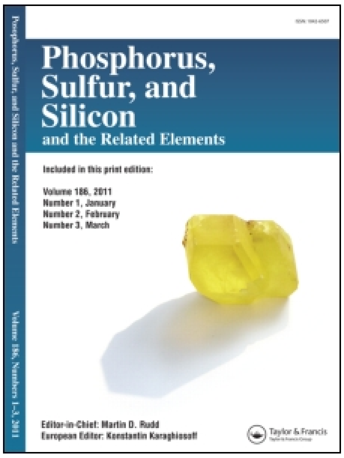

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KINETICS OF THE REACTION OF SULFIMIDES WITH POTASSIUM HYDROXIDE IN METHANOL

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KINETICS OF THE REACTION OF SULFIMIDES WITH POTASSIUM HYDROXIDE IN METHANOL

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The reaction of sulfimides with hydroxide ion in methanol gave the corresponding sulfoxide (the solvolysis product) and/or the corresponding α-methoxysulfide (the Pummerer type product). The pseudo first order rates for the solvolysis reaction and the Pummerer type reaction were determined using a large excess of potassium hydroxide. The rates of the solvolyses are correlated with σ values and the values of $\rho_X = +1.2$ and $\rho_Y = +0.8$ were obtained for aryl methyl *N*-arylsulfonylsulfimides (p-$XC_6H_4S(NSO_2C_6H_4Y$-$p)CH_3$), and both the activation enthalpy and entropy calculated are $\Delta H^{\neq} = 18.8$ kcal mol^{-1} and $\Delta S^{\neq} = -23.9$ e.u. ($PhS(NSO_2C_6H_4CH_3$-$p)CH_3$), respectively. Hammett correlation with σ values for the Pummerer type reaction gave $\rho_Z = +2.0$ for *N*-aryl-sulfonyltetramethylenesulfimides ($(CH_2)_4SNSO_2C_6H_4Z$-p), and the activation enthalpy and entropy are $\Delta H^{\neq} = 27.9$ kcal mol^{-1} and $\Delta S^{\neq} = +13.3$ eu ($(CH_2)_4SNSO_2C_6H_4CH_3$-p), respectively. All these observations suggest that the solvolysis reaction proceeds via the initial nucleophilic attack of hydroxide ion on the sulfur atom of the sulfimide namely via an S_N2 process at the sulfur atom whereas the Pummerer type reaction proceeds by way of the *E*1*cb* mechanism.

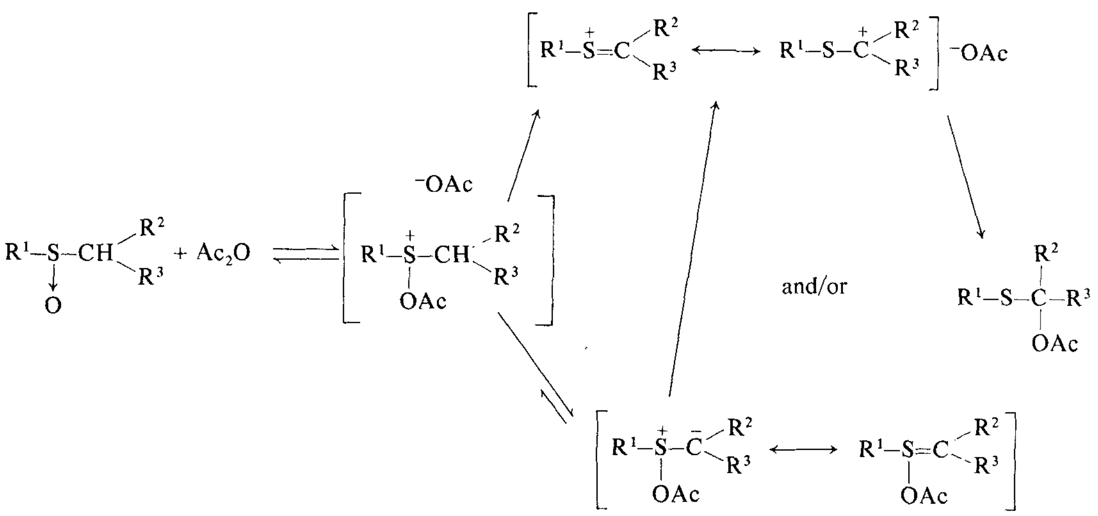
Earlier, Cram and his co-workers[1] reported that the reaction of methyl *p*-tolyl *N*-*p*-tosylsulfimide with hydroxide ion in methanol gave the corresponding sulfoxide in high yield. This reaction has been considered to be a typical S_N2 type reaction on the sulfur atom of the tricoordinated sulfur compound having a semipolar bond. However, unexpectedly, we found that the reactions of other sulfimides under similar conditions afford either the corresponding sulfoxide or the corresponding α-methoxysulfide alone, or a mixture of both products.[2] Our previous investigations showed that the products obtained by the reaction vary depending upon the structure of the sulfimide; namely, in the case of methyl, *p*-tolyl, or cyclopropyl phenyl *N*-*p*-tosylsulfimide, the sulfoxide is the sole product, whereas in the case of *N*-*p*-tosyltetra- or hexamethylenesulfimide, only the rearranged product was obtained.[2] On the other hand, the reaction of the sulfimide with hydroxide ion in methanol generally gives a mixture of both the substituted and rearranged products.[2] Thus, this reaction is quite attractive for the investigation of both the nucleophilic substitution on the tricoordinated sulfur atom and the elimination reaction involving the sulfur atom.

Although the nucleophilic substitutions on the sp^3 carbon or the dicoordinated sulfur atom have been studied extensively, those on the tricoordinated sulfur atom such as in the sulfoxide or the sulfimide have been investigated rather little.[3] Furthermore, kinetic studies on the acid-catalyzed nucleophilic substitution on the sulfur atoms of sulfoxide[3] or sulfimide[4] were reported by several investigators and the reactions have been revealed to proceed via the initial formation of the sulfonium compound. Whereas, the reaction of the sulfimide with cyanide ion[5] or triphenylphosphine[6] to give the corresponding sulfide has been shown by kinetic study to proceed via the initial formation of the sulfurane as the intermediate. However, the accompanying rearrangement which takes place in the present reaction of the sulfimide with hydroxide ion seems to involve the Pummerer type reaction of the sulfoxide,[7] sulfimide,[8] and sulfonium ylid.[9] The generally accepted mechanism for the Pummerer reaction of the sulfoxide is illustrated as shown below (Scheme 1).

RESULTS AND DISCUSSION

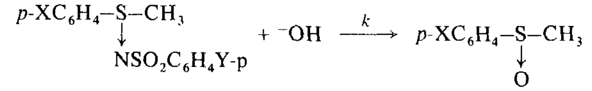
Kinetics of the Solvolysis Reaction

The sulfimides selected for the investigation of the solvolysis are para-substituted aryl methyl derivatives since these compounds under the reaction conditions used afforded the corresponding sulfoxide as the sole product. The kinetic study was carried out in the presence of a large excess of



SCHEME 1

TABLE I
Rate constants of the reaction of *N*-arylsulfonylsulfimides (p-$XC_6H_4S(NSO_2C_6H_4Y$-$p)CH_3$) with potassium hydroxide in methanol
[Sulfimide] = 0.050 mol l^{-1}



$$p\text{-}XC_6H_4\text{-}\underset{\downarrow \atop NSO_2C_6H_4Y\text{-}p}{S}\text{-}CH_3 + {}^-OH \xrightarrow{k} p\text{-}XC_6H_4\text{-}\underset{\downarrow \atop O}{S}\text{-}CH_3$$

X	Y	[KOH] mol l^{-1}	Temp. (°C)	$10^5\,k_{app}$ (sec^{-1})	$10^5\,k$ (l mol^{-1} sec^{-1})
H	Me	0.843	50.00 ± 0.05	0.84 ± 0.02	1.00 ± 0.02
H	Me	0.843	55.20 ± 0.05	1.29 ± 0.07	1.53 ± 0.08
H	Me	0.843	59.90 ± 0.05	2.07 ± 0.15	2.46 ± 0.18
H	Me	0.653	59.90 ± 0.05	1.60 ± 0.15	2.45 ± 0.08
H	Me	0.440	59.00 ± 0.05	1.03 ± 0.12	2.34 ± 0.27
Me	Me	0.843	59.90 ± 0.05	1.32 ± 0.24	1.57 ± 0.28
Cl	Me	0.843	59.90 ± 0.05	4.35 ± 0.14	5.16 ± 0.17
H	H	0.843	59.90 ± 0.05	2.60 ± 0.15	3.08 ± 0.18
H	Br	0.843	59.90 ± 0.05	4.20 ± 0.26	4.98 ± 0.31

$\Delta H^{\neq} = 18.8$ kcal mol^{-1}; $\Delta S^{\neq} = -23.9$ eu ($X = H$, $Y = Me$); $\rho_X = +1.2$; $\rho_Y = +0.8$.

potassium hydroxide for the sake of simplicity in following the increase of the amount of the sulfoxide formed in the reaction. The rate constants for the aryl methyl *N*-*p*-tosylsulfimides were calculated by the pseudo first order kinetic equation.† The results obtained are summarized in Table I.

Furthermore, by plotting [KOH] against k_{app} a straight line was obtained ($\gamma = 0.999$) (Figure 1). Thus, the solvolysis reaction obeyed 2nd order kinetics; namely, first order with respect to both [sulfimide] and [KOH] concentrations. The activation parameters for the reaction of methyl phenyl *N*-*p*-tosylsulfimide with hydroxide ion in methanol are $\Delta H^{\neq} = 18.8$ kcal mol^{-1} and $\Delta S^{\neq} = -23.9$ eu. These activation parameters are of similar magnitude to those of the acid-catalyzed solvolysis reaction of methyl phenyl *N*-*p*-tosylsulfimide ($\Delta H^{\neq} = 19.5$ kcal mol^{-1}, $\Delta S^{\neq} = -19.0$ eu.).[4] The pseudo first order rate constants of the reactions for the para-substituted aryl methyl *N*-*p*-tosylsulfimides (p-$XC_6H_4S(NSO_2C_6H_4CH_3$-$p)CH_3$) and the methyl

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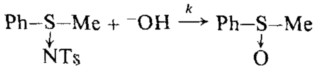
† Product analyses and kinetic results lead to the reaction scheme (i). Based on this the kinetic equations (ii) and (iii) are obtained.



$$Ph\text{-}\underset{\downarrow \atop NTs}{S}\text{-}Me + {}^-OH \xrightarrow{k} Ph\text{-}\underset{\downarrow \atop O}{S}\text{-}Me \qquad \text{(i)}$$

$$\text{Rate} = k.[{}^-OH].[\text{Sulfimide}] \qquad \text{(ii)}$$

if [Sulfimide] ≪ [⁻OH]

$$\text{Rate} = k_{app}.[\text{Sulfimide}] \qquad \text{(iii)}$$

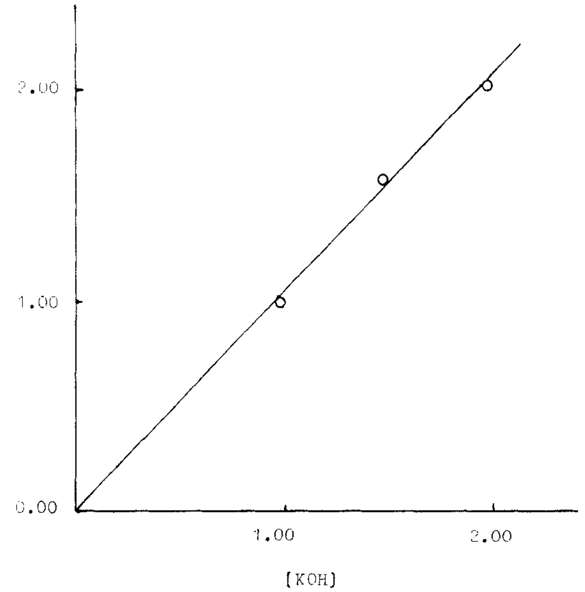
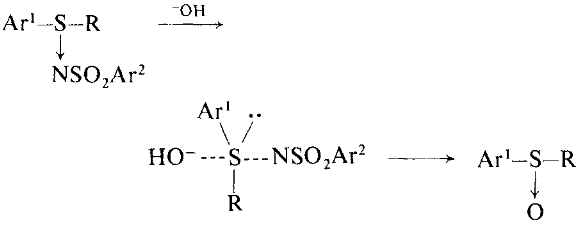


FIGURE 1 Correlation of K_{app} and [KOH] at 59.90 ± 0.05°C.

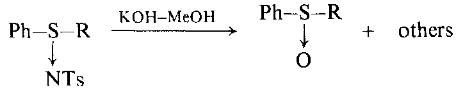
phenyl N-para-substituted arylsulfonylsulfimides ($C_6H_5S(NSO_2C_6H_4Y\text{-}p)CH_3$) are correlated with σ values giving Hammett plots[10] with $\rho_X = +1.2$ and $\rho_Y = +0.8$. These results reveal that the rate determining step of the solvolysis reaction is the nucleophilic attack of hydroxide ion on the tricoordinated sulfur atom and hence the process is an S_N2 type reaction on the tricoordinated sulfur atom.



SCHEME 2

This mechanism seems to be supported further by the investigation of the steric effect of alkyl substituents in the reactions of several alkyl phenyl N-p-tosylsulfimides ($C_6H_5S(NSO_2C_6H_4CH_3\text{-}p)R$, R: Me, Et, i-Pr, and –△) with hydroxide ion in methanol. The relative rates obtained from the competitive reactions of these sulfimides with methyl phenyl N-p-tosylsulfimide as a standard are shown in Table II. The magnitude of the steric effect in these reactions is consistent with those of other substitution reactions on the tricoordinated sulfur atom of the sulfoxide and the sulfimide.

TABLE II
Steric effect of several alkyl phenyl N-p-tosylsulfimides at 59.90 ± 0.05°C



$$\underset{\substack{\downarrow\\ \text{NTs}}}{\text{Ph–S–R}} \xrightarrow{\text{KOH–MeOH}} \underset{\substack{\downarrow\\ \text{O}}}{\text{Ph–S–R}} + \text{others}$$

R	Relative Rates	I	II	III
Me	(1)	(1)	(1)	(1)
Et	0.24	0.1	0.26	0.28
i-Pr	0.01	0.06	0.08	0.02
–◁	0.12			

I; PhS(NTs)R + $^-$CN Reduction[5]
II; p-Tol$\overset{*}{\text{S}}$(O)R + HCl Racemization[3b]
III; PhS(NTs)R + H_3O^+ Hydrolysis[4b]

Kinetics of the Pummerer Type Reaction

The Pummerer type reaction of cyclic N-p-tosylsulfimides afforded the corresponding α-methoxysulfides as nearly the sole products (Table III). The analysis of the products suggests that the rearrangement of the sulfimide to the corresponding α-methoxysulfide proceeds via a mechanistic route quite similar to the Pummerer reaction of the sulfoxide.

As indicated in the experimental section, the kinetic study was carried out in the presence of a large excess of potassium hydroxide by following the increase of the amount of the α-methoxysulfide which was formed during the reaction. The rate constants for cyclic N-p-tosylsulfimides were calculated by the pseudo first order kinetic equation.† The results obtained are summarized in Table IV.

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† According to the proposed mechanism for the reaction as shown in Scheme (iv), the kinetic equations (v)–(vi) are derived by the steady state method; namely, the rates should be calculated from Eq. (vi).

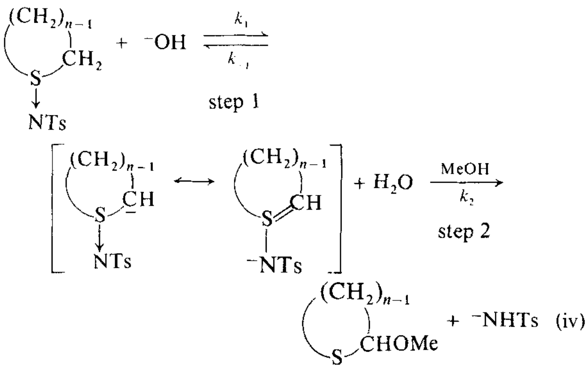
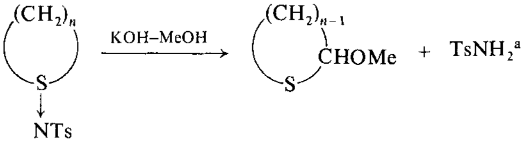
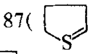
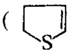
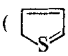
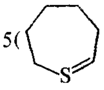
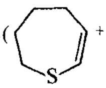
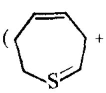
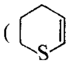


TABLE III
The reaction of cyclic sulfimides with potassium hydroxide in methanol at room temperature for 48 h



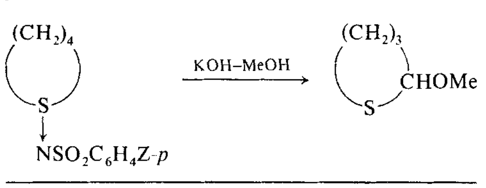
n	Yields of Product(%)[b]	ir Spectra (cm^{-1})	nmr Spectra (CCl_4), δ = ppm)	mass Spectra (m/e)
4	38[c]	1090	1.6–2.4(4H, m, $-(CH_2)_2-$), 2.5–3.2(2H, m, $-CH_2S-$),	118(M^+), 87( +),
		1130	3.22(3H, s, $-OCH_3$), 5.0–5.2(1H, m, $-CH(OCH_3)S-$)	86( +),
		1160		85( +)
5	30[d]	1065 1110 1140	1.4–2.2(6H, M, $-(CH_2)_3-$), 2.2–3.2(2H, m, $-CH_2S-$), 3.35(3H, s, $-OCH_3$), 4.2–4.4(1H, m, $-CH(OCH_3)S-$)	
6	35[c]	1060	1.4–2.3(8H, m, $-(CH_2)_4$), 2.3–3.0(2H, m, $-CH_2S-$),	146(M^+), 115( +),
		1090	3.29(3H, s, $-OCH_3$), 4.4(1H, t, $-CH(OCH_3)S-$)	114( +),
		1120		113( +)

[a] In the reactions, *p*-toluenesulfonamide was obtained quantitatively.
[b] These values are those of the isolated yields by the preparative glc.
[c] In the glc analysis, α-methoxysulfides were obtained in nearly quantitative yields.
[d] In the glc analysis, α-methoxysulfide was obtained in about 70% yield and other product was vinylic sulfide ().

The activation parameters for the Pummerer type reaction of *N*-*p*-tosyltetramethylenesulfimide with hydroxide ion in methanol are $\Delta H^{\neq} = 27.9$ kcal mol^{-1} and $\Delta S^{\neq} = +13.3$ eu, respectively. The pseudo first order rate constants of the reactions of the *N*-para-substituted arylsulfonyltetramethylenesulfimides ($(CH_2)_4SNSO_2C_6H_4Z$-*p*) give a Hammett correlation with $\rho_Z = +2.0$ for σ values.

In order to ascertain the rate determining step of the reaction, the hydrogen–deuterium kinetic isotope effect (k_H/k_D) was determined by comparing the rates of *N*-*p*-tosyltetramethylenesulfimide and its 2,2,5,5-tetra-deuterated compound and found to be

TABLE IV
Rates of the reaction of para-substituted cyclic *N*-arylsulfonylsulfimides with potassium hydroxide in methanol
[KOH] = 2.55 mol l^{-1}, [Sulfimide] = 0.125 mol l^{-1}



Z	Temp. (°C)	$10^4\ k_{app}$ (sec^{-1})
Me	30.10 ± 0.05	0.37 ± 0.02
Me	33.60 ± 0.05	0.67 ± 0.03
Me	39.80 ± 0.05	1.62 ± 0.05
H	30.10 ± 0.05	0.89 ± 0.03
Br	30.10 ± 0.05	1.98 ± 0.08

$\Delta H^{\neq} = 27.9$ kcal mol^{-1}; $\Delta S^{\neq} = +13.3$ eu (Z =Me); $\rho_Z = +2.0$.

Footnote (*cont.*)
if step 2 is the rate determining step

$$\text{Rate} = \frac{[\text{MeOH}]}{k_{-1}[\text{H}_2\text{O}] + k_2[\text{MeOH}]}.k_1.k_2.[\text{Sulfimide}].[^-\text{OH}] \quad \text{(v)}$$

if [MeOH], [H_2O], [^-OH] $\gg$ [Sulfimide]

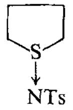
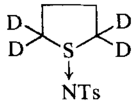
$$\text{Rate} = k_{app}.[\text{Sulfimide}] \quad \text{(vi)}$$

The lack of hydrogen–deuterium kinetic isotope effect in the reactions with both *N*-*p*-tosyltetramethylenesulfimide and its 2,2,5,5-tetra-deuterated compound suggests that the rate-determining step should be step 2.

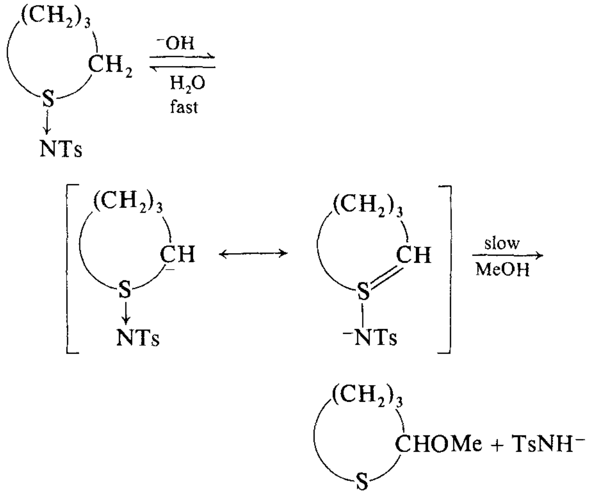
TABLE V

Rates of the reaction of undeuterated *N*-*p*-tosyltetramethylenesulfimide and its 2,2,5,5,-tetradeuterated compound with potassium hydroxide in methanol at 30.10 ± 0.05°C

[KOH] = 2.55 mol l^{-1}; [Sulfimide] = 0.125 mol l^{-1}

Sulfimide	$10^4 k_{app}$ (sec^{-1})	
	0.37 ± 0.02	$k_H/k_D = 1.09$
	0.34 ± 0.02	

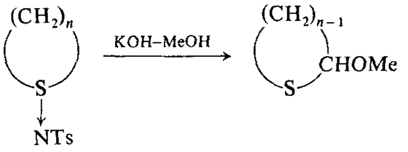
only 1.09 (Table V). Apparently the proton removal is not the rate determining step. Moreover, after the reaction proceeded about 10% with the 2,2,5,5-tetradeuterated *N*-*p*-tosyltetramethylenesulfimide, the deuterium content of the recovered sulfimide was found to have decreased to 85% from the original 95% (the starting deuterium content). The negligible isotope effect and the facile hydrogen–deuterium exchange suggest that the rate determining step is not the initial proton abstraction by hydroxide ion but the step involving the S—N bond cleavage. This is supported by the large substituent effects ($\rho_Z = +2.0$) as described before. Thus, the reaction of the sulfimide with hydroxide ion in methanol is considered to proceed via the *E*1*cb* route.



SCHEME 3

TABLE VI

The relative rates of the reaction of 5–7 membered cyclic *N*-*p*-tosylsulfimides with potassium hydroxide in methanol at 35.00 ± 0.05°C



n	$10^4 k_{app}$ (sec^{-1})	Relative Rates
4	0.80 ± 0.02	(1)
5	0.23 ± 0.01	0.29
6	0.90 ± 0.04	1.13

The ring size effects for the 5–7 membered cyclic *N*-*p*-tosyltetra-, penta-, and hexamethylenesulfimides were examined. The relative rates were calculated from the pseudo 1st order rates of the reactions of these sulfimides with hydroxide ion in methanol based on that of *N*-*p*-tosyltetramethylenesulfimide. The relative rates of the 5–7 membered ring sulfimides were found to fall in the following order 6 < 5 ~ 7 (Table VI).

EXPERIMENTAL

Materials

Sulfimides All the sulfimides used were prepared from the corresponding sulfides and the sodium salt of *N*-chloroarylsulfonamides by a modified Mann–Pope reaction.[2,11] The melting points, ir and nmr spectra of the sulfimides are all identical to those prepared earlier.[2,11]

Potassium hydroxide Potassium hydroxide was of commercial grade used without further purification.

Solvent Methanol was purified by the usual procedure. The concentration of the potassium hydroxide–methanol solution was determined by titration with aqueous 1N–HCl solution just before the kinetic measurement.

Reaction of Sulfimides with Potassium Hydroxide in Methanol

The solvolysis reaction of sulfimides This reaction has been already described.[2b]

The Pummerer reaction of cyclic N-p-tosylsulfimides with potassium hydroxide in methanol The reaction was carried out as follows. A cyclic *N*-*p*-tosylsulfimide (58 mmol) was allowed to react with a 20 mol excess of potassium hydroxide in 200 ml of methanol at room temperature for 48 h. Then the solution was poured onto a large amount of ice water and extracted with chloroform. After drying, the solvent was evaporated. The products obtained were isolated by glc (1% silicone OV-17; 1 m; 6 mm i.d.; stainless steel tube; temperature 100°C; H_2 flow 40 ml min^{-1}) and identified by comparing their ir, nmr and mass spectra with those of the authentic samples[12] which were prepared by the reaction of the corresponding α-chlorosulfides with methanol in the presence of pyridine. The products obtained and their yields are summarized in Table IV.

Kinetics

The solvolysis reaction of the sulfimide with potassium hydroxide in methanol A typical kinetic procedure was as follows. 25 ml of a potassium hydroxide (1.686 mol l^{-1})–methanol solution and 25 ml of a methanol solution of methyl phenyl *N-p*-tosylsulfimide (2.5 mmol) and benzyl phenyl sulfide (0.2 mmol) as an internal standard were placed separately into a thermostatted bath. The two solutions were then mixed and aliquot portions (5 ml) were pipetted at suitable intervals into an aqueous 0.2N–HCl solution (25 ml) into which chloroform (25 ml) was added. The chloroform layer was removed and after the solvent was evaporated, the residue was dissolved in benzene (3 ml). The solution was directly injected into the glc column (5% diethyleneglycol succinate on Celite; 1 m; 3 mm id; stainless steel tube; temperature 150°C; He flow 40 ml min^{-1}). The rate constants were calculated by the well-known pseudo first order kinetic equation.

$$k_{\text{app}} = \frac{1}{t}.\ln(X_{\infty}/X_{\infty} - X)$$

Here X_{∞} and X are calculated from the relative peak areas of methyl phenyl sulfoxide and benzyl phenyl sulfide (internal standard) at infinite time t_{∞} and t, respectively. The kinetic measurements of other sulfimides were carried out as described above. Activation parameters are determined as usual and the Hammett plots were drawn against σ values.

Steric effect 25 ml of a potassium hydroxide (1.686 mol l^{-1})–methanol solution and 25 ml of a methanol solution of alkyl phenyl *N-p*-tosylsulfimide (1.25 mmol) and methyl phenyl *N-p*-tosylsulfimide (1.25 mmol) were placed separately into a thermostatted bath (bath temperature; 59.9°C). The two solutions were then mixed and after allowing to react for 5 h, the reaction mixture was quenched immediately with aqueous 1N–HCl solution (50 ml) and then chloroform (50 ml) was added. The chloroform layer was removed and after the solvent was evaporated, the residue was dissolved in ether (3 ml). The solution was directly injected into the glc column.

The Pummerer type reaction of the sulfimide with potassium hydroxide in methanol A typical kinetic procedure was as follows. 3 ml of a potassium hydroxide (6.79 mol l^{-1})–methanol solution and 5 ml of a *N-p*-tosyltetramethylenesulfimide (1 mmol) and ethyl phenyl ether (0.25 mmol) as an internal standard were placed separately into a thermostatted bath. The two solutions were then mixed and aliquot portions (0.5 ml) were pipetted at suitable intervals and quenched immediately with aqueous 1N–H_2SO_4 solution (3 ml) into which benzene (2 ml) was added. The benzene layer was directly injected into glc column. The rate constants were calculated by the well-known pseudo first order kinetic equation. The kinetic measurements of other cyclic sulfimides were carried out as described above. Activation parameters are determined as usual and the Hammett plots were drawn against σ values.

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