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EFFECT OF PRESSURE ON THE RATE OF SOLVOLYSIS. FORMOLYSIS OF 1-(P-SUBSTITUTED BENZYL)ETHYL TOSYLATES1)

Chisako YAMAGAMI and Akira SERA
Department of Chemistry, Faculty of Science
Kyoto University, Kyoto

The pressure dependence of the formolysis rates of the title compounds was examined and activation volumes, $\Delta V^{\ddagger}$, were calculated. Electron donating substituents in the aryl rings gave rise to less negative values of $\Delta V^{\ddagger}$.

We have been interested in the dependence of the rates of solvolytic reactions on hydrostatic pressure. Schleyer2) has successfully estimated the relative magnitudes of the anchimerically assisted (Fk_{Δ}) and the unassisted (k_s) pathways in the formolysis of 1-(p-substituted benzyl)ethyl tosylates (I). Activation of the aryl rings in (I) by sufficiently electron donating substituents was found to facilitate aryl participation. le Noble3) has shown that somewhat less negative activation volumes, $\Delta V^{\ddagger}$, observed in solvolyses must indicate the presence of aryl participation. However, little is known about the dependence of $\Delta V^{\ddagger}$ on substituents.

$X\text{-}C_6H_4\text{-}CH_2CH(OTs)CH_3$ (I); X=p-OCH_3, p-CH_3, H, p-Cl, p-NO_2

We wish to present here the pressure dependence of the formolysis rates of (I). Efforts were directed to an examination of the substituent effect on $\Delta V^{\ddagger}$. One can anticipate from the electrostriction theory that a charge developement in the transition state of solvolysis must result in a volume contraction of the system. Accordingly, the more delocalized the change in the transition state, the less negative the magnitude of $\Delta V^{\ddagger}$ becomes.

Reactions were followed by a conductometric method and $\Delta V^{\ddagger}$ was estimated from the first order rate constants under pressure by the following equation.

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = \frac{-\Delta V^{\ddagger}}{RT}$$

Formolysis Rates of 1-(p-Substituted benzyl)ethyl
Tosylates, (I), under Pressure at 25.0°C

Pressure (kg/cm^2)	$10^5 k (sec^{-1})$ *)				
	X=p-OCH_3	p-CH_3	H	p-Cl	p-NO_2
1	47.8	9.84	1.60	0.229	0.0394
100	48.7	10.1	1.66	0.239	0.0427
300	52.2	10.8	1.76	0.257	0.0467
500	55.0	11.3	1.87	0.275	0.0515
700	-	-	-	0.296	-
1000	-	12.6	2.13	-	0.0630
$\Delta V^{\ddagger}$ (cc/mole)	-7.3	-7.1	-7.8	-9.1	-13.1

*) Reliable to 2-3%

The observed values of $\Delta V^{\ddagger}$ enhibit considerable dependence on the substituents. In the aryl assisted (Fk_{Δ}) process, the extent of charge delocalization into the participating aryl moiety should be considerable. Consequently, less negative values of $\Delta V^{\ddagger}$ should be resulted. This is the case as shown in Table. This trend is in good accordance with the prediction[4,5] that an anchimerically assisted (Fk_{Δ}) process has less negative $\Delta S^{\ddagger}$ than an unassisted (k_s) process. A detailed analysis for partioning the apparent $\Delta V^{\ddagger}$ into the anchimerically assisted ($\Delta V_{\Delta}^{\ddagger}$) and the unassisted ($\Delta V_{s}^{\ddagger}$) components will be reported elsewhere.

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