Table I: Rate Constants for the Solvolysis of Benzyl Chloride in Water–Glycerol Mixtures

Vol % glycerol at 25°	10^6k, sec^{-1}								
	50.00°			59.78°			70.00°		
0.0	218.9	219.1		566.0	565.9		1442	1446	
5.0	206.7	207.1		534.7	535.8		1348	1342	
12.5	190.6	190.3		489.4	489.3		1231	1228	
25.0	162.7	162.7	162.0	415.4	415.5		1034	1038	
50.0	107.0	108.0	108.0	274.1	273.4	273.5	687.0	689.1	690.8
75.0	58.62	58.58		148.3	149.1	148.4	376.4	375.1	

capacitance–conductance bridge and digital readout. The range of conductance used was about 160–440 μmhos, and the measurement accuracy was increased by connecting to the bridge a reference conductance of about 300 μmhos so that the digital readout was then the conductance of the sample less the reference conductance. The readout covered the range −140 to +140 μmhos and could be obtained to 10 nmhos, or about 30 ppm of the change of conductance during a run. The bridge was calibrated against Sullivan and Griffiths nonreactive resistors and against resistors calibrated from time to time against an Anthony pattern Wheatstone bridge at 1 kcps. No corrections to the bridge readout were necessary. There is no doubt that this bridge greatly facilitates kinetic measurements by conductance, particularly if several conductance cells are used simultaneously, as they were in this work.

The conductances were converted to conductances at infinite dilution by means of the limiting law (for details see Baliga and Whalley[22]) and were analyzed by digital computer by the Guggenheim method using least squares. The deviations did not differ significantly from random, and the standard errors from internal consistency were about ±0.2%. The rate constants are summarized in Table I. At least two values were obtained at each temperature and solvent composition. The standard error from consistency between runs appears to be about ±0.2%.

The activation parameters in pure water, obtained by least squares from these results together with the values obtained by others, are given in Table II. The agreement is satisfactory.

Table II: Activation Parameters for the Solvolysis of Benzyl Chloride in Water at 60.00°

$\Delta H_p^{\ddagger}$, kcal mol^{-1}	$\Delta S_p^{\ddagger}$, cal deg^{-1} mol^{-1}	Ref
19.90 + 0.05	13.7 ± 0.16	*a*
19.80 ± 0.08	13.5 ± 0.25	*b*
20.12 ± 0.10	13.2 ± 0.3	*c*

[a] Reference 10. [b] R. E. Robertson and J. M. W. Scott, *J. Chem. Soc.*, 1596 (1961). [c] This work.

Since the main purpose of the work was to investigate the effect of solvent on the activation parameters rather than the activation parameters themselves, the measurements in aqueous glycerol were analyzed by plotting log (k_1/k_2) against $1/T$, where k_1 and k_2 are rate constants in pure water and in a mixed solvent, respectively, and alternatively T log (k_1/k_2) against T. The slopes and intercepts then give the change $\Delta\Delta H_p^{\ddagger}$ and $\Delta\Delta S_p^{\ddagger}$ of the enthalpy and entropy of activation directly according to the relation

$$\ln (k_1/k_2) = \Delta\Delta H_p^{\ddagger}/RT - \Delta\Delta S_p^{\ddagger}/R$$

The graphs of log (k_1/k_2) against $1/T$ are given in Figure 1 to indicate the reproducibility of the work. The values of $\Delta\Delta H_p^{\ddagger}$ and $\Delta\Delta S_p^{\ddagger}$ are listed in Table III, together with estimates of the standard error, and are plotted in Figure 2 with vertical bars showing the estimated standard error. The corresponding values for the solvolysis of benzyl chloride in ethanol–water mixtures obtained by Hyne, Wills, and Wonkka[10] are also plotted in Figure 2 for comparison.

Table III: Change with Solvent Composition of the Activation Parameters for the Solvolysis of Benzyl Chloride in Water–Glycerol

Vol % glycerol	$\Delta\Delta G_p^{\ddagger}$ ($\pm\sim 4$), cal mol^{-1}	$\Delta\Delta H_p^{\ddagger}$ ($\pm\sim 100$), cal mol^{-1}	$T\Delta\Delta S_p^{\ddagger}$ ($\pm\sim 100$), cal mol^{-1}	$10^6\alpha$ deg^{-1}
0				523
5.0	37	−157	−194	517
12.5	96	−231	−327	522
25.0	204	−361	−565	547
50.0	480	−400	−880	560
75.0	886	−300	−1186	540

3. Discussion

The effect of solvent on the activation enthalpy and entropy for the solvolysis of benzyl chloride in water–glycerol and water–ethanol mixtures at 60° are compared in Figure 2. The difference between the two

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[22] B. T. Baliga and E. Whalley *J. Phys. Chem.*, in press.

systems is striking. There is a minimum in the activation enthalpy about 400 cal mol^{-1} deep in water–glycerol contrasted with one about 1700 cal mol^{-1} deep in water–ethanol. There is no minimum but only a steady decrease in $T\Delta S_p^{\ddagger}$ in water–glycerol, compared with a minimum of about 2700 cal mol^{-1} in water–ethanol. Furthermore, Figure 3 shows that the high enthalpy–entropy compensation in the region of the minimum in water–ethanol is greatly reduced in water–glycerol.

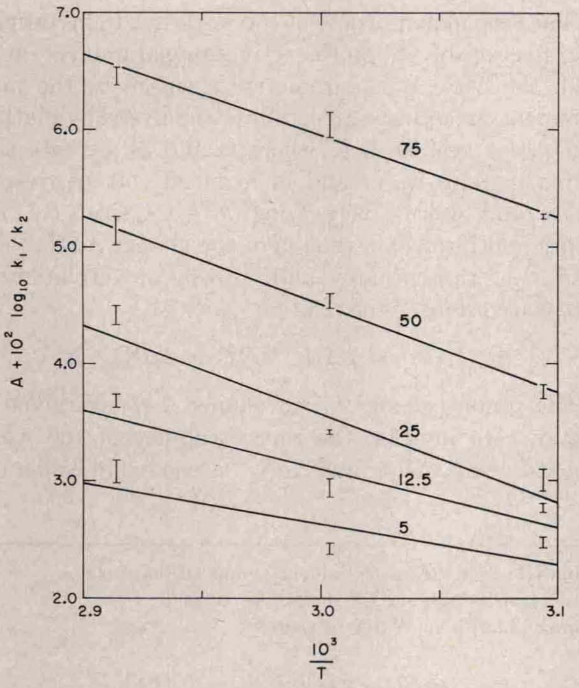

Figure 1. Graphs of log (k_1/k_2), where k_1 and k_2 are rate constants in pure water and a mixed solvent, respectively, against $1/T$. The numbers attached to the curves are the volume per cent at 25° of glycerol. For 5% glycerol, $A = 0.0$; 12.5%, $A = 0.033$; 25%, $A = 0.100$; 50%, $A = 0.270$; 75%, $A = 0.520$.

It is not easy to associate this difference with anything but the relative variations in the thermal expansivity with solvent composition. In the first place, glycerol and ethanol are chemically similar, and solvation dependent on chemical properties should not differ greatly. In the second place, the static dielectric constants are 24 and 42, respectively, at 25° and so they would tend to solvate by multipole-dielectric energies in a similar way. Furthermore, neither the chemical properties nor the dielectric constants of the pure organic components seems to be a major factor, as the activation parameters vary in acetone–water, dioxane–water, and ethanol–water in similar ways.[6,10]

The observed variation in the activation parameters is closer to that for the constant-volume parameters for water–ethanol mixtures[21] than to the constant-pressure parameters. This strongly suggests, according to the argument in the next to the last paragraph in the Introduction, that the constant-volume parameters are more appropriate than the constant-pressure parameters for a fundamental understanding of this reaction in these solvents. Furthermore, the measurements appear to confirm that the minimum in the constant-pressure enthalpy and entropy is at least partly connected with the large variation of the thermal expansivity of the water–organic solvent mixtures with composition. Presumably, the greater the thermal expansivity, the greater the reduction of solvating power when the temperature is increased at constant pressure. A monotonic fall in the solvating power with increasing organic content, combined with a constant-volume energy that at a low organic content is almost independent of composition but that rises ever more steeply as the organic content increases,[19] explains the observed minima. It is of course quite possible that

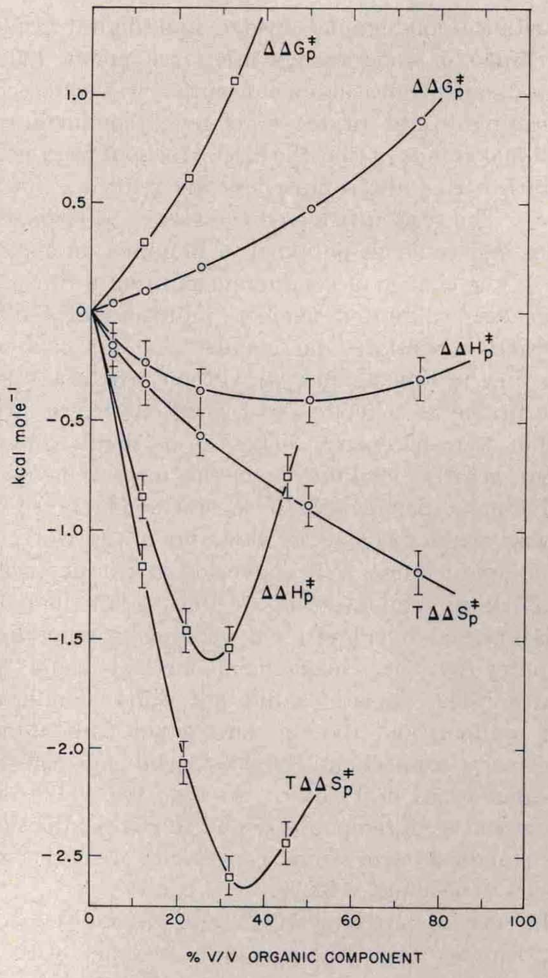

Figure 2. Comparison of effect of solvent composition on the constant-pressure activation enthalpy and entropy for the solvolysis of benzyl chloride in water–glycerol and water–ethanol:[10] ○, water–glycerol; □, water–ethanol.