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ANOMALOUS SUBSTITUENT EFFECT ON ACTIVATION VOLUME OF ACETOLYSIS OF 2-METHYL-2-(p-SUBSTITUTED PHENYL)PROPYL TOSYLATES

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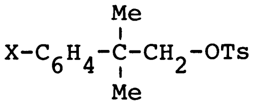
The acetolysis rates of 2-methyl-2-(p-substituted phenyl)-propyl tosylates at 75°C have been determined at various pressure and the activation volumes were calculated. The activation volume of this solvolysis showed an unexpected substituent dependence, being more negative for faster solvolyzing substrates.

General usefulness of activation volume($\Delta V^{\ddagger}$) as a diagnostic probe for organic reaction mechanism elucidation has been well recognized in recent years.[1)] Detailed reaction mechanisms have been discussed by scrutinizing activation volumes under variable conditions(substituents, solvents, temperature, etc.). All solvolysis reactions of alkyl halides and arenesulfonates were reported to have negative values of activation volume.[1)] This is what would be expected if one assumes aggregation of solvent molecules around the partially charged transition states species. These electrostatic volume contractions are in general governed by the degree of charge delocalization by substituents, hence a more activating substituent(with more negative σ value) should give a less negative activation volume, and vice versa.[2-4)] We wish to report here an outstanding violation of the above mentioned understanding for the substituent dependence of activation volume.

The pressure effect on the acetolysis rates of 2-methyl-2-(p-substituted phenyl)propyl tosylates(neophyl tosylates) at 75°C was carefully investigated. The presence of neighboring aryl participation was exemplified for these solvolyses. Accordingly, we expected to have somewhat less negative activation volumes for these tosylates in testinony that the intervention of more charge delocalized transition state should accompany the less negative activation volume. The experimental results, however, showed this was not the case(see Table). Surprizingly all the tosylates seemed to solvolyze with rather large negative activation volume.[5)] In addition, there observed an unexpectedly reverse order of activation volume, being $\Delta V^{\ddagger}_{(\underline{p}\text{-Me})} < \Delta V^{\ddagger}_{(\text{H})} < \Delta V^{\ddagger}_{(\underline{p}\text{-Br})}$. This observation is the first example of violation of the general understanding, because in all reported solvolyses, plots of activation volumes against σ values revealed roughly linear correlation, where the signs of the slopes were all negative without exception.[2,3)]

Table Activation Volumes of Acetolysis of  $X\text{-}C_6H_4\text{-}C(Me)_2\text{-}CH_2\text{-}OTs$ at 75°C.

	Acetolysis Rate Constants, $\times 10^{-5} s^{-1}$						Activation Volume
Pressure	1	200	400	600	800	1000bar	
X = p-Me	14.6	18.4	23.9	27.5	30.3	33.8	-39.3 $cm^3 mol^{-1}$
H	2.21	2.78	3.33	3.82	4.38	5.03	-31.5
p-Br	0.414	0.499	0.645	0.714	0.871	0.956	-24.5

The origin of this phenomenon has not been elucidated yet. There will be some particular reasons; a) a special temperature dependence of activation volume($\delta\Delta V^{\ddagger}/\delta T$) accidentally made the values of activation volume confused, b) the contribution of the initial state partial molar volumes played a key role in determining the values of activation volume, c) the experimental conditions employed here were rather special because of the combination of fully participating substrates and a k_c-k_s hybrid solvent, acetic acid, d) some particular properties of the solvent(hydrogen bonding ability, nucleophilicity, etc.) revealed its unexpected solvating power at higher pressure, e) solvation mode was quite different at the transition state of the participated solvolyses because of their special geometry(pseudo triangular), and/or others.

Active investigations are in progress to elucidate the origin of this astonishing observation.$^{6)}$

References and notes:

1) T.Asano and W.J.LeNoble, Chem. Rev., 78, 407 (1978).
2) A.Sera, T.Miyazawa, T.Matsuda, Y.Togawa, and K.Maruyama, Bull. Chem. Soc. Jpn. 46, 3490 (1973).
3) A.Sera, C.Yamagami, and K.Maruyama, ibid., 46, 3860 (1973); 47, 704 (1974).
4) K.J.Laidler and R.Martin, Int. J. Kinetics, 1, 113 (1969).
5) Activation volumes for the solvolyses of alkyl tosylates have been reported to be in a range of -7 to -20 $cm^3 mol^{-1}$, approximately.$^{1)}$
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