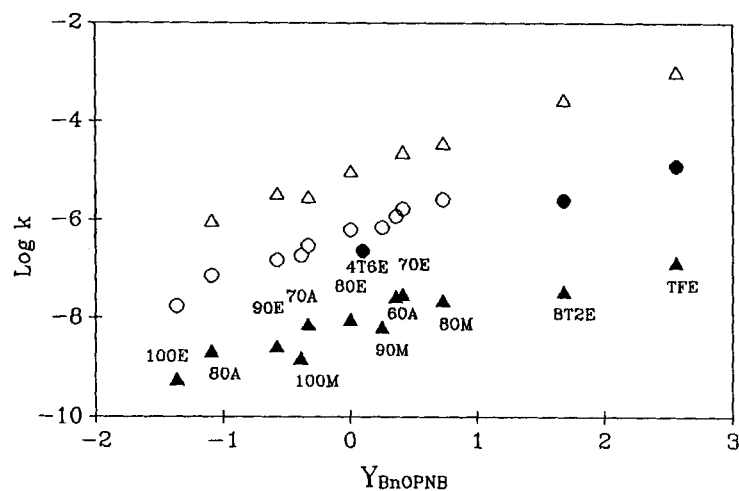
Figure 3. Plot of logarithms of rate constants for ($\circ$ and $\bullet$) 2, ($\triangle$) 3 and ($\blacktriangle$) 4 versus Y_{BnOPNB}. For abbreviations, see Table 1

log k vs Y_{OTs} plot for benzhydryl p-nitrobenzoate in ethanol–water and in trifluoroethanol–water[2] might be the result of the limited types of solvents examined.

This study suggests that significant delocalization of a cationic transition state may be detected by treating the rate data with suitable Y scales, Y_X or Y_{BnX}. Consequently, it might be used as an effective tool to elucidate the solvolytic mechanism for many systems. More work on this aspect and on the confirmation of nucleophilic solvent assistance is in progress.

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