## **Supporting Information**

for

## β-Hydroxy carbocation intermediates in solvolyses of

## di- and tetra-hydronaphthalene substrates

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This Supporting Information contains two items: The first is plots of log k versus  $Y_{OTs}$  for the solvolysis of substrates considered in the main manuscript to allow extrapolation of measurements in aqueous acetonitrile mixtures to pure water. The second is a table of rate constants arising from measurements of salt effects on the solvolysis reactions.

The only solvent parameter measured for acetonitrile water mixtures is  $Y_{OTs}$  [1,2]. This parameter was used to correlate kinetic measurements, therefore even though the leaving groups studied were chloride or trichloroacetate rather than tosylate. Indeed  $Y_{OTs}$  has only been measured in the range 0–60% acetonitrile. We extended this range by studying the solvolysis of 1-chloro-2,3-cyclohexene in both methanol

water mixtures and acetonitrile water mixtures. The measurements in aqueous methanol were correlated by the relationship log  $k = -1.34 + 1.123 Y_{OTs}$ , From measurements for the same substrate in aqueous acetonitrile, values of  $Y_{OTs}$  were inferred from the relationship  $Y_{OTs} = (\log k + 1.34)/1.123$  [3]. The derived values (-0.14, 80% MeCN; 0.44, 70% MeCN; 0.87, 60% MeCN; 1.40, 50% MeCN; 1.81, 40% MeCN; 2.21, 30% MeCN) were deemed satisfactory for extrapolating a value of log *k* for 1-chloro-1,2,3,4-terahydronaphthalene in pure water. Plots of log *k* versus  $Y_{OTs}$  for this substrate (filled circles) and for *trans*-1-trichloroacetoxy-1,2-dihdyronaphthalene (open circles) are shown in Figure S1. For the latter substrate directly measured values of  $Y_{OTs}$  were used, although values appropriate to solvents mixed by volume had to be interpolated from measurements recorded for solvent mixtures made up by weight. The equations for the two correlations are log  $k = -2.93 + 1.045 Y_{OTs}$  for the 1-chlorotetrahydronaphthalene. Rate constants in water were interpolated by taking  $Y_{OTs}$  for water as 3.9.



**Figure S1:** Plots of log *k* versus  $Y_{OTs}$  for solvolysis of 1-chloro-1,2,3,4-terahydronaphthalene (filled circles) and *trans*-1-trichloroacetoxy-1,2-dihdyro-naphthalene (**10**-*trans*, open circles) in acetonitrile water mixtures at 25 °C.

Salt effects on the solvolysis of *cis*-1-trichoracetoxy-2-hydroxy-1,2dihydronaphthalene. Table S1 lists measurements of rate constants for solvolysis in 80:20 (v:v) aqueous acetonitrile in the presence of varying concentrations of sodium perchlorate, sodium acetate, sodium azide and sodium trichloroacetate in the concentration range 0–0.8 M. The rate constant in the absence of added salt is  $6.75 \times 10^{-3} s^{-1}$ .

**Table S1:** First order rate constant (s<sup>-1</sup>) for the solvolysis of *cis*-1-trichoracetoxy-2hydroxy-1,2-dihydronaphthalene at different concentrations of added salts in 80% aqueous acetonitrile at 25 °C.

Concn	$10^3 k_{\rm obs}$	$10^3 k_{\rm obs}$	$10^3 k_{\rm obs}$	$10^3 k_{\rm obs}$
М	NaClO <sub>4</sub>	NaN <sub>3</sub>	NaOAc	NaOOCCCI <sub>3</sub>
0.2	7.39	7.61	7.94	5.85
0.4	7.90	8.21	10.7	4.75
0.6	8.10			4.12
0.8	8.44			

## References

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