

TABLE 3

Constant-volume parameters of activation for the solvolysis of benzyl chloride in aqueous glycerol at 50 °C

Volume fraction glycerol	$10^6 \alpha^*$ deg ⁻¹	$T\alpha\Delta V^\ddagger/\kappa$ cal mole ⁻¹ ± ~100	$\Delta\Delta H_p^\ddagger$ cal mole ⁻¹ ± ~100	$T\Delta\Delta S_p^\ddagger$ cal mole ⁻¹ ± ~100	$\Delta U_v\Delta^\ddagger$ cal mole ⁻¹ ± ~140	$T\Delta\Delta S_v^\ddagger$ cal mole ⁻¹ ± ~140
0.0	458	-851				
0.05	460	-882	-157	-194	-126	-163
0.125	475	-962	-231	-327	-120	-216
0.25	490	-1027	-361	-565	-185	-389
0.50	557	-1392	-400	-880	+141	-339
0.75	543	-1501	-300	-1186	+350	-536

*From the data in ref. 5.

found here. If the possibility of a negative $\partial\Delta V^\ddagger/\partial p$ is ignored, the best line through Hynes, Golinkin, and Laidlaw's points agrees reasonably well with our value. The reason for the apparent discrepancy is unknown.

In order to calculate the constant-volume energy and entropy of activation according to the equations

$$\Delta U_v^\ddagger = \Delta H_p^\ddagger - T\alpha\Delta V^\ddagger/\kappa$$

$$\Delta S_v^\ddagger = \Delta S_p^\ddagger - \alpha\Delta V^\ddagger/\kappa$$

it is necessary to know the thermal expansivity α and the compressibility κ of the solvent. The thermal expansivity was obtained graphically from data in the literature (5). The compressibility was obtained from measurements in this laboratory (6) at 60 °C. These values were taken as appropriate for 50 °C; the compressibility of pure water at 50 °C is less than 1% smaller than that at 60 °C, and that of pure glycerol is about 4% smaller. The true values of $-T\alpha\Delta V^\ddagger/\kappa$ are therefore somewhat larger than the values in Table 3, but are probably within the claimed error. The constant-pressure parameters from ref. 1 and the constant-volume parameters derived from them are listed in Table 3.

Discussion

1. Activation Volume and its Solvent Dependence

The activation volume in water is similar to the values for the hydrolysis of methyl and isopropyl amides (3). The important contributions probably arise from an increase in the C—Cl bond length, a contraction due to a possible formation of a new C—O bond by incoming water, and a contraction of the solvent and the transition state caused by the increased electro-

static interaction with the solvent due to the electric moments of the transition state. There is no firm evidence about the relative values of the various contributions.

The activation volume does not change significantly with composition in the range 0 to 0.75 volume fraction glycerol in water. For the same reaction in ethanol–water (4) there is a large change of activation volume with solvent composition which appears to be largely caused by a change with solvent composition of the partial volume of the initial state (7). On the basis of the dipole-in-dielectric model of the transition state, no great change in the volume of solvation of the transition state is expected (8). In glycerol–water, the partial volumes of benzyl chloride and the transition state vary with solvent composition in the same way, and both may be almost independent of solvent composition.

2. Energy and Entropy of Activation at Constant Volume

The constant-pressure and constant-volume activation parameters are plotted in Fig. 3. There is a minimum in ΔH_p^\ddagger about 400 cal mole⁻¹ deep which is reduced to less than 200 cal mole⁻¹ in ΔU_v^\ddagger , and may even be zero. $T\Delta S_p^\ddagger$ decreases by about 500 cal mole⁻¹ from water to 75% v/v glycerol–water compared to a decrease of about 1200 cal mole⁻¹ for $T\Delta S_p^\ddagger$ under the same conditions.

The question must be asked "which is to be considered the more fundamental, the constant-pressure or the constant-volume parameters, or are they to be considered equally fundamental?" The dependence of the constant-volume parameters on the solvent can be readily understood in the terms used by Baliga and Whalley (2) for the solvolysis of benzyl chloride in ethanol–water.