

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

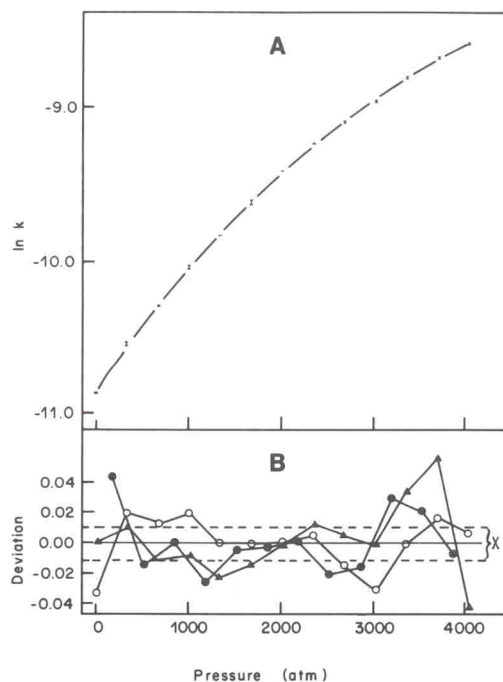


FIG. 3. Solvolysis of benzyl chloride in 0.10 mol fraction aqueous *t*-butyl alcohol at 60.50 °C. (A) Pressure dependence of rate ($\ln k$); (B) deviation between $\ln k_{\text{obs}}$ and $\ln k_{\text{calc}}$ for various expressions. ○, Quadratic; ▲, Benson-Benson; ●, incremental; ×, experimental uncertainty.

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-