Effect of Pressure on the Rates of Solvolysis. Hydrolysis of Some Sterically Hindered Chlorides

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The effect of pressure on the rates of solvolyses of substituted 1-phenylethyl and benzyl chlorides has been investigated in an ethanol–water mixture at 25 °C. The activation volumes have been calculated and the dependence of these values on the number and size of the substituents have been interpreted in terms of the competitive contribution of the steric inhibition of resonance and steric hindrance to solvation in the transition states.

The effect of hydrostatic pressure on the rates of solvolytic displacement reactions have been investigated by many research groups.[1–12] In general, the solvolyses of alkyl halides and arenesulfonates have negative activation volumes ascribable to the electrostriction of solvent molecules by the polar transition states. Attention has also been paid to the substituent dependence of activation volume.[7–12] In most cases, the activation volume was linearly related to the substituent constants, σ^+ and σ^*.[7,8,11] These observations were interpreted in terms of the degree of charge delocalization, taking into account the contribution of electrostrictive volume contraction, *i.e.*, the more the charge delocalizes in the transition state, the less negative the values of activation volume become.[7]

A further characteristic is the rate acceleration of sterically hindered reactions by pressure. It has been said that a more sterically hindered reaction revealed a more negative activation volume.[13,14]

The present investigation concerns the pressure effect on the hydrolysis rates of some substituted 1-phenylethyl and benzyl chlorides in order to elucidate the relationships between steric and pressure effect in solvolytic reactions.

Experimental

The high pressure apparatus has been described elsewhere.[7] The kinetic solvent was ethanol–water (80: 20, v/v) and all reactions were conducted at 25.00±0.02 °C, and followed conductimetrically under pressure. The initial concentration of the kinetic solution was approximately 0.01 mol per liter. Rate constants were calculated by the Guggenheim method[15] or by the first-order rate equation.[16]

Results and Discussion

Solvolyses of the substrates under pressure followed first-order kinetics. In the case of 1-arylethyl chlorides, plots of the logarithm of the rate constants against pressure showed linearity over the range of pressure employed. Accordingly, activation volumes were calculated by the following equation; $RT(\delta \ln k/\delta P)_T = -\Delta V_0^*$, where k is the rate constant and ΔV_0^* is the activation volume at atmospheric pressure and 25 °C. For trialkylbenzyl chlorides, plots of $\ln k$ against pressure revealed curvatures. In these cases the activation volume was calculated assuming the following second-order polynomial equation; $\ln k = a + bP + cP^2$ and the curves fitted using the least-squares method. Since the enthalpies and entropies of activation for the hydrolyses of 1-arylethyl chlorides in 80% ethanol were not available, solvolyses have been conducted at 15.00, 25.00, 35.00, and 45.00±0.01 °C under atmospheric pressure.

For solvolytic reactions, the relationship between steric hindrance and activation volume has not been fully investigated. LeNoble and Shurpic examined the pressure effect on the solvolysis of several sterically hindered cycloalkyl arenesulfonates but unfortunately the difference in the values of the activation volume for hindered and unhindered substrates was small.[4]

TABLE 1. PRESSURE DEPENDENCE OF FIRST-ORDER RATE CONSTANTS FOR THE SOLVOLYSIS OF 1-ARYLETHYL CHLORIDES IN ETHANOL–WATER (80: 20, v/v) AT 25.0 °C

Pressure / kg cm^{-2}	Rate constant/10^{-5} s^{-1} Ar			
	Phenyl	*o*-Tolyl	*p*-Tolyl	2,6-Xylyl
1	1.14	12.8	54.9	26.5
250	1.27	14.9	63.2	30.2
500	1.58	17.6	72.3	34.2
750	1.64	18.6	78.9	38.2
1000	1.87	23.0	85.2	42.5
ΔV_0^* / cm^3/mol	−12.6	−14.1	−11.1	−11.8

The activation volumes for the hydrolyses of 1-arylethyl chlorides are listed in Table 1. The activation volume of the parent 1-phenylethyl chloride was found to be −12.6 cm^3/mol. For 1-(*p*-tolyl)ethyl chloride a rather loose solvation shell might be expected in the transition state where the developing charge is highly delocalized by the resonance effect and hence the activation volume became less negative (−11.4 cm^3/mol). The introduction of one methyl group at the ortho position in the parent chloride showed a rate enhancement of 11 fold, a value lower than expected due to the steric inhibition of resonance (compare to 45 fold by *p*-methyl group). Thus, the activation volume was found to be −14.1 cm^3/mol, more negative than the parent chloride. The volume contraction in this case resulted from a tight transition state solvation shell around the reaction center where some charge localization appears as a result of the steric inhibition of

Table 2. First-order rate constants for the solvolysis of 1-arylethyl chlorides in ethanol–water (80: 20, v/v)

Temperature °C	Rate constant/10^{-5} s^{-1} Ar			
	Phenyl	*o*-Tolyl	*p*-Tolyl	2,6-Xylyl
15.0	—	3.60	15.3	9.00
25.0	1.14	12.1	51.8	25.9
35.0	3.10	43.3	198	98.9
45.0	9.82	—	—	—
$\Delta H^{\neq}_{25°C}$ / kcal mol^{-1}	21.3	21.3	21.8	20.5
$\Delta S^{\neq}_{25°C}$ / e.u.	−10.2	−4.9	−0.3	−10.2

resonance. This violation of a general understand ing—the more reactive, the less negative,[7,8]—stems from steric reasons.

The additional introduction of the second methyl group at the ortho position revealed a smaller rate enhancement (2 fold); *i.e.* the steric inhibition of resonance operated more strongly making the charge more localized. Consequently, electrostrictive interaction with the solvent molecules should be strong so that a more negative activation volume is expected. However, this was not the case. The observed value was −11.8 cm^3/mol, less negative than that for 1-(*o*-tolyl)-ethyl chloride. A reasonable explanation is that the solvation at the reaction center is strongly restricted by the two ortho substituents and thus the desolvation effect is responsible for the less contracted transition state volume.

Recently, the hydrolyses of 2,4,6-trialkylbenzyl chlorides have been reported,[17] and these chlorides offer a good model to demonstrate sterically hindered solvolysis. As shown in Table 3, the hydrolysis rate of 2,4,6-triisopropylbenzyl chloride was somewhat smaller than that of 2,4,6-trimethylbenzyl chloride. The reason of this rate retardation is complex: the possible operation of steric inhibition of resonance, decreasing hyperconjugative effect, and increasing inductive effect. Considering the bulkiness of the isopropyl groups, the steric effect may predominate. The value of the activation volume for the triisopropyl compound was found as −18.4 cm^3/mol, a value more negative than that for the trimethyl compound (−17.3 cm^3/mol). Again, sterically inhibited resonance is associated with a more negative activation volume. The reactivity of tri-*t*-butylbenzyl chloride was unexpectedly high as shown in Table 3. The presence of steric acceleration in this solvolysis is highly possible,[15] and the value of the activation entropy implies the existence of steric hindrance to solvation. The examination of solvolysis under pressure gave an activation volume of −15.7 cm^3/mol. Thus, as in the case of 1-(2,6-xylyl)ethyl chloride, the presence of bulky substituents near the reaction center results in a less negative activation volume. This observation should be strong evidence for the large steric hindrance by substituents to solvation.

Table 3. Pressure dependence of first-order rate constants for the solvolysis of trialkylbenzyl chlorides in ethanol–water (80: 20, v/v) at 25.0 °C

Pressure bar	Rate constant/10^{-5} s^{-1}		
	2,4,6-Trimethyl-	2,4,6-Triisopropyl-	2,4,6-Tri-*t*-butyl-
1	3.61	0.996	19.8
250	4.29	1.16	24.2
500	5.12	1.42	26.4
750	5.70	1.61	29.7
1000	6.83	1.87	32.8
1250	7.54	2.25	35.7
1500	8.45	2.50	37.3
$\Delta V^{\neq}_0$ / cm^3 mol^{-1}	−17.3	−18.4	−15.7
$\Delta S^{\neq}_{25°C}$ [a] / e.u.	−11.0	−10.4	+0.3

a) See Ref. 17.

Electrostriction is the phenomenon where a strong electrostatic interaction is exerted between a highly polar species and solvent molecules, and consequently the entropy of the system in general decreases. Actually in some reactions which have large negative activation volumes, the activation entropies are large and negative.[1] In some instances, an approximate proportionality between activation volume and activation entropy has been observed.[7] In the present reactions, however, Tables 2 and 3 show that there is no correlation between these two activation parameters.

In conslusion, it appears that the steric inhibition of resonance results in a more negative activation volume. However, with bulkier substituents the steric hindrance to solvation becomes predominant, and consequently a less negative activation volume is observed.

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