Kinetic Study of the Pyrolysis of 1- and 2-Phenylethyl Phenyl *N*-Tosylsulfilimines[1]

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The pyrolysis of 1-phenylethyl phenyl *N*-tosylsulfilimine was found to proceed more than 10^3 times faster than that of ethyl phenyl derivative. The large rate enhancement suggests that the mechanism changes from an ideal *cis*-elimination to nearly E1 type. However, substituent effect, kinetic isotope effect with 1-phenylethyl-2,2,2-d_3 phenyl *N*-tosylsulfilimine and solvent effect clearly reveal that the reaction proceeds *via* an intramolecular concerted process.

In a previous paper we reported that the pyrolysis of alkyl *N*-tosylsulfilimine having β-hydrogen gives olefin in a high yield,[2] and the reaction was suggested to proceed through a concerted *cis*-elimination process based on both kinetic and stereochemical results.[3]

When the sulfilimine having both α and β phenyl groups was subjected to pyrolysis, the rate of the reaction was found to be accelerated by a factor of 10^3 times higher than the unsubstituted sulfilimine. This enormously large rate enhancement by the phenyl groups gives rise to a consideration of the nature of the concerted process for the pyrolysis namely, whether or not the reaction proceeds *via* an internal concerted *cis*-elimination route[4] or through a different mechanism such as E1 type mechanism[5] or radical pair mechanism[6] involving the rate-determining C–S bond cleavage or through some alternative pathway which involves the rate-determining C–H bond fission at the transition state[7] (nearly carbanion type mechanism). All the possible mechanistic pathways are schematically shown in Fig. 1.

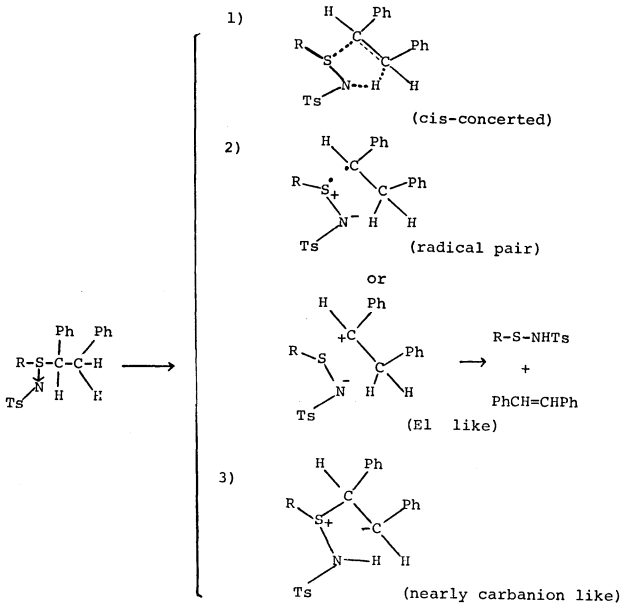
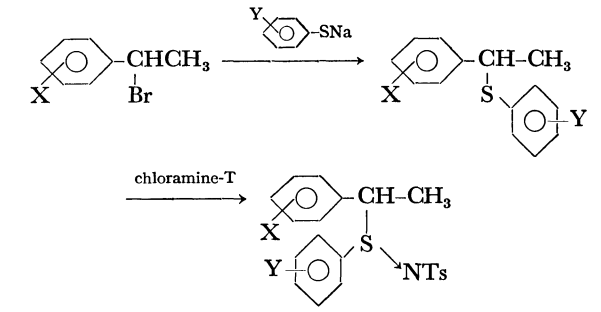


Fig. 1. Possible mechanistic scheme for the E1 reaction.

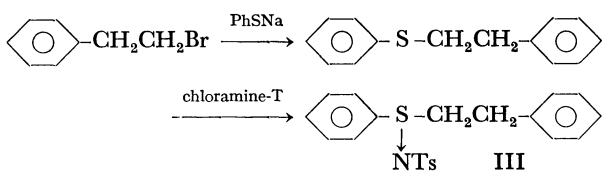
In order to understand the nature of the pyrolysis and thus be able to make a choice of mechanism, 1- and 2-phenylethyl phenyl *N*-tosylsulfilimines were prepared and subjected to pyrolysis. This paper gives a detailed account of the kinetic study of the pyrolysis and implication of the data for understanding of the mechanism.

Results and Discussion

Preparation of Sulfilimine. The sulfilimines used for the pyrolysis were 1-(substituted)phenylethyl phenyl-(I), 1-phenylethyl(substituted)phenyl (II) and 2-phenylethyl phenyl *N*-tosylsulfilimines (III) prepared by treating the corresponding sulfides with chloramine-T in methanol solution, as shown below. The mp, elemental analyses, and IR spectra are listed in Table 1.



I : X=*p*-CH_3, H, Cl, *m*-NO_2, Y=H
II: X=H, Y=*p*-CH_3O, *p*-CH_3, H, *p*-Cl



1) Part IV of Ei reaction.

2) S. Oae, K. Tsujihara, and N. Furukawa, *Tetrahedron Lett.*, **1970**, 2663.

3) K. Tsujihara, N. Furukawa, and S. Oae, *Tetrahedron*, **27**, 4921 (1971); K. Tsujihara, K. Harada, N. Furukawa, and S. Oae, *ibid.*, **27**, 6101 (1971).

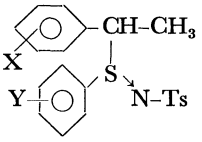
4) For Ei reaction, D. V. Banthorpe, "Elimination Reactions," Elsvier Publish., Co., N. Y. (1963), p. 167.

5) R. Taylor and G. G. Smith, *Tetrahedron*, **19**, 937 (1963); R. Taylor, G. G. Smith, and W. H. Wetzel, *J. Amer. Chem. Soc.*, **84**, 4817 (1962).

6) C. A. Kingsbury and D. J. Cram., *ibid.*, **82**, 1810 (1960).

7) A. C. Cope, N. A. Lebel, H. H. Lee, and W. R. Moore, *ibid.*, **79**, 4720 (1957).

TABLE 1.



X	Y	Mp (°C)	Elemental analysis Calcd C%	Calcd H%	Calcd N%	Found C%	Found H%	Found N%	IR (cm^{-1}) (-S=N-)
p-CH_3	H[a)]	91—91.5	66.50,	5.80,	3.53	65.73	5.57	3.65	960
H	H	102.5—103							960
p-Cl	H	111—111.5	60.00	4.78	3.36	60.03	4.73	3.36	960
m-NO_2	H	113—114	58.80,	4.67	6.55	58.58	4.43	6.50	965
H	*p*-OCH_3	73.5—74	63.37	5.57	3.44	63.39	5.47	3.40	948
H	*p*-CH_3	94.5—95	66.60	5.80	3.53	66.40	5.73	3.67	955
H	*p*-Cl	83—83.5			3.46			3.75	975

a) The compound is unstable at room temperature and decomposes gradually during the course of purification.

Kinetics and Product Analysis. The pyrolysis was carried out by heating a solution of the desired sulfilimine in benzene. Products were not isolated after reaction except in the case of 2-phenylethyl phenyl *N*-tosylsulfilimine, from which styrene was isolated in more than 60% yield. However, the products derived from (I) and (II) were found to be both substituted styrene and arenesulfenyl *p*-toluenesulfonamide, since the NMR spectrum of the reaction mixture in $CDCl_3$, which had been left to stand for some days until the signals of methine and methyl protons of the sulfilimine disappeared, showed a complete 1:1 mixture of substituted styrene and arenesulfenyl *p*-toluenesulfonamide as shown in Fig. 2. We can thus conclude that the yield of olefin is nearly quantitative. The kinetic measurements were carried out by following the IR absorption band of the product, *i.e.* the -NH- band of arenesulfenyl *p*-toluenesulfonamide appeared at 3280 cm^{-1}. The rates of the pyrolysis were correlated with the first-order rate equation. The kinetic data obtained from the above reaction are summarized in Tables 2 and 3.

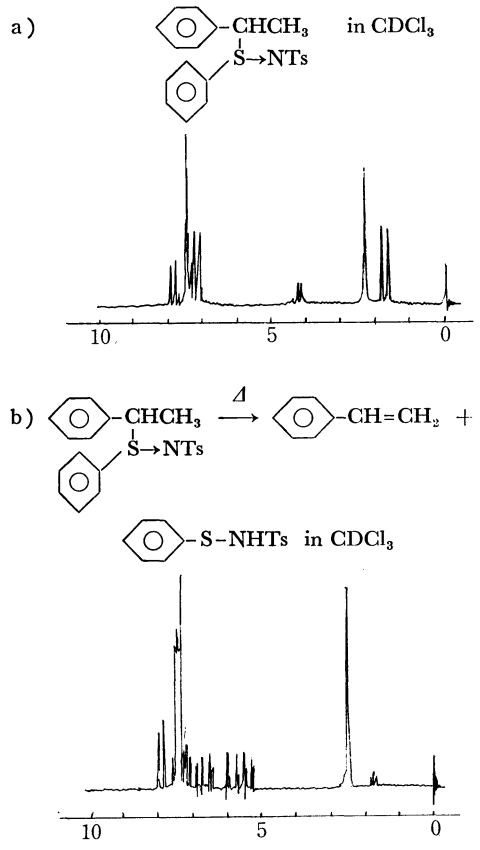


Fig. 2. NMR Spectra of 1-phenylethyl phenyl sulfilimine (a) and the products after the Reaction (b).

Solvent Effect. The pyrolysis was carried out in various solvents, the rate constants obtained being summarized in Table 4. We see that the pyrolysis is not much affected by solvent. Even the change in polarity of the solvent from benzene (ε=2.27) to nitrobenzene (ε=34.6) or acetonitrile (ε=37.5) changes the rate not more than five fold. This seems to indicate that the transition state of the reaction is neither ionic nor radical. In ethanol, the reaction proceeded slowly and the yield of olefin was low. Apparently the initial C–S bond cleavage took place concurrently with the elimination giving rise to some substitution products such as 1-phenyl ethyl ethyl ether. The rate is also low in chloroform suggesting that the hydrogen bond formation between imino nitrogen and acidic hydrogen of chloroform prevents an attack of the terminal nitrogen to β-proton. This is also the case with ethanol. Acetonitrile also retards the reaction slightly. As in a similar retardation of pyrolysis in DMSO, the dipolar

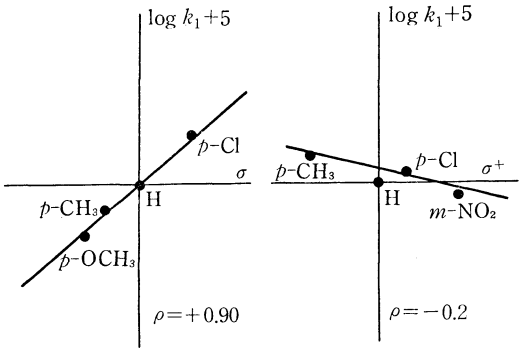
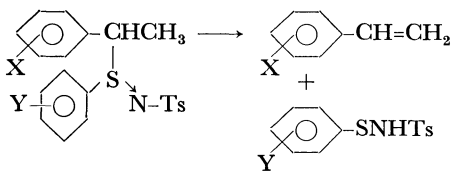


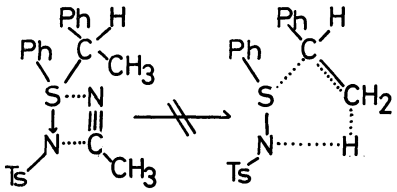
Fig. 3. Hammett equation.

TABLE 2. SUBSTITUENT EFFECTS



X	Y	Temp (°C)	$k_1 \times 10^5$ (sec^{-1})	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$(e.u.)
H	H	10.0±0.05	1.27		
		25.0	7.87	20.8	−7.2
		35.0	24.2		
p-CH_3	H	10.0	1.60		
		15.0	4.68	22.6	−2.7
		25.0	17.8		
		28.0	20.2		
p-Cl	H	10.0	1.31		
		15.0	2.75	22.8	−2.1
		25.0	11.1		
		28.0	15.1		
m-NO_2	H	9.5	0.90	24.4	+3.2
		15.0	7.43		
		25.0	9.55		
		28.0	13.6	$\rho_X = -0.20$	
H	*p*-Cl	25.0	10.1		
H	*p*-CH_3	25.0	5.16	$\rho_Y = 0.90$	
H	*p*-OCH_3	25.0	3.69		
$PhCHCD_3$ (PhS, NTs)		25.0	2.67	$k_H/k_D = 2.90$ (solvent; benzene)	

interaction between acetonitrile and the sulfilimine shown schematically below would be responsible for the small retardation.



Hammett Equation and Isotope Effect. The substituent effects (Table 2) seem to be correlated nicely with Hammett σ values. Substituents Y gave a good straight line with $\rho_Y = +0.90$, while the effect of X is very small and gave hardly any correlation with either σ or σ^+ values. Apparently the electron-donating substituent such as *p*-CH_3 accelerated the reaction while the electron-withdrawing substituent retarded it. The ρ values though small, indicate a negative trend and is roughly estimated to be $\rho = -0.2$. The Hammett relation is shown in Fig. 3. The kinetic isotope effect was measured from the rate constants of 1-phenylethyl 2,2,2-d_3 phenyl *N*-tosylsulfilimine and the corresponding undeuterated compound, and found to be $k_H/k_D = 2.90$. The data in Table 3 indicate that the rate promotion in the pyrolysis is found to be mainly due to α-phenyl group which accelerates the reaction around 10^3 times as compared to one without it, while the β-phenyl group accelerates the reaction only 1.5 times or at most 2.5 times, though correcting the number of available β hydrogen atoms. The following conclusions can be obtained. (1) The rather small rate-enhancing effect of the β-phenyl group rules out the nearly carbanion like mechanism, since either E1 or E2 reaction which is presumed to proceed *via* nearly carbanion-like mechanism[7] should show an enormous large rate enhancement by β-phenyl group. For example, ethyl methyl phenethyl amine oxide undergoes E1 reaction more than 10^2 times faster than the phenyl unsubstituted derivative, while dimethyl ethyl phenethyl quarternary ammonium hydroxide decomposes 2.7×10^4 times faster than the compound having no β-phenyl group. (2) Although a large rate enhancement by the α-phenyl group could suggest an E1 route, this is

TABLE 4. SOLVENT EFFECT ON PYROLYSIS OF 1-PHENYLETHYL PHENYL *N*-TOSYLSULFILIMINE

Solvents	Reaction Temp (°C)	ε	k_1 (sec^{-1})
Benzene	40.0	2.27	2.55×10^{-4}
Toluene	40.0	2.38	5.41
Chlorobenzene	40.0	5.61	3.24
Nitrobenzene	40.0	34.6	2.29
CH_3CN	40.0	37.5	1.20
EtOH	40.0	24.3	not measured
$CHCl_3$	40.0	4.7	1.42

TABLE 3. THE RELATIVE RATES OF PYROLYSIS OF SULFILIMINES

Sulfilimine	Temp (°C)	k_1 (sec^{-1})	Rel.Rates	$\Delta H^{\ddagger}\left(\frac{\text{kcal}}{\text{mol}}\right)$	$\Delta S^{\ddagger}$ (e.u)
Ph–SCH_2CH_3 (NTs)	60.5	0.01×10^{-5}			
	80.3	1.08	1	26.5	−5.8
	100.5	9.85			
Ph–SCH_2CH_2Ph (NTs)	90.2	2.84			
	95.2	6.28			
	100.0	10.3	1.5	25.7	−8.6
$PhSCH(Ph)CH_3$ (NTs)	22.4	5.40			
	31.0	16.0	10^3	20.8	−7.2
	35.0	24.2			
Ph–S(NTs)–CH(Ph)–CH(Ph)–OCH_3					
erythro-	60.0	10.1	10^2		
threo-		16.5	1.5×10^2		

ruled out since both N–H bond forming and C–S bond breaking are apparently involved in the transition state in view of the relatively large β-hydrogen kinetic isotope effect. Recently an E1-like mechanism was proposed by Burgess, Penton, and Taylor for the solvolyitic internal elimination reaction of 1,2-diphenylethyl-*N*-carbomethoxysulfamate triethylammonium salt. In this case the kinetics suggests that although stereospecificity is maintained, only a small β-hydrogen kinetic isotope effect (1.05~1.08) is obtained.[8] The small negative ρ_x value might suggest the involvement of a radical pair mechanism proposed by Cram[6] for the pyrolysis of the four diastereomeric 1,2-diphenyl-1-propyl phenyl sulfoxides. However, this is also ruled out since the free radical mechanism involving the prior C–S bond cleavage is not in accord with the relatively large kinetic isotope effect. The ESR taken with the reaction conditions did not show any signals and there was no particular effect by oxygen or radical scavenger. Styrene placed in the reaction vessel did not polymerize under the reaction conditions. Thus, the radical type mechnism can be ruled out. (3) Recently we found that optically active benzyl *p*-tolyl *N*-tosylsulfilimine undergoes very facile thermal racemization apparently *via* pyramidal inversion[9] without involving C–S bond fission. This result together with the solvent effect on the pyrolysis indicates that either the initial radical or the ionic C–S bond fission mechanism (2) can be neglected. Thus, the present data are consistent with the *cis*-concerted mechanism which we predicted.[2,3] Although the relative rate of α-phenyl substituted sulfilimine is 10^3 times larger than that of the unsubstituted one, both ρ_y and isotope effects are nearly identical in both series. *i.e.*, $\rho_y=+0.90$ (α-phenyl), $+0.90$ (α-H); $k_H/k_D=2.90$ (α-phenyl), 3.03 (α-H) respectively. Therefore, the pyrolysis of these sulfilimines appears to proceed *via* an ideal five-membered transition state during the course of reaction regardless of the structural change. The large rate enhancement by the α-phenyl group is undoubtedly associated with the stabilization of the transition state by the effective conjugation with the developing double bond at the transition state.[10] The small negative trend of ρ_x value appears somewhat strange, but it may be due to the change of transition state with the change of substituent on the phenyl ring, namely the timing of C–S bond fission and C–H bond fission differs with substituent, compensating the substituent effect. This phenomenon is also observed in the case of E2 reaction of α-substituted phenethyl bromide.[11] These results suggest that the pyrolysis of sulfilimine proceeds *via* an internal concerted *cis* elimination involving a five membered transition state though the reaction is accelerated 10^3 times by the α-phenyl group.

8) E. M. Burgess, H. R. Penton, Jr., and E. A. Taylor, *J. Amer. Chem. Soc.*, **92**, 5224 (1970).

9) N. Furukawa, K. Harada, and S. Oae, *Tetrahedron Lett.*, **1972**, 1377.

10) The substitution of a phenyl group, e.g., phenethyl halide or tosylate, is known to accelerate the solvolysis reaction around 10^3 times.

11) T. Yoshida, Y. Yano, and S. Oae, *Tetrahedron*, **27**, 5343 (1971).

Table 5. Kinetics of 1-(*p*-chlorophenyl)ethyl phenyl *N*-tosylsulfilimine in benzene at 25°C

	min	log I_0/I	log C_0/C	k	sec^{-1}
1)	0	0.0464	0.1464		
	30	0.0653	0.2269	1.18	
	60	0.0856	0.3308	1.05	
	90	0.0916	0.4546	1.22	
	120	0.1066	0.4742	1.17	
	150	0.1212	0.6107	1.03	
		0.1605			1.13×10^{-4}
2)	0	0.0306	0.1057		
	20	0.0453	0.1667	1.17	
	40	0.0580	0.2278	1.17	
	60	0.0650	0.2655	1.02	
	80	0.0747	0.3239	1.04	1.10×10^{-4}
		0.1421		av. $k=1.11\pm0.01$	

Activation parameters were calculated by the usual method.

Experimental

Preparation of Sulfilimine. 1- And 2-arylethyl bromides were prepared according to the known method.[12] They were treated with sodium thiophenoxide in ethanol solution to afford the corresponding sulfide in a 70% yield. The sulfilimines were prepared by treating the sulfides with chloramine-T.[13] A typical example is as follows. 1-Phenylethyl phenyl sulfide (2 g) was dissolved in 25 ml of methanol containing a drop of acetic acid. To this was added 2.9 g of chloramine-T in methanol at 0 °C. After being stirred for 1 hr, methanol was removed at room temperature. The residue was added to ice–water containing a dilute sodium hydroxide solution. The precipitates were separated and dried. The crude crystals were recrystallized from methanol. The yield was 50%. The IR spectral data are summarized in Table 1.

Product Analysis. The products were not actually isolated. The identification of substituted styrenes and arenesulfenyl *p*-toluenesulfonamide was carried out by means of NMR and IR spectra. Sulfilimine was dissolved in $CDCl_3$ in an NMR tube. The tube was kept standing at room temperature or heated at 50 °C until the methyl doublet or methine quartet of phenylethyl protons completely disappeared. The spectra obtained were all of 1:1 mixture of styrene and the sulfenamide. In benzene solution, the products were the same as those in $CDCl_3$.

Preparation of 1-Phenylethyl-2,2,2-d_3 *Phenyl N-Tosylsulfilimine.* *Acetophenone-*d_3: Acetophenone (5.0 g) was dissolved in 15 ml of dioxane containing 5.0 g of deuterium oxide, and 0.5 g of triethylamine. The mixture was heated at 100 °C for 10 hr. Water was removed as a dioxane azeotrope and dioxane was removed by distillation. A new mixture of dioxane, deuterium oxide, and triethylamine was added to the residue. The procedure was repeated four times. The NMR spectra showed no protons in the methyl group (2.5 ppm) bp 87 °C/2 mmHg.

*1-Phenylethyl Alcohol-*2,2,2-d_3: The deuterated acetophenone (5.0 g) was reduced with lithium alminum hydride by the usual method. Bp 90 °C/10 mmHg, yield 55%.

*1-Phenylethyl Bromide-*2,2,2-d_3: The deuterated alcohol was

12) H. C. Brown, I. Moritani, and Y. Okamoto, *J. Amer. Chem. Soc.*, **78**, 2193 (1956).

13) K. Tsujihara, N. Furukawa, K. Oae, and S. Oae, This Bulletin, **42**, 2631 (1969).

converted into the bromo compound with phosphorus tribromide. The NMR showed no protons in the methyl group. Bp 67 °C/3 mmHg, yield 60%.

1-Phenylethyl-2,2,2-d_3 *Phenyl* N-*Tosylsulfilimine*: The sulfilimine was prepared from the sulfide and chloramine- T. Mp 102.0—103 °C, yield 73%.

Kinetics. A pre-cooled solution of 0.5~1% sulfilimine in anhydrous solvents was prepared and sealed into 2 ml ampoules, which were immersed in a constant temperature bath. At an appropriate time, the ampoules were taken out one by one and frozen in a dry-ice–acetone bath to stop the reaction. The reaction rate was then calculated by following the increase of the IR intense –NH– stretching absorption band at 3280 cm^{-1} due to sulfenamide produced. The reaction was found to follow a good first-order kinetic equation. A typical example of the kinetics is shown in Table 5.