The cyclization of 4-chlorobutanol in water was found by Heine *et al.*[13] to have a rate constant of $2 \cdot 87 \times 10^{-4}$ sec^{-1} at $70 \cdot 5°$. More recent measurements[14] at $50 \cdot 3°$ have shown a rate constant of $3 \cdot 60 \times 10^{-5}$ sec^{-1} in good agreement with our measurements at atmospheric pressure. Our values of ΔH^* and ΔS^* are in agreement with the earlier measurements.[13] The values of ΔV^* in Table 2 show that the acceleration by pressure is comparatively small and decreases with increasing pressure. The acceleration is greater in 50% by volume acetone/water and is much greater again in methanol.

The neutral hydrolyses of methyl bromide, ethyl bromide, and n-butylchloride in water are closely analogous to the cyclization reaction of CBL. The absolute rate constant for the reaction of methyl bromide was not determined because the initial concentration of methyl bromide was not known accurately. The relative values given in Table 1 should however be accurate as they were found by using the same solution at different pressures. Our rate constant for the hydrolysis of ethyl bromide is in good agreement with the results of Robertson *et al.*[15] The value of ΔV^* for the methyl bromide and ethyl bromide hydrolyses are very similar to the value of -14 ml/mole which can be derived from the measurements of these reactions by Strauss[16] in 80% by volume ethanol/water.

The rate constant found for the hydrolysis of benzyl chloride in 50% by volume acetone/water at 1 atm agrees with the value of $2 \cdot 2 \times 10^{-7}$ sec^{-1} extrapolated from the measurements of Bensley and Kohnstam[17] at higher temperatures. This reaction has recently been studied at several pressures in aqueous ethanol[18] containing up to $0 \cdot 4$ mole fraction ethanol. The volume of activation was found to vary between -17 and -23 ml/mole with change of solvent composition with a maximum at $0 \cdot 3$ mole fraction. The solvent used in our measurements contained $0 \cdot 20$ mole fraction of organic component (acetone) and ΔV^* was found to be the same as that found in aqueous ethanol of the same composition.[18] Although the reaction is classed as an S_N2 reaction,[19] it has some characteristics in common with S_N1 reactions and an unusually polar transition state has been postulated for it.[17] This is supported by the volume of activation which is comparable with that of the S_N1 hydrolysis of t-butyl chloride in the same solvent.

The rate constants for the hydrolysis of t-butyl chloride in 50% and in 92% by volume acetone/water ($0 \cdot 20$ and $0 \cdot 74$ mole fraction respectively) at atmospheric pressure agree with the values found by Winstein and Fainberg[20] at the lower concentration of acetone, and, by making a slight extrapolation, with those of Tommila *et al.*[21] at the higher concentration of acetone. The effect of pressure on this reaction

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TABLE 1

KINETIC MEASUREMENTS AT HIGH PRESSURES

Pressures at which the experiments were conducted are in atmospheres and are printed in **bold** numerals

Temp.	Constant	Results at Stated Pressures					
	(1) Cyclization of 4-Chlorobutanol in Water; $[CB]_0$ 0·01M						
	P (atm)	**1**	**500**	**1500**	**3000**		
39·8°	10^5k_1 (sec^{-1})	1·03	1·15	1·35	1·67		
49·7		3·26	3·54	4·54	5·62		
54·7		5·48	6·15	7·78	9·80		
59·6		9·95	10·7	12·8	16·7		
50	ΔH_p^* (kcal mole^{-1})	22·1	22·3	22·9	23·4		
50	ΔS_p^* (e.u.)	−13·8	−12	−9	−7		
	(2) Hydrolysis of n-Butyl Chloride in Water; $[Bu^nCl]_0$ 0·1M						
		1	**1000**	**2000**	**3000**		
25·0	10^8k_1 (sec^{-1})	1·5			2·8		
40·1		7·8					
45·0		12·9			25·2		
65·0		96·5	137	167	186		
	(3) Hydrolysis of Methyl Bromide in Water; $[MeBr]_0$ 0·001M						
		1	**700**	**1500**	**3000**		
30·0	$k_{1,P}/k_1$ (±1%)	1·00	1·51	1·96	3·03		
	(4) Hydrolysis of Ethyl Bromide in Water; $[EtBr]_0$ 0·05M						
		1	**1000**	**1700**	**2000**	**3000**	
30·0	10^6k_1 (sec^{-1})	5·85	8·53	10·2	11·1	13·6	
	(5) Cyclization of Chlorobutanol in Acetone/Water (50% v/v); $[CB]_0$ 0·05M						
		1	**500**	**1000**	**1500**	**2000**	**3000**
25·09	10^7k_1 (sec^{-1})	3·95	4·63	5·60	6·55	7·43	9·03
	(6) Neutral Hydrolysis of Benzyl Chloride in Acetone/Water (50% v/v); $[PhCH_2Cl]_0$ 0·05M						
		1	**1000**	**1500**	**2500**		
25·1	10^7k_1 (sec^{-1})	2·38	4·90	6·60	10·3		
	(7) Neutral Hydrolysis of t-Butyl Chloride in Acetone/Water (50% v/v); $[Bu^tCl]_0$ 0·05M						
		1	**470**	**1020**	**1330**		
25·0	10^7k_1 (sec^{-1})	2·37	3·20	4·36	5·1		
	(8) Neutral Hydrolysis of t-Butyl Chloride in Acetone/Water (90% w/w); $[Bu^tCl]_0$ 0·1M						
		1	**1000**	**1500**	**2000**		
50·0	10^7k_1 (sec^{-1})	5·90	12·6	15·9	18·9		
	(9) Cyclization of 4-Chlorobutanol in Methanol; $[CB]_0$ 0·1M						
		1	**1500**	**3000**			
25·0	10^8k_1 (sec^{-1})	1·92	4·92	7·75			
40·0		17·1	41·1	69·7			
49·7		70					
59·6		238					
	(10) Neutral Methanolysis of Ethyl Chloride in Methanol; $[EtCl]_0$ 0·5M						
		1	**850**				
60·0	10^8k_1 (sec^{-1})	2·56	6·11				
	(11) Neutral Methanolysis of t-Butyl Chloride in Methanol; $[Bu^tCl]_0$ 0·05M						
		1	**500**	**1500**	**3000**		
25·0	10^7k_1 (sec^{-1})	7·3	12·6	22·7	49·5		
50·0		210	370	805			
	(12) Cyclization of Bromobutylcatechol Monoether in Alkaline Methanol; $[BBCE]_0$ 0·01M, $[OCH_3^-]_0$ 0·05M						
		1	**450**	**750**	**1500**		
32·1	10^5k_1 (sec^{-1})	1·16	1·1	1·2	1·22		