A Maximum in a Grunwald–Winstein Plot for a Limiting S_N1 Solvolysis

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The Grunwald–Winstein *Y* values for acetone–methanol mixtures vary appreciably and in a uniform manner but the specific rates of solvolysis of 2-adamantyl perchlorate vary by less than threefold over a range of from 5 to 100% methanol content and a shallow maximum is observed.

Recently, it was reported[1] that the S_N2 solvolysis[2,3] of methyl perchlorate in aqueous acetone or aqueous dioxan exhibits a maximum in the Grunwald–Winstein plot. Methyl derivatives are good models for S_N2 solvolyses and, indeed, a *Q*-parameter scale[4,5] has been developed for situating the solvolysis mechanism for alkyl derivatives within a spectrum intermediate

Table 1. Specific rates of solvolysis of t-butyl chloride[a] and Grunwald–Winstein Y values for acetone–methanol mixtures at 25.0 °C.

MeOH (v/v)	10^7k_1 (s^{-1})[b]	Y
100	7.53[c]	−1.099
80	5.77 ± 0.15	−1.206
60	2.84 ± 0.06	−1.513
40	1.01 ± 0.02	−1.962
20	0.187 ± 0.012	−2.695

[a] [Bu^{t}Cl] = *ca.* 0.01 M. [b] With estimated standard deviations and all runs performed in duplicate. [c] From A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, 1956, **78**, 2770.

Table 2. Specific rates of solvolysis of 2-adamantyl perchlorate[a] in hydroxylic solvents at 0.0 °C.

Solvent[b]	10^6k_1 (s^{-1})[c]	Y[d]
CF_3CH_2OH[e]	610.3 ± 4.0	+1.045
MeOH	4.77 ± 0.14	−1.090
AcOH	(1.48)[f]	−1.675
EtOH	0.451 ± 0.011	−2.033
Pr^{i}OH	0.123 ± 0.003	−2.73
Bu^{t}OH	(0.071)[g]	−3.26

[a] [2-AdOClO$_3$] = *ca.* 0.005 M. [b] On volume–volume basis, 98% of indicated solvent plus 2% pentane. [c] With estimated standard deviations and all runs performed in duplicate. [d] From P. R. Wells, *Chem. Rev.*, 1962, **62**, 171, except for value for CF_3CH_2OH which is from V. J. Shiner, Jr., W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rapp, *J. Am. Chem. Soc.*, 1969, **91**, 4838. [e] 2% dioxan replacing 2% pentane. [f] Extrapolated value obtained from Arrhenius plot of four determinations at 17—42 °C. [g] Extrapolated value obtained from Arrhenius plot of three determinations at 26—50 °C.

Table 3. Specific rates of solvolysis[a] of 2-adamantyl perchlorate[b] in acetone–methanol mixtures.[c]

Methanol % (v/v)	10^6k_1 (25.0 °C)	10^6k_1 (0.0 °C)
100	227 ± 4	4.77 ± 0.14
90		5.12 ± 0.12
80	299 ± 5	5.96 ± 0.19
60	345 ± 4	
40	317 ± 2	
20	236 ± 2	
10	171 ± 3	
5	138 ± 2	

[a] In units of s^{-1} and with estimated standard deviations; all runs performed in duplicate. [b] [2-AdOClO$_3$] = *ca.* 0.005 M. [c] On volume–volume basis, solvent is 98% of mixture indicated plus 2% pentane.

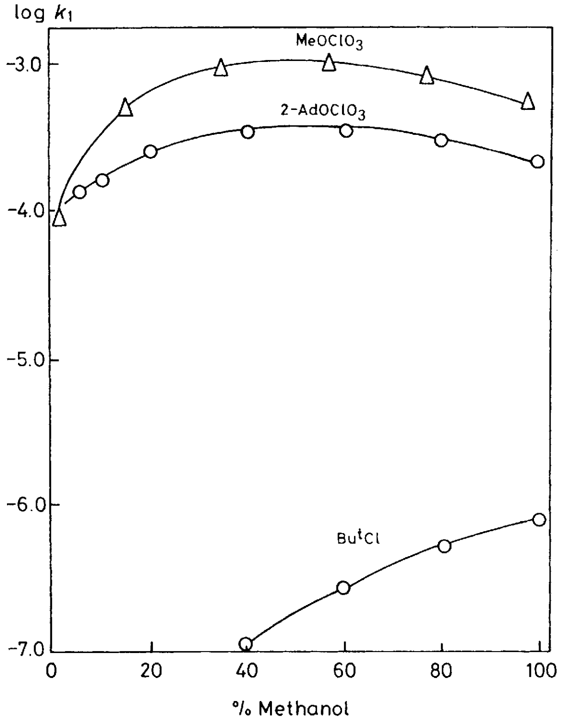

Figure 1. Solvolyses in acetone–methanol mixtures at 25.0 °C of methyl perchlorate (data from ref. 9), 2-adamantyl perchlorate, and t-butyl chloride.

between methyl derivatives and 2-adamantyl (2-Ad) derivatives, considered as limiting S_N1 substrates.[6]

Especially since 2-adamantyl methanesulphonate in aqueous acetone mixtures gives a shallow curve with gradually *increasing m* value,[7] it is of interest to see whether perchlorate esters exhibit a maximum in Grunwald–Winstein plots for solvolyses at the S_N1 mechanistic extreme. The 2-adamantyl perchlorate[8] was prepared by heterogenous reaction of 2-adamantyl bromide with silver perchlorate in pentane. Unfortunately, 2-adamantyl perchlorate (after transfer to dioxan) is of very limited solubility and very short half-life in solvents containing in excess of 50% water. However, it is soluble in all compositions of acetone–methanol mixtures, a system for which specific rates of solvolysis of methyl perchlorate have been reported.[9]

Methanol is considerably more polar than acetone as is indicated by higher E_T, Z, and log k_{ion} values[10] and Grunwald–Winstein Y values for acetone–methanol mixtures (Table 1) show the expected trend of decreasing value with increasing acetone content. As with the acetone–water system, a Grunwald–Winstein plot of the methyl perchlorate data[9] has a maximum, showing that the presence of water is not essential for this phenomenon to be observed.

The specific solvolysis rates (acid formation) for 2-adamantyl perchlorate in five hydroxylic solvents (Table 2) show the normal behaviour for a limiting S_N1 solvolysis with an m value of 0.989 ± 0.020 (standard error), inclusion of the t-butyl alcohol solvolysis (requiring a rather lengthy Arrhenius plot extrapolation) leads to a value of 0.941 ± 0.041. It is noteworthy that the acetolysis specific rate falls on the plot described by the alcoholyses; for 1-adamantyl toluene-*p*-sulphonate, the acetolysis rate[11] was faster than predicted based upon the alcoholyses.[12] Presumably, the specific electrophilic assistance for the perchlorate leaving group is less than that for toluene-*p*-sulphonate and comparable to that for the chloride of the standard substrate.

Surprisingly, the specific rates of solvolysis of 2-adamantyl perchlorate in acetone–methanol mixtures (Table 3) show characteristics very similar to those for methyl perchlorate (Figure 1). In the range of 5 to 100% methanol, there is a less than three-fold variation in specific rate with a shallow maximum in plots against either solvent composition or Y values. The specific rates with 100 and 20% methanol content are essentially identical, despite a difference in Y value of 1.6.

We are currently investigating 2-adamantyl perchlorate in other mixed systems in an attempt to rationalize this highly unusual behaviour for a solvolysis involving a substrate of a type universally accepted as a good model for limiting S_N1 character.

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