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TEMPERATURE DEPENDENCE OF ACTIVATION VOLUME FOR ACETOLYSIS OF 2-ARYL-2-METHYLPROPYL TOSYLATES

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The activation volume of the acetolysis of the title compounds was found to have an unexpectedly large temperature dependence. The activation volume—temperature profile of a steep concave was observed which was responsible for the previously reported anomaly of the substituent dependence of the activation volume.

The electrostatic volume contraction generally gives rise to negative values of the activation volume in solvolytic reactions.[1)] Accordingly, an electron donating substituent should give a less negative value of the activation volume, because it leads to charge delocalization in the transition state of the reaction.[2)] Recently however, we reported that the activation volumes of the acetolyses of 2-aryl-2-methylpropyl tosylates(1) were found to be -39.3 for 2-(4-methylphenyl), -31.5 for phenyl, and -25.5 cm^3mol^{-1} for 2-(4-bromophenyl) derivatives at 75°C.[3)] Thus the substituent effect on the activation volume in these solvolyses was seemingly in the reverse order to what would be expected for ionic reactions under pressure. We wish to report here an outstanding temperature dependence of the activation volume, $\delta\Delta V^{\ddagger}/\delta T$, which accidentally resulted in the above mentioned anomaly of the substituent dependence of the activation volume at 75°C.

The acetolysis rates of the tosylates(1) were measured under pressure(1--1000 bar) at 65°, 75°, and 85°C, and the activation volumes were calculated as described elsewhere.[4)] Table 1 shows an unexpectedly large temperature dependence of the activation volume, and as is depicted in Figure the activation volume—temperature profile reveals a surprisingly steep concave. It must be recognized that the temperature dependence of the activation volume is a second order derivative of the experimentally obtained rate constants, and hence the inherent uncertainty in such a parameter is expected to be sizable. However, the results shown in Table 1 are quite indisputable, being the largest temperature dependence of the activation volumes ever reported.

Table 1 Rate Constants and Activation Volumes for Acetolyses of 2-Aryl-2-methylpropyl Tosylates(1).

Temperature	65°C		75°C		85°C	
Ar =	Ph	4-Me-Ph	Ph	4-Me-Ph	Ph	4-Me-Ph
Pressure (bar)	Rate Constants ($k \times 10^5$ s^{-1})					
1	0.69	5.13	2.21	14.6	6.43	60.7
200	0.85	6.14	2.78	20.6	8.34	70.3
400	1.03	7.46	3.33	23.9	9.43	77.8
600	1.26	8.63	3.82	27.5	10.3	88.3
800	1.35	9.66	4.38	30.3	11.7	93.0
1000	1.45	11.5	5.03	33.8	15.6	101.5
Activation Volume($\Delta V^{\ddagger}$) ($cm^3 mol^{-1}$)	-36.8	-26.9	-31.5	-39.3	-21.4	-21.6

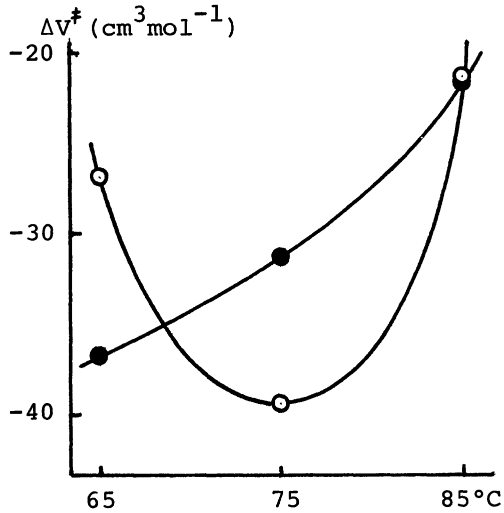

Figure Plot of Activation Volume($\Delta V^{\ddagger}$) against Pressure

● : Ar = Ph

○ : Ar = 4-Me-Ph

Up to date, little is known about the temperature dependence of activation volumes. Hyne and his coworkers[5,6] reported that the activation volume of the hydrolysis of benzyl chloride was slightly temperature dependent. The activation volume became more negative at lower temperatures. Similar tendency was also observed for the hydrolyses of 1-methyl-1-phenylethyl chloride.[2] The hydrolyses of methanesulfonyl chloride in H_2O and D_2O were claimed to have slightly convex activation volume—temperature profiles in the temperature range of 0°-25°C.$^{6)}$ This behavior was interpreted in terms of changes in structuredness of light and heavy water with temperature. In the present case, however, no one can expect any change in structuredness of acetic acid at temperatures employed.

It has been accepted that the tosylates(1) are acetolyzed through the wholly anchimerically assisted (k_Δ) path to give the rearranged acetates(2) and olefins (3 and 4).$^{7)}$ No detectable contribution of the anchimerically unassisted (k_s) path was observed. In K_s-k_Δ concurrent solvolyses, the activation volumes of the k_Δ-solvolyses were known to have less negative values than those of the k_s-solvolyses.$^{8)}$ This means that under higher pressure the unassisted k_s-path will become a more favorable solvolytic process. Accordingly, there may arise one possibility , which sheds light on the above mentioned anomalous activation volume behavior, that the acetolysis mechanism changed partly to favor the k_s-path under higher pressure. The product analysis of the reaction was achieved under atmospheric pressure and 1000 bar at the reaction temperatures in order to examine if this mechanistic change actually occured. Table 2 clearly shows that this was not the case, but the acetolyses proceeded through the k_Δ-path only even under high pressure. Investigations are in progress to elucidate the origin of this anomaly.

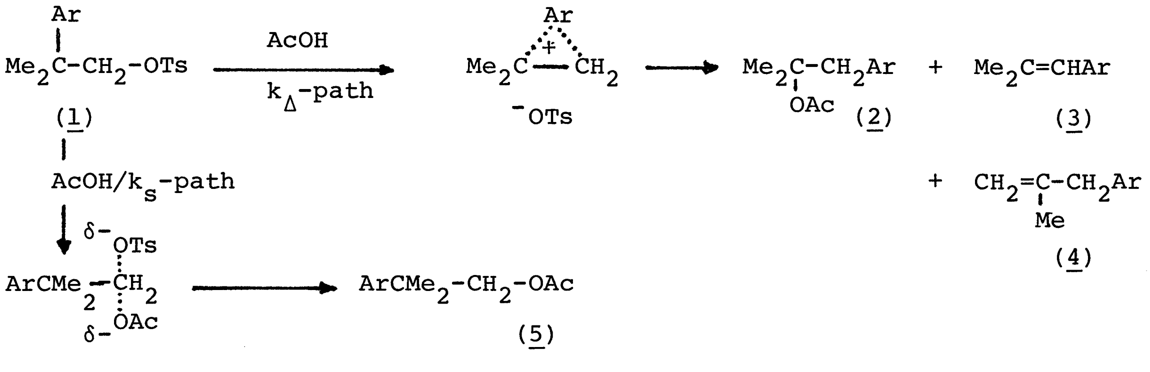

Table 2 Product Distribution of Acetolysis of 2-Methyl-2-phenylpropyl Tosylate

Temperature (°C)	Pressure (bar)	k_s-Product (5) %	k_Δ-Products (2) %	(3)+(4) %
65	1	trace	31	69
65	1000	trace	39	61
85	1	trace	25	75
85	1000	trace	27	73

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