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INVESTIGATION OF TRIFLUOROACETOLYSIS OF SOME 2-BROMOETHANOL ARYLSULFONATES

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542.952.1:547.549.2

During solvolysis of some complex esters of haloalkanols isomerization with halogen migration is observed for which an ion-pair mechanism has been proposed [1, 2]. In this work trifluoroacetolysis (TFA) of 2-bromoethyl-p-toluenesulfonate and 2-bromo-p-anisolesulfonate was studied in order to explain the influence of the departing sulfonate group on the mechanism and kinetics of the reaction. The reaction was investigated by PMR. In order to monitor the bromine 1,2-migration a deuterated substrate was prepared by the following scheme

$$CD_3COOD \xrightarrow{Br_2,\ P} BrCD_2COBr \xrightarrow[Et_2O]{LiAlH_4} BrCD_2CH_2OH \xrightarrow{RSO_2Cl} RSO_2OCH_2CD_2Br$$

$$PhOH + CD_3I \xrightarrow[Me_2CO]{K_2CO_3} PhOCD_3 \xrightarrow{HOSO_2Cl} p\text{-}CD_3OC_6H_4SO_2Cl \xrightarrow{(I),\ (II)}$$

$$\xrightarrow{HOCH_2CD_2Br} p\text{-}CD_3OC_6H_4SO_2OCH_2CD_2Br$$

$$R = p\text{-}MeOC_6H_4\ (I),\ p\text{-}MeC_6H_4\ (II).$$

The CD_3O group serves to eliminate the MeO signal at 3.6 ppm thus simplifying the spectrum of the investigated compounds.

TFA was carried out at 70°C directly in sealed NMR tubes, which allows analysis of the reaction mixture without isolation of the individual components. The reaction was observed until complete transformation of the starting materials (I) and (II) into 2-bromoethyltrifluoroacetate (III) (520 and 400 h respectively). Initially in the PMR spectra of the reaction mixtures only singlets at 4.04 and 4.07 ppm due to the starting (I) and (II) are observed. After reaction was complete the mixtures were composed of equal amounts of the isomer resulting from 1,2-migration of bromine (3.20 ppm, s, CH_2Br) and the nonisomerized product (III) (4.36 ppm, s, SH_2OCOCF_3). However, before the appearance of trifluoroacetates in the reaction mixture (16 h for (I) and 12 h for (II)) isomerization of the starting sulfonates begins by 1,2-migration of Br ((I): 3.12 ppm, s, CH_2Br; (II): 3.10 ppm, s, CH_2Br). This can be explained by assuming an ion-pair mechanism of solvolysis, according to which ion pairs upon reaction with solvent can give either product (III) or return to the initial covalent sulfonates (I) and (II) with isomerization of the latter [1].

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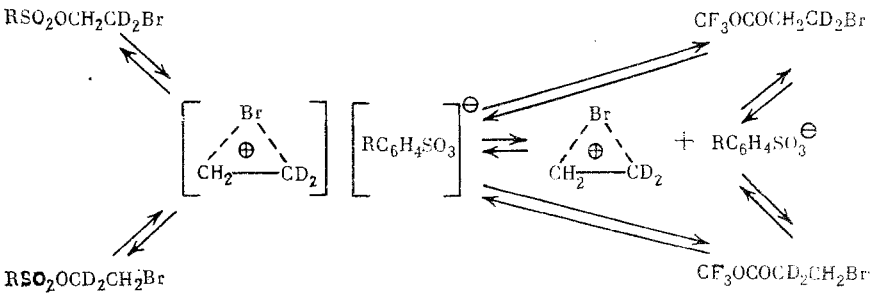

Study of the dependence of solvolysis rate on the initial concentration of sulfonates showed that the solvolysis constant k_{solv} and the isomerization rate constant of the initial compound k_{is}* for both sulfonates do not depend on the initial concentration of the substrates, which proves the pseudomolecularity of the reaction.

In order to determine the type of ionic pairs participating in TFA of (I) and (II) we investigated the dependence of the reaction kinetics on the amount of added $LiClO_4$. The obtained data are shown in Table 1 and in Fig. 1 and 2.

In the case of TFA of (I) a special salt effect was found, which according to the generally accepted ion-pair mechanism of nucleophilic substitution, testifies to the formation of solvent separated ion pairs in the solvolysis process. During solvolysis of (II) in the presence of $LiClO_4$ only a normal salt effect is observed – a linear dependence of reaction rate on the ionic strength of the solution, i.e., upon TFA of (II) solvent separated ion pairs are not found.

In order to examine the possibility of formation of free carbonium ions the TFA of 2-bromoethylsulfonates (I) and (II) was studied in the presence of the corresponding lithium sulfonate ROLi (R = p-$CD_3OC_6H_4SO_2$ and p-$MeC_6H_4SO_2$) (common ion effect). The data are shown in Table 2.

From the obtained data it follows with increase of salt concentration in both cases some depression of the reaction rate is observed, which is an argument in favor of the existence of free ions. The actual retardation of the TFA rate is probably greater than the observed retardation since two opposite factors are working: the retarding common ion effect and the accelerating normal salt effect.

In order to confirm the conclusion on formation of free carbonium ions a special experiment on the study of anion exchange was carried out with 2-bromoethyltosylate (II). For this 2-bromoethyl-2,2-d_2-toluene-d_7-sulfonate was synthesized from toluene-d_8 by the following scheme.

$$CD_3C_6D_5 \xrightarrow{HOSO_2Cl} CD_3C_6D_4SO_2Cl \xrightarrow{HOCH_2CD_2Br} CD_3C_6D_4SO_3CH_2CD_2Br$$

TFA of a 1 M solution of this sulfonate in the presence of nondeuterated 0.1 M lithium toluenesulfonate (H served as isotopic marker) was investigated. At 30% reaction 15% of "light" tosylate was found in the recovered sulfonate. Such a substitution can be realized at the stage of external ionic return during reaction of the free carbocation with $MeC_6H_4SO_3^-$ anion. Thus, isomerization of 2-bromoethyl-2,2-d_2-toluene-d_7-sulfonate is realized both during return of the contact ionic pairs and upon recombination of free ions.

Generalizing the obtained data and the results of study of the TFA of 2-bromoethyl-p-chloro- and 2-bromoethyl-p-nitrobenzenesulfonates [1, 2] one can conclude that all these processes occur by an ion-pair mechanism, according to which the reversible ionization of the starting compound in general passes through the following stages: covalent compound ⇌ contact ion-pairs ⇌ solvent-separated ion-pairs ⇌ free ions. However the formation of solvent-separated ion-pairs are realized only in the case of 2-bromoethyl-p-anisolesulfonate. This is associated with the various types of para-substituent in the benzenesulfonate group: in the studied series of sulfonates the methoxy group has the biggest electron donating effect.

*k_{is} calculated by [2].

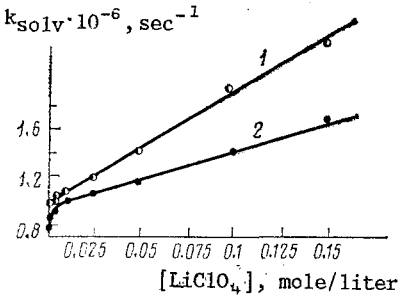

Fig. 1

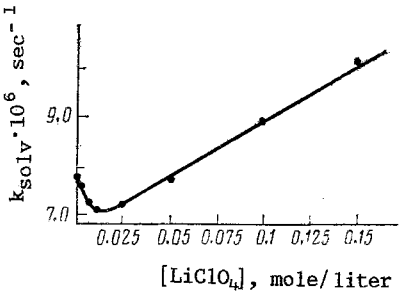

Fig. 2

Fig. 1. Dependence of k_{solv} on $LiClO_4$ concentration during TFA: 1) 2-bromoethyl-2,2-d_2-toluenesulfonate; 2) 2-bromoethyl-2,2-d_2-anisolesulfonate.

Fig. 2. Dependence of k_{is} on $LiClO_4$ concentration during TFA of 2-bromoethyl-2,2-d_2-anisolesulfonate.

TABLE 1. Dependence on $LiClO_4$ concentration of k_{solv} and k_{is} during Trifluoroacetolysis of 1 M Solutions of Sulfonates (I) and (II)

$[LiClO_4]$, mole/l	(I)		(II)		$[LiClO_4]$ mole/l	(I)		(II)	
	k_{solv}	k_{is}	k_{solv}	k_{is}		k_{solv}	k_{is}	k_{solv}	k_{is}
	$10^6 \cdot sec^{-1}$					$10^6 \cdot sec^{-1}$			
0.000	0.82	9.2	0.97	10.3	0.025	1.15	7.3	1.18	11.4
0.001	0.85	7.7	1.00	10.3	0.050	1.12	7.6	1.45	12.8
0.005	0.93	7.4	1.05	10.5	0.100	1.38	8.9	1.97	13.8
0.010	0.98	7.0	1.08	10.8	0.150	1.72	10.2	2.24	18.3

TABLE 2. Trifluoroacetolysis of 2-Bromoethylsulfonates-2,2-d_2 in the Presence of the Corresponding Lithium Sulfonates ROLi

[ROLi], mole/liter	(II)	(I)	[ROLi], mole/liter	(II)	(I)
	$k_{solv} \cdot 10^6$, sec^{-1}			$k_{solv} \cdot 10^6$, sec^{-1}	
0.10	0.872	0.732	0.04	0.896	0.760
0.07	0.885	0.746	0.01	–	0.779

TABLE 3. Data on Synthesis of 2-Bromoethyl-2,2-d_2-Sulfonates

Sulfonate	Amount of reagents, mole			Reaction time, h	Yield, %	Boiling point, °C (p, mm, Hg)	Literature data reference
	CD_2CH_2BrOH	RSO_2Cl	C_6H_5N				
(I)	0.05	0.05	0.22	3	75	150 ($6 \cdot 10^{-3}$) melting point 32	206° (1 mm) [7]
(II)	0.05	0.05	0.22	3.5	72	130 ($5 \cdot 10^{-4}$)	melting point, 35° [7]

EXPERIMENTAL

Preparation of 2-bromoethyl-2,2-d_2-sulfonates

2,2-d_2-Bromoacetyl bromide. A mixture of 20 g (0.312 mole) in industrial grade CD_3COOD and 3.5 g (0.112 mole) of dry red phosphorus was treated with 230 g (1.48 mole) Br_2 and heated for 5 h on a boiling water bath. The fraction distilling at 145-153°C was redistilled under vacuum to yield 39.6 g (58%) of 2,2-d_2-bromoacetyl bromide with b.p. 48-49°C (15 mm) (see [3]).

2-Bromoethanol-2,2-d_2. To a suspension of 5.23 g (0.43 mole) of $LiAlH_4$ in 150 ml absolute ether at −75°C an ether solution of 28 g (0.127 mole) 2,2-d_2-bromoacetyl bromide was added dropwise. The mixture was stirred for 0.5 h at −70°C and at the same temperature 140 ml water and 140 ml 6 N H_2SO_4 were added. The ether layer was separated and the water was extracted with ether. The ether solutions were combined and dried with calcined $MgSO_4$. By distillation under vacuum 9.5 g (59%) of 2-bromoethanol-2,2-d_2 was obtained with b.p. 56-59°C (23 mm) (see [4]).

p-Anisolesulfonyl chloride-d_3. a) Anisole-d_3. To a solution of 21.6 g (0.23 mole) of phenol in acetone 38 g (0.276 mole) of finely ground K_2CO_3 and 40 g (0.276 mole) CD_3I were added. The mixture was heated on a boiling water bath. After ether addition the K_2CO_3 was separated on a Buchner funnel. The ether extract was dried over $MgSO_4$. By distillation 20 g (79%) of anisole-d_3 with boiling point 152-153°C was isolated (see [5]).

b) p-Anisole-d_3-sulfonyl chloride. To a solution of 40.56 g (0.343 mole) anisole-d_3 in $CHCl_3$ at −8°C 87.5 g (0.75 mole) of chlorosulfonic acid was added dropwise for 40 min. The mixture was kept for 50 min at 20°C and poured into a beaker with ice. The sulfonyl chloride was extracted with chloroform and dried above roasted $MgSO_4$. After solvent removal 56.4 g (80%) of anisole-d_3-sulfonyl chloride with m.p. 39°C was obtained by recrystallization from hexane (see [6]).

2-Bromoethyl-2,2-d_2-sulfonates. To a mixture of 2-bromoethanol-2,2-d_2 and the corresponding sulfonyl chloride at 0-5°C absolute pyridine was added with careful stirring. Stirring was prolonged for 2-3 h at 0°C. Then the reaction mixture was poured into ice water and extracted with ether. The extract was washed with cold dilute H_2SO_4, ice water, and dried with $MgSO_4$. The ether was distilled off and the residue was distilled under vacuum or recrystallized (depending on the type of sulfonate). Data on synthesis are shown in Table 3.

CONCLUSIONS

By PMR spectroscopy the kinetics of trifluoroacetolysis of 2-bromoethyl-2,2-d_2-toluene- and 2-bromoethyl-2,2-d_2-anisole sulfonates, the dependence of rate constant on the presence of lithium perchlorate and on salts with a common ion were investigated. The trifluoroacetolysis of 2-bromoethyl-2,2-d_2-toluene-d_7-sulfonate in the presence of the lithium salt of nondeuterated toluenesulfonic acid was investigated. It was shown that reaction is accompanied by isomerization of the initial sulfonate (1,2-migration of bromine) and occurs by an ion-pair mechanism.

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