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THE MECHANISM OF SOLVOLYSIS OF METHYL PERCHLORATE IN HYDROXYLIC SOLVENTS: CALCULATION OF THE CAVITY TERMS

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Abstract. From standard Gibbs energies of transfer, corrected for cavity or nonelectrostatic effects, it is concluded that the solvolysis of methyl perchlorate takes place through a looser-than-usual S_N2 transition state with a charge separation of about 0.52 units.

A number of mechanistic proposals have been made for the hydrolysis of methyl perchlorate in water. The original S_N1 assignment by Koskikallio[1] does not seem to be in agreement with a number of experimental observations,[2-4] but there have been explanations both in terms of an ion-pair mechanism[4,5] and in terms of a traditional S_N2 mechanism in which the transition state is rather loose.[6] Thus Abraham and McLennan[6] were able to rationalise the secondary isotope effect by suggesting that in the hydrolyses of methyl halides and methyl perchlorate the nucleophile-to-substrate separation remained almost constant in the transition state, but that the methyl-to-perchlorate distance was greater than expected. Kevill and Adolf[7] have recently provided further experimental information by obtaining rate constants for the solvolysis of methyl perchlorate in several hydroxylic solvents. They observed a low Grunwald-Winstein m-value for the solvolysis (m=0.11 to 0.33, c.f. also ref. 4) and concluded that the solvolysis took place by a classical S_N2 mechanism. Having available rate constants and hence ΔG values for the solvolysis in water and alcohol solvents, we thought it might be instructive to apply our recent[8] method of analysis to the methyl perchlorate reaction.

It is necessary first to separate out the solvent effect on ΔG into initial-state and transition-state values through eqn. (1), where $\delta\Delta G = \Delta G$ (solvent) - ΔG (methanol), and ΔG°_t is the standard Gibbs energy of transfer of a given species from methanol to another solvent.[9] In view of the nature of methyl perchlorate, it is not practicable to determine the $\Delta G^\circ_t(\mathrm{MeOC\ell O_3})$ values experimentally. Fortunately, ΔG°_t values are available for

$$\Delta G^\circ_t(\mathrm{Tr}) = \Delta G^\circ_t(\mathrm{MeOC\ell O_3}) + \delta\Delta G \qquad (1)$$

nitromethane,[10] and so we used these as an approximation to the required values for methyl perchlorate and thence calculated the $\Delta G^\circ_t(\mathrm{Tr})$ terms, Table 1.

Table 1. Calculation of transition-state ΔG°_t values in the methyl perchlorate solvolysis in kcal $\mathrm{mol^{-1}}$ at 298 K

Solvent	Water	MeOH	EtOH	i-PrOH	t-BuOH
$10^4\ k/s^{-1}$ [a] :	17.4	6.80	3.42	1.87	1.29
$\delta\Delta G$:	-0.56	0.0	0.41	0.76	0.98
$\Delta G^\circ_t(\mathrm{MeOC\ell O_3})$ [b] :	1.04	0.0	0.16	0.33	0.32
$\Delta G^\circ_t(\mathrm{Tr})$:	0.48	0.0	0.57	1.09	1.30

[a] Values from ref. 7 except for water, ref. 4.

[b] Using values for nitromethane from ref. 10.

As we have pointed out before,[8-11] there is little that can be deduced from ΔG°_t values themselves, especially for transfers to and from water, because of effects associated with the size of the solute such as the creation of suitable cavities in the solvents. However, we have successfully used a number of methods for subtracting out the cavity or nonelectrostatic effects to leave the required effects due to the interaction of the solute with the solvent, ΔG_{INT}, or to electrostatic forces, ΔG_E, through eqns(2) and (3):[8]

$$\Delta G^\circ_t = \Delta G_{\mathrm{CAV}} + \Delta G_{\mathrm{INT}} \qquad (2)$$

$$\Delta G^\circ_t = \Delta G_N + \Delta G_E \qquad (3)$$

We calculate G_{CAV} by both scaled-particle theory (SPT) and by the method of Reisse, Moura-Ramos, and Sinanolgu (SRMR),[8] and from the known $\Delta G^\circ_t(Tr)$ values deduce the ΔG_{INT} term for the transition state. Similarly, we can obtain the ΔG_N values as before,[8] and then deduce ΔG_E for the transition state. In these calculations we took the molar volume and diameter of the transition state as 85 cm^3 mol^{-1} and 5.20 Å respectively, but calculations showed that these values are not critical. It is necessary also to calculate ΔG_{CAV} and ΔG_E values for a suitable model solute; since the perchlorate ion and iodide ion have very similar Gibbs energies of transfer from methanol to other hydroxylic solvents,[12] we used the known ΔG°_t values for the Me_4NI ion-pair[13] and then calculated by the same methods the ΔG_{CAV} and ΔG_E values for the ion-pair. Results are given in Table 2.

Table 2. Values of ΔG_{CAV} and ΔG_E for the methyl perchlorate transition state and the Me_4NI ion-pair in kcal mol^{-1} at 298 K

	SRMR		SPT			
Solvent	$\Delta G_{INT}(Tr)$	$\Delta G_{INT}(Me_4NI)$	$\Delta G_{INT}(Tr)$	$\Delta G_{INT}(Me_4NI)$	$\Delta G_E(Tr)$	$\Delta G_E(Me_4NI)$
Water	-7.49	-12.02	-2.77	-5.32	-3.02	-6.48
MeOH	0	0	0	0	0	0
EtOH	0.74	0.98	0.71	0.93	0.93	1.29
i-PrOH	1.75	2.34	1.49	2.20	1.63	2.33
t-BuOH	2.37	4.29	1.76	3.60	2.16	4.15

Plots of $\Delta G_{INT}(Tr)$ against $\Delta G_{INT}(Me_4NI)$, or similar plots in ΔG_E, yield good straight lines; the average value of the slopes of these lines, excluding the result for the SRMR calculations in water, is 0.52 which can be taken as a measure of the charge separation in the transition state. Comparison with the much higher average value found for the t-butyl chloride solvolysis transition state by the same methods (0.81)[8] indicates that the mechanism of the methyl perchlorate solvolysis is well away from the S_N1 end of the spectrum. However, the corresponding values for methyl halides are only about 0.30 units,[9,11] so that the methyl perchlorate solvolysis transition state is appreciably more polar. This seems to fit well with the suggestion of Abraham and McLennan[6] that the CH_3----$OC\ell O_3$ bond is longer than expected in the transition state, and we conclude that the methyl perchlorate solvolysis proceeds through a looser-than-usual S_N2 type transition state.

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