Reactions of Cyclopropylmethyl Benzenesulfonate. Energies and Entropies of Activation

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The solvolyses of cyclopropylmethyl derivatives are accelerated and seem to proceed through the formation of non-classical carbonium ions[1-5]. These reactions are also very often accompanied by extensive rearrangements[6]. Thus, the acetolysis of cyclopropylmethyl benzenesulfonate proceeds simultaneously with a competitive *internal rearrangement* to products which are 250 times less reactive than the starting material[7]. In the course of our investigation of the mechanism of these two closely related reactions, we wanted to gain some information about the corresponding free energies and entropies of activation. Therefore, cyclopropylmethyl benzenesulfonate was synthesized in the usual manner[1] and its ethanolysis and acetolysis rate constants determined titrimetrically at different temperatures. The relative unreactivity of the internal rearrangement products permitted an accurate estimation of the acetolysis *infinity titer* (after 8 halflives) and thus of the rate constant. The results, given in Table I, are those which could be expected for first order reactions. In order to determine the corresponding values for the reaction of *internal rearrangement* the following procedure was used. An aliquot of an about 0.03 N solution of the sulfonate ester in acetic acid was titrated after eight acetolysis half-lives at the given temperature. Another aliquot was titrated after a few hours of heating to 100⁰. The first titer corresponds to the amount of material which underwent acetolysis (a) and the second titer to the total amount of material which underwent both, acetolysis and internal rearrangement ($a+r$)[7]. The values a/r for different temperatures are given in Table II. Using the expression (1) and the least squares treatment, the energy and entropy terms were calculated from equation (2) and (3).

(1) $a/r = k_a/k_r$ k_a = *acetolysis rate constant*
k_r = *internal rearrangement rate constant*

$$(2)\ log\ \frac{k_a}{k_r} = log\ \frac{A_a}{A_r} + \frac{E_A^r - E_A^a}{RT} \cdot 2.303$$

$$(3)\ A = e \cdot \frac{RT}{Nh} \cdot e^{\Delta S^{\ddagger}/R}$$

The results are given in Table I.

The increase of the quotient a/r with temperature is significant. This result indicates that the energy of activation is smaller for the slower

internal rearrangement than for the faster acetolysis. The difference in reaction rates must therefore be caused by a difference in frequency factors indicating that a higher degree of order is required for the formation of the transition state in the internal rearrangement than in the acetolysis reaction.

TABLE I

Free Energies and Entropies of Activation for Reactions of Cyclopropylmethyl Benzenesulfonate

Reaction	t	$k \cdot 10^4 \cdot sec^{-1}$	E_A kcal/mole	$\Delta S^{\ddagger}$ e.u.	log A
Ethanolysis	20⁰	0.581	21.80	— 2.0	11 93
	30⁰	2.118			
	40⁰	6.272			
Acetolysis	20⁰	2.248	24.24	+ 9.0	14.41
	25⁰	4.576			
	30⁰	8.438			
Internal rearrangement			23.40	+ 5.3	13.51

TABLE II

Acetolysis of Cyclopropylmethyl Benzenesulfonate to Internal Rearrangement Products Ratio (a/r) for Different Temperatures

t	a/r			
	1. series	2. series	3. series	mean
20⁰	1.51	1.46	1.45	1.47
25⁰	1.55	1.51		1.53
30⁰	1.54	1.53	1.59	1.55
35⁰		1.61		1,61
40⁰	1.62	1.64	1.61	1.63
45⁰		1.67		1.67
50⁰	1.68	1.70	1.70	1.69

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IZVOD

Reakcije ciklopropilmetil benzensulfonata. Energije i entropije aktiviranja

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Mjerene su konstante brzina reakcija za etanolizu i acetolizu uz popratno unutarnje pregrađivanje ciklopropilmetil benzensulfonata kod različitih temperatura. Izračunate su odgovarajuće slobodne energije i entropije aktiviranja. Pronađeno je, da ove veličine odgovaraju reakcijama prvoga reda. Iz promjene entropija kod acetolize odnosno unutarnjeg pregrađivanja zaključeno je, da su stupnjevi slobode prelaznoga stanja veći kod prve nego kod druge reakcije.