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Effect of pressure on the rates of hydrolysis of allyl chlorides

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The pressure dependence of the rates of hydrolysis of allyl chloride and α-, β-, and γ-methyl allyl chlorides has been examined. The significance of the activation volumes, ΔV^*, and their pressure dependence, $d\Delta V^*/dP$, is discussed. These activation parameters indicate an S_N2 mechanism for allyl and β-methyl allyl chloride and an S_N1 or intermediate character mechanism for the other methyl substituted allyl chlorides investigated. The results are compared with the corresponding ΔH^* and ΔC_P^* measurements of Robertson and co-workers. The temperature dependence of the activation volume, $d\Delta V^*/dT$, for the solvolysis of the parent allyl chloride has been measured and found to be small and negative.

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Introduction

DeWolfe and Young (1) have reviewed the extensive investigations of various workers on the solvolysis of allylic type halides. It has been suggested (2) that solvolysis reactions of this type represent a continuous spectrum of mechanism, ranging from bimolecular S_N2 to the limiting unimolecular S_N1 type ionization process.

Although the effect of pressure on the rates of reaction in solution has been under investigation for some time, the significance of the activation volume as a mechanistic probe has been recognized only recently (3–5). Whalley (4) has reviewed the significance of activation volumes in the determination of reaction mechanism, and has suggested that the volume of activation is probably easier to rationalize in terms of reaction mechanism than the other important parameters of activation, i.e. the free energy, enthalpy, and entropy. Improvements in the precision with which the pressure dependence of reaction rates can be determined has also permitted the evaluation of the second pressure differential of the rate, namely the pressure dependence of the activation volume, $d\Delta V^*/dP$. Robertson (6) has demonstrated the value of the second temperature differential of the rate, ΔC_P^*, as a measure of reaction mechanism type and it will be shown in this paper that $d\Delta V^*/dP$ may be an equally important and informative activation parameter. Table I summarizes the various activation parameters that may be obtained for a given system by a combination of pressure and temperature effect studies.

There are very few solvolysis reactions for which all of these pseudo thermodynamic activation parameters are available. In order to examine the relative significance of these various activation parameters, as far as reaction mechanism is concerned, it is important to have a complete set for a given system. Robertson *et al.* (7) have examined the solvolysis of methyl substituted allyl chlorides and reported the activation parameters with respect to temperature. The primary purpose of this work was to determine the activation parameters with respect to pressure for this same system, and to illustrate the inter-relationship of all of these activation parameters in indicating the variation of mechanism as the structure of the reacting substrate changes.

TABLE I

Thermodynamic parameters of activation

Variable	First derivative	Second derivative
Temperature	ΔH^* (ΔS^*)	ΔC_P^*
Pressure	ΔV^*	$d\Delta V^*/dP$

Experimental

Kinetic Method

The rate of production of HCl resulting from the hydrolysis of the various allyl chlorides was followed conductimetrically. Details of the in situ conductimetric technique have been reported previously (8). In this work an automatic balancing a.c. conductance bridge with digital print out (GR Type 1680-A) was used, providing improved accuracy and reproducibility, particularly with faster reactions. The high pressure vessel, pressure control, and conductance cell have been described in earlier papers (8). Temperature control was maintained to better than ±0.01 °C by oil bath thermostating. At temperatures below ambient, an auxiliary refrigerated cooling coil immersed in the oil bath was employed. The temperature sensing device controlled both the cooling unit and the heating element. Pseudo first order rate constants were extracted from conductance/time data by the Guggenheim method (9).

TABLE II

Rate constants for the hydrolysis of substituted allyl chlorides as a function of pressure

Allyl chloride 50.25 °C		β-Methyl allyl chloride 50.25 °C		*trans*-γ-Methyl allyl chloride 12.02 °C	
Pressure (atm)	$10^5 \times k$ (s^{-1})	Pressure (atm)	$10^5 \times k$ (s^{-1})	Pressure (atm)	$10^4 \times k$ (s^{-1})
1.0	2.540[a]	1.0	5.706[a]	1.0	1.140±0.002
680.5	3.355±0.008	313.0	6.478±0.018	340.0	1.386±0.016
1360.9	4.340±0.024	680.5	7.546±0.060	510.3	1.518±0.018
2041.4	5.346±0.021	1360.9	9.296±0.065	680.5	1.696±0.020
2721.8	6.557±0.073	2041.4	11.560±0.22	850.6	1.811±0.017
		2721.8	14.350±0.100	1020.7	1.949±0.030
ΔV^* ml/mole	−11.40±0.13		−10.16±0.21		−14.83±0.05
$d\Delta V^*/dP \times 10^4$ ml/atm mole	16.11±1.44		9.85±1.03		46.66±4.69

[a]Calculated from the data of Robertson and co-workers (12, 7). N.B. The rate constants reported in Robertson's paper (7) are correct. However the values for the coefficients A, B, and C in the temperature dependence equation for β-methyl allyl chloride are in error. The correct values are $A = -8006.0996$, $B = -23.3571$, and $C = 79.13099$, as obtained from Robertson in a private communication.

Materials

Water

House distilled water was first passed through Ilco-way de-ionizing resin and then redistilled in Pyrex apparatus from which atmospheric carbon dioxide was excluded; storage was in polyethylene containers.

Allyl Chloride

Matheson, Coleman, and Bell material was redistilled at 10^{-3} mm, and the center cut stored for later use. Purity was checked by gas–liquid chromatography (g.l.c.).

β-Methyl Allyl Chloride

Eastman Organic Chemicals sample redistilled in small quantities at 10^{-3} mm, as required. Gas–liquid chromatography indicated no significant impurities.

trans-γ-Methyl Allyl Chloride

The crotyl chloride purchased from Aldrich Chemical Co. was found to be a mixture of *cis*- and *trans*-γ-methyl allyl chloride. The *trans*-γ-methyl allyl chloride was separated by preparative g.l.c. as described by Robertson *et al.* (7). The preparative column used was 9 ft × ⅜ in., packed with 15% β,β′-oxydipropionitrile on Chromosorb P(80–100 mesh), which is capable of separating the *cis* and *trans* isomers. The separation was carried out under the following conditions: injector 100 °C, oven 45 °C, detector 140 °C, flow rate 90 cc nitrogen per min. The purity of the sample of *trans*-γ-methyl allyl chloride was checked on an analytical column of 6 ft × ¼ in. packed with the same material, under the following conditions: injector 100 °C, oven 41 °C, detector 197 °C, nitrogen flow 28 cc per min. The sample of *trans*-γ-methyl allyl chloride was found to have less than 0.3% impurity.

α-Methyl Allyl Chloride

A pure sample of this substrate was kindly provided by R. E. Robertson. The purification method was as described in ref. 7.

Preparation of Working Solutions

All reaction solutions were prepared by weighing required amounts of the various allyl chlorides and dilution in standard flasks to yield 10^{-4} M concentrations. Solutions were degassed by repetitive freezing and melting before being loaded into conductance cells.

Results

Pseudo first order rate constants for the hydrolysis of allyl chloride, β-methyl allyl chloride, and *trans*-γ-methyl allyl chloride at various pressures to 2700 atm are reported in Table II. Attempts to measure the pressure dependence of the rate of hydrolysis of α-methyl allyl chloride were unsuccessful, due to the relatively rapid intramolecular rearrangement of this substrate to a mixture of *cis*- and *trans*-γ-methyl allyl chloride (10). Rearrangements of this kind have been shown (4, 11) to be particularly pressure sensitive and to have rates in excess of the rate of hydrolysis of the parent halide. Accordingly, any attempt to observe the rate of hydrolysis of α-methyl allyl chloride, particularly at elevated pressures, rapidly becomes an observation of the combined rate of hydrolysis of a rearranged mixture of methyl substituted allyl chlorides. The complication is clearly demonstrated by failure to obtain linear first order kinetic behavior in the case of α-methyl allyl chloride.

Allyl chloride and β-methyl allyl chloride were studied at 50.25 °C; at this temperature the reaction proceeded at a rate which permitted considerable pressure variation without increas-

TABLE III

Rate constants for the solvolysis of allyl chloride as a function of pressure at various temperatures

Pressure (atm)	Rate constant, $10^5 \times k$ (s^{-1}), at temperatures			
	29.34 °C	40.00 °C	50.25 °C	60.50 °C
1.0	0.210[a]	0.793[a]	2.540[a]	7.440±0.100
680.5		1.043±0.023	3.355±0.008	10.31 ±0.300
1360.9	0.343±0.012	1.329±0.012	4.340±0.024	13.060±0.250
2041.4			5.346±0.021	
2721.8	0.488±0.014	2.027±0.016	6.557±0.073	21.050±0.360
ΔV^* ml/mole	−10.20±0.74	−10.69±0.19	−11.40±0.13	−12.58±0.25
$d\Delta V^*/dP \times 10^4$ ml/atm mole	18.46±1.50	13.49±1.22	16.11±1.44	16.30±1.87

[a]Calculated from ref. 12.

ing the rate beyond a measurable value. *trans*-γ-Methyl allyl chloride, however, hydrolyzes at a considerably faster rate even at room temperature and atmospheric pressure. Accordingly, it was necessary to study the effect of pressure on the hydrolysis of this substrate at 12.02 °C. Since the purpose of this study was to compare the pseudo thermodynamic parameters of activation of the complete set of allyl chlorides, this experimentally dictated temperature difference required that a check of the temperature dependence of the pressure-derived activation parameters be carried out. This was done in the case of allyl chloride. Table III reports the dependence of the rate of hydrolysis of allyl chloride on pressure at four temperatures over the range of 30–60 °C. The activation volume and its pressure dependence derived from these results for each temperature shows a remarkable constancy as the temperature is varied. While this observation in itself is interesting, its main value is to serve as a good indication of the magnitude of any correction that should be applied when comparing the pressure-derived activation parameters obtained from kinetic data at different temperatures.

In any study in which the derivation of the measured rate constants with respect to pressure or temperature is extracted, the error associated with these derived parameters is strictly dependent on the accuracy of the rate determinations themselves. Selected rate data determined at atmospheric pressure in the apparatus used in this work were in excellent agreement with the previously reported values of Robertson and co-workers (7, 12). The values shown at atmospheric pressure in Tables II and III are those calculated from the rate/temperature dependence equation published by Robertson (6). All rate constants reported at elevated pressures are the average values of at least four separate rate determinations. The uncertainties associated with each value were obtained by the method previously described by Golinkin *et al.* (13), and are normally better than ±1.0%. Activation volumes and their pressure dependence were extracted from the rate/pressure data reported in Table II by obtaining a computer best fit to the rate/pressure quadratic equation.

$$\log k = A + BP + CP^2$$

This method has been described in detail in a previous paper (13). Figure 1 is a typical plot of $\log k$ vs. pressure for data reported in this paper. The error bars shown on each point illustrate the typical uncertainty associated with the rate

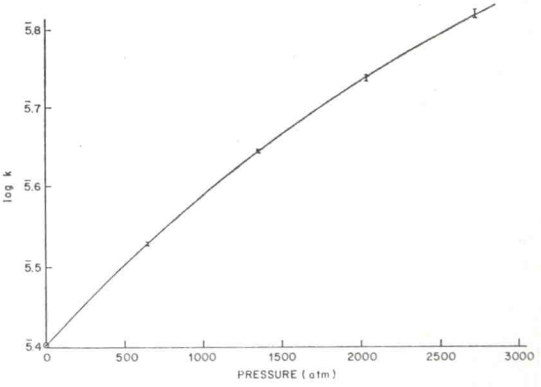

FIG. 1. Plot of $\log k$ vs. pressure for the hydrolysis of allyl chloride at 50.25 °C.

TABLE IV

Activation parameters derived from pressure and temperature dependence of rate for the solvolysis of various allyl chlorides

Substrate chloride	Pressure parameters		Temperature parameters[a]	
	ΔV^* (ml/mole)	$(d\Delta V^*/dP) \times 10^4$ (ml/atm mole)	ΔH^* (kcal/mole)	$(d\Delta H^*/dT)\Delta C_P^*$ (cal mole deg)
Allyl-	-11.40 ± 0.13 (50.25°) -8.0 (approx.) (12.0°)	16.11 ± 1.44	21.99 ± 0.01 (50.0°)	-49.6 ± 1.2
β-Methyl allyl-	-10.16 ± 0.21 (50.25°)	9.85 ± 1.03	20.98 ± 0.08 (50.0°)	-48.39 ± 4.5
α-Methyl allyl-			23.87 ± 0.01 (15°)	-91.6 ± 3.1
trans-γ-Methyl allyl-	-14.83 ± 0.05 (12.02°)	46.66 ± 4.69	23.93 ± 0.01 (15°)	-81.6 ± 3.3

[a]Robertson's data, ref. 7.

determinations at pressures above atmospheric, and the plot clearly establishes the non-linearity of the log k vs. pressure relationship. This curvature is reflected in the non-zero valued C coefficient in the quadratic equation used to describe the pressure dependence and yields the $d\Delta V^*/dP$ values shown in Tables II and III.

Discussion

All volumes of activation measured for the allyl halides studied in this work are negative. This observation is in keeping with the fact that where an S_N1 or S_N2 type mechanism is operative, the transition state is normally a more polar species than the initial state. Accordingly, volume reduction by electrostriction of solvent will tend to outweigh any volume increase due to bond extension in the activation process. Furthermore, it might be expected that the ΔV^* associated with the more ion-like transition state of an S_N1 mechanism would be more negative than in the case of an S_N2 mechanism.

Robertson and co-workers (7) have suggested, on the basis of their ΔH^* and ΔC_P^* values (see Table IV), that *trans*-γ-methyl allyl chloride hydrolyzes by a more S_N1 like mechanism while the parent allyl and β-methyl allyl chlorides are more S_N2 type reactions. The ΔV^* values reported in Table II for these three compounds suggest that the two S_N2 type reactions do indeed have volumes of activation somewhat less negative than that for the S_N1 type *trans*-γ-methyl allyl chloride. It is important at this point to recall the temperature dependence of ΔV^* as illustrated in Table III. If the ΔV^* value for allyl chloride is corrected to 12.02 °C a value of approximately -8 ml/mole is obtained, to be compared with a corresponding value for *trans*-γ-methyl allyl chloride of -14.8 ml/mole at the same temperature. Accordingly, the temperature difference between the data reported in Table II tends to obscure the differences in the ΔV^* values rather than accentuate them. Whether or not the ΔV^* values for allyl and β-methyl allyl chlorides reflect a true S_N2 type mechanism cannot be established conclusively. However, le Noble (11) has reviewed the volumes of activation of a number of bimolecular reactions for which other evidence suggests a simultaneous bond-making and bond-breaking reaction mechanism and has suggested that for such limiting S_N2 reaction types, a ΔV^* value between -5 and -10 ml/mole is to be expected. The ΔV^* values reported here suggest that allyl and β-methyl allyl chloride hydrolyze by a mechanism that might be termed non-limiting S_N2. In reactions for which the rate is controlled by an S_N1 type ionization process, the ΔV^* is expected to be of the order of -15 ml/mole (14). Hence the -14.8 ml/mole value of ΔV^* for the hydrolysis of *trans*-γ-methyl allyl chloride suggests an S_N1 type mechanism.

By far the most instructive presentation of the available data on the allyl chloride system is that presented in Table IV. Here are presented in summary form all of the activation parameters for allyl, β-methyl, and *trans*-γ-methyl allyl chlorides. It was on the basis of ΔC_P^* values shown, that Robertson and co-workers (7) classified the allyl and β-methyl allyl chlorides as S_N2 like and α-methyl and *trans*-γ-methyl allyl chlorides as

S_N1. While a classification of this type could be based on ΔH^* values, the relative differences in these parameters was not great. The more sensitive of the two temperature-derived activation parameters was the second differential ΔC_P^*. While it is unfortunate that rate/pressure data for α-methyl allyl chloride proved to be unobtainable in this work, the remaining three allyl chloride substrates provide sufficient data to compare ΔV^* and $d\Delta V^*/dP$ with ΔH^* and ΔC_P^* values. A very similar picture emerges. As discussed above, a classification into S_N1 and S_N2 type mechanisms is possible on the basis of ΔV^* alone, but a much clearer separation of types becomes apparent when the second derivative $d\Delta V^*/dP$ values are examined. It is, therefore, clear from Table IV that first derivatives of the rate with respect to pressure (ΔV^*) and temperature (ΔH^*) are considerably inferior to second derivatives, $d\Delta V^*/dP$ and ΔC_P^*, as activation parameters for use as mechanistic probes.

The main reason for examining the temperature dependence of activation volume in the case of the allyl chloride was to permit appropriate compensation to be made for the considerable temperature difference between the pressure studies of the three allyl systems. However, the observed small value for $d\Delta V^*/dT$ is, in itself, an interesting observation. Walling and Schugar (15) have previously commented on the apparent lack of temperature sensitivity of ΔV^* although Laidler and Chen (16) reported that ΔV^* for the hydrolysis of ethyl acetate changed from −9.9 ml/mole at 25 °C to −4.8 ml/mole at 2.4 °C. Even in the latter case, however, $d\Delta V^*/dT$ is less than 0.25 ml/mole deg compared with a value of less than 0.1 ml/mole deg in the case of allyl chloride hydrolysis. It is worth noting that in the ethyl acetate case, although the reaction mechanism differs from solvolysis, the temperature range involved includes the temperature of maximum density of water and, if ΔV^* in any way reflects solvent reorganization, it might be expected to show its maximum temperature dependence passing through the Td(max) of water. Whatever the explanation of the lack of temperature sensitivity of ΔV^* may be, it can at least be said, that since ΔV^* is the difference in volume between the initial and the transition states, the volumes of both of these states respond in a remarkably similar manner to temperature change. This observation is noteworthy since if the solvent is deemed to be more highly electrostricted around the more polar transition state, it might be reasoned that the volume of the transition state entity would be significantly less sensitive to temperature than the more "loosely solvated" initial state. The apparent lack of sensitivity of ΔV^* to temperature might, therefore, be interpreted as suggesting that the solvent cage around the initial state is a good deal more rigid and temperature stable than has heretofore been believed.

Conclusions

The heat capacity and pressure dependence of volume of activation appear to be more sensitive to variations in the reaction mechanism for the allyl chloride solvolyses studied than are the first derivative parameters, enthalpy and volume of activation. The temperature dependence of the enthalpy and volume of activation makes it advisable to determine these parameters at comparable temperatures before using their relative values as indicators of likely mechanistic types.

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