

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.

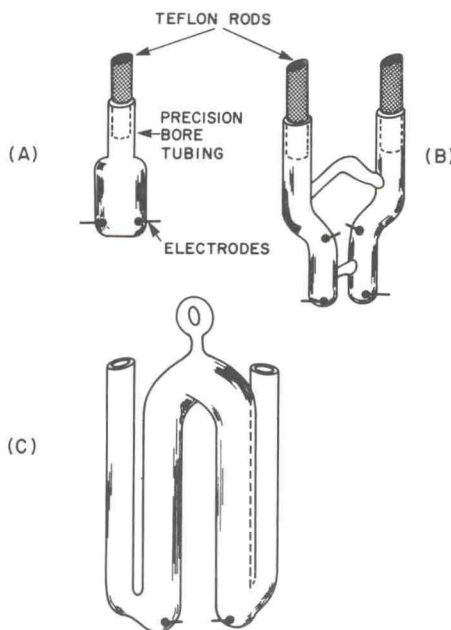


FIG. 2. Conductivity reaction cells.

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, $\Delta\bar{H}_s^*$, 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