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The Pseudo Thermodynamics of Solvolysis. A Detailed Study of the Pressure and Temperature Dependence of Benzyl Chloride Solvolysis in *t*-Butyl Alcohol – Water Mixtures

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The pseudo first order rate constants for the solvolysis of benzyl chloride in aqueous *t*-butyl alcohol (*t*-BuOH) are reported at 40.00, 50.25, and 60.50 °C at various pressures up to 4084 atm. From these data the first temperature derivatives (ΔH^* and ΔS^*), the first (ΔV^*) and second pressure derivatives, $\partial\Delta V^*/\partial P$, and the mixed second derivative, $\partial\Delta V_o^*/\partial T$, of the rate are evaluated. These activation parameters exhibit extremum behavior in the highly aqueous solvent region. This behavior is discussed in terms of solvent structure variation. The signs of the pressure dependence of ΔH^* and ΔS^* are shown to be consistent with those required by the Maxwell type relationships for classical thermodynamic systems.

Les constantes de vitesse du pseudo premier ordre pour la solvolysé du chlorure de benzyle dans l'alcool tertiobutyllique (*t*-BuOH) sont rapportées à 40.00, 50.25, et 60.50 °C pour différentes pressions supérieures à 4084 atm. A partir de ces données, les dérivées premières de la vitesse par rapport à la température (ΔH^* et ΔS^*), ses dérivées première (ΔV^*) et seconde par rapport à la pression, $\partial V^*/\partial P$, et sa dérivée seconde $\partial\Delta V_o^*/\partial T$ sont calculées. Ces paramètres d'activation montrent un comportement extrême dans la région des solvants fortement aqueux. Ce comportement est analysé en fonction de la variation de structure du solvant. On montre que les signes de ΔH^* et ΔS^* dépendant de la pression sont compatibles avec ceux requis par les relations du type relations de Maxwell pour des systèmes thermodynamiques classiques.

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Introduction

In recent years a number of researchers (1–3) have investigated the behavior of the first derivative pseudo thermodynamic activation parameters. Their efforts have demonstrated that many interesting phenomena are concealed in free energy parameters by the compensatory behavior of enthalpy and entropy. More recently the extremum behavior exhibited by ΔH^* and ΔS^* in aqueous binary solvent mixtures has been observed for the volume, ΔV^* , (4–6) and the heat capacity, ΔC_p^* , (7) of activation. The particular sensitivity of ΔC_p^* , the second derivative of the rate with respect to temperature, to variation of the binary solvent composition suggests that the parameter may be even more valuable than ΔH^* or ΔS^* for the investigation of solvent effects on reaction rates. This increased sensitivity of a second derivative parameter also prompts investigation of the second pressure derivative of the rate, $\partial\Delta V^*/\partial P$.

A major difficulty in understanding the solvent dependence of the various pseudo thermodynamic parameters has arisen because no single system has been examined exhaustively to obtain values

for all of the accessible activation parameters. Accordingly, it was decided to examine the solvolysis of benzyl chloride in *t*-butyl alcohol – water binary solvent mixtures with a view to determining ΔH^* , ΔS^* , ΔV^* , $\partial\Delta V^*/\partial P$, $\partial\Delta V^*/\partial T$, $\partial\Delta H^*/\partial P$, and $\partial\Delta S^*/\partial P$. A summary of the relationship between the various derivatives is demonstrated in Fig. 1. The ΔC_p^* value was not included in this study since the accurate determination of this parameter requires that the rate be measured at many more than the three temperatures used in this work.

The technique of dissecting the differential pseudo thermodynamic parameters of activation into their component initial and transition state parts has been previously employed (4, 8). In this study the enthalpy and volume of activation were so dissected by determining the partial molal enthalpies and volumes of solution of the initial state benzyl chloride as a function of binary solvent composition. Such dissections establish whether the initial state or transition state is primarily responsible for the observed behavior of the differential activation parameter.

The Maxwell relationships shown in eqs. 1 and

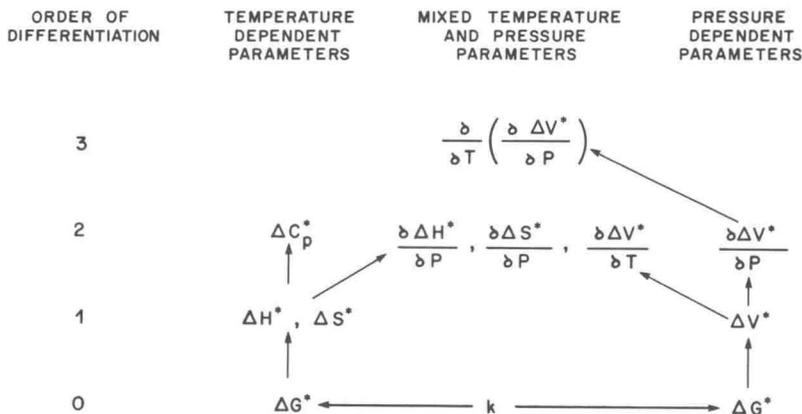


FIG. 1. Inter-relationship of pseudo thermodynamic parameters of activation.

2 can also be tested for a pseudo thermodynamic

$$[1] \quad (\partial \Delta S / \partial P)_T = -(\partial \Delta V / \partial T)_P$$

$$[2] \quad (\partial \Delta H / \partial P)_T = \Delta V - T(\partial \Delta V / \partial T)_P$$

system since the parameters $\partial \Delta S^* / \partial P$, $\partial \Delta V^* / \partial T$, $\partial \Delta H^* / \partial P$, and ΔV^* are available from the rate–pressure–temperature data.

The solvolysis of benzyl chloride in aqueous *t*-butyl alcohol solvent mixtures was chosen for this investigation for the following reasons. The solvolysis of benzyl chloride has been extensively investigated (4–6, 9–11) in other solvent media and a wide range of other activation parameters are available. The solvolysis reaction velocity is also convenient for the precision rate determinations required in second derivative rate studies. In addition, aqueous *t*-butyl alcohol solvent mixtures are known to display the most marked extremum behavior of any aqueous binary mixture both in activation parameters and other physical properties (12). Consequently, it was hoped that large changes in the parameters studied might be observed with variation of the composition of this aqueous binary.

Experimental

Kinetics

All rate constants were determined by following the change of conductance of the reaction mixture due to HCl formation as a function of time. With the exception of the conductivity cells, the high pressure apparatus and techniques employed in this work have been described previously (13). Some comments on the types of conductance cell employed are, however, justified. The three different types of conductivity cells which were used

to determine the reaction rates are illustrated in Fig. 2. For the majority of the slower reactions studied the cell shown in Fig. 2A was used. This cell had a capacity of about 10 ml. Occasionally during the course of a slow reaction the teflon rods moved to the end of the precision bore glass tubing and into the electrode compartment changing the cell characteristics and producing discontinuities in the rate data plots. In order to reduce the risk of this happening the cells shown in Fig. 2B were employed for the slowest reactions. These cells had the advantage of having a longer length of precision bore tubing and removed the danger of the pistons dropping into the cell compartment between the electrodes.

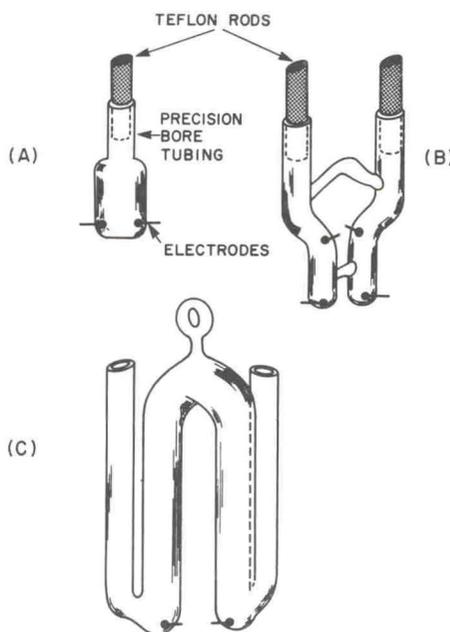


FIG. 2. Conductivity reaction cells.

TABLE 1. Rate constants for the solvolysis of benzyl chloride at 40.00 °C as a function of *t*-BuOH - H₂O solvent composition and pressure

Pressure (atm)	$k \times 10^5 \text{ s}^{-1}$		$k \times 10^6 \text{ s}^{-1}$		$k \times 10^7 \text{ s}^{-1}$	
	Mol fraction <i>t</i> -BuOH		Mol fraction <i>t</i> -BuOH		Mol fraction <i>t</i> -BuOH	
	0	0.025	0.05	0.10	0.20	0.30
1	7.538 ± 0.005	4.88 ± 0.04	15.27 ± 0.02	2.323 ± 0.004	6.150 ± 0.004	2.96 ± 0.06
341	8.33 ± 0.09	5.44 ± 0.02	21.68 ± 0.01	—	—	—
681	9.64 ± 0.03	6.28 ± 0.04	28.63 ± 0.05	4.528 ± 0.003	9.99 ± 0.02	4.75 ± 0.08
1021	10.74 ± 0.06	—	—	—	—	—
1362	12.3 ± 0.2	7.86 ± 0.10	43.6 ± 0.1	7.827 ± 0.007	15.49 ± 0.01	7.47 ± 0.06
2042	14.94 ± 0.08	9.76 ± 0.10	58.7 ± 0.4	11.8 ± 0.1	22.3 ± 0.1	10.52 ± 0.02
2722	18.86 ± 0.07	11.67 ± 0.06	74.3 ± 0.2	17.4 ± 0.1	29.8 ± 0.2	13.9 ± 0.2
3403	23.9 ± 0.3	—	—	—	—	17.7 ± 0.2
4084	—	—	102.2 ± 0.9	31.53 ± 0.35	51.98 ± 0.09	—

TABLE 2. Rate constants for the solvolysis of benzyl chloride at 50.25 °C as a function of *t*-BuOH - H₂O solvent composition and pressure

Pressure (atm)	$k \times 10^5 \text{ s}^{-1}$		$k \times 10^6 \text{ s}^{-1}$		$k \times 10^7 \text{ s}^{-1}$	
	Mol fraction <i>t</i> -BuOH		Mol fraction <i>t</i> -BuOH		Mol fraction <i>t</i> -BuOH	
	0*	0.025	0.05	0.10	0.20	0.30
1	21.35 ± 0.04	12.23 ± 0.06	38.4 ± 0.7	6.79 ± 0.06†	18.68 ± 0.02†	9.10 ± 0.05†
341	24.3 ± 0.1	14.67 ± 0.01	54.44 ± 0.06	—	—	—
681	28.1 ± 0.3	17.5 ± 0.1	69.8 ± 0.9	13.03 ± 0.03	32.3 ± 0.2	15.2 ± 0.3
1021	31.3 ± 0.2	—	—	—	—	—
1362	35.54 ± 0.01	22.3 ± 0.3	110.8 ± 0.4	21.1 ± 0.5	47.5 ± 1.3	22.1 ± 0.5
2042	46.6 ± 0.7	28.2 ± 0.2	155.9 ± 0.8	31.8 ± 0.4	70.6 ± 0.1	32.53 ± 0.08
2722	61.0 ± 1.1	35.5 ± 0.3	203 ± 2	44.5 ± 0.2†	95.0 ± 0.3	43.4 ± 0.1
4084	—	—	—	77.9 ± 0.3†	157 ± 1	69.2 ± 0.8†

*Temperature recorded for rates in pure water was 50.10 not 50.25 °C.

†Data taken from ref. 4.

The cell used for the fastest ($k = 10^{-3}$ to 10^{-4} s^{-1}) solvolysis reactions in pure water had a capacity of 25 ml and is shown in Fig. 2C. It was found that if the small cells were employed to measure the fast reaction rates, the differences in successive resistance values were close to zero after thermal and pressure equilibration had been attained. The larger cells, having a path length about 20 times greater than the smaller cells, were preferred because of the increased differences in successive resistance values and hence increased experimental sensitivity.

Duplicate kinetic runs carried out in the three different types of conductivity cells yielded rates which agreed within the maximum experimental uncertainty of $\pm 1\%$.

Enthalpy and Volume of Solution

The modified dilatometric technique employed in this study for the measurement of the partial molal volume (\bar{V}°) of the benzyl chloride as a function of solvent composition has been discussed previously (4). The partial molal heat of solution of the initial state, $\Delta\bar{H}_s^{\circ}$, was determined using the method described by Arnett and coworkers (8). As reported by Arnett, limited solubility of benzyl chloride in highly aqueous solvent systems precluded enthalpy determinations in this composition region.

Results

Rates

The pseudo first order rate constants for the solvolysis of the benzyl chloride (10^{-3} M maximum concentration) under various conditions of temperature, pressure, and solvent composition were obtained by analyzing the conductance-time data by the method of Guggenheim (14) using a computerized least mean squares calculation (13). Rate constants and associated uncertainties are presented in Tables 1–3. In all cases the rate constants are the average of a minimum of three duplicate runs. The deviations listed are the average deviations of the individual rate determinations from the mean value and in general represent an uncertainty of less than $\pm 1\%$. In some instances the rate vs. pressure data are incomplete; although it was desirable, it was not always possible to record rate data over the entire pressure range (1–4084 atm). The rate of reaction increased as the temperature and

TABLE 3. Rate constants for the solvolysis of benzyl chloride at 60.50 °C as a function of *t*-BuOH - H₂O solvent composition and pressure

Pressure (atm)	$k \times 10^5 \text{ s}^{-1}$		$k \times 10^6 \text{ s}^{-1}$		$k \times 10^7 \text{ s}^{-1}$	
	Mol fraction <i>t</i> -BuOH		Mol fraction <i>t</i> -BuOH		Mol fraction <i>t</i> -BuOH	
	0	0.025	0.05	0.10	0.20	0.30
1	58.75±0.08	30.3 ±0.1	92.1±0.5	18.88±0.1	53.56±0.01	26.1±0.3
171	62.5 ±0.1	—	—	—	—	—
341	66.4 ±0.7	36.88±0.09	130.9±0.5	26.3 ±0.3	—	33.5±0.1
511	71.5 ±0.3	—	—	—	—	—
681	74.9 ±0.4	45.0 ±0.2	170.7±0.9	33.96±0.08	89.7±1.5	42.5±0.5
851	81.09±0.09	—	—	—	—	—
1021	86.3 ±0.5	50.6 ±0.9	—	43.7 ±0.2	—	—
1191	94.3 ±1.1	—	—	—	—	—
1362	100.2 ±0.3	59.5 ±0.2	259.7±0.7	53.9 ±0.1	137 ±1	63.1±0.9
1532	106.7 ±0.1	—	—	—	—	—
1702	112.6 ±0.4	—	—	66.7 ±0.8	—	—
1872	122.6 ±1.5	—	—	—	—	—
2042	—	79.8 ±0.7	365 ±1	81.3 ±0.1	202.1±0.2	92.8±1.2
2382	—	—	—	97.75±0.08	—	—
2722	—	—	493 ±1	113.0 ±0.9	258 ±5	125 ±1
3062	—	—	—	128.9 ±0.2	—	—
3403	—	—	—	151.3 ±0.7	—	—
3742	—	—	—	173 ±1	—	—
4084	—	—	—	189 ±1	373 ±6	184.8±0.3

pressure increased, and consequently at the higher temperatures and pressures the rate could not always be measured with the conventional apparatus employed. For each system studied the rate was determined at a minimum of six pressures.

Golinkin *et al.* (4) have reported rate constants for the solvolysis of benzyl chloride in aqueous *t*-butyl alcohol mixtures at 50.25 °C. It will be noted that some of the data used here have been measured by Golinkin (5). The general effects studied by Golinkin *et al.* required less accurate data than was considered essential for this study. Consequently, if the uncertainty in Golinkin's rate constants was greater than ±1%, or if the data did not lie on a smooth $\ln k$ vs. pressure curve, it was redetermined in this study. In the majority of instances in which repetition was deemed necessary the data lay within the limits of uncertainty claimed by the earlier workers.

The solvolysis of benzyl chloride in 0.10 mol fraction of *t*-butyl alcohol at 60.50 °C was examined in considerable detail as a specific test of the adequacy of the rate-pressure relationship used in this work. The $\ln k$ vs. pressure plot for this system is shown in Figure 3A. Two important points should be noted. Firstly, this plot indicates that $\ln k$ is a smooth monotonic function of pressure. Secondly, because the uncertainties in

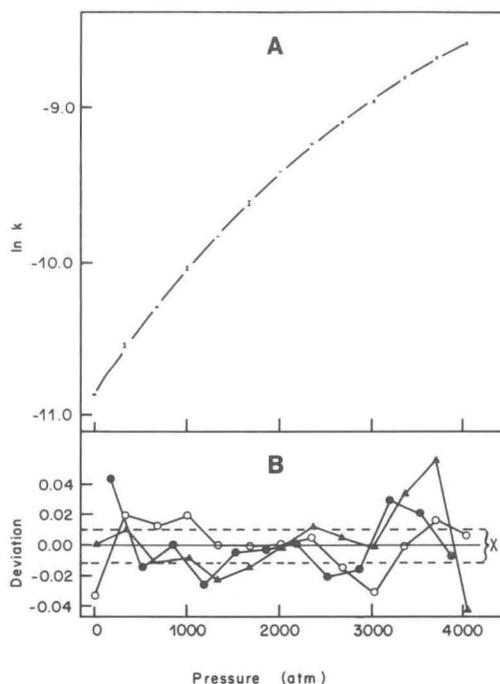


FIG. 3. Solvolysis of benzyl chloride in 0.10 mol fraction aqueous *t*-butyl alcohol at 60.50 °C. (A) Pressure dependence of rate ($\ln k$); (B) deviation between $\ln k_{\text{obs}}$ and $\ln k_{\text{calc}}$, for various expressions. ○, Quadratic; ▲, Benson-Benson; ●, incremental; ×, experimental uncertainty.

TABLE 4. Dependence of ΔH^* (ΔS^*) on pressure and solvent composition

Pressure (atm)	ΔH^* kcal mol ⁻¹ (ΔS^* cal deg ⁻¹ mol ⁻¹)†					
	Mol fraction <i>t</i> -BuOH					
	0	0.025	0.05	0.10	0.20	0.30
1	20.1±0.2 (13.1±0.7)	17.9±0.1 (21.4±0.4)	17.6±0.2 (24.6±0.7)	20.6±0.2 (18.7±0.6)	21.3±0.2 (19.1±0.6)	21.4±0.1 (20.1±0.4)
341	20.4±0.2 (12.2±0.6)	18.7±0.2 (18.3±0.5)	17.6±0.2 (23.9±0.7)	—	—	—
681	20.1±0.2 (12.7±0.7)	19.3±0.2 (16.2±0.6)	17.4±0.2 (23.8±0.7)	19.8±0.2 (19.9±0.7)	21.6±0.3 (17.1±1.0)	21.5±0.2 (18.7±0.5)
1021	20.5±0.2 (11.4±0.7)	—	—	—	—	—
1362	20.6±0.1 (10.8±0.1)	19.9±0.1 (14.0±0.4)	17.4±0.2 (22.9±0.6)	18.9±0.2 (21.7±0.7)	21.5±0.3 (16.7±0.9)	21.0±0.3 (19.8±0.9)
2042	—	20.6±0.2 (11.1±0.6)	17.9±0.1 (20.9±0.4)	18.9±0.1 (20.9±0.4)	21.7±0.2 (15.2±0.6)	21.4±0.3 (17.6±0.9)
2722	—	—	18.5±0.3 (18.3±1.1)	18.3±0.2 (22.0±0.6)	21.2±0.3 (16.0±1.1)	21.6±0.2 (16.3±0.5)
4084	—	—	—	17.5±0.1 (23.4±0.3)	19.3±0.3 (21.0±1.1)	—

†All entropies negative.

the rate determinations are extremely small, it is possible to establish with confidence the magnitude of the curvature in these plots, *i.e.* $\partial\Delta V^*/\partial P$.

The Enthalpy and Entropy of Activation

The enthalpies of activation used in this work were all calculated using eq. 3.

$$[3] \quad \Delta H^* = -R \left(\frac{\ln k_2/T_2 - \ln k_1/T_1}{1/T_2 - 1/T_1} \right)$$

The temperatures, T_2 and T_1 , in this case are 60.50 and 40.00 °C respectively. The extracted enthalpies of activation can then be associated with the mean temperature of 50.25 °C (15). The values obtained for ΔH^* in pure water are in excellent agreement with the results of other researchers (15–17). The uncertainties associated with each ΔH^* value listed in Table 4 are shown.

The entropies of activation used in this work were calculated by substituting the rate constant k at 50.25 °C, and the corresponding ΔH^* value into eq. 4, where k_b is Boltzmann's constant, and

$$[4] \quad \Delta S^* = R \ln k - R \ln k_b T/h + \Delta H^*/T$$

h is Planck's constant.

It should be noted that the hydrolyses in water were carried out at 40.00, 50.10 (not 50.25), and 60.50 °C. The difference between this intermediate temperature, 50.10 °C, and that at which ΔH^*

was calculated, 50.25 °C, is sufficiently small to render any correction insignificant compared with the experimental uncertainty.

The Volume of Activation

According to the transition state theory (18) the volume of activation, ΔV^* , for a reaction is related to the pressure dependence of the rate constant by eq. 5.

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

Before the evaluation of ΔV^* from a set of rate constants is possible, the functional dependence of $\ln k$ on pressure must be established. The four main algebraic expressions that have been employed are given by eqs. 6–9 (19).

$$[6] \quad \text{Linear: } \ln k = A + BP$$

$$[7] \quad \text{Quadratic: } \ln k = A + BP + CP^2$$

$$[8] \quad \text{Benson-Berson: } \frac{\ln k/k_0}{P} = A + BP^{0.523}$$

$$[9] \quad \text{Incremental: } \frac{\ln k_{n+1}/k_n}{P_{n+1} - P_n} = A + B \left(\frac{P_{n+1} + P_n}{2} \right)$$

Golinkin *et al.* (19) have examined the relative merits of these empirical equations, and con-

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

Mol fraction <i>t</i> -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 <i>t</i> -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 $\ln k_{(\text{observed})}$ and $\ln k_{(\text{calculated})}$ 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.

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

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

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

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

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

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

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

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

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

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

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 (\bar{V}^{\ddagger}) and partial molal heat of solution ($\Delta\bar{H}_s^{\ddagger}$) of the benzyl chloride initial state

Mol fraction <i>t</i> -BuOH	\bar{V}^{\ddagger} (ml mol ⁻¹) (50.25 °C)	$\Delta\bar{H}_s^{\ddagger}$ (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, \bar{V}^{\ddagger} , and the partial molal heats of solution, $\Delta\bar{H}_s^{\ddagger}$, of benzyl chloride in aqueous *t*-butyl alcohol mixtures are listed in Table 6. The values of $\Delta\bar{H}_s^{\ddagger}$ 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.

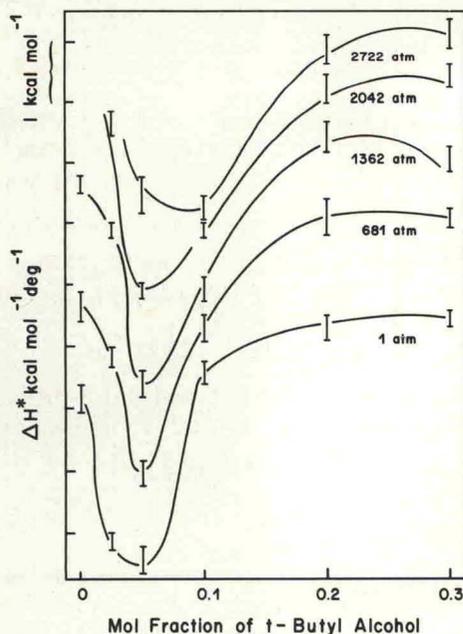


FIG. 4. Solvent dependence of activation enthalpy at various pressures.

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 ($\Delta\bar{H}_s^{\ddagger}$) 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, $\delta\Delta\bar{H}_s^{\ddagger}$, using eq. 16.

$$[16] \quad \delta\Delta\bar{H}_s^{\ddagger} = \delta(\Delta H^* + \Delta\bar{H}_s^{\ddagger})$$

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

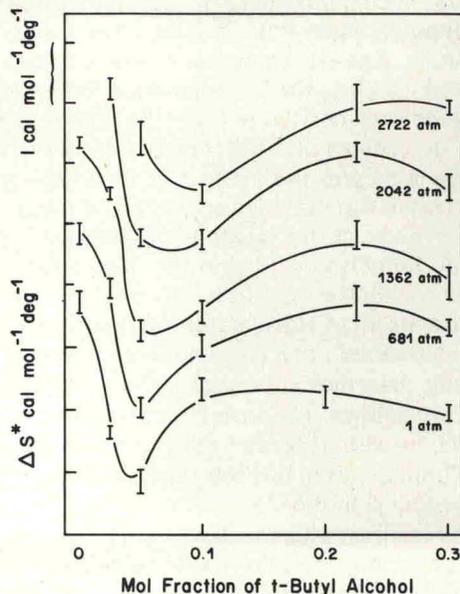


FIG. 5. Solvent dependence of activation entropy at various pressures.

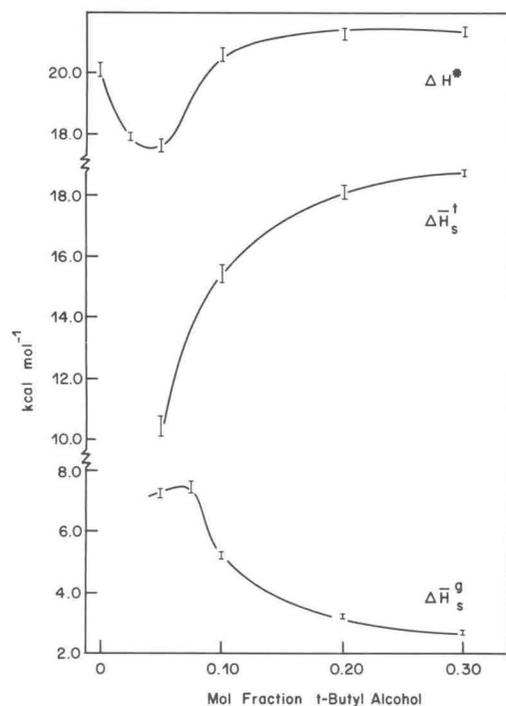


FIG. 6. Dissection of activation enthalpy. Solvent dependence of activation (ΔH^*) and initial ($\Delta \bar{H}_s^\ddagger$) and transition state ($\Delta \bar{H}_s^\ddagger$) enthalpies at 50.25 °C.

less than 0.05 mol fraction alcohol. For this reason one cannot be dogmatic about concluding that the extremum in ΔH^* is due to a corresponding extremum in the enthalpy behavior of the initial state $\Delta \bar{H}_s^\ddagger$. However, there is every indication in the limited data available at 0.05 and 0.075 mol fraction *t*-butyl alcohol that this may indeed be so.

In Figs. 4 and 5 the positions of minima in ΔH^* and ΔS^* appear to be pressure dependent and move to higher alcohol compositions as the pressure is increased. If the extremum in ΔH^* is due to the difference in the structure making and breaking abilities of the initial and transition states, as Arnett has suggested (21), then this observation is not surprising. The application of pressure itself is known to influence the structure of aqueous binary solutions (22) and hence presumably the additional structural influence of solute molecules, such as benzyl chloride, would be expected to vary with pressure.

The concurrent shift of the position of the extremum in ΔS^* is in keeping with the generally observed compensatory behavior of enthalpy

and entropy changes, but also suggests that the order-disorder phenomena which produce the observed extrema have their optimum effect at higher alcohol compositions at higher pressures.

The Pressure Derivatives of the Rate, ΔV^* and $\partial \Delta V^* / \partial P$

The volumes of activation obtained in this work are plotted against solvent composition in Fig. 7. The negative values of ΔV_0^* are characteristic for solvolyses of alkyl halides in aqueous binary solvents (4-6). The negative sign corresponds to increased electrostriction of the kinetically important immediate solvent environment around the more polar transition state compared with the initial state (23-25).

The volume of activation is defined by eq. 17 and thus can be "dissected" in a similar manner to enthalpy. Values of \bar{V}^\ddagger were calculated from

$$[17] \quad \Delta V_0^* = \bar{V}^\ddagger - \bar{V}^g$$

the measured values of ΔV_0^* and \bar{V}^g . The solvent dependences of these three parameters at 50.25 °C are shown in Fig. 8. It is apparent that the minimum in the behavior of the activation parameter, ΔV_0^* , is primarily, but not exclusively, the result of a maximum in \bar{V}^g rather than in the extremum behavior of the transition state volume, \bar{V}^\ddagger , as a function of solvent composition.

The extremum behavior of \bar{V}^\ddagger of benzyl chlo-

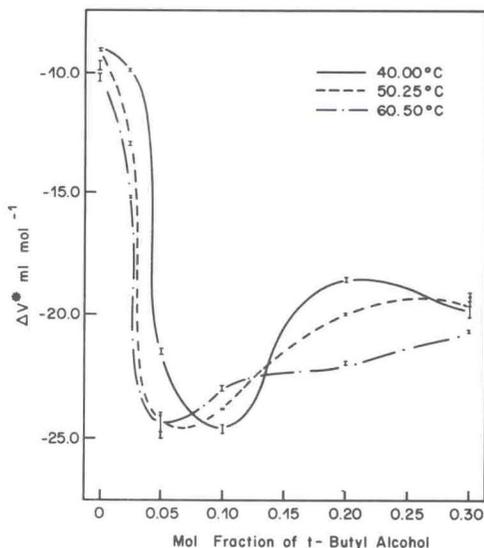


FIG. 7. Solvent dependence of activation volume at three temperatures.

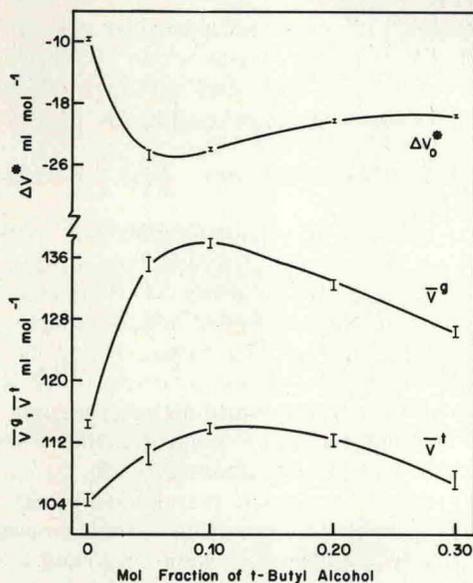


FIG. 8. Dissection of activation volume. Solvent dependence of activation (ΔV_0^*) and initial (\bar{V}^a) and transition state (\bar{V}^T) volumes at 50.25 °C.

ride in aqueous *t*-butyl alcohol is actually typical of several other non-electrolytes in aqueous alcohol mixtures. In aqueous ethyl alcohol, for example, benzyl fluoride, benzyl chloride and *p*-chloro benzyl chloride all pass through a maximum in \bar{V}^a near 0.3 mol fraction alcohol (26). These maxima occur at a solvent composition which has been suggested to possess minimum structuredness (27). If it is valid to draw an analogy between the behavior of the benzyl chloride initial state in aqueous ethyl alcohol and in aqueous *t*-butyl alcohol, then the maximum in \bar{V}^a in the latter solvent may indicate that the solvent possesses a minimum of structuredness at 0.1 mol fraction of alcohol. The observed minima in ΔV_0^* in the 0.05–0.10 mol fraction alcohol region would then be largely attributed to solvent structural changes.

Since 0.1 mol fraction *t*-butyl alcohol corresponds to 30% alcohol by volume it is hardly surprising that relatively little water-like open structuredness remains in such a binary and hence non-electrostricting solutes such as benzyl chloride must displace solvent molecules on dissolution resulting in a maximization of partial molal volume of solution.

In Fig. 7 it is apparent that an increase in temperature from 40.00 to 50.25 °C causes the

minimum in ΔV_0^* to move to a less alcoholic composition. Whether the further increase in temperature from 50.25 to 60.50 °C produces any further shift in the extremum is not conclusive. An increase in temperature also causes the minimum in the partial molal volume of *t*-butyl alcohol in aqueous *t*-butyl alcohol mixtures, $\bar{V}_{t\text{-BuOH}}$, to move to lower alcohol compositions (12). Since $\bar{V}_{t\text{-BuOH}}$ presumably reflects the solvent structure, the parallel effect of temperature on the extremum in ΔV_0^* and $\bar{V}_{t\text{-BuOH}}$ strengthens the argument that this activation parameter reflects solvent structural changes.

Figure 9 illustrates the effect of solvent and temperature variation on $\partial\Delta V^*/\partial P$ the second pressure derivative of the rate. The values of $\partial\Delta V^*/\partial P$ are generally positive and exhibit a pronounced maximum at about 0.05 mol fraction of *t*-butyl alcohol.

The pressure dependence of ΔV^* is defined by eq. 18. This dissection is analogous to the Arnett

$$[18] \quad \partial\Delta V^*/\partial P = \partial\bar{V}^T/\partial P - \partial\bar{V}^a/\partial P$$

et. al. (8) and Golinkin *et al.* (4) dissections of ΔH^* and ΔV_0^* respectively.

In pure water $\partial\Delta V^*/\partial P$ is approximately zero indicating that the partial molal volumes of the initial and transition states responded similarly to pressure, *i.e.* $\partial\bar{V}^T/\partial P \doteq \partial\bar{V}^a/\partial P$. This appar-

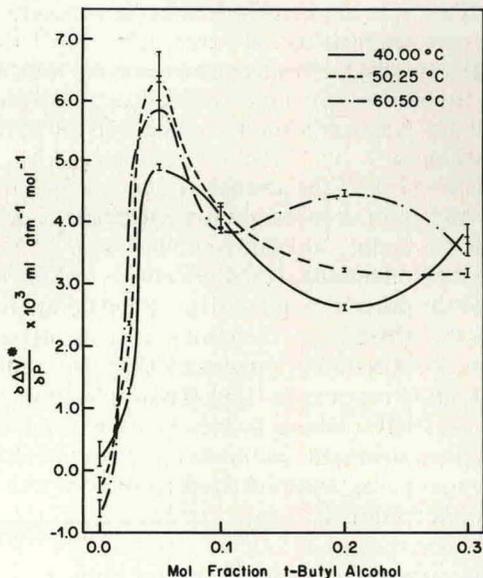


FIG. 9. Pressure dependence of activation volume as a function of solvent composition at three temperatures.

TABLE 7. The relative signs of $\partial\Delta V_0^*/\partial T$, $\partial\Delta S^*/\partial P$, $(\Delta V_0^* - T\partial\Delta V_0^*/\partial T)$ and $\partial\Delta H^*/\partial P$ at 50.25°C and atmospheric pressure

Mol fraction <i>t</i> -BuOH	ΔV_0^*	$-T\partial\Delta V_0^*/\partial T$	$\partial\Delta S^*/\partial P$	$\partial\Delta H^*/\partial P$	$(\Delta V_0^* - T\partial\Delta V_0^*/\partial T)$
0	-9.9	+20	+	+	+10
0.025	-13.0	+75	+	+	+60
0.05	-24.7	?	+	0	?
0.10	-24.0	-25	-	-	-50
0.20	-20.2	+50	+	+	+30
0.30	-19.5	?	+	0	?
		Maxwell relationship		Maxwell relationship	

ently equal "compressibility" of the transition state and initial state solvent shells is particularly interesting since it implies that the *electrostricted* solvent shell around the strongly dipolar transition state is no "harder" than the solvation shell around the initial state which presumably is primarily the result of *hydrophobic* type interactions.

Until experimental techniques are developed to enable the transition and initial state contributions to $\partial\Delta V^*/\partial P$ to be determined, any interpretation of the solvent dependence of this parameter is perhaps premature. It is nonetheless interesting to note that the compression of aqueous *t*-butyl alcohol passes through a minimum at 0.03 mol fraction alcohol (28), close to the composition possessing a maximum in $\partial\Delta V^*/\partial P$. This must surely be yet a further indication that the extremum behavior of these activation parameters primarily reflects changes in solvent structure.

The sharp extremum behavior of $\partial\Delta V^*/\partial P$, a *second pressure derivative* of the rate, for the solvolysis of benzyl chloride in aqueous *t*-butyl alcohol, is remarkably similar to the solvent dependence of the second temperature derivative of the rate, ΔC_p^* , for the solvolysis of *t*-butyl chloride in the same solvent mixtures as reported by Robertson and Sugamori (7). It would appear that the extremum behavior of such second derivative pseudo thermodynamic parameters of activation is both more pronounced and more complex than is the case for the corresponding first derivative parameters (ΔH^* , ΔS^* , ΔV^*) where single extrema of modest amplitude are more characteristic.

Mixed Temperature and Pressure Derivatives,

$$\partial\Delta S^*/\partial P, \partial\Delta H^*/\partial P, \text{ and } \partial\Delta V_0^*/\partial T$$

It should be recognized at once that the pa-

rameters under consideration in this section are second derivatives of the measured rate and are subject to the accumulated errors of rate, pressure, and temperature measurements. It is, therefore, hardly surprising that the errors associated with such mixed second derivatives are sizeable. The values shown in Table 7 should therefore be viewed primarily as indications of the sign of the parameter (*i.e.* the slope, positive or negative, of the plots in Figs. 10 and 11) with little significance being attached to the numerical values where these are shown.

The entropy and enthalpy of activation are plotted against pressure in Figs. 10 and 11. The plots indicate that both these activation parameters are pressure dependent and at some compositions the dependence is non-linear. This non-linearity presents difficulties in obtaining numerical values of the pressure dependence of the entropy, $\partial\Delta S^*/\partial P$, and the enthalpy, $\partial\Delta H^*/\partial P$. Because of these difficulties the signs, as obtained from the *initial* slopes of Figs. 10 and 11, but not the magnitudes of $\partial\Delta S^*/\partial P$ and $\partial\Delta H^*/\partial P$ are reported in Table 7.

Examination of Figs. 10 and 11 and also the signs in Table 7 reveals that the solvent dependence of $\partial\Delta S^*/\partial P$ and $\partial\Delta H^*/\partial P$ are very similar. This would tend to suggest that the well known compensatory behavior of ΔH^* and ΔS^* (27) is still in evidence when the second derivatives are compared. This is in fact to be expected. The differences in the intermolecular interactions, of the initial state and the transition state with the solvent environment, that resulted in the compensatory behavior of the first derivative parameters are still operative in the second derivatives.

The volumes of activation for the solvolysis of benzyl chloride in aqueous *t*-butyl alcohol mixtures were determined at 40.00, 50.25, and

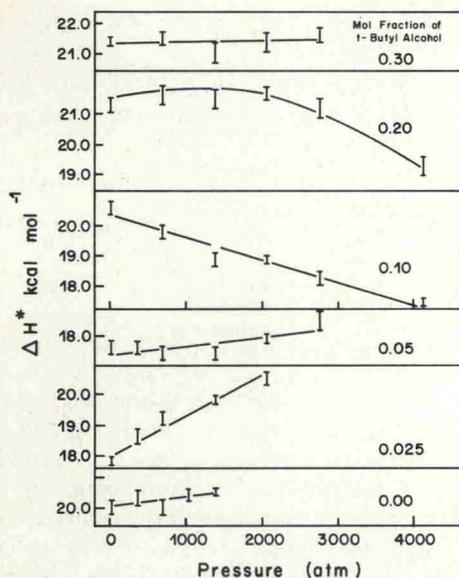


FIG. 10. Pressure dependence of activation enthalpy at various *t*-butyl alcohol mol fractions.

60.50 °C (Table 5). The temperature dependence, $\partial\Delta V_0^*/\partial T$, can thus be evaluated. Values of $\partial\Delta V_0^*/\partial T$ are not reported for 0.05 or 0.30 mol fraction of *t*-butyl alcohol since it appears that at these solvent compositions the dependence of ΔV_0^* on temperature is markedly non-linear. The values of $\partial\Delta V_0^*/\partial T$ obtained at other solvent compositions are listed in Table 7, and it is apparent that this second derivative of the rate is extremely sensitive to solvent composition changes.

The solvent dependence of $\partial\Delta V_0^*/\partial T$ is due to the different responses of the temperature dependence of the volume of the component initial and transition states to solvent changes. The solvent dependence of the initial and transition state contributions, and hence of the activation parameter itself, may well be a reflection of the changing structural stability of the solvent medium as cosolvent is added to water.

Maxwell Type Pseudo Thermodynamic Relationships

The availability of a large number of temperature and pressure derived pseudo thermodynamic parameters of activation for the single system examined in this work permits the application of classical thermodynamic identity tests to these "kinetic" parameters. In particular the following well established thermodynamic relationships

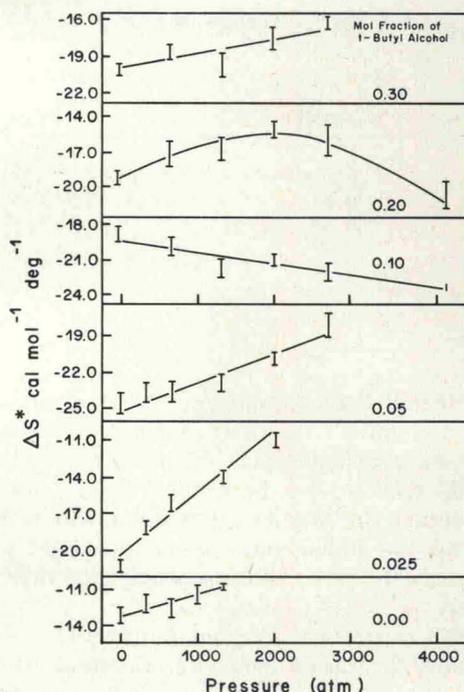


FIG. 11. Pressure dependence of activation entropy at various *t*-butyl alcohol mol fractions.

may be tested using the pseudo thermodynamic parameters obtained in this work.

$$[19] \quad (\partial\Delta S^*/\partial P)_T = -(\partial\Delta V^*/\partial T)_P$$

$$[20] \quad (\partial\Delta H^*/\partial P)_T = \Delta V^* - T(\partial\Delta V^*/\partial T)_P$$

The high experimental accuracy required to obtain meaningful values of the mixed second derivative parameters in eq. 19 has limited the testing of this identity to establishing that the parameters have indeed opposite signs in the case of the Menshutkin reaction (29) and some hydrolyses (30).

The present work offers the opportunity of examining this Maxwell relationship as a function of solvent composition. Unfortunately, as was noted above, the determination of a numerical value of $\partial\Delta S^*/\partial P$ was not possible. It was possible, however, to determine the sign of $\partial\Delta S^*/\partial P$. The signs of both $\partial\Delta S^*/\partial P$ and $\partial\Delta V_0^*/\partial T$ are shown in Table 7 and demonstrate again that these parameters have opposite signs as required by eq. 19.

The present data also enables eq. 20 to be tested. The numerical evaluation of $\Delta V_0^* - T\partial\Delta V_0^*/\partial T$ is shown in Table 7. Numerical values of $\partial\Delta H^*/\partial P$ could not be obtained but again its

sign should be determined. It is apparent, from the results listed in Table 7, that the signs of $\partial\Delta H^*/\partial P$ and $\Delta V_0^* - T\partial\Delta V_0^*/\partial T$ are in agreement with eq. 20.

Although it is not presently justifiable to extract numerical values which would permit rigorous checks of the validity of eqs. 19 and 20 for pseudo thermodynamic parameters, the agreement of signs obtained in these complex second derivative relationships serves to establish further the credibility and reality of the mixed second derivative parameters obtained from exhaustive examination of the temperature and pressure dependence of the rate of this solvolytic reaction.

Conclusion

(1) The extremum behavior exhibited by the activation parameters, as a function of solvent composition, holds clues to our understanding of kinetic solvent effects. Explanation of these extrema requires knowledge of both the initial and transition state solvent dependences.

(2) The extrema observed in ΔH^* , ΔS^* , and ΔV^* are also present in the second derivative parameters. These latter exhibit more pronounced extremum behavior and, as in the study of ΔH^* and ΔS^* behavior, may further aid our comprehension of these systems.

(3) The analogous behavior of the activation parameters and non-kinetic properties of the solvent itself indicate that the extrema in the former are related to solvent structure.

(4) The validity of Maxwellian type relationships in this pseudo thermodynamic system supports the application of real state thermodynamics to kinetic systems.

(5) The evaluation of a third derivative of the rate, the temperature dependence of $\partial\Delta V^*/\partial P$ is at present premature. Figure 9 suggests that $\partial\Delta V^*/\partial P$ is temperature dependent, but this dependence is small. This demonstrates that, in spite of the extreme accuracy of the data, still greater reproducibility will be necessary to permit the determination of third derivative pseudo thermodynamic parameters.

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