Secondary Hydrogen Isotopes Effects. V. Internal Rearrangement in the Acetolysis of Deuterium Labeled Cyclopropylmethyl Benzenesulfonates[1]
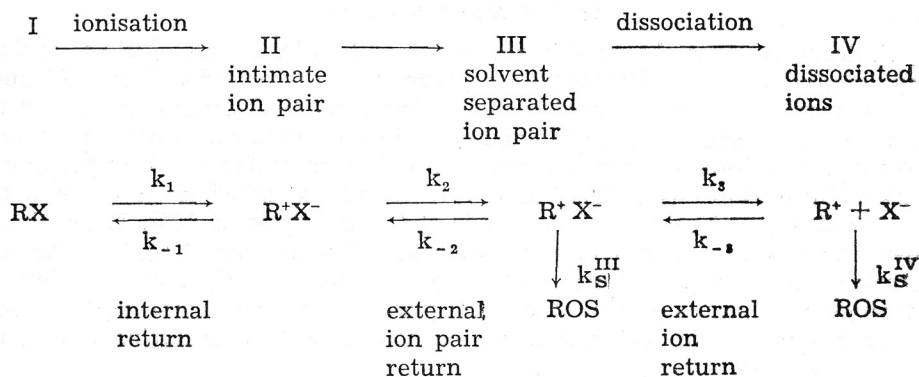
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The acetolysis *vs.* internal rearrangement products ratio was determined for cyclopropylmethyl, cyclopropylmethyl-1,1-d_2 and -3,3-d_2 benzenesulfonate and was found to remain constant within the experimental error. The results confirm that both concurrent reactions proceed through a common intermediate in which the bond between the carbonium ion and the leaving group must be purely ionic.

For the understanding of the mechanism of the solvolysis reaction Winstein[2] presented the following useful scheme:
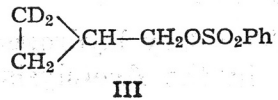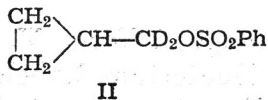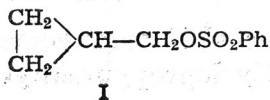
$$
\text{I} \xrightarrow{\text{ionisation}} \underset{\substack{\text{intimate}\\\text{ion pair}}}{\text{II}} \xrightarrow{\qquad} \underset{\substack{\text{solvent}\\\text{separated}\\\text{ion pair}}}{\text{III}} \xrightarrow{\text{dissociation}} \underset{\substack{\text{dissociated}\\\text{ions}}}{\text{IV}}
$$

$$
\text{RX} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} R^+X^- \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} R^+ X^- \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} R^+ + X^-
$$

$$
\underset{\substack{\text{internal}\\\text{return}}}{} \qquad \underset{\substack{\text{external}\\\text{ion pair}\\\text{return}}}{} \;\; \Big\downarrow k_S^{III} \quad \underset{\substack{\text{external}\\\text{ion}\\\text{return}}}{} \;\; \Big\downarrow k_S^{IV}
$$

$$\qquad\qquad\qquad\qquad\qquad\qquad \text{ROS} \qquad\qquad\qquad\qquad \text{ROS}$$

ROS = Solvolysis products

It was observed that some compounds may rearrange during solvolysis to products bearing the leaving group[3]. This, so called internal rearrangement has been explained[3a-d] by the formation of the intimate ion pair (R^+X^-) as the first intermediate which may rearrange giving by the return process the rearranged starting materials.

The acetolysis of cyclopropylmethyl benzenesulfonate appears to be suitable for the investigation of the internal rearrangement as the resulting benzenesulfonates are unreactive under the specified conditions[1]. Since it has been shown that deuterium labeling affects the acetolysis rate of cyclopropylmethyl benzenesulfonate[1] it was of interest to investigate if and how it would affect the accompanying internal rearrangement. For this purpose the acetolysis *vs.* internal rearrangement products ratio was determined for compounds

I, II and III. With this experiment it was hoped to gain some information about (1) the amount of ionisation resp. covalency of the bond between R and X in the intimate ion pair and (2) the structure of the carbonium ion in the intimate ion pair and at later stages of the reaction.

$$
\begin{array}{ccc}
\underset{\mid}{\overset{CH_2}{\underset{CH_2}{\diagdown}}}CH{-}CH_2OSO_2Ph & \underset{\mid}{\overset{CH_2}{\underset{CH_2}{\diagdown}}}CH{-}CD_2OSO_2Ph & \underset{\mid}{\overset{CD_2}{\underset{CH_2}{\diagdown}}}CH{-}CH_2OSO_2Ph \\
\textbf{I} & \textbf{II} & \textbf{III}
\end{array}
$$

EXPERIMENTAL

The preparation of cyclopropylmethyl benzenesulfonates I, II, and III containing 0, 1.88, and 1.76 atoms of deuterium per molecule respectively is described elsewhere[1].

Benzenesulfonates were dissolved in anhydrous acetic acid (50 ml.) so as to obtain about 0.05 M solutions. A part of each solution (30 ml.) was left in a thermostat at 20.0 ± 0.1⁰ for 10 acetolysis halflives. The remaining part of each solution was sealed in an ampule and left in a boiling water bath for 48 hrs. Aliquots of both sets of solutions were then titrated for benzenesulfonic acid with a 0.03 M solution of sodium acetate in acetic acid and bromphenolblue as indicator.

Solutions (0.03 M) of benzenesulfonates in anhydrous ethanol were left in a thermostat at 20.0 ± 0.1⁰ for 10 ethanolysis halflives and the liberated benzenesulfonic acid titrated with a 0.03 M sodium hydroxide solution in anhydrous ethanol and methyl red as indicator.

The amount of unsaturated products formed during the acetolysis of I at 20.0⁰ was determined by bromide-bromate titration.

RESULTS AND DISCUSSION

A difference was observed in the *infinity* titers in the acetolysis of cyclopropylmethyl benzenesulfonates if the reaction was carried out at 100⁰ and 20.0⁰ respectively. This fact could be due to the presence of less reactive benzenesulfonates in the starting materials and/or to their formation during the reaction. The purities of the starting cyclopropylmethyl benzenesulfonates were therefore checked by ethanolysis at 20.0⁰ and were found, as indicated in Table I, to correspond very closely to those obtained by acetolysis at 100⁰. From these observations it can be concluded (1) that the only impurities in the starting materials are inert compounds which do not solvolyse, (2) that an internal rearrangement occurs during the acetolysis of cyclopropylmethyl benzenesulfonate and (3) that such a rearrangement does not occur during the ethanolysis reaction.

The difference in the infinity titers in acetolyses at 100⁰ and 20⁰ corresponds to the amount of rearranged benzenesulfonates formed in the reaction at 20.0⁰. The acetolysis *vs.* internal rearrangement products ratios (A/R) as calculated by equation 1 are given in the Table I.

$$
(1) \qquad \frac{A}{R} = \frac{a}{b-a}
$$

a = infinity titer in the acetolysis at 20.0⁰
b = titer after acetolysis at 100⁰ for 48 hrs.

In the calculation of the A/R values it should be considered that some benzenesulfonic acid liberated in the acetolysis at 20.0⁰ may arise from rearranged benzenesulfonates. It is known[4] that cyclopropylmethyl derivatives can rearrange to homoallyl and cyclobutyl derivatives. By bromide-bromate titration the amount of unsaturated products formed during the reaction was found to be 3—5 per cent. Therefore, it can be assumed that in the internal

rearrangement practically only cyclobutyl benzenesulfonate is formed. The acetolysis rate constant (k_{ac}) of the latter compound at 20.0° is not known but can be computed approximatively. By the Arrhenius equation k_{ac} for

TABLE I

Internal Rearrangement in the Acetolysis of Cyclopropylmethyl Benzenesolfonates at 20.0°

R—O$_3$S Ph R =	Purity (in per cent)[a] 1	2	Concentration moles/l.	$k_{ac} \cdot 10^4$[b] sec^{-1}	A/R[c]	$k_t \cdot 10^4$[d] sec^{-1}
CH$_2$\ | >CH—CH$_2$ CH$_2$/	87.8	89.0	0.0484	2.19	1.644 ± 0.035	1.33
CH$_2$\ | >CH—CD$_2$ CH$_2$/	88.4	89.4	0.0501	1.68	1.646 ± 0.035	1.02
CH$_2$\ | >CH—CH$_2$ CH$_2$/	87.6	86.8	0.0485	2.25	1.613 ± 0.034	1.39

a) Calculated from the *infinity* titers of 1. the acetolysis at 100° 2. ethanolysis at 20.0° b) Acetolysis rate constant at 20.0°, see reference 1. c) Acetolysis *vs.* internal rearrangement products ratio calculated by equation 1. d) Internal rearrangement rate constant at 20.0° calculated by equation $k_r = k_{ac} : A/R$.

cyclobutyl *p*-toluenesulfonate at 20.0° and 50.0° was evaluated to be $0.84 \cdot 10^{-6}$ resp. $4.22 \cdot 10^{-5}$ sec^{-1} from the data given for 55.1° and 60.1°.[5] The k_{ac} of the rearranged benzenesulfonates are close to this values as demonstrated by a rate measurement at 50.0° ($k_{ac} = (5.55 \pm 0.11) \cdot 10^{-5}$ sec^{-1}). In this way, it can


REACTION COORDINATE
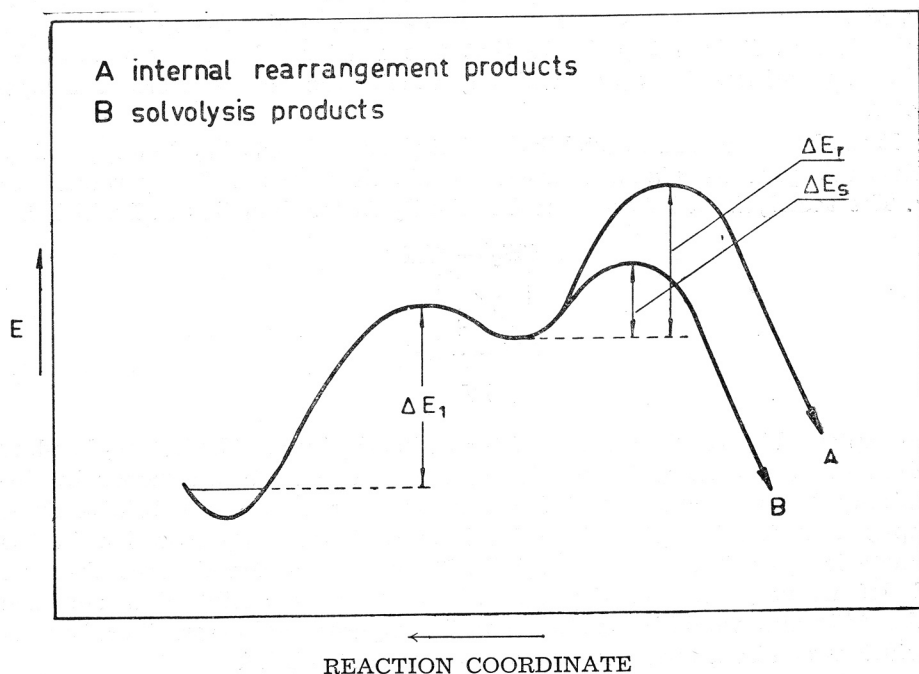
be calculated that about 3.5 per cent of the benzenesulfonic acid titrated after 10 acetolysis halflives of cyclopropylmethyl benzenesulfonates at 20.0⁰ arise from solvolysed rearranged benzenesulfonates. The A/R values and the internal rearrangement rate constants given in Table I should therefore be corrected accordingly. However, the comparison of these values is possible as the error implied must be very much the same for each compound.

An interesting result of the present investigation is that the A/R value is the same with I, II and III. As the acetolysis of II has been shown to display an isotope effect $(k_H/k_D = 1.30)$[1] it is obvious that the concurrent internal rearrangement must be equally retarded. This can be well understood by considering the scheme and plotting the free energy of activation against the reaction coordinate as shown in the diagram.

The first energy barrier (ΔE_1) corresponds to the formation of the intimate ion pair (R^+X^-) which can either rearrange and return to the starting material (ΔE_r) or solvolyse further (ΔE_s). If deuterium labeling of carbon atom 1 affects only the first energy barrier the A/R value which is determined by the energy difference $\Delta E_r - \Delta E_s$ will remain constant. The rehybridisation of the carbon-deuterium bonding orbitals which causes the isotope effect in the acetolysis of II[1,6], must therefore be already complete in the intimate ion pair. If this were not the case, any further rehybridisation would affect ΔE_s thus causing a change of the A/R value. The carbon-hydrogen (deuterium) bonding orbitals being essentially sp^2 hybridised on carbon atom 1 in the intimate ion pair, the bond between R and X (at least in the case examined) must be purely ionic in character.

De La Mare and Vernon[3e] proposed a mechanism involving two distinct reaction paths for internal rearrangement and solvolysis of α,α-dimethylallyl chloride. The results of this work cannot be well accounted for by an analogous mechanism as it is not probable that two reactions involving structurally different transition states would display exactly the same deuterium isotopes effects.

It can be considered as established that the solvolyses of cyclopropylmethyl derivatives proceed *via* non-classical carbonium ions probably resembling IV[7]. The acetolysis of III seems to be slightly faster than this of I which has

$$
\begin{array}{ccc}
CH_2 & \!\!\!\!-\!\!\!\!- & CH \\
| & \diagup\!\!| & || \\
| & +| & \\
CH_2 & \!\!\!\!-\!\!\!\!-\!\!\!\!- & CH_2
\end{array}
$$
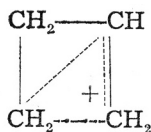
IV

been explained by rehybridisation of the carbon-hydrogen (deuterium) bonding orbitals on carbon atom 3 towards more p character[1]. It was hoped by determining the A/R value with III to find out how far this rehybridisation is completed at the ion pair stage *i.e.* how well the carbonium ion in the intimate ion pair is represented by IV. However, the rate changes observed with III are very small (2—4 per cent)[1] so that is is possible that a change in the A/R value would be smaller than the experimental error. Therefore, no conclusions can be drown from the measurements with III.

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IZVOD

Sekundarni hidrogenski izotopski efekti. V. Unutarnje pregrađivanje kod acetolize deuteriranih ciklopropilmetil benzensulfonata

S. Borčić i D. E. Sunko

Određen je omjer produkata acetolize i unutarnjega pregrađivanja za ciklopropilmetil, ciklopropilmetil-1,1-d_2 i -3,3-d_2 benzensulfonat te je nađeno da taj omjer ostaje konstantan u granicama eksperimentalne pogreške. Rezultati potvrđuju da obje reakcije idu preko zajedničkoga međuprodukta u kojemu je veza između karbonium iona i benzensulfonske skupine potpuno ionskoga karaktera.