Effect of Pressure on the Rate of Solvolysis. Formolysis of 1-(*p*-Substituted benzyl)ethyl Tosylates[1,2]

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The effect of pressure on the formolysis of 1-(*p*-substituted benzyl)ethyl tosylates was investigated, and the activation volumes, $\Delta V_0^{\neq}$ were estimated. The apparent values of activation volume were found to correlate nicely with σ^*. Because the present substrates were believed to be formolyzed through two separate processes, anchimerically assisted (k_Δ) and unassisted (k_s), the apparent values of activation volume were partitioned into the corresponding activation volumes, $\Delta V_\Delta^{\neq}$ and $\Delta V_s^{\neq}$. The dependence of $\Delta V_\Delta^{\neq}$ and $\Delta V_s^{\neq}$ on the substituents was examined, and the correlation between the mechanisms of solvolysis and $\Delta V_\Delta^{\neq}$ and $\Delta V_s^{\neq}$ was discussed.

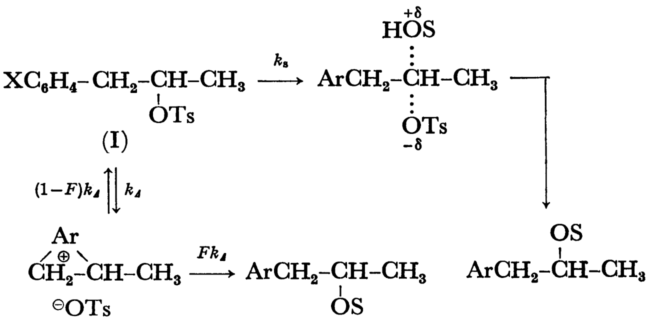
In a previous paper we have shown the utility of the activation volumes as a diagnostic tool for studying solvolytic reaction mechanisms.[3]

The activation volume, $\Delta V^{\neq}$, defined as difference in the partial molal volumes between the transition and the initial states, can be determined experimentally from the rate data under pressure by means of the following equation;

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

In general, solvolytic reactions of neutral substrates are characterized by activation volumes with a negative sign; that is, the rate constant increases by the application of pressure. This volume contraction is known to be caused mainly by the electrostrictive reorientation of the solvent molecules around the newly-charged transition state species.[4] The magnitude of activation volume is considered to reflect the charge density of the transition state species; a more delocalized charge yields a less negative value of $\Delta V^{\neq}$. It may, then, be anticipated that the application of this concept to neighboring group participation reactions could provide a more comprehensive understanding of the carbonium-ion problem. le Noble and his co-workers studied the solvolysis of *exo*-2- and *endo*-2-norbornyl systems and showed that the less negative value of $\Delta V^{\neq}$ observed for the *exo*-epimer could be well reconciled with the σ-participation.[5] The aryl participations were also studied for primary substrates, and it was shown that the participation processes resulted in less negative activation volumes than the non-participation processes.[6]

However, little is known about the substituent effects on the activation volume for reactions proceeding through the participation mechanism. It seems that a series of *β*-arylalkyl compounds would be a suitable model for the investigation of this problem because the solvolytic behavior of *β*-arylalkyl arenesulfonates has been extensively studied[7] since the first proposal of phenonium-ion intermediate[7a] and because the presence of the aryl participation has been actually proved in some cases.[7c~e] Accordingly, we chose the formolysis of 1-(*p*-substituted benzyl)ethyl tosylates (System I) as our model reaction. It is now accepted that tosylates (I) are solvolyzed through two distinct pathways, the anchimerically assisted (k_Δ) and anchimerically unassisted (k_s) routes, as shown in Scheme 1.[7c,8]



$$k_t = Fk_\Delta + k_s$$

Scheme 1.

In this paper, we shall describe an attempt to partition the activation volume ($\Delta V^{\neq}$) of the reaction into the activation volume for the anchimerically assisted process ($\Delta V_\Delta^{\neq}$) and that for the anchimerically unassisted process ($\Delta V_s^{\neq}$) in order to obtain a further insight into the reaction mechanism in terms of the activation volume.

Results

The apparent activation volumes at atmospheric pressure, $\Delta V_0^{\neq}$, for the formolysis of I and some typical secondary alkyl tosylates (System II) at 25.0 °C are summarized in Table 1, together with their rate constants at atmospheric pressure. These data were taken from our previous papers.[2,3] In order to examine the effect of an aryl moiety on the activation volume, the formolysis of *γ*-phenylalkyl tosylates (System III), a model possessing a non-participating aryl ring, was also studied (see Table 4). Their activation volumes, $\Delta V_0^{\neq}$, were determined according to Eq. (1) by using the following first-order expression;

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

The slope b was calculated by the method of least-squares in the range from 1 to 700 kg/cm², as has previously been described.[3] The results are given in Table 1.

As is shown in Table 1, the activation volume is dependent on the substituents in all systems. Figure 1 shows the correlations between $\Delta V_0^{\neq}$ and σ^*_{add}.[9] Two systems, I and II, were found to give approximately parallel correlation lines. The plot of $\Delta V_0^{\neq}$ against σ^*_{add} for System III gave another correlation line with a slope similar to the two others, whereas

Table 1. Formolysis rate constants and activation volumes for secondary tosylates at 25.0 °C

$XC_6H_4CH_2CH(OTs)CH_3$ (I)[a]			$R_1CH(OTs)R_2$ (II)[b]				$C_6H_5CH_2CH_2CH(OTs)R$ (III)[c]		
X	10^5k[d]	$\Delta V_0^{\neq}$[e]	R_1	R_2	10^5k[d]	$\Delta V_0^{\neq}$[e]	R	10^5k[d]	$\Delta V_0^{\neq}$[e]
p-OCH_3 (**1**)	47.8	−7.3	Me	Me (**6**)	2.47	−14.7	Me (**9**)	1.42	−9.8
p-CH_3 (**2**)	9.84	−7.1	Me	Et (**7**)	6.04	−12.9	Et (**10**)	4.15	−8.5
H (**3**)	1.60	−7.8	Et	Et (**8**)	13.1	−11.2			
p-Cl (**4**)	0.229	−9.1							
p-NO_2 (**5**)	0.0394	−13.1							

a) Ref. 2. b) Ref. 3. c) For rate constants at other pressures, see Experimental. d) Rate constant at atmospheric pressure, s^{-1}. e) Activation volume at atmospheric pressure, cm^3/mol. Accurate to within 1 cm^3/mol.

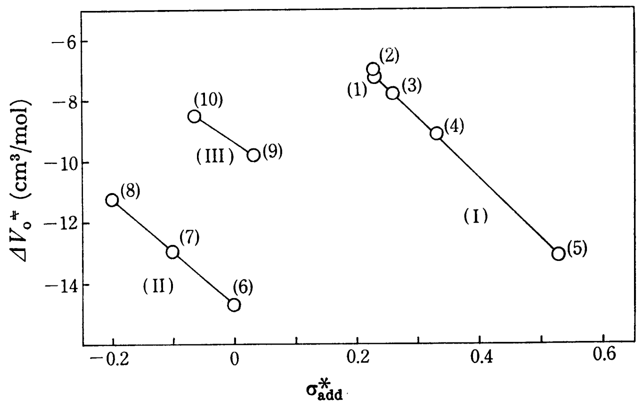


Fig. 1. Correlation of activation volume ($\Delta V_0^{\neq}$) with σ^*_{add}. Roman numerals indicate system numbers and arabic numerals correspond to substrate numbers in Table 1.

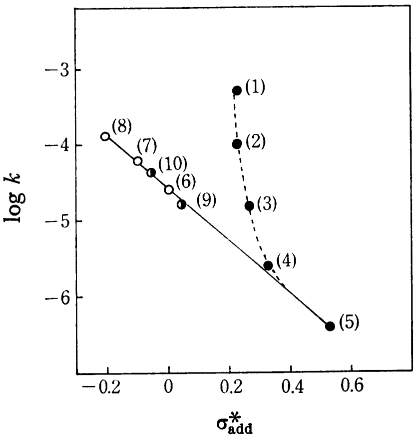


Fig. 2. Hammett-Taft plot of formolysis of secondary alkyl tosylates at atmospheric pressure.

●: $XC_6H_4CH_2CH(OTs)CH_3$, (system I); ○: $R_1CH(OTs)R_2$, (system II); ◑: $C_6H_5CH_2CH_2CH(OTs)R$, (system III). Numerals correspond to substrate numbers in Table 1.

the Hammett-Taft plot of log k against σ^*_{add} revealed a single correlation line including the points for System II (Fig. 2).

Partitioning of the Activation Volume. In order to partition solvolysis rates (k_t) for the β-arylalkyl system into anchimerically assisted (k_Δ) and unassisted (k_s) rate constants (Scheme 1), Schleyer and his coworkers[7c] have successfully utilized the deviation from the Hammett-Taft relation of the reaction rates for the substrates with activating substituents. The present method of partition of $\Delta V_0^{\neq}$ into $\Delta V_s^{\neq}$ and $\Delta V_\Delta^{\neq}$ was essentially the same in principle. The plot of log k against σ^*_{add} (Fig. 2) shows that four substrates, **5**, **6**, **7**, and **8**, define a nicely correlated k_s line with the ρ^*-value of −3.475.[8b] From this correlation line we estimated the k_s values for the other substrates with activating substituents. The values of Fk_Δ were then readily calculated from the relationship; $k_t = Fk_\Delta + k_s$. The same treatments of the rate-data at other pressures allow us to estimate the values of k_s and Fk_Δ at the given pressure. By knowing the values of k_s and Fk_Δ at each pressure, we can evaluate the magnitudes of $\Delta V_\Delta^{\neq}$ and $\Delta V_s^{\neq}$ by means of the same method employed to determine the apparent $\Delta V_0^{\neq}$. The representative results obtained for the unsubstituted compound (**3**) are presented in Table 2; the ρ^*-value at each pressure is also given. Table 3 summarizes the activation volumes thus evaluated and the partitioned rate constants at atmospheric pressure for all the substrates. A set of parameters, $\Delta V_0^{\neq}$, $\Delta V_\Delta^{\neq}$, and $\Delta V_s^{\neq}$, allows us to calculate the fraction undergoing the k_Δ process, X_Δ, from the equation; $\Delta V_0^{\neq} = X_\Delta \cdot \Delta V_\Delta^{\neq} + (1 - X_\Delta) \cdot \Delta V_s^{\neq}$. The results are presented in the last column in Table 3. The rate ratio, Fk_Δ/k_t, is considered to be an alternative parameter providing the fraction of the contribution of the k_Δ-process. The excellent agreement of these two values (see Table 3) may confirm the reliability of the present analysis.

Table 2. Partitioning of formolysis rates for $PhCH_2CH(OTs)CH_3$ and ρ^*-values under pressure at 25.0 °C

Pressure (kg/cm²)	$10^5 k_t$ (s^{-1})	$10^5 k_s$ (s^{-1})	$10^5 Fk_\Delta$ (s^{-1})	ρ^*[a]
1	1.60	0.336	1.26	−3.475
300	1.76	0.396	1.36	−3.467
500	1.87	0.433	1.44	−3.450
700	2.01[b]	0.488	1.52	−3.446
	$\Delta V_0^{\neq} = -7.8$[c]	$\Delta V_s^{\neq} = -13.2$[c]	$\Delta V_\Delta^{\neq} = -6.5$[c]	

a) Established from **5**, **6**, **7**, and **8**, see text and Fig. 2. b) Extrapolated from data at other pressures. c) Activation volume at atmospheric pressure, cm³/mol.

Discussion

All the activation volumes shown in Table 1 are negative as had been predicted. Figure 1 shows that

TABLE 3. ESTIMATE OF $\Delta V_s^{\neq}$- AND $\Delta V_\Delta^{\neq}$- VALUES FOR $XC_6H_4CH_2CH(OTs)CH_3$ AT 25.0 °C

X	$10^5 k_t$ a)	$\Delta V_0^{\neq}$ b)	$10^5 k_s$ a)	$\Delta V_s^{\neq}$ b)	$10^5 Fk_\Delta$ a)	$\Delta V_\Delta^{\neq}$ b)	Fk_Δ/k_t	X_Δ c)
p-OCH_3 (**1**)	47.8	−7.3	0.420	−13.3	47.4	−7.3	0.99	1.0
p-CH_3 (**2**)	9.84	−7.1	0.441	−13.4	9.40	−6.8	0.96	0.96
H (**3**)	1.60	−7.8	0.336	−13.2	1.26	−6.5	0.79	0.80
p-Cl (**4**)	0.229	−9.1	0.192	−13.6	0.04	—	0.17	—
p-NO_2 (**5**)	0.0394	−13.1	0.0394	−13.1	—	—	—	—

a) Rate constant at atmospheric pressure, s^{-1}. (b) Activation volume at atmospheric pressure, cm^3/mol.
c) Calculated from $\Delta V_0^{\neq}=X_\Delta \cdot \Delta V_\Delta^{\neq}+(1-X_\Delta)\cdot \Delta V_s^{\neq}$.

all the systems presently studied exhibit a considerable dependence of the $\Delta V_0^{\neq}$ on σ^*_{add}. The conformity of $\Delta V_0^{\neq}$ to the Hammett-type correlation for II was previously discussed in terms of the k_c-k_s hybrid nature of the substrates.[3] The reaction of I is known to be accelerated more effectively by an electron-donating substituent. Accordingly, the shown trend that a less negative activation volume is associated with a more electron-donating substituent is in good accordance with the general concept that the transition state accompanying the neighboring group participation is sufficiently stabilized by the charge delocalization into the aryl moiety. The results of the partition of $\Delta V_0^{\neq}$ clearly indicate that the anchimerically assisted process (k_Δ) is characterized by a less negative activation volume (about $-7\ cm^3/mol$) than the value (about $-13\ cm^3/mol$) evaluated for the non-assisted process (k_s). This trend seems to correspond to the prediction that a k_Δ-process has a less negative activation entropy, $\Delta S^{\neq}$, than a k_s-process.[10] The difference of about $6\ cm^3/mol$ observed between the two processes is noteworthy. This magnitude is thought to be large enough for us to distinguish these two reaction mechanisms.

It should be noted that the values of $\Delta V_\Delta^{\neq}$ and $\Delta V_s^{\neq}$ were found to be independent of the substituents in spite of the presence of a significant substituent effect on the apparent activation volumes, $\Delta V_0^{\neq}$. Since the $\Delta V_0^{\neq}$-σ^* correlation was observed for secondary alkyl tosylates,[3] the dissimilar features between Systems I and II will require some consideration. In the present treatments, the accumulation of errors causes the values of $\Delta V_0^{\neq}$ to be less precise. Hence, it is obscure whether $\Delta V_\Delta^{\neq}$ reveals a substituent effect or not.[11] Therefore, we will here discuss only the case of the non-assisted pathway. The independence of $\Delta V_s^{\neq}$ on the substituents for System I must result from the presence of the aryl ring in these substrates. As has been presented in Table 1 and Fig. 1, the substituent effect on $\Delta V_0^{\neq}$ for System III was actually observed. Accordingly, the possibility that the aryl moiety functions in some way effectively to exhibit a leveling effect on $\Delta V_s^{\neq}$ for System I could be excluded. Another effect induced by the presence of the aryl moiety is an inductive rate deceleration. Therefore, the most likely explanation of the insensitivity of $\Delta V_s^{\neq}$ to σ^*_{add} may be that the anchimerically unassisted reaction in the system under consideration actually undergoes a solvent assisted process, that is, a nearly pure k_s-process,[12] whereas simple alkyl tosylates are solvolyzed with some k_c-character.[3] The leveling effect on the activation volumes associated with the k_s-mechanism (solvent assisted) has already been discussed in the case of methanolyses.[3] The k_s-character (solvent assisted) of the non-participating process of β-arylalkyl system has been accepted by several workers;[7c,7e] another evidence can be supplied on the basis of activation volume parameters. We have suggested that, as a reaction mechanism shifts from a k_c- to k_s-process, its activation volume becomes more negative.[3,13] The study of the formolyses of *n*-propyl and isopropyl tosylates at 45.0 °C yielded the activation volumes of $-16.5\ cm^3/mol$ for the former and $-15.6\ cm^3/mol$ for the latter.[14] These two values agree well with each other within the limits of experimental error. These results lead us to conclude that the reaction of isopropyl tosylate, even in formolysis, has a sufficient k_s-character rather than a k_c-character.[15] It may, then, be reasonably predicted that the non-participating process of I, for all substituents, is actually nearly the pure k_s-process (solvent assisted) because the rate-retarding inductive effect of the aryl ring makes it more difficult for the reaction to proceed *via* a carbonium-ion intermediate (k_c-character).

As has been shown above, the apparent slope associated with System I (Fig. 1) does not reflect the substituent dependence of $\Delta V_\Delta^{\neq}$ and/or $\Delta V_s^{\neq}$. From Table 3, the value of X_Δ is seen to vary with the substituents. Therefore, it is the change in X_Δ which is responsible for the apparent substituent dependence of $\Delta V_0^{\neq}$. In other words, the slope of the correlation line for System I is determined by the change in the degree of the contribution of each process, k_Δ and k_s, to the over-all reaction. The fact that the correlation lines between $\Delta V_0^{\neq}$ and σ^*_{add} for Systems I and II show similar slopes is also of interest. In the discussion of the $\Delta V_0^{\neq}$-σ^*_{add} correlation for the formolysis of secondary alkyl tosylates, we have suggested the importance of the k_c-character of the reaction.[3] Therefore, it may be considered that the difference in the degree of the solvent assistance in contributing to the over-all reactions decides the correlation slope. The similarity of the slopes for Systems I and II implies that the change in the degree of the solvent assistance is controlled by the substituents in a similar manner in these two cases. This interpretation supports the k_c-k_s hybrid mechanism proposed for secondary alkyl tosylates.

The comparison of the activation volumes for System II with those for System III indicates that the introduction of a non-participating aryl substituent into the alkyl system results in an increase in $\Delta V_0^{\neq}$ by several cubic centimeters/mol (see Fig. 1). Since all the points for the substrates of System II and III fall on a single

Hammett-Taft correlation line (Fig. 2), it is hard to consider that the observed increase in $\Delta V_0^{\neq}$ is a result of a change in the mechanism. Accordingly, the presence of an aryl group is considered to result in the difference in solvation. The activation volume is represented as follows;

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

where $\bar{V}_g$ and $\bar{V}_t$ are the partial molal volumes of the initial and the transition sates respectively. The measurements of the partial molal volumes of the substrates can provide information on this problem.[16] A rough estimate of $\bar{V}_g$ in formic acid gave the values of 194.6 cm^3/mol for (**6**) and 295 cm^3/mol for (**10**).[14] These data indicate that, taking into account the molar volumes (V_m) of 188.2 cm^3/mol for neat (**6**) and 287 cm^3/mol for neat (**10**), the volume changes in the solvent system accompanied by the addition of the solute ($\bar{V}_g - V_m$) are nearly the same. Hence, the difference in $\Delta V_0^{\neq}$ between the two systems (II and III) can be thought to reflect the difference in $\bar{V}_t$ rather than that in $\bar{V}_g$. This means that, in the transtion state, System III reveals a less significant volume contraction than System II. An explanation is possible in terms of the steric effect; that is, the bulky aryl group exerts some effect in hindering the electrostrictive solvation. Unfortunately, unambiguous evidence supporting this interpretation is now lacking.

Experimental

Materials. Formic acid was purified as has been described previously.[8] All the tosylates were prepared from the corresponding alcohols in the usual way. The purity of all the tosylates was confirmed by NMR analysis. Tosylate (**10**) was found to contain a small amount of impurity, but it did not interfere with the kinetic measurements.

Rate Measurements. A high-pressure apparatus described previously[17] was used without further modification. The bath temperature was kept at 25.0±0.01 °C. The reactions were followed by a conductometric method described previously.[8] The rate constants of γ-phenyl tosylates at various pressures are given in Table 4.

TABLE 4. FORMOLYSIS RATE CONSTANTS OF $PhCH_2CH_2CH(OTs)R$ UNDER PRESSURE AT 25.0 °C

Pressure (kg/cm^2)	R=Me 10^5k(s^{-1})	R=Et 10^5k(s^{-1})
1	1.42	4.15
300	1.60	4.53
500	1.73	4.86
700	—	5.25
1000	2.07	—

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9) $\sigma^*_{add} = \sigma^*_{R_1} + \sigma^*_{R_2}$ for R_1-CH(OTs)-R_2. R. W. Taft, Jr., "Steric Effects in Organic Chemistry", ed. by M. S. Newman, John Wiley and Sons, Inc., New York (1956), p. 556.

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11) It should be noted that in the present system the partitioned Fk_Δ-values do not correlate well with σ^+-constants, see also D. S. Noyce and R. L. Castenson, *J. Amer. Chem. Soc.*, **95**, 1247 (1973). In order to examine the substituent effect on $\Delta V_\Delta^{\neq}$, therefore, a model system in which a linear Fk_Δ-σ^+ relationship is fulfilled must be chosen.

12) In the present discussion, the definition of the term k_s is somewhat troublesome To refer to the solvent assisted pathway, a word "solvent assisted" was parenthesized.

13) For such a generalization, the partial molal volume of the initial state must be, of course, taken into account. Details will be presented elsewhere.

14) Unpublished data.

15) For the difference in k_s-characters between primary and secondary systems, see ref. 7e and the references cited therein.

16) For the studies of initial state volumes in solvolytic reactions, see for example, H. S. Golinkin, I. Lee, and J. B. Hyne, *J. Amer. Chem. Soc.*, **89**, 1307 (1967).

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