

Structural Interpretation of Solvolysis of t-Butyl Chloride and t-Butyl Bromide in t-Butanol Based on Temperature and Pressure Dependence of Rate Constants

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Pressure and temperature effects on the rate constants of t-butyl chloride and t-butyl bromide in t-butanol have been studied over the intervals 1-1000 bar and 27-60°C, respectively. An exceptionally low absolute value of ΔV^\ddagger connected with a very high and negative ΔC_p^\ddagger is observed for t-butyl chloride, contrary to t-butyl bromide which presents much more common values for those functions.

Some conclusions are drawn in terms of solvent structure and its involvement in the transition state.

Thermodynamic analysis based on temperature and pressure dependence of rate constants are often used to interpret reaction mechanisms in solution. However, the usefulness of such analysis is dependent on both the sensitivity and discrimination of the resulting thermodynamic functions to structural and solvent changes between the initial and the transition states.

In a former paper, a very large and negative ($\Delta H^\ddagger, T$) variation was reported by us for the solvolysis of t-butyl chloride in t-butanol.¹ Such behaviour was explained in terms of a large and unexpected increase of solvation during the activated complex formation. The same point of view is reinforced by the simultaneous observation of a large loss of entropy of activation with increasing temperature which certainly reflects a restriction on the freedom of the solvent molecules at the transition state level.

A new and independent set of experiments concerning pressure effects on the rate constants of the same system is now presented. This permits discussion of the reaction mechanism in terms of the volume of activation, generally accepted as a highly discriminative parameter in the study of solvent involvement in this type of chemical system.^{2, 3} Rate constants of a similar system, t-butyl bromide in t-butanol, were also obtained for comparative purposes.

EXPERIMENTAL

An *in situ* conductimetric technique described previously was used to obtain rate constants at one atm.^{1, 4, 5} A high pressure technique has already been described by one of us.⁶ A conductivity cell support was internally attached to the pressure vessel head where the electrical leads pass through, as shown in fig. 1. It was not possible to extend our studies to pressures in excess of 1000 atm because of the high melting point of t-butanol and its large temperature coefficient.⁷ Gas chromatography, i.r. spectroscopy and refractometry were used to analyse t-butanol, t-butyl chloride and t-butyl bromide purity (B.D.H. AnalaR).

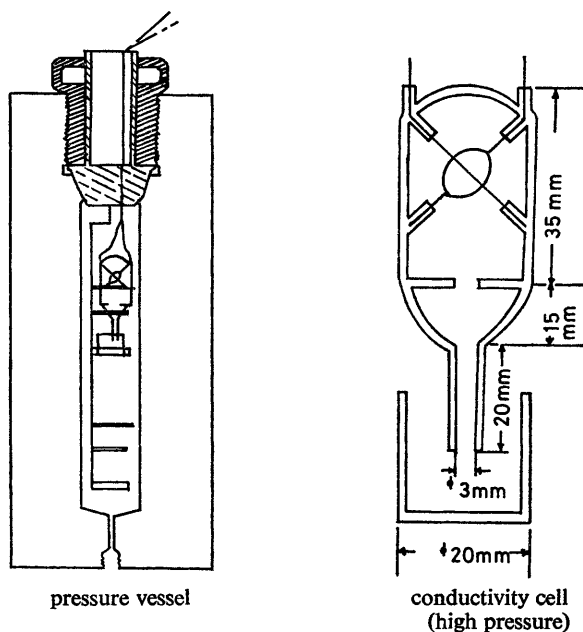


FIG. 1.—Pressure vessel and conductivity cell, showing fitting of conductivity cell in pressure vessel.

The solution preparation has been described previously.¹

The “time-lag” method^{8,9} was satisfactorily applied to obtain first-order rate constants and their standard deviations.

Typical equations, $\ln k = A X + B Y + C$, where A , B and C are constants and X and Y are either temperature or pressure dependent, were used to obtain different thermodynamic parameters. The Hynes-Robertson equation for $(\ln k, T)$ variation¹⁰ and a quadratic equation to study pressure effects on rate constants¹¹ were found to be adequate for our results. In a few cases, a linear relationship $(\ln k, P)$ was equally accurate. Correlation coefficients were always found to be better than 0.995. A Fortran program, REGPK : *** (Honey Bull), was used to solve the multiple linear regression. From the values of A , B and C parameters and their standard deviations (σ), the values of the thermodynamic functions of activation were obtained (table 1).

TABLE 1.—EQUATIONS RELATING RATE CONSTANTS WITH TEMPERATURE AND PRESSURE

$$\ln k = A_1/T + B_1 \ln T + C$$

$$\Delta H^\ddagger = R[(B_1 - 1)T - A_1]$$

$$\sigma(\Delta H^\ddagger) = R[T^2\sigma(B_1)^2 + \sigma(A_1)^2 - 2T \text{cov}(A_1, B_1)]^{1/2}$$

$$\Delta S^\ddagger = R[\ln h/k + B_1 + C_1 - 1 + \ln T(B_1 + 1)]$$

$$\sigma(\Delta S^\ddagger) = R[\sigma(C_1)^2 + (1 + \ln T)^2\sigma(B_1)^2 + 2(1 + \ln T) \text{cov}(B_1, C_1)]^{1/2}$$

$$\Delta C_p^\ddagger = R(B_1 - 1)$$

$$\sigma(\Delta C_p^\ddagger) = R\sigma(B_1)$$

$$\ln k = A_2P + B_2P^2 + C_2$$

$$\Delta V^\ddagger = -RT(A_2 + 2B_2P)$$

$$\sigma(\Delta V^\ddagger) = RT[\sigma(A_2)^2 + 4P^2\sigma(B_2)^2 - 4P \text{cov}(A_2, B_2)]^{1/2}$$

RESULTS AND DISCUSSION

Rate constants and activation functions for the two systems are shown in table 2 and 3. These results indicate an almost constant value of ΔG^\ddagger over the entire range of temperature and pressure. However, very different behaviour between the two systems is observed when the corresponding pressure and temperature derivatives are analysed. Contrary to observation on the t-BuCl-t-BuOH system, a relatively small and negative ΔC_p^\ddagger as well as a much smaller entropy change over the studied temperature interval was obtained for the t-BuBr-t-BuOH system. The pressure derivatives also show quite different behaviour for the two systems: ΔV_0^\ddagger varies from $-5 \text{ cm}^3 \text{ mol}^{-1}$ (t-BuCl) to $-23 \text{ cm}^3 \text{ mol}^{-1}$ (t-BuBr).

Such results certainly reflect different mechanisms of solvent involvement in those reactions to form the transition state. t-BuOH is a "globular" type solvent.¹² Its molecular radius is $\approx 3 \text{ \AA}$ while the sum of C—O plus O—H bond lengths is

TABLE 2.—SOLVOLYSIS OF t-BUTYL HALIDES IN t-BUTANOL

<i>T</i> /K	$\ln k^a \pm \text{dln } k^b$		$\Delta G^\ddagger \pm \text{d}\Delta G^\ddagger$ /kcal mol ⁻¹		$\Delta H^\ddagger \pm \sigma(\Delta H^\ddagger)$ /kcal mol ⁻¹		$\Delta S^\ddagger \pm \sigma(\Delta S^\ddagger)$ /cal mol ⁻¹ K ⁻¹	
(a) Solvolysis of t-BuCl (0.02 mol dm ⁻³) in t-BuOH at 1 atm.								
300	-12.40	0.32	24.96	0.19	26.4	0.9	+2	2
303	-11.90	0.18	24.91	0.11	24.5	0.7	-2	2
308	-11.45	0.05	25.06	0.03	21.2	0.5	-12	2
313	-10.84	0.00	25.09	0.00	17.9	0.3	-23	1
315	-10.57	0.04	25.09	0.03	16.6	0.3	-27	1
317	-10.43	0.06	25.16	0.04	15.2	0.3	-31	1
318	-10.37	0.02	25.20	0.01	14.5	0.3	-33	1
320	-10.27	0.00	25.30	0.00	13.3	0.3	-38	1
322	-10.08	0.04	25.35	0.02	11.9	0.4	-42	1
323	-10.06	0.02	25.41	0.02	11.3	0.4	-44	1
324	-10.00	0.01	25.45	0.01	10.6	0.5	-46	1
325	-9.99	0.02	25.53	0.02	10.0	0.5	-48	2
326	-9.91	0.02	25.56	0.01	9.3	0.6	-50	2
327	-9.83	0.02	25.58	0.01	8.6	0.6	-52	2
328	-9.75	0.03	25.61	0.02	8.0	0.7	-54	2
331	-9.70	0.01	25.82	0.01	6.0	0.8	-60	3
333	-9.68	0.02	25.97	0.01	4.7	0.9	-64	3
(b) Solvolysis of t-BuBr (0.02 mol dm ⁻³) in t-BuOH at 1 atm.								
300	-11.20	0.04	24.24	0.03	23.2	2.6	-4	8
303	-10.99	0.04	24.36	0.03	23.0	2.2	-4	7
308	-10.04	0.04	24.19	0.02	22.6	1.4	-5	4
313	-9.55	0.05	24.29	0.03	22.4	0.8	-6	2
318	-9.12	0.04	24.41	0.03	22.0	0.8	-7	2
323	-8.54	0.05	24.44	0.03	21.7	1.4	-8	4
328	-7.90	0.01	24.41	0.00	21.4	2.1	-9	6
333	-7.43	0.04	24.48	0.02	21.1	2.9	-10	8

$$\Delta C_p^\ddagger (\text{t-BuCl}) \approx -659 \text{ cal mol}^{-1} \text{ K}^{-1} \quad \Delta C_p^\ddagger (\text{t-BuBr}) \approx -61 \text{ cal mol}^{-1} \text{ K}^{-1}.$$

^a Mean value from four to eight experiments. ^b Maximum deviation from the mean value.

$\approx 2.4 \text{ \AA}$.¹³ This implies a large steric hindrance of the OH group which is actually confirmed by the small association by hydrogen bonding that t-BuOH shows in comparison with other alcohols. Nevertheless, there is some bidimensional association possibly due to cyclic polymerization.¹⁴

Considering ΔC_p^\ddagger values and $(\Delta S^\ddagger, T)$ variation, a much higher degree of solvation of the transition state is expected relative to t-BuCl. However, $\Delta V_0^\ddagger = -5 \text{ cm}^3 \text{ mol}^{-1}$ for t-BuCl seems to correspond to a small increase in the number of molecules

TABLE 3.—SOLVOLYSIS OF t-BUTYL HALIDES (0.02 mol dm^{-3}) IN t-BUTANOL (HIGH PRESSURE CONDUCTIVITY CELLS)

T/K	P/atm	t-BuCl				t-BuBr			
		$\ln k^a \pm \text{dln } k^b$		$\Delta V^\ddagger \pm \sigma(\Delta V^\ddagger)$ / $\text{cm}^3 \text{ mol}^{-1}$		$\ln k^a \pm \text{dln } k^b$		$\Delta V^\ddagger \pm \sigma(\Delta V^\ddagger)$ / $\text{cm}^3 \text{ mol}^{-1}$	
313	0			-5	1				
	1	-10.86	0.02	-5	1				
	99	-10.84	0.01	-5	1				
	197	-10.83	0.01	-5	1				
	395	-10.78	0.01	-5	1				
	494	-10.76	0.01	-5	1				
323	0			-5	1			-23	1
	1	-10.14	0.03	-5	1	-8.54	0.04	-23	1
	99	-10.12	0.01	-5	1				
	197	-10.12	0.04	-5	1	-8.40	0.03	-21	1
	296	-10.10	0.04	-5	1	-8.30	0.00	-19	2
	395	-10.07	0.01	-5	1				
	444					-8.22	0.02	-18	2
	494	-10.04	0.01	-5	1				
	543					-8.14	0.01	-16	2
	642	-10.01	0.02	-5	1	-8.08	0.02	-15	2
	790	-9.97	0.02	-5	1	-8.01	0.01	-13	3
	938	-9.95	0.06	-5	1	-7.93	0.04	-12	3

^a Mean value from four to eight experiments. ^b Maximum deviation from the mean value.

of solvent around the activated complex. According to former calculations made by one of us,² it must be, approximately, one extra molecule which can only be a consequence of a very small free volume associated with each solvent molecule. Having regard to the globular form of the solvent molecules and its small degree of association, we can assume that a structure of close-packing is adequate for t-BuOH. t-BuCl can easily enter either within the structural holes or in the middle of the polymeric associations; the same is not possible with t-BuBr due to its higher volume. Some extra work against the solvent structure has to be realized by these molecules as this work is endothermic in nature and will contribute positively to ΔC_p^\ddagger . Only then does solvation become possible, the solute-solvent intermolecular energy being smaller in the case of t-butyl bromide than in the case of t-butyl chloride due to the different charge development on the transition states.

Further work, based on $\Delta \bar{H}_s^\circ$ values, discriminates the influence of the solvent and of the temperature in the structure of the ground and transition states.¹⁵

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(PAPER 9/409)