

TABLE 1

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

p/bar	Composition, % v/v at 25 °C					
	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
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

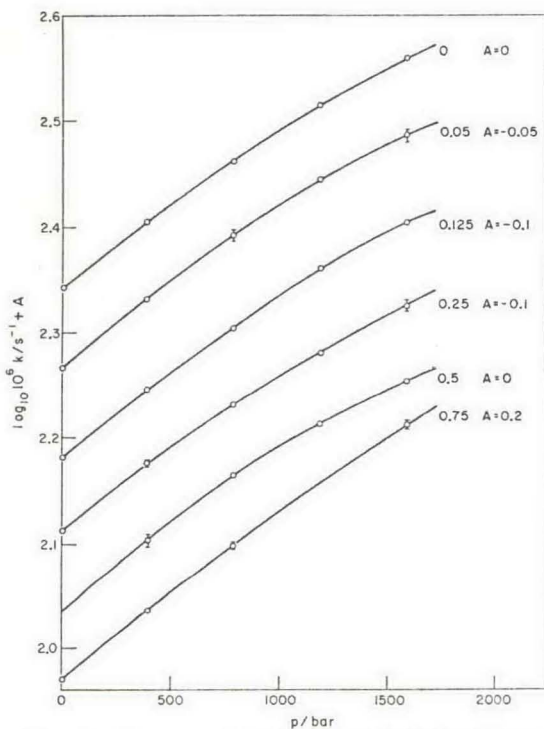


FIG. 1. Rate constants for the solvolysis of benzyl chloride in several glycerol-water mixtures at 50 °C and pressures up to 1.6 kbar. The numbers attached to the curves are the volume fractions of glycerol.

$-(RT \ln k_1/k_2)/(p_1 - p_2)$ , 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

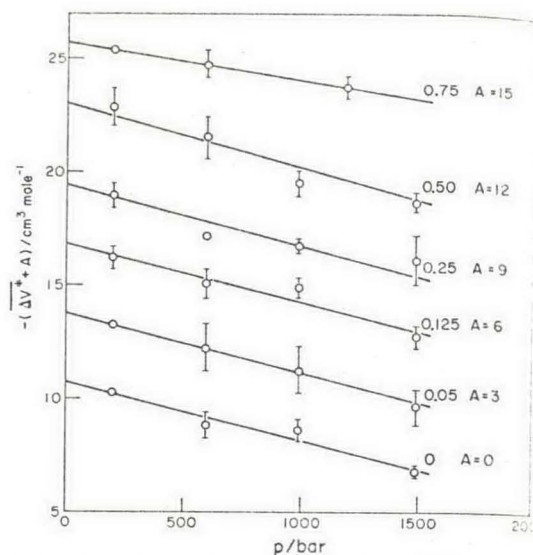
FIG. 2. Mean volumes of activation  $\Delta V^\ddagger$  [ $= (RT \ln k_2/k_1)/(p_2 - p_1)$ ] against  $\frac{1}{2}(p_2 + p_1)$  for the solvolysis of benzyl chloride in glycerol-water at 50.0 °C. The numbers attached to the curves are the volume fractions of glycerol.

TABLE 2

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

Volume fraction glycerol	$\Delta V^\ddagger$
	$\text{cm}^3 \text{ mole}^{-1}$ $\pm \sim 0.4$
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  $0.4 \text{ cm}^3 \text{ mole}^{-1}$ . The pressure variation of the activation volume is about  $2.6 \text{ cm}^3 \text{ mole}^{-1} \text{ kbar}^{-1}$  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  $-8 \pm 1 \text{ cm}^3 \text{ mole}^{-1}$  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

Constant

Volume fraction glycerol

0.0  
0.05  
0.125  
0.25  
0.50  
0.75

\*From the

found here. I  
 $\Delta \Delta V^\ddagger / \partial p$  is ign  
Golinkin, and I  
well with our v  
discrepancy is u

In order to  
energy and ent  
the equations

 $\Delta U_v^\ddagger$  $\Delta S_v^\ddagger$ 

it is necessary to  
and the compr  
thermal expans  
from data in t  
ibility was obt  
laboratory (6) a  
as appropriate  
pure water at 50  
that at 60 °C, an  
4% smaller. The  
therefore somev  
Table 3, but an  
error. The con  
ref. 1 and the  
derived from the

### 1. Activation Volume Dependence

The activation  
values for the hy  
bromides (3).  
probably arise f  
bond length, a  
formation of a  
water, and a con  
transition state c