Kinetics and Mechanism of the Olefin-Forming Elimination Producing Phenylsulfonylethene

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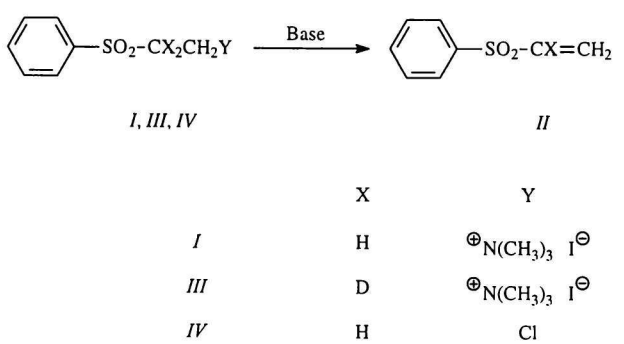
[2-(Phenylsulfonyl)ethyl]trimethylammonium iodide, its 2,2-dideuterio derivative, and 1-chloro-2-(phenylsulfonyl)ethane have been synthesized, and the kinetics of their elimination reaction giving phenylsulfonylethene have been studied in methanolic solutions of acetate, triethylamine, morpholine, and butylamine buffers. The kinetic experiments show that the reaction is specific-base-catalyzed and its rate is independent of the ionic strength, and the primary isotope effect is 3.5. The results of kinetic measurements are discussed from the point of view of the E1cB mechanism.

Elimination represents one of the basic types of organic reactions, and according to the present knowledge [1—3] it can proceed by one of three possible mechanisms: E1, E2, or E1cB. The aim of the present paper was to find which of the mechanisms is operating in the reaction of formation of phenylsulfonylethene (*II*) from [2-(phenylsulfonyl)ethyl]trimethylammonium iodide (*I*), its 2,2-dideuterio derivative (*III*), and 2-phenylsulfonylchloroethane (*IV*) (Scheme 1).

The substrates used (*I* and *III*) are characterized by the presence of a strong electron-acceptor phenylsulfone group at β-carbon atom and a poor leaving group at α-carbon atom, *i.e.* quaternary ammonium group which, however, is strongly polar: hence it can be presumed that the said elimination will proceed *via* the conjugate base. In this type of E1cB mechanism the first step is splitting off of the proton from β-carbon atom by a base with production of the corresponding carbanion, which either is reprotonated or splits off trimethylamine (Scheme 2).

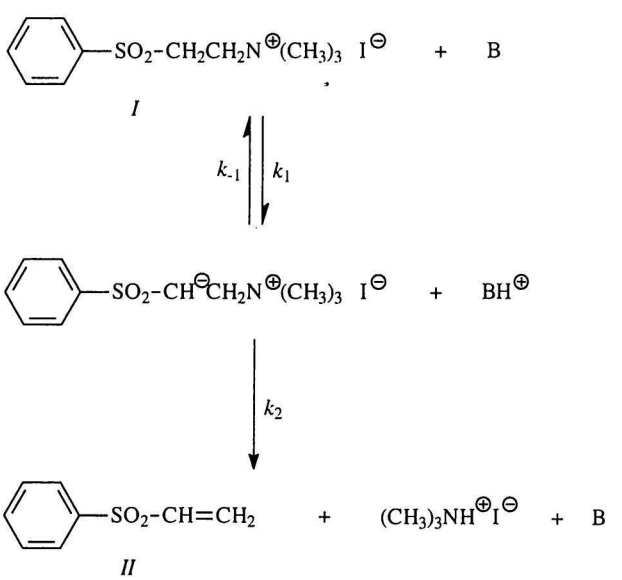
This elimination reaction followed under the pseudo-first-order conditions can be described by the overall reaction rate equation (eqn (*1*)) derived from Scheme 2, and the observed rate constant k_{obs} is given by eqn (*2*).

$$\nu = k_{obs} \cdot [I] \qquad (1)$$



	X	Y
I	H	$^{\oplus}N(CH_3)_3\ I^{\ominus}$
III	D	$^{\oplus}N(CH_3)_3\ I^{\ominus}$
IV	H	Cl

Scheme 1



Scheme 2

$$k_{obs} = \frac{k_1 k_2[B]}{k_{-1}[BH^{\oplus}] + k_2} \quad (2)$$

It is possible to consider two extreme cases for the denominator of eqn (*2*). In the first case, the first reaction step is very fast, hence $k_{-1}[BH^{\oplus}] \ll k_2$ and $k_{obs} = k_1[B]$, which means that the reaction is subject to general base catalysis. This case is referred to as irreversible E1cB reaction or, according to *Bordwell* [4], as $(E1cB)_i$. In the second extreme case it is $k_{-1}[BH^{\oplus}] \gg k_2$ and hence the value $k_{obs} = K_1 k_2[B]/[BH^{\oplus}]$, *i.e.* the E1cB mechanism is reversible and is denoted as $(E1cB)_r$. The value $K_1 = k_1/k_{-1}$ expresses the dissociation constant of the substrate in the given medium. This means that the reaction is now subject to specific base catalysis, but the opposite need not be true, *i.e.* the specific base catalysis need not necessarily mean that the reaction goes by the $(E1cB)_r$ mechanism.

Despite the fact that elimination reactions have been described in a number of works, the E1cB mechanism was specified for the first time by *Hine* [5] as late as 1961. The author has proved its existence convincingly in reactions producing olefins. *Crosby* and *Stirling* [6] have carried out a systematic study of substrates containing various electron-acceptor groups and the phenoxide anion in the role of the leaving group Y. They have found rate constant values covering a broad interval of eleven orders of magnitude depending on the type of substituents [7]. The E1cB mechanism usually makes itself felt when there is a strong activating group at β-carbon atom and a bad leaving group Y at α-carbon atom (which slows down the reaction going by the E2 mechanism). From this point of view a number of substrates were studied with Y = PhO [6], MeO [8], and RSO [9].

The evidence for an elimination reaction going by E1cB mechanism most often involves the deuteration at β-carbon atom, the isotope effect of solvent, the primary isotope effect, the base catalysis, and the effect of leaving group Y [10, 11].

EXPERIMENTAL

2-Hydroxyethyl phenyl sulfide (b.p. (1870 Pa) = 138—140 °C, n(D, 25 °C) = 1.5900 in accordance with literature [12]) was used.

The elimination reactions were followed in methanolic solutions of respective buffers at 25 °C. The ionic strength was adjusted by adding sodium perchlorate. The resulting concentration of substrate was 1×10^{-4} mol dm^{-3}. The kinetic measurements were carried out spectrophotometrically with a Specord UV VIS apparatus (Zeiss, Jena). A 2 cm quartz cell with lid was charged with buffer (2 cm^3) and placed in thermostat cell compartment of the apparatus; after reaching the required temperature, 2 cm^3 solution of substrate (*I*, *III* or *IV*) was added from a pipette. The observed rate constants k_{obs} were calculated from the absorbance change $\Delta A = (A_\infty - A_t)$ measured at λ = 278 nm using the relationship $k_{obs}\ t = -2.3 \log (\Delta A) + \text{const.}$

1-Chloro-2-(phenylsulfonyl)ethane (*IV*). 2-Hydroxyethyl phenyl sulfide (12 g; 0.078 mol) was suspended in 100 cm^3 of cold water and 120 cm^3 of 35 % HCl. The mixture was then treated with sodium hypochlorite (153 cm^3, 10 % solution) added during 3 h at the temperature of 0 °C. Then the reaction mixture was left to stand overnight at room temperature. The product was poured in acidified water and extracted with dichloromethane. The extract was washed with sodium hydrogen sulfite, dried with Na_2SO_4, and dichloromethane was distilled off. Yield 12.1 g (75 %), m.p. = 52 °C in accordance with literature [13].

[2-(Phenylsulfonyl)ethyl]trimethylammonium iodide (*I*). 1-Chloro-2-(phenylsulfonyl)ethane (2 g; 0.0056 mol) was added to a solution of dimethylamine (2.5 cm^3; 0.036 mol) in methanol (25 cm^3). After 24 h, the methanol was distilled off and the obtained raw 1-dimethylammonium-2-phenylsulfonylethane chloride (2.3 g; 92 %) was recrystallized from ethanol (m.p. = 184 °C). The hydrochloride thus obtained (2.5 g) was added to a mixture of water (40 cm^3), sodium hydrogen carbonate (2 g), and sodium chloride (10 g). After shaking, the mixture was extracted with ether and the extract was treated with methyl iodide (2.8 g; 0.02 mol). After 3 h, the separated crystalline solid was collected by filtration (3.4 g; m.p. = 198—200 °C) and recrystallized from ethanol (m.p. = 200—201 °C in accordance with literature [14]).

[2,2-Dideuterio-2-(phenylsulfonyl)ethyl]trimethylammonium iodide (*III*). Sodium metal (0.23 g; 0.01 mol) was carefully added to deuterium oxide (D_2O; 25 cm^3) and the sodium deuteroxide formed was treated with (2-phenylsulfonylethyl)trimethylammonium iodide (*I*; 1.1 g; 0.003 mol). After 24 h, the solution was saturated with sodium chloride and extracted with 3 × 40 cm^3 of ether. The extract was dried with Na_2SO_4 and the ether solvent was distilled off. The distillation residue (*ca.* 40 cm^3) was treated with methyl iodide (0.3 cm^3) and left to stand overnight. The white crystalline product was collected by filtration; m.p. = 182—184 °C [15].

RESULTS AND DISCUSSION

Compounds *I*, *III*, and *IV* were prepared by modified procedures which gave the same yields but purity of the products was much better than that given in Refs. [13—15].

The rate constants of elimination reactions were measured in methanolic solutions of triethylamine, morpholine, and butylamine buffers. The concentration of both buffer components was much higher than that of the substrate, hence no pH decrease occurred throughout the measurement. The reactions proceeded under the pseudo-first-order conditions and

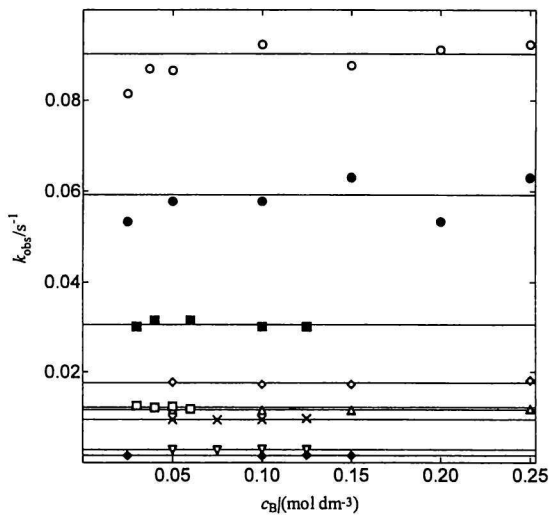


Fig. 1. Dependence of k_{obs} of the elimination ($I \rightarrow III$) on the concentration of basic component c_B of basic triethylamine buffers ([B]/[BH$^{\oplus}$]): ○ 10 : 1, ● 10 : 1.5, ■ 10 : 3, □ 10 : 6, basic morpholine buffers ([B]/[BH$^{\oplus}$]): ◇ 10 : 1, △ 10 : 2, × 10 : 4, and basic butylamine buffers ([B]/[BH$^{\oplus}$]): ▽ 10 : 4, ◆ 10 : 8.

the dependences of $\log(\Delta A)$ upon time were linear in the whole interval followed (more than 95 % conversion). All the measurements were carried out at constant ionic strength despite the fact that separate experiments showed that the observed rate constant was independent of ionic strength. The observed rate constants were independent of the basic buffer component concentration (Fig. 1) and increased with increasing pH value (*i.e.* with increasing [B]/[BH$^{\oplus}$] ratio in a given series).

This means that the reaction is subject to specific base catalysis and the $(E1cB)_r$ mechanism can be considered with $k_{-1}[BH^{\oplus}] \gg k_2$ and $k_{obs} = K_1 k_2 [B]/[BH^{\oplus}]$. However, the experimental proof of specific base catalysis does not clearly prove the mechanism going *via* the conjugate base. It is also compatible with a case of general base catalysis with the Brønsted coefficient close to 1. In such a case, the rates of base-catalyzed splitting of C—H bond are much lower than those of the bond splitting by methoxide ion, which means that the concentration of basic buffer component will not make itself felt kinetically. Beside the above-mentioned study of base catalysis we have made use of still another method frequently applied to mechanistic studies of elimination reactions, *viz.* the primary isotope effect. For this purpose, we prepared [2,2-dideuterio-2-(phenylsulfonyl)ethyl]trimethylammonium iodide (*III*) and studied its elimination reactions in the same media as above with derivative *I*. The elimination reactions proceeding by the E2 mechanism are characterized by the activated complexes with the same extent of bond splitting at both α- and β-carbon atoms, and their values of primary kinetic isotope effect k_H/k_D vary in the interval of 7—10 [4, 16]. If the C^{β}—H bond is split to a greater extent than the C^{α}—Y bond in the activated complex, then the k_H/k_D ratio is lower. The value $k_H/k_D = 3.5$ found by us unambiguously indicates that the rate-limiting step involves the C—H bond splitting but it cannot be decided whether the reaction goes by an E2 mechanism with unsymmetrical activated complex or by the $(E1cB)_r$ mechanism. Therefore we further studied the elimination reaction of 1-chloro-2-(phenylsulfonyl)ethane (*IV*). If the elimination proceeded by the E2 mechanism, then the reaction rate of chloro derivative *IV* would be many times higher than that of ammonium salt *I* because the chloride anion is a much better leaving group [17]. On the other hand, in the case of $(E1cB)_i$ mechanism we can expect a retardation because the $-I$ effect of chloro substituent is substantially lower than that of trimethylammonium group, hence the splitting of

Table 1. Observed Rate Constants k_{obs} at 25 °C and Ion Strength 0.25 mol dm^{-3} for Elimination Reaction *IV* → *II* in Methanolic Amine Buffers

[B]/[BH$^{\oplus}$]	$c_B \cdot 10^3$/(mol dm^{-3})	$k_{obs} \cdot 10^4/s^{-1}$
Triethylamine buffer (10 : 6)	40	8.7
	50	8.5
	63	8.8
Morpholine buffer (10 : 4)	50	6.8
	75	7.1
	125	6.8

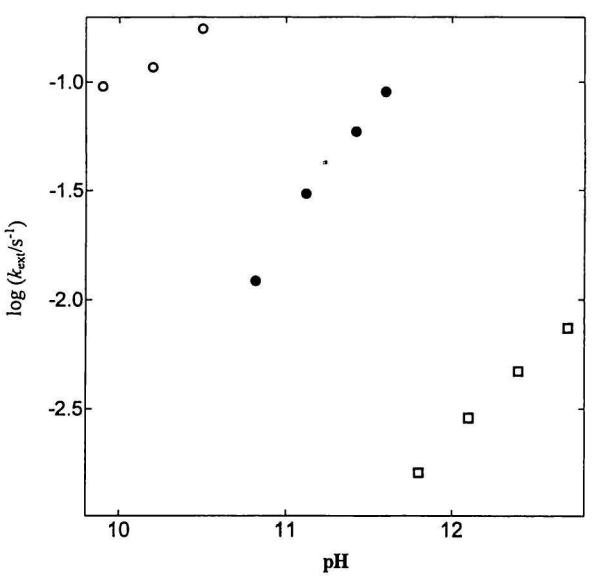


Fig. 2. Dependence of log (k_{ext}/s^{-1}) of the elimination ($I \rightarrow III$) on the pH values of amine buffers: ○ morpholine, ● triethylamine, □ butylamine.

C—H bond would be more demanding energetically. The rate of elimination of chloro derivative *IV* was measured in triethylamine and morpholine buffers. In both cases, the observed rate constants were one order of magnitude lower than those of ammonium salt *I*, which corresponds to the $(E1cB)_i$ mechanism (Table 1).

When comparing the rates of elimination in various buffers, we have found an anomaly for which we have no explanation yet. Available literature does not mention such behaviour either. Our extrapolated rate constants from Fig. 1 (*i.e.* the constants of methoxide-ion-catalyzed reaction) plotted against pH for the individual buffers give linear dependences (linear dependences on the acid-to-base buffer component ratio in each buffer) but they also depend on the type of buffer used (Fig. 2). This finding indicates that the base of buffer specifically affects the reactivity of substrate *I*.

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