April, 1974] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(4), 881—884 (1974) 881

Effect of Pressure on the Rate of Solvolysis. Volume Parameters and Solvolysis Mechanism[1)]

Chisako YAMAGAMI, Akira SERA, and Kazuhiro MARUYAMA
Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606

(Received September 10, 1973)

The effect of pressure on the solvolysis rates of representative primary, secondary, and tertiary tosylates was investigated in three representative solvents—formic acid, aqueous acetone, and methanol. The calculated activation volumes for these reactions were found to depend on the substrate structure and on the nature of solvent in a systematic manner. The activation volumes for k_c-like reactions were less negative than those for k_s-like reactions. In the case of the nearly k_s-like reactions, the activation volume was found to be governed by the partial molal volume of the initial state.

In previous papers concerning the pressure dependence of the solvolytic rates of secondary tosylates,[2)] we have discussed some correlations between the activation volumes, $\Delta V^{\neq}$, and the reaction mechanisms. It was suggested that the activation volume for the reactions of a series of substrates in a given solvent became less negative with an increase in the k_c-character of the substrate. It was also found that a reaction in formic acid resulted in a less negative value of activation volume than the corresponding reaction in methanol. If these observations are common to various types of substrates and solvents, this activation parameter could be expected to provide an additional criterion for examining the detailed reaction mechanisms. However, much of the published data on the activation volume is of limited usefulness for this purpose; there has been no systematic investigation of the activation volume upon changes in the type of substrate and the nature of solvent.

From this point of view, in this report we wish to extend our solvolytic studies under pressure to primary, secondary, and tertiary substrates in three different types of solvent—formic acid, 85% aqueous acetone (v/v), and methanol. It is generally accepted that primary substrates are solvolyzed by a solvent assisted pathway (k_s), and tertiary substrates by a solvent unassisted pathway (k_c). It may, then, be anticipated from our previous assumption[2)] that the activation volume for a tertiary system is less negative than for a primary system. Methyl, isopropyl, and adamantyl tosylates were chosen as model compounds for primary, secondary, and tertiary systems respectively. Methyl tosylate, possessing the lowest m-value[3)] of 0.30, has often been used as a reference standard for k_s-type behavior.[4)] On the other hand, adamantyl system has been well established to exhibit limiting behavior (k_c).[5)] Formic acid was chosen as a polar solvent which facilitates the k_c-process, whereas methanol was employed as a solvent of high nucleophilicity promoting the k_s-process. An aqueous organic solvent was expected to be intermediate in character between the above two solvents. The composition of the aqueous binary solvent (85%, v/v) was adopted so as to give appropriate rate constants at the temperatures employed in this investigation.

Results and Discussion

The solvolysis rate constants of typical primary, secondary, and tertiary alkyl tosylates were measured at various pressures (Table 1), and the activation volumes, $\Delta V^{\neq}$, were estimated by means of the following equations;

$$\Delta V^{\neq} = -RT(\partial \ln k/\partial P)_T \qquad (1)$$

$$\ln k = a + bP \qquad (2)$$

The parameter b in Eq. (2) was determined by the least-squares method in the range from 1 to 700 kg/cm^2.

The activation volumes obtained at atmospheric pressure, $\Delta V_0^{\neq}$, are summarized in Table 2 and are also illustrated in Fig. 1. As the wide range of reactivities of the substrates prevented rate measurements at a common temperature, two temperatures were employed for each solvent (25 °C and 45 °C for formolysis, and 25 °C and 40 °C for methanolysis and hydrolysis). The check of the temperature dependence of $\Delta V_0^{\neq}$ was performed in the case of isopropyl tosylate. The results indicate that an increase in the temperature results in a slight decrease in $\Delta V_0^{\neq}$ (Table 2).[6)] However, these differences are considered to be small enough to advance our argument without any corrections. In the case of formolysis, 2-adamantyl tosylate was used in the place of 1-adamantyl tosylate because all tertiary tosylates are too reactive to be measured at 25 °C. This replacement is reasonable since secondary 2-adamantyl tosylate is well known to behave like tertiary substrates.[5)]

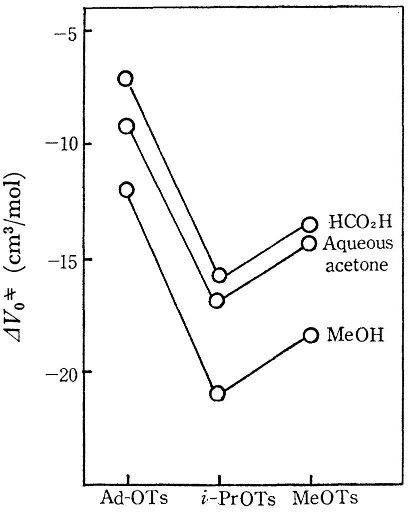

Fig. 1. Dependence of activation volume on substrate structure and solvent.

TABLE 1. SOLVOLYSIS RATE CONSTANTS OF PRIMARY, SECONDARY AND TERTIARY ALKYL TOSYLATES UNDER PRESSURE

Solvent	Temperature (°C)	Pressure (kg/cm^2)						
		1	100	200	300	500	700	1000
		Methyl tosylate 10^6k (s^{-1})[a]						
HCOOH	45.0	—[c]	0.684	—	0.757	0.834	0.924	—
aq-Acetone[b]	40.0	1.12	1.14	—	1.27	1.41	1.57	—
MeOH	40.0	3.72	4.05	—	4.76	5.36	6.03	—
		Isopropyl tosylate 10^6k (s^{-1})[a]						
HCOOH	45.0	265	286	—	321	363	397	—
aq-Acetone[b]	40.0	1.62	1.70	—	1.97	2.21	2.50	—
MeOH	40.0	7.08	7.72	—	9.22	10.6	12.3	—
		Adamantyl tosylate 10^4k (s^{-1})[a]						
HCOOH[d]	25.0	0.275	—	—	0.300	0.318	0.332	0.354
aq-Acetone[b,e]	25.0	1.88	2.00	—	2.19	2.35	2.48	—
MeOH[e]	25.0	5.63	6.13	6.57	6.87	7.42	—	—

a) The average of duplicate runs. b) 15% Water-85% acetone (v/v). c) An accurate value was not obtained due to the decomposition of formic acid. d) 2-Adamantyl. e) 1-Adamantyl.

TABLE 2. ACTIVATION VOLUMES FOR SOLVOLYSIS OF PRIMARY SECONDARY AND TERTIARY TOSYLATES IN VARIOUS SOLVENTS

ROTs R=	$\Delta V_0^{\ddagger}$ (cm^3/mol)[a]		
	HCOOH	aq-Acetone[b]	MeOH
Methyl	−13.4(45°)	−14.2(40°)	−18.2(40°)
Isopropyl	−14.7(25°)[c]	—	−18.9(25°)[c]
	−15.6(45°)	−16.7(40°)	−20.9(40°)
2-Adamantyl	−6.9(25°)	—	—
1-Adamantyl	—	−9.0(25°)	−11.8(25°)[d]

a) Accurate to within 1 cm^3/mol. b) 15% Water-85% acetone (v/v). c) Taken from Ref. 2a. d) See Ref. 2a, footnote 8.

TABLE 3. PARTIAL MOLAL VOLUMES AND MOLAR VOLUMES OF METHYL AND ISOPROPYL TOSYLATES AT 25.0±0.001 °C

ROTs R=	Solvent	$\bar{V}_g$[a]	V_m[b]	$\bar{V}_g-V_m$[c]
Methyl	HCOOH	154.4	151.8	2.6
	MeOH	142.9		−8.9
Isopropyl	HCOOH	194.5	188.2	6.3
	MeOH	181.6		−6.6

a) Partial molal volume of the initial state, cm^3/mol. The average deviation from the mean of several trials is ±0.5 cm^3/mol. b) Molar volume of substrate, cm^3/mol. c) cm^3/mol.

The partial molal volumes ($\bar{V}_g$) of methyl and isopropyl tosylates were measured at 25.0±0.001 °C by the dilatometric method.[7] The results are presented in Table 3, together with the molar volumes of the substrates (V_m).

Dependence of Activation Volume on the Nature of Solvent. All the activation volumes listed in Table 2 are negative. The invariable observation of negative activation volumes in solvolyses of neutral substrates is consistent with the view that the volume contraction by the electrostriction of the solvent predominates over the volume expansion due to bond extension during the activation process.[8] Accordingly, the activation volume which reflects the degree of solvation should, of course, be sensitive to the solvent change. In fact, Fig. 1 clearly shows the solvent dependence of $\Delta V_0^{\ddagger}$. The magnitude of $\Delta V_0^{\ddagger}$ for a given substrate is seen to decrease in the order; formic acid, aqueous acetone, and methanol. Such behavior is compatible with the previous observation in the Menschutkin reactions that the change in solvent from a non-polar to a polar one causes a remarkable increase in $\Delta V_0^{\ddagger}$.[9] The explanation was given that a polar solvent should be less constricted by the partly ionic transition state because of its low compressibility. Our results may also be considered to conform to this generalization.

In the case of limiting adamantyl systems, in which the volume contraction due to the partial bond formation is negligible, it may be said that the change in $\Delta V_0^{\ddagger}$ with solvent directly reflects the difference in the degree of the electrostrictive volume contraction of the solvent. Accordingly, the magnitude of the difference in $\Delta V_0^{\ddagger}$ between any two solvents could be regarded as a measure of the relative solvating ability of the solvent.

It is also interesting to note that a more favorable solvent for the k_c-process gives a less negative activation volume. Two solvent parameters, Y-[3] and N_{BS}-[4] values, are useful for describing the solvent character under discussion. The comparison of the Y-values (Y=2.05, −1.27,[10] and −1.09 for formic acid, aqueous acetone, and methanol respectively) indicates that formic acid is the most favorable for the k_c-process, whereas the N_{BS}- values, recently established solvent nucleophilicity parameters (N_{BS}=−2.05, −0.4,[10] and 0.01 for formic acid, aqueous acetone, and methanol respectively), indicate that methanol is the most favorable for the k_s-process.

The above-mentioned behavior will become more obvious if we examine the volumes of the initial state ($\bar{V}_g$) presented in Table 3.[11] The most important point to be noted is that $\bar{V}_g$ in formic acid is greater than V_m for a given substrate, while the reverse trend is observed in methanol. The observed increase in the volume of the solution in the case of formic acid, when one mole of a solute was dissolved in the solvent, is most likely attributable to the inherent structuredness of the solvent. On dissolving the solute, the polar formic acid, already highly oriented itself, should be compelled to expand in order to make a "hole" to accept the solute. On the other hand, in methanol, a less structured medium, the process of the reorientation of solvent molecules around the dissolved solute becomes more important than the hole-making process; hence, the total contraction of the solvent system may result. As the activation volume is represented by the following equation;

$$\Delta V^{\neq} = \overline{V}_t - \overline{V}_g \tag{3}$$

the partial molal volume of the transition state species, $\overline{V}_t$, can be calculated from the values of $\overline{V}_g$ and $\Delta V_0^{\neq}$. Calculations were made for $\overline{V}_t$ of isopropyl tosylate to give rise to values of 162.7 cm^3/mol in methanol and 179.8 cm^3/mol in formic acid. The difference in $\overline{V}_t$ for isopropyl tosylate in these two solvents amounts to 17 cm^3/mol. This large difference in $\overline{V}_t$ is understandable in terms of the general concept in organic chemistry that methanol has a powerful solvating ability, while formic acid is a solvent of low nucleophilicity.

Dependence of Activation Volume on the Structure of Substrate. An inspection of Fig. 1 indicates that the variation in $\Delta V_0^{\neq}$ with the substrate structure reveals a similar behavior in all solvents. In each case, the $\Delta V_0^{\neq}$ for adamantyl tosylate is less negative by about 8 cm^3/mol than that for isopropyl tosylate. This finding is compatible with our assumption that the more k_c-like process results in a less negative activation volume.[2)] However, a conflicting tendency was observed in the case of the primary system; a change in structure from isopropyl to methyl is accompanied by an increase in $\Delta V_0^{\neq}$ by 2—3 cm^3/mol, in spite of the fact that the latter is inevitably a more k_s-like substrate than the former. This observed discrepancy can be explained by assuming a larger contribution of the initial state volume to $\Delta V_0^{\neq}$ in the case of methyl tosylate than in that of isopropyl tosylate. In our previous discussion we have considered the activation volume to reflect chiefly the degree of solvation in the transition state. Such a view is quite reasonable as long as the systematic change of the substrate structure can govern the systematic alteration of solvation, in situation and degree, in the transition state. However, once the intensely solvated transition state is attained, that is, when the reaction is thought to be classifiable as a nearly pure k_s-process, the transition state volume ($\overline{V}_t$) can no longer be expected to be modified by a further change in the substrate structure. In this case, the contribution of the initial state volume becomes important, and the activation volume, $\Delta V_0^{\neq}$, must be controlled by $\overline{V}_g$ rather than by $\overline{V}_t$. This may be the case for methyl tosylate. In order to get information about the initial state contribution,[7)] it would be useful to examine the quantity of $\overline{V}_g - V_m$. It may be seen from Table 3 that the value of $\overline{V}_g - V_m$ for methyl tosylate is smaller than that for isopropyl tosylate in each solvent. Although $\Delta V_0^{\neq}$ and $\overline{V}_g$ were not measured at the same temperature, the observed decreases in $\overline{V}_g - V_m$ with the substrate change from isopropyl to methyl tosylate (about 4 cm^3/mol for formic acid and about 2 cm^3/mol for methanol at 25 °C) seem to correspond approximately to the increases in $\Delta V_0^{\neq}$ in the same structural change (2—3 cm^3/mol for both of the solvents at either 40 or 45 °C). This suggests that $\overline{V}_g$ is more sensitive to the change in the substrate structure from the secondary to primary system than is $\overline{V}_t$. That is, the transition state of isopropyl tosylate constricts the surrounding solvent to nearly the same extent as that of methyl tosylate. The importance of the k_s-character of isopropyl tosylate has already been described in the case of methanolysis.[2)] It is worthwhile to note again that the behavior of isopropyl tosylate is far from limiting solvolysis, even in formic acid. The same conclusion has been reported by Schleyer and hiscoworkers[5)] on the basis of a scrutiny of the relative rates of the corresponding substrates.

It can be seen from our results that the change in mechanism from a k_s- to a k_c-process causes a considerable variation in $\Delta V_0^{\neq}$ (about 8 cm^3/mol). As has been reported,[2a)] this mechanistic change in the case of formolysis was achieved by means of the successive introduction of alkyl groups into the parent substrate, isopropyl tosylate. A good linear regression of the activation volume with the characteristics of the substrate was actually observed; the more k_c-like substrate was characterized by the less negative activation volume. The most k_c-like substrate, 2-adamantyl tosylate, gave the least negative-value (−6.9 cm^3/mol), while the most k_s-like substrate, isopropyl tosylate, gave the most negative value (−14.7 cm^3/mol). The others exhibited values between these two. However, the leveling effect on the activation volume[2a)] in the case of the pure k_s-substrate, methyl tosylate, embosses the importance of the initial state partial molal volume. These observations lead us to conclude that the activation volume is a quite useful parameter or criterion for the study of solvolytic reaction mechanisms, especially for a series of reactions in which the degree of the k_s-contribution to the whole kinetic process varies.

Experimental

Materials. Methyl tosylate was a commercial material. Isopropyl and 2-adamantyl tosylates were prepared from the corresponding alcohols by the usual method. 1-Adamantyl tosylate was prepared from 1-adamantyl iodide and silver *p*-toluenesulfonate according to the procedure in the literature.[12)] All the tosylates were found by NMR analysis to be satisfactorily pure.

Formic acid and methanol were purified as has previously been described.[2a)] Acetone was dried over Drierite and distilled. The distilled water used was stored out of contact with air.

Rate Measurements. The high-pressure apparatus has previously been described.[6c)] Temperature was controlled within 0.03 °C for all the kinetic runs. The reaction rate was measured using the conductance technique.[2a)] The concentrations of the kinetic solutions were 0.019, 0.005, and 0.003 M for formolysis, hydrolysis, and methanolysis respectively. The rate constants for all the reactions of adamantyl tosylates and for the formolysis of isopropyl tosylate were determined by the Guggenheim method.[13] Pre-cooling of the medium in the high-pressure vessel was required to establish the thermal equilibrium rapidly.[2a] For the other slow reactions, we employed the procedure previously described for the methanolysis of secondary alkyl tosylates.[2a]

Partial Molal Volume Measurements. The technique used here was the dilatometric method recommended by Hyne and his co-workers.[7] 30 μl of tosylate was injected into a dilatometer consisting of a 190 cm³ bulb containing a magnetic spin bar and fitted with precision bore capillary, 25 cm in length. The bath temperature during the measurement was kept within 0.002 °C. The density of the substrate used in calculating the molar volume was determined by the usual picnometer technique.

The present work has been supported by a Grant-in-aid for Scientific Research from the Ministry of Education.

References

1) Organic Reaction under High Pressure XIV. Part XIII, A. Sera, C. Yamagami, and K. Maruyama, This Bulletin, **47**, 704 (1974).

2) a) A. Sera, C. Yamagami, and K. Maruyama, *ibid.*, **46**, 3864 (1973); b) *Idem*, *ibid.*, **47**, 704 (1974).

3) a) S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1120, (1952); b) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770, (1956).

4) T. W. Bentley, F. L. Schadt, and P. v. R. Schleyer, *ibid.*, **94**, 992 (1972).

5) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **92**, 2538 (1970), and references cited therein.

6) This is the expected result because the volume of the transition state in solvolysis is less sensitive to the temperature change than the initial state, see a) A. B. Lateef and J. B. Hyne, *Can. J. Chem.*, **47**, 1369 (1969); b) M. J. MacKinnon, and J. B. Hyne, *ibid.*, **49**, 3840 (1971); c) A. Sera, T. Miyazawa, T. Matsuda, Y. Togawa, and K. Maruyama, This Bulletin, **46**, 3490 (1973).

7) H. S. Golinkin, I. Lee, and J. B. Hyne, *J. Amer. Chem. Soc.*, **89**, 1307 (1967).

8) a) S. D. Hamman, "Physico-Chemical Effects of Pressure," Butterworths Scientific Publications, London (1957); b) W. J. le Noble, "Progress in Physical Organic Chemistry," Vol. 5, ed. A. Streitwieser, Jr. and R. W. Taft, Jr. by Interscience Publisher, New York (1967), p. 207.

9) K. R. Brower, *J. Amer. Chem. Soc.*, **85**, 1401 (1963), and references cited therein.

10) Estimated value.

11) For the study of the initial state contribution to the activation volume, see Ref. 7.

12) D. N. Kevill, K. C. Kolwyck, and F. L. Weitl, *J. Amer. Chem. Soc.*, **92**, 7300 (1970).

13) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).