TABLE 5. Activation volume parameters for the solvolysis of benzyl chloride in aqueous t-butyl alcohol as a function of temperature

Mol fraction t-BuOH	ΔV_0^* (ml mol^{-1})		
	40.00 °C	50.25 °C	60.50 °C
0.0000	-9.09 ± 0.01	-9.9 ± 0.1	-10.3 ± 0.2
0.0250	-10.07 ± 0.06	-13.0 ± 0.1	-15.20 ± 0.04
0.0500	-21.54 ± 0.05	-24.7 ± 0.6	-24.5 ± 0.05
0.1000	-24.7 ± 0.1	-23.97 ± 0.01	-23.1 ± 0.1
0.2000	-18.66 ± 0.06	-20.22 ± 0.03	-22.03 ± 0.04
0.3000	-19.8 ± 0.5	-19.5 ± 0.2	-20.71 ± 0.01

Mol fraction t-BuOH	$(\partial \Delta V^*/\partial P)_T \times 10^3$ (ml atm^{-1} mol^{-1})		
	40.00 °C	50.25 °C	60.50 °C
0.0000	0.2 ± 0.2	-0.3 ± 0.2	-0.6 ± 0.2
0.0250	1.27 ± 0.04	2.09 ± 0.02	2.36 ± 0.01
0.0500	4.92 ± 0.06	6.4 ± 0.4	6.0 ± 0.5
0.1000	4.2 ± 0.1	4.12 ± 0.02	3.88 ± 0.06
0.2000	2.62 ± 0.03	3.21 ± 0.01	4.44 ± 0.07
0.3000	3.7 ± 0.3	3.15 ± 0.07	3.70 ± 0.02

cluded that for the solvolysis of benzyl chloride in aqueous alcohol mixtures the quadratic (eq. 7) gives the best representation of the data. Nevertheless, it was considered necessary to recheck these expressions to determine which one gave a best fit for the present data. The linear eq. 6 was eliminated because of the obvious non-linear pressure dependence of ln k (see Fig. 3A). The constants A, B, and C in the other three equations were evaluated by fitting the 0.1 mol fraction alcohol rate data to each expression in turn using a computer programmed least mean squares technique. The deviations between ln $k_{(observed)}$ and ln $k_{(calculated)}$ for each equation were determined as previously reported (13). These deviations are shown in Fig. 3B as a function of experimental pressure for each of the three equations tested. Similar analyses were performed on all the rates at the several temperatures and solvent compositions employed. The deviations for the quadratic equation, when taken for all mol fractions of solvent, at all temperatures, were considered to be more random functions of pressure than those obtained by using the other two expressions. The standard deviations were smaller for the quadratic equation than for the other functions. On this basis the quadratic form was preferred to the other relationships.

A possibility which deserves consideration is whether or not the data could be better represented by a polynomial of higher than second order (see ref. 20). In view of the fact that most of the deviations shown in Fig. 3B are of the

same order of magnitude as the experimental uncertainty ($\pm 1\%$), the extension of the polynomial to powers higher than two seems unjustified in this particular instance.

Substitution of the quadratic expression (eq. 7) into eq. 5 produces eq. 10 and enables ΔV^* to be evaluated.

[5] $\qquad \Delta V^* = -RT (\partial \ln k/\partial P)_T$

[10] $\qquad = -RT \, \partial(A + BP + CP^2)/\partial P$

[11] $\qquad = -RT(B + 2CP)$

The volume of activation at atmospheric pressure (zero applied pressure) is therefore given by eq. 12.

[12] $\qquad \Delta V_0^* = -RTB$

The pressure dependence of ΔV^* is given by differentiation of eq. 11 with respect to pressure.

[13] $\qquad \partial \Delta V^*/\partial P = -2RTC$

The uncertainties in ΔV_0^* and $\partial \Delta V^*/\partial P$ were calculated using eqs. 14 and 15 respectively,

[14] $\qquad \delta \Delta V_0^* = -RT\delta B$

[15] $\qquad \delta \partial \Delta V^*/\partial P = -2RT\delta C$

where δB and δC are the uncertainties in the B and C coefficients of eq. 7 given by the least squares analysis. The values of ΔV_0^* and $\partial \Delta V^*/\partial P$ and their limits of uncertainty are shown in Table 5.

TABLE 6. The partial molal volume ($\overline{V}^g$) and partial molal heat of solution ($\Delta \overline{H}^g$) of the benzyl chloride initial state

Mol fraction t-BuOH	$\overline{V}^g$ (ml mol^{-1}) (50.25 °C)	$\Delta \overline{H}_s^g$ (kcal mol^{-1}) (25.0 °C)
0	115*	—
0.05	135.1±0.9	7.21±0.10
0.075	—	7.41±0.11
0.10	137.7±0.6	5.16±0.06
0.20	132.5±0.6	3.15±0.01
0.30	126.5±0.6	2.65±0.02

*Reference 4.

Enthalpies and Volumes of the Initial State

The partial molal volumes, $\overline{V}^g$, and the partial molal heats of solution, $\Delta \overline{H}_s^g$, of benzyl chloride in aqueous t-butyl alcohol mixtures are listed in Table 6. The values of $\Delta \overline{H}_s^g$ were determined at 25.0 °C (not 50.25 °C) to minimize solvolysis of the reacting solute. The determination of the solvent dependence of the partial molal heat of solution of the benzyl chloride transition state in the following section is therefore based on the difference between two enthalpies determined at two different temperatures. While this may have a small effect on absolute magnitude of the transition state enthalpies, it is unlikely to effect the general form of the solvent dependence.
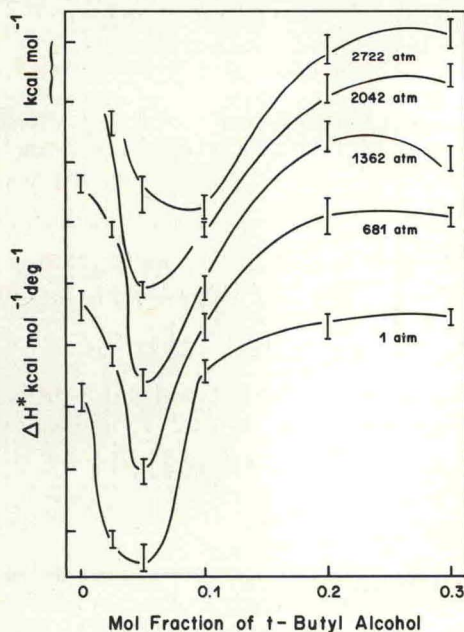
Discussion

The Temperature Derivatives of the Rate, ΔH^* and ΔS^*

The enthalpies and entropies of activation are plotted against binary solvent composition in Figs. 4 and 5 respectively. The main feature of both plots is the appearance of deep minima in the range 0.05–0.10 mol fraction t-butyl alcohol.

Arnett (21) has offered the most comprehensive explanation of this extremum behavior. For the solvolysis of t-butyl chloride in aqueous ethyl alcohol, Arnett was able to demonstrate that the minimum in ΔH^* was due, in large part, to the variation of the partial molal heat of solution of the *initial state* with solvent composition.

In Fig. 6 the solvent dependences of ΔH^*, at atmospheric pressure, and the partial molal heat of solution of the initial state ($\Delta \overline{H}_s^g$) across the same solvent composition range are compared for the solvolysis of benzyl chloride in aqueous t-butyl alcohol. This data permits the extraction of the solvent dependence of the enthalpy of the transition state, $\delta \Delta \overline{H}_s^t$, using eq. 16.

$$[16] \qquad \delta \Delta \overline{H}_s^t = \delta(\Delta H^* + \Delta \overline{H}_s^g)$$

The solubility of benzyl chloride in highly aqueous t-butyl alcohol was insufficient to permit measurement of $\Delta \overline{H}_s^g$ at compositions containing

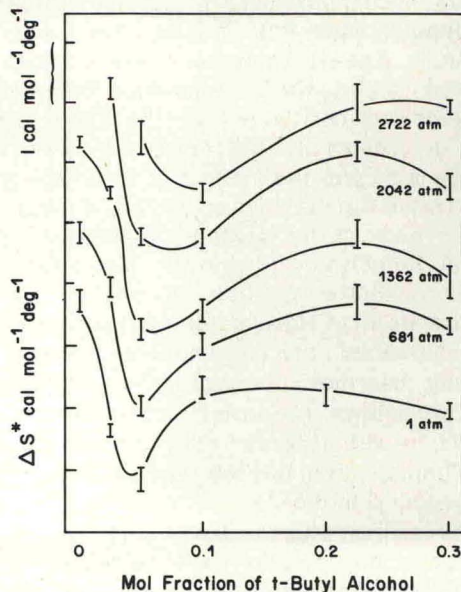FIG. 4. Solvent dependence of activation enthalpy at various pressures.

FIG. 5. Solvent dependence of activation entropy at various pressures.