TABLE 1

First-order rate constants (10^6 k/s^{-1}) for the solvolysis of benzyl chloride in aqueous glycerol at 50 °C

|	Composition, % v/v at 25 °C					
p/bar	0	5.0	12.5	25.0	50.0	75.0
1	219.6	207.5	190.7	163.1	108.3	58.82
	219.4	207.0	191.2	162.5	108.3	58.87
				163.1	108.7	
395	253.5	240.7	223.0	189.5	128.6	68.71
	255.5	240.4	220.2	187.2	125.4	68.40
	255.0	240.9				68.45
792	290.0	276.1	253.7	214.1	146.3	79.77
	288.4	272.2	252.4	214.2	145.8	78.65
		272.6			145.9	
1190	328.2	311.4	287.2	241.2	162.0	—
	329.8	312.5	289.7	239.1	164.0	
	327.0					
1590	361.2	347.7	319.7	270.0	179.6	103.7
	363.4	339.6	318.1	270.3	180.1	102.0
		345.9		263.6		103.2
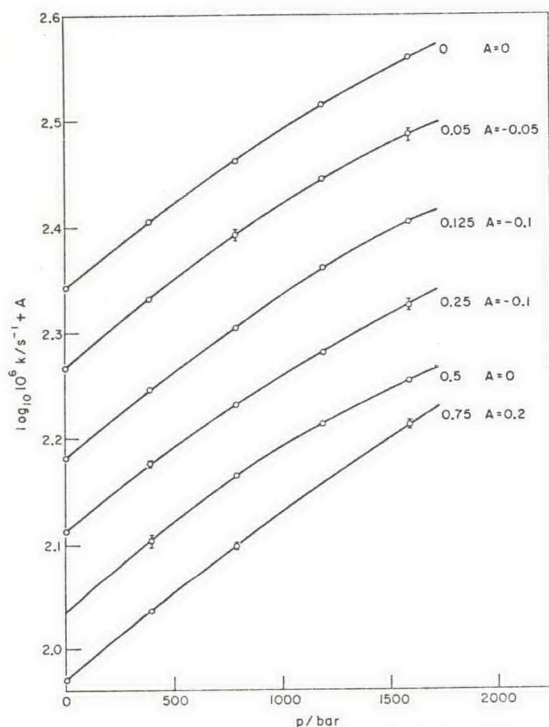
FIG. 1. Rate constants for the solvolysis of benzyl chloride in several glycerol–water mixtures at 50 °C and pressures up to 1.6 kbar. The numbers attached to the curves are the volume fractions of glycerol.

FIG. 2. Mean volumes of activation $\overline{\Delta V^{\ddagger}}$ [$=$ (RT ln $k_2/k_1)/(p_2 - p_1)$)] against $\frac{1}{2}(p_2 + p_1)$ for the solvolysis of benzyl chloride in glycerol–water at 50.0 °C. The numbers attached to the curves are the volume fractions of glycerol.

TABLE 2

Volumes of activation for the solvolysis of benzyl chloride in aqueous glycerol at 50 °C

	$\Delta V^{\ddagger}$
Volume fraction glycerol	cm³ mole⁻¹ $\pm \sim 0.4$
0.0	−10.7
0.05	−10.7
0.125	−10.8
0.25	−10.4
0.50	−11.0
0.75	−10.7

activation are summarized in Table 2. The accuracy appears to be about $\pm$ 0.3 or 0.4 cm³ mole⁻¹. The pressure variation of the activation volume is about 2.6 cm³ mole⁻¹ kbar⁻¹ for all solvents except perhaps 0.75 volume fraction glycerol, where it appears to be smaller.

The only activation volume for comparison is one by Hyne, Golinkin, and Laidlaw (4) who report −8 $\pm$ 1 cm³ mole⁻¹ in water at 50.25 °C, based on a least-squares fit of four rate constants to a quadratic of ln k in the pressure. Surprisingly, the pressure coefficient of the volume of activation in water was negative, that is, the activation volume became more negative with increasing pressure, in contrast to the positive values in aqueous ethanol, and the positive value in water

$-(RT \ln k_1/k_2)/(p_1 - p_2)$, where k_1 and k_2 are the rate constants at pressures p_1 and p_2, against the mean pressure and extrapolating to zero pressure. The plots are given in Fig. 2 and the volumes of
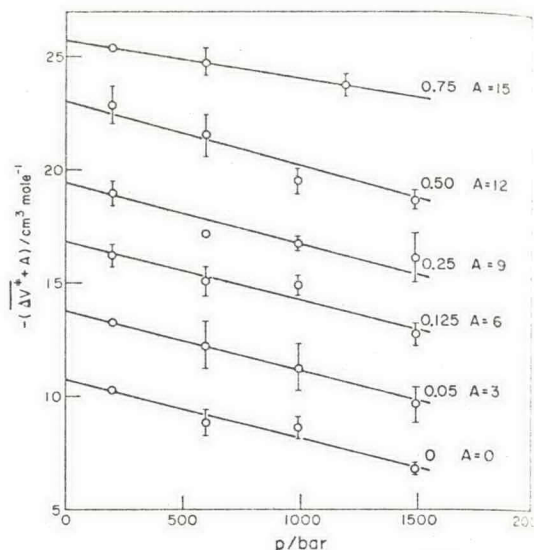
Constant

Volume fraction glycerol
0.0
0.05
0.125
0.25
0.50
0.75

*From th

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In order to energy and ent the equations

$$\Delta U_v^{\ddagger}$$

$$\Delta S_v^{\ddagger}$$

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I. Activation Vo
  Dependence

The activation values for the hy bromides (3). probably arise bond length, a formation of a ater, and a co ransition state