KINETICS OF THE ALKALINE HYDROLYSIS OF 3-SULFOLANOL PHENYL ETHERS

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A scheme for the elimination of aryloxy groups via an E1cB mechanism is proposed on the basis of data on the kinetics of the alkaline hydrolysis of 3-sulfolanol phenyl ethers in H_2O and D_2O.

Under the influence of basic catalysts, 3-sulfolanol ethers readily split out alcohol to give 2-sulfoline or react with nucleophilic reagents with exchange of alkoxy or aryloxy groups [1]. It has been shown in the case of 3-methoxysulfolane [2] that the introduction of an alkoxy group into the sulfolane molecule raises the lability of the hydrogen atoms of the methylene group in the 2-position. Their isotopic exchange with D_2O reaches equilibrium at 20-25°C in 0.006 N alkali solution after 30-40 min. In this case, the rate of isotopic exchange is considerably higher than the rate of elimination. These data make it possible to propose the intermediate formation of carbanions (E1cB mechanism), which has been established for many elimination and cleavage-addition reactions (for example, see [3-5]), for the elimination and substitution reactions of β-substituted derivatives of sulfolane.

The results of an investigation of the kinetics of the alkaline hydrolysis of 3-sulfolanol phenyl ethers (Ia-f), which confirm this assumption, are presented below.

The hydrolysis of all of the investigated ethers in excess alkali is described by a first-order kinetic equation (Fig. 1). The first-order reaction with respect to the ether is confirmed by the constancy of the observed rate constants when the starting concentration of ethers I changes. The first-order rate constant is linearly related to the activity of the OH^- ions (Fig. 2). Thus, the kinetic equation of the reaction has the form

$$-\frac{d[I]}{dt}=k_2[I][a_{OH^-}].$$

The activation parameters of the hydrolysis, which are presented in Table 1 together with the rate constants, were found from the temperature dependence of the reaction rate at 30, 40, and 50°C.

A comparison of the k_2 values for various ethers I shows that electron-acceptor substituents in the para position of the phenyl ring accelerate the reaction, while electron-donor substituents in this position inhibit it. The k_2 values satisfy the Hammett equation with σ^p substituent constants [6]: $\log k = -1.3010 + 1.27\,\sigma^p$ ($r = 0.942$; $s = 0.036$).

Inasmuch as the magnitude of the kinetic isotope effect may serve as one of the criteria of a carbanion mechanism [3, 7, 8], we carried out two parallel series of experiments with ether Ia in D_2O and H_2O with catalysis by NaOH in 50% dioxane–water solutions. At 30°, $k_2(H) = 0.0436$, $k_2(D) = 0.072$ liter · mole^{-1} · sec^{-1}, and $k_H/k_D = 0.61$. The observed acceleration of the reaction in D_2O is in agreement with the results of calculations [3] from the shift in the protolytic equilibria on passing from H_2O to D_2O (from 0.3 to 0.8), with the values of the isotope effect in the elimination of a phenoxy group from a 2-phenoxyethylsulfonium salt (0.66) and a sulfoxide (0.78) [3], and also with the values observed in the elimination of a

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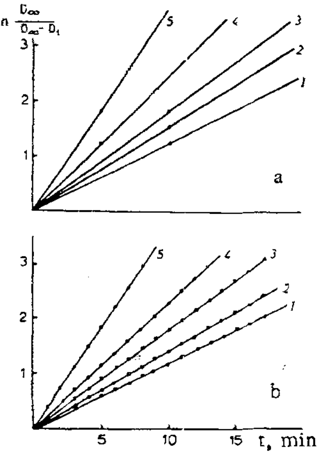


Fig. 1

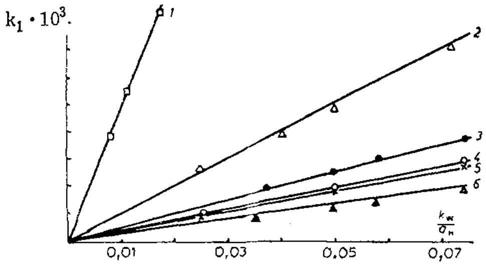


Fig. 2

Fig. 1. Change in the concentration of ether Ia during hydrolysis at 30° [a) $c_I = 2.4 \cdot 10^{-3}$ mole/liter; b) $c_I = 4 \cdot 10^{-3}$ mole/liter: 1) 0.032 N KOH; 2) 0.405 N KOH; 3) 0.047 N KOH; 4) 0.061 N KOH; 5) 0.009 N KOH.

Fig. 2. Dependence of the pseudo-first-order rate constant (k_1) on the alkali concentration during the alkaline hydrolysis of ethers I with various substituents: 1) p-NO_2; 2) p-Br; 3) H; 4) p-CH_3; 5) m-CH_3; 6) o-CH_3.

methoxy group from methoxy ketones (0.75-0.88) [7], for which an E1cB mechanism has been proved. One should have expected inhibition of the reaction in D_2O for an E2 mechanism (k_H/k_D = 3) [3]. The entropy of activation of the alkaline hydrolysis of ethers is somewhat lower than for ketones [7]; in the case of identical mechanisms, this can be explained by the lower acidity of sulfolane derivatives and reinforcement of the steric hindrance to solvation of the transition state [9].

A comparison of the results of the present study with the data in [8] makes it possible to arrange the investigated phenyl ethers in the following order of decreasing activity in alkaline hydrolysis:

	$C_6H_5SO_2CH_2OPh$ >	I >	$C_6H_5SOCH_2CH_2OC_6H_5$
k_2 liter · mole^{-1}·sec^{-1}	$3.5\cdot10^{-1}$ (at 25.4°)	$5\cdot10^{-2}$ (at 30°)	$1.1\cdot10^{-3}$ (at 25.4°)
ρ	+1.5	+1.27	+1.2

The ρ values are close in all cases, while the rate constants differ between adjacent members of the series; this is characteristic for an E1cB carbanion mechanism [8].

On the basis of the materials set forth above, the alkaline hydrolysis of ethers I can be represented by the scheme

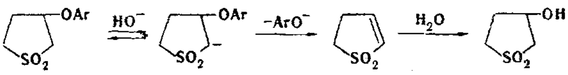
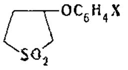


TABLE 1. Rate Constants of the Alkaline Hydrolysis of 

Compound	X	I concn., mole/liter · 10^{-4}	k, liter·mole^{-1}·sec^{-1}			E_a, kcal/mole	$\Delta S^{\neq}$, eu
			30°	40°	50°		
Ia	H	4	0,0506	0,124	0,278	16,6	−11,7
Ib	4-CH_3	3,99	0,0392	0,0891	0,252	18,2	−7,0
Ic	3-CH_3	3,76	0,0381	0,101	0,262	18,8	−5,0
Id	2-CH_3	3,55	0,0272	0,0705	0,156	17,0	−11,6
Ie	4-Br	3,95	0,101	0,249	0,515	15,8	−12,8
If	4-NO_2	1,28*	0,425	—	—	12,6	−20,6

*At 22°, k_2 = 0.269; at 9°, k_2 = 0.0848.

TABLE 2. Properties of Aryloxysulfolanes

Compound	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
			C	H	S	C	H	S	
Ia	125,5—126,5	$C_{10}H_{12}O_3S$	56,8	5,7	15,3	56,6	5,7	15,1	10
Ib	128—129	$C_{11}H_{14}O_3S$	57,7	5,9	14,2	58,4	6,2	14,2	19
Ic	103,5—104	$C_{11}H_{14}O_3S$	58,5	6,5	14,2	58,4	6,2	14,2	16
Id	89— 90	$C_{11}H_{14}O_3S$	58,3	6,2	14,5	58,4	6,2	14,2	16
Ie	150,5—151,5	$C_{10}H_{11}BrO_3S$	41,4	3,9	10,7	41,3	3,8	11,0	70
If	144,5—145,5	$C_{10}H_{11}NO_3S$	45,4	4,2	13,2	46,7	4,3	12,5	<5
Ig	192—193	$C_{10}H_{10}N_2O_7S$	39,5	3,3	10,8	39,7	3,3	10,6	95

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* Compound Id was crystallized from ether, Ig was crystallized from methanol–dioxane, and the remaining compounds were crystallized from methanol.

EXPERIMENTAL

3-Phenoxy- (Ia) and 3-tolyloxysulfolanes (Ib-d) were obtained by reaction of phenols and cresols with 2-sulfolene in the presence of sodium metal (in a ratio of 2 : 1 : 0.5), while 3-(4-bromophenoxy)sulfolane (Ie) was obtained by bromination of ether Ia with dioxane dibromide. 3-(4-Nitro)- (If) and 3-(2,4-dinitrophenoxy)sulfolane (Ig) (Table 2) were isolated in the nitration of ether Ia with a mixture of 53% nitric acid and 83% sulfuric acid.

The hydrolysis was carried out in 10% aqueous dioxane. A constant ionic strength was maintained in the solutions by means of 1 M KCl solution. The kinetic measurements were made with an SF-16 spectrophotometer, the thermostatted cuvette (1 cm thick) of which was used as the reaction vessel. The course of the reaction was followed from the change in the potassium phenoxide concentration. Inasmuch as the difference in the absorption of the potassium phenoxide and ethers I in the absorption maxima of the phenoxides is very large, the absorption of ethers I was not taken into account in the calculations. The experiments were repeated no less than three times, and the data were averaged.

The rate of hydrolysis was investigated under pseudomonomolecular conditions in the presence of a considerable (1 : 100) excess of KOH. The rate constant was calculated from the first-order reaction equation

$$\ln \frac{D_\infty}{D_\infty - D_t} = k_{\text{obs}} \cdot t,$$

where D_∞ and D_t are the optical densities of the solution in the case of 100% hydrolysis and at time t. The D_∞ values observed in the hydrolysis of Ia, b were in agreement with the values calculated from the molar absorption coefficient of the corresponding phenoxide and the starting ether concentration; this indicates the practical irreversibility of the reaction and the absence of side processes. The experimental D_∞ values were therefore subsequently used in the calculations of the rate constants.

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