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SULFUR-OXYGEN VERSUS CARBON-OXYGEN BOND FISSION IN THE SOLVOLYSIS OF BENZYL SULFENATES

S. Braverman and D. Reisman
Department of Chemistry, Bar-Ilan University
Ramat-Gan, Israel

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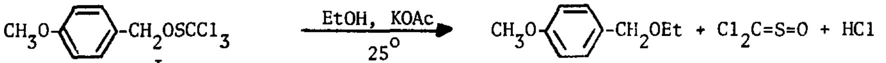
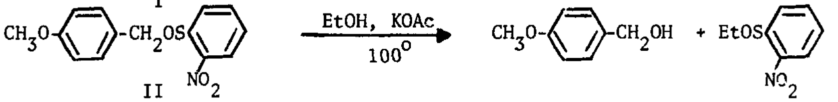
While the solvolysis of sulfonates[1] and sulfinates[2], by either sulfur-oxygen or carbon-oxygen bond fission is well documented, only sulfur-oxygen bond fission has been reported so far for the solvolysis of sulfenates[3]. This can be explained by the relatively greater electrophilicity of the sulfur atom in the sulfenate[4], and the poor leaving group ability of its anion[5]. Prompted by our observation of an ionization mechansim for the rearrangement of benzyl trichloromethanesulfenates to sulfoxides and chlorides[6], we examined the possible operation of such a mechanism during the solvolysis of these and related benzyl sulfenates.

We have found that p-anisyl trichloromethanesulfenate[7] (I, m.p. 28°) readily undergoes ethanolysis at room temperature with complete carbon-oxygen bond cleavage (eq.1)[8]. In sharp contrast, the ethanolysis of p-anisyl 2-nitrobenzenesulfenate[7] (II, m.p. 75°) proceeds at a similar rate only at 100°, and involves complete sulfur-oxygen bond cleavage (eq.2).


I (1)


II (2)

Further details about the mechanisms of solvolysis of the two esters can be obtained from inspection of the kinetic data presented in the Table. While the reaction of I showed first-order kinetics, the reaction of II was second-order: first-order with respect to each, ester and added base. The rate of solvolysis of II decreases by a factor of 3.5 on going from 100% to 80% ethanol and by a factor of 5 by using pyridine instead of acetate as base. These results are consistent with an S_N2 type mechanism involving nucleophilic displacement on sulfur by the base or lyate ion to yield a reactive intermediate or final product, respectively. This interpretation parallels that suggested for the solvolysis of related systems[2a,3a,9]. As indicated in the Table, the rate of solvolysis of I is greatly enhanced by increasing the ionizing power of the solvent. A graph of log k for solvolysis of this ester against log k for ionization of p-methoxyneophyl tosylate[10], for the four solvent systems mentioned in the Table gives a straight line with a slope of 1.33. No organic azide could be detected on addition of NaN_3 to the reaction mixture of I in ethanol at 25°. In the light of this evidence, we feel that the solvolysis of I proceeds by an ionization mechansim to the stage of some ion pair species.

TABLE

Summary of Solvolysis Rate Constants [a] of p-Anisyl Sulfenates.

Sulfenate	Solvent	Temp °C	Added base	[Base],M	10^5k_1 sec^{-1}	10^3k_1/[Base] $l\ mole^{-1}sec^{-1}$
I[b]	MeOH	0	KOAc	0.1998	2.3	
	MeOH	0	2,6-Lutidine	0.2000	2.1	
	80%EtOH-H_2O	0	KOAc	0.2035	7.3	
	80%MeOH-H_2O	0	KOAc	0.2127	23.6	
	60%EtOH-H_2O	0	KOAc	0.2093	30.3	
	60%EtOH-H_2O	0	2,6-Lutidine	0.2093	29.5	
II[c]	EtOH	100	KOAc	0.0499	6.7	1.34
	EtOH	100	KOAc	0.0834	11.8	1.41
	EtOH	100	KOAc	0.1139	15.4	1.35
	EtOH	100	KOAc	0.1273	16.7	1.31
	EtOH	100	Pyridine	0.0562	1.3	0.23
	80%EtOH-H_2O	100	KOAc	0.0553	1.8	0.33

a) Determined by nmr b) [Ester]=0.05M c) [Ester]=0.0275M

The unique S_N1 mechanism and the high reactivity of I, exceeding even that of the corresponding chloride (e.g. in MeOH at 0°. $k=1.51\times10^{-5}sec^{-1}$) and benzenesulfinate[2b], are a result of the relatively high acid strength of Cl_3CSOH. However, the stability of the carbonium ion is of crucial importance, as indicated by the similarity in reactivity of I and its benzhydryl and furfuryl analogues, and by the extensive S-O bond fission involved in the solvolysis of the corresponding benzyl, p-chloro-, and p-methylbenzyl esters. For this reason, and/or due to the use of strong acid or base catalysis, the mechanism reported above for the reaction of I has not been observed in previous studies on the solvolysis of trichloromethanesulfenates[11].

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