Sulfene Mechanism in the Pyridine-catalysed Reactions of Alkanesulfonyl Halides with Phenols

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The influence of pyridine bases upon the rate and mechanism of the interaction of alkanesulfonyl halides with phenols in organic solvents has been studied. Two competing routes have been shown to be followed under the reaction conditions, *i.e.* elimination–addition (the sulfene mechanism) and nucleophilic substitution at the sulfonyl group sulfur (predominantly general-base catalysis). The influence of the substrate, reactant and catalyst structure, as well as the nature of the medium, upon the rate and relationship between the competing routes have been investigated.

The elimination–addition mechanism is of substantial importance for acyl transfer reactions involving derivatives of aliphatic acids,[1–3] in particular, alkanesulfonic acids (*i.e.* anhydrides, sulfonyl halides, esters). In the latter case the intermediate is a sulfene (thioaldehyde dioxide).

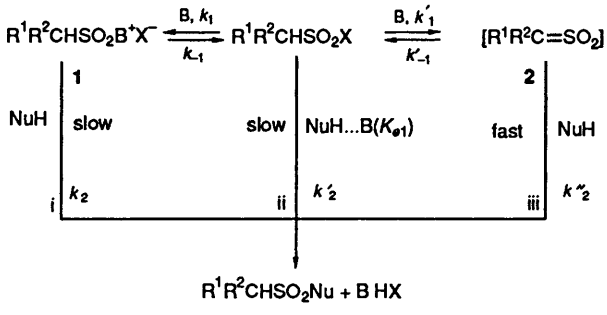
The study of sulfenes originated from Vedekind's[4] and Staudinger's[5] papers, which postulated sulfene formation in a number of synthetic reactions involving alkanesulfonyl chlorides, and described the first attempts at its preparative isolation. In spite of the fact that synthetic reactions of sulfenes are sufficiently studied by now, attempts to obtain stable sulfenes at ambient temperature have failed and the knowledge of these compounds is based on reactions *in situ*.

The number of papers devoted to quantitative aspects of realization of the sulfene mechanism is rather limited. The works by Williams and co-workers,[6–8] King and co-workers[9,10] and those of our laboratory[11,12] in the 1970s and 1980s enabled one to study quantitatively the sulfene mechanism by kinetic methods in a number of cases. However, all new research in this field is of great interest.

The presence of the electrophilic sulfur atom and the labile α-hydrogen atoms in the molecules of alkanesulfonyl derivatives results, as a rule, in the potential to realize several mechanisms for interaction of these compounds with nucleophiles (Scheme 1), *i.e.* the nucleophilic mechanism (i), general-base catalysis (ii) (nucleophilic substitution routes at the sulfur atom) and the sulfene mechanism (iii) (that of elimination–addition). This requires the development of approaches for quantitative separation of these routes by kinetic methods.

Previously we studied the catalytic effect of trialkylamines in reactions of formation of alkanesulfonyl acid esters in non-aqueous media.[11,12] It was found that, depending on the reactants structure and other conditions, the reaction may proceed predominantly by any one of the competing routes, *i.e.* those of elimination–addition and nucleophilic substitution. The experimental data are indicative of the general-base-catalysed nature of the substitution route competing with the sulfene mechanism (iii). However, to our mind it was worthwhile to study the possibility of realization of the elimination–addition mechanism and the nature of the route competing with it, in the presence of pyridines, which are less basic but more nucleophilic than trialkyl amines and referred to as predominantly nucleophilic catalysts in literature,[13,14] the more so as pyridine catalysts are widely used in synthetic practice.

The aim of the present paper is to determine the limits for realization of the sulfene mechanism in the reaction of alkanesulfonyl halides with phenols in non-aqueous media,



B = HO^-, Py, $N(Alk)_3$; NuH = H_2O, AlkOH, ArOH, RNH_2

Scheme 1

catalysed by pyridine bases, the nature of the nucleophilic substitution route competing with the sulfene mechanism, as well as the rules for the quantitative effect of the substrate, reactant and catalyst structure and the medium upon the rate and relationship of the competing routes.

Experimental

Proceeding from Scheme 1 the equations for the competing route rates under constant concentrations of intermediates **1** and **2** can be written in the form of eqns. (1)–(3) where [H], [P]

$$(dx/dt)_i = \frac{k_1 k_2[H][P][B]}{k_{-1} + k_2[P]} \quad (1)$$

$$(dx/dt)_{ii} = K_{e1} k'_2[H][P][B] \quad (2)$$

$$(dx/dt)_{iii} = \frac{k''_1 k''_2[H][P][B]}{k''_{-1} + k''_2[P]} \quad (3)$$

and [B] are sulfonyl halide, phenol and catalyst concentrations, respectively; $K_{e1} = k'_1/k'_{-1}$ is an equilibrium constant for formation of the hydrogen-bonded complex ArOH ··· Py; and k_1, k_{-1}, k_2, k'_2, k''_2, k''_1, k''_{-1} are the constants for individual steps of the competing routes.

Bearing in mind that in a low polarity medium $k_{-1} \gg k_2[P]$,[14] as well as the fact that phenol reacts with sulfene in the fast step,[1,2,12] *i.e.* $k''_{-1} \ll k''_2[P]$, the equation for the total process rate takes the form of eqn. (4) where $k_s = k''_1$; $k_n = K_{e1}k'_2 + K_{e2}k''_2$, and $K_{e2} = k_1/k_{-1}$ is an equilibrium constant for

$$\Sigma(dx/dt) = (k_s + k_n[P])[H][B] = k_{obs}[H][B] \quad (4)$$

Table 1 The influence of structure of phenols (XC_6H_4OH) and pyridines (YC_5H_4N) upon the rate of ester formation[a]

X in XC_6H_4OH Y=H	$k_s/10^{-4}$ dm^3 mol^{-1} s^{-1}	$k_n/10^{-4}$ dm^6 mol^{-2} s^{-1}	Y in YC_5H_4N X=H	$k_s/10^{-4}$ dm^3 mol^{-1} s^{-1}	$k_n/10^{-5}$ dm^6 mol^{-2} s^{-1}
4-MeO	1.15	8.44	3-CN	0.04	0.34
4-Me	1.19	8.60	3-Br	0.45	3.16
3-Me	1.20	11.4	4-PhCO	1.79	12.3
H	1.27	14.7	3-CHO	3.6	20.4
4-F	1.10	17.1	*b*	48.8	72.5
4-I	1.17	20.1	3-$PhCH_2$	159	154
4-Cl	1.21	25.9	H	127	147
4-Br	1.19	25.4	*c*	444	211
3-Cl	1.24	32.7	3-Et	647	149
3-NO_2	1.18	81.6	4-$PhCH_2$	510	310
4-NO_2	1.15	89.2	2-Et	526	238
2-Me	0.76	3.83	2-Me	306	616
2,6-$(Me)_2$	0.52	2.32	4-Pr^i	1 010	560
2,4,6-$(Me)_3$	0.53	1.01	4-Me	1 120	688
2,4-$(NO_2)_2$	1.20	31.8	3-Pr^i	546	450
			2,4-$(Me)_2$	2 540	850
			2,4,6-$(Me)_3$	12 600	2 720
			4-$N(Me)_2$	1×10^7	negligible

[a] The substrate is phenylmethanesulfonyl chloride, the solvent is chlorobenzene; the reactant concentrations are [H] 0.01, [B] 0.05, [P] 0.05–0.15 mol dm^{-3}. [b] Quinoline. [c] Isoquinoline.

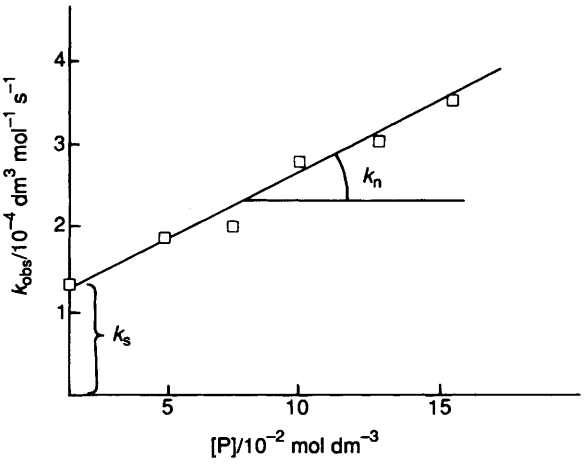


Fig. 1 Plot of the pseudo-first-order rate constants obtained by the potentiometric titration method *versus* phenol concentration: [H] (phenylmethanesulfonyl chloride) 0.01; [B] (pyridine) 0.05 mol dm^{-3}; the solvent is chlorobenzene

the formation of sulfonylonium salt **1**. Routes (i) and (ii) are described by similar formal kinetic equations and under conditions when intermediate **1** is not accumulated in the system, they cannot be separated quantitatively, k_n including two summands relating to routes (i) and (ii), respectively. However, it is possible to separate quantitatively two trends in the reaction, *i.e.* the elimination–addition (sulfene) mechanism and that of nucleophilic substitution at the sulfur atom of the sulfonyl group (the general-base and/or nucleophilic catalysis) by varying the phenol concentration under constant concentrations of sulfonyl halide and pyridine (Fig. 1).

To make the study of kinetics more convenient, the reaction was carried out under pseudo-first-order conditions with respect to sulfonyl halide ([H] ≪ [B] < [P]).

The contributions of the competing routes were estimated by eqns. (5) and (6).

$$D_s = k_s/(k_s + k_n[P]) \quad (5)$$

$$D_n = 1 - D_s \quad (6)$$

The rate of the ester-formation process was monitored using the gas–liquid chromatography method, by following the accumulation of sulfonyl acids phenyl esters, and by potentiometric titration of chloride ions formed in the course of the reaction. All rate constants were measured at 30 ± 1 °C. Standard deviations in the rate constants did not exceed 3–6%.

Results and Discussion

The Influence of the Structure of Phenols and Pyridines.— Comprehensive information on the existence of competing reaction routes can only be obtained when the routes proceed simultaneously in the system under study. This specifies the requirements for the choice of the model reaction. Optimal conditions for studying the effect of X in XC_6H_4OH upon the rate of ester formation are obtained when unsubstituted pyridine is used as a catalyst, and those for studying the effect of Y in YC_5H_4N are provided when unsubstituted phenol is used as a reactant, with the substrate (phenylmethanesulfonyl chloride) and the solvent (chlorobenzene) being identical in each case (Table 1).

As seen from Table 1, an increase in the electronegativity of substituent X in XC_6H_4OH (*i.e.* an increase in phenol acidity) does not actually affect the rate of the elimination–addition route which confirms that the reactive sulfene adds to phenol in the fast step. For the nucleophilic substitution route competing with the sulfene route, an increase in phenol acidity results in substantial growth of k_n which appears to be caused by facilitation of formation of the reaction complex $XC_6H_4OH \cdots Py$.

The kinetic results obtained for sterically unhindered phenols can be roughly described by the Brønsted equation ($\beta = -0.35 \pm 0.04$, r 0.95, s_0 0.12) and much better described by the Hammett equation:

$$\log k_n = (-2.85 \pm 0.01) + (1.03 \pm 0.03)\sigma, r\ 0.99, s_0\ 0.03 \quad (7)$$

The use of sterically-hindered phenols results in a decrease in the rate of both competing routes at the expense of disturbing the interaction of the reactant with the catalyst, or intermediate **1** or sulfene, at the step of their mutual collapse. In the latter case the yield of the reaction product, *i.e.* sulfonyl acid phenyl ester,

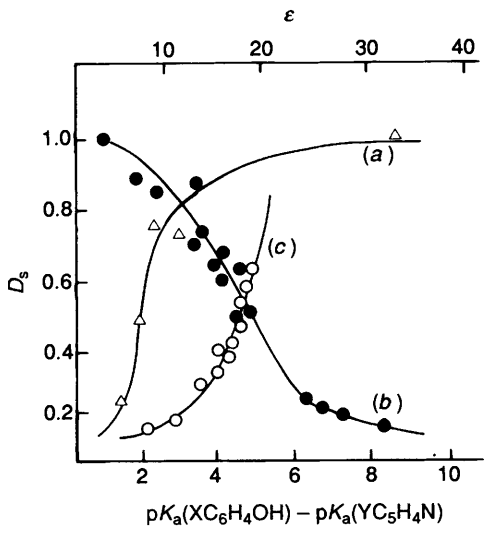


Fig. 2 Contribution of sulfene route as a function of solvent polarity (*a*) and pK_a differences of pyridines (*b*) (X = H) and phenols (*c*) (Y = H). Concentrations of substrate and catalyst as in Table 1; [P] 0.10 mol dm^{-3}.

decreases at the expense of the side-reaction of sulfene oligomerization.

To estimate the contributions of the inductive (σ^0) and mesomeric (σ^+) effects of the influence of substituents X in XC_6H_4OH to the rate of ester formation, kinetic results were calculated by the two-parameter equation taking into account both effects [eqn. (8)]. Analysis of contributions of individual

$$\log k_n = (-2.86 \pm 0.02) + (0.83 \pm 0.09)\sigma^0 + (0.21 \pm 0.07)\sigma^+ \quad (8)$$
$$r\ 0.99,\ s_0\ 0.04$$

parameters made on a standard scale proves that the contribution of the mesomeric effect is about three times less than that of the inductive one.

The obtained values for ρ^0 and ρ^+ indicate simultaneous O–H bond rupture and S–O bond formation in the transition state of the substitution route. Increased electronegativity of substituent X in XC_6H_4OH results in an increase in phenol acidity, facilitation of O–H bond rupture and, therefore, an acceleration of the ester formation.

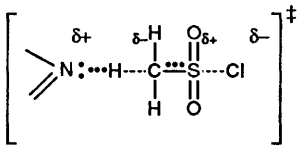
When the basicity of pyridines increases, the contribution of the sulfene route increases sharply (Fig. 2). When pyridines with $pK_\alpha < 5$ are used, the nucleophilic substitution route dominates, and with $pK_\alpha > 5$ it is the sulfene route that prevails.

Treatment of the kinetic data by the Brønsted equation yields eqns. (9) and (10). The greater value for the β coefficient for the

$$\log k_s = (-9.0 \pm 0.2) + (1.00 \pm 0.03)\,pK_\alpha,\ r\ 0.99,\ s_0\ 0.26 \quad (9)$$

$$\log k_n = (-6.2 \pm 0.1) + (0.64 \pm 0.03)\,pK_\alpha,\ r\ 0.99,\ s_0\ 0.15 \quad (10)$$

sulfene route indicates a higher degree of proton transfer in the transition state of this route.



For the nucleophilic substitution route the value of $\beta = 0.64$ is in greater agreement with the general-base catalysis mechanism, which is confirmed by the weak effect of steric hindrances in the pyridine molecule upon the rate of this route [the data were treated by the modified Taft equation[15] considering the inductive ($\Sigma\sigma^*$) and the steric (E_N) influence of the substituents in pyridine upon the reaction rate]. The weak

$$\log k_s = (0.47 \pm 0.13) - (3.16 \pm 0.09)\Sigma\sigma^* + (0.12 \pm 0.06)E_N \quad (11)$$
$$r\ 0.99,\ s_0\ 0.19$$

$$\log k_n = (0.11 \pm 0.01) - (2.16 \pm 0.08)\Sigma\sigma^* + (0.09 \pm 0.04)E_N \quad (12)$$
$$r\ 0.99,\ s_0\ 0.13$$

influence of steric hindrance in pyridine is understandable for the sulfene mechanism when, in the transition state, the base attacks a sterically accessible α-hydrogen atom of the sulfonyl chloride; however, this is not in agreement with the knowledge of the nucleophilic catalysis mechanism for the substitution route.[13] In the latter case the influence of steric hindrance in the amine is rather considerable and should manifest itself both in the formation of the sulfonylonium salt, and during the interaction of the latter with nucleophilic reactants.

It should be noted that the sulfene route is much more sensitive to the inductive influence of the substituents in the amine than the competing route. When amines with high basicity [*e.g.* 4-(*N*,*N*-dimethylamino)pyridine] are used, the contribution of the nucleophilic substitution route [path (i) and (ii)] can be neglected, and the reaction rate is no longer dependent on the phenol concentration (i.e. the reaction proceeds completely by the sulfene route). Such a situation was observed earlier[11,12] when the catalytic effect of trialkylamines in the formation of alkanesulfonyl acid esters was studied.

The Effect of the Substrate Structure.—When using alkanesulfonyl chlorides $AlkSO_2Cl$ (Alk = Me; Et; Pr; Pr^i; cyclo-C_6H_{11}) in the pyridine-catalysed reaction with phenol in chlorobenzene medium, only the nucleophilic substitution route is observed, with the ester formation rate decreasing more than 10^3 times on varying Alk from Me to cyclo-C_6H_{11}. This is likely to be due to the simultaneous action of two factors, *i.e.* an increase in the donor properties and the steric volume of the substituents. When it is only the inductive effect (σ_R^*) of the substituents in $AlkSO_2Cl$ that is taken into account, the correlation between $\log k_n$ and σ_R^* is poor. Calculation of the results obtained by the Taft equation considering the inductive and steric influence of Alk, however, yields eqn. (13). Analysis of contributions of individual parameters in eqn. (13) made to a

$$\log k_n = -(3.74 \pm 0.15) + (6.1 \pm 1.5)\sigma_R^* + (2.11 \pm 0.22)E_s^0 \quad (13)$$
$$r\ 0.99;\ s_0\ 0.17$$

standard scale proves substantial domination (about 2.5 times) of the effect of steric factors over inductive ones upon the rate of ester formation.

During catalysis by pyridines the transition from alkanesulfonyl chlorides $AlkSO_2Cl$ to arylmethanesulfonyl chlorides $RC_6H_4CH_2SO_2Cl$ in the reaction with phenol is accompanied by the appearance of the elimination–addition route (Table 2), competing with nucleophilic substitution.

Increased electron-accepting ability of the substituent R in $RC_6H_4CH_2SO_2Cl$ yields acceleration in both routes of the ester formation reaction, being more pronounced in the sulfene path. With R = 3-Cl, 4-NO_2 it is only the sulfene mechanism that is

realized; this is manifested in the fact that phenol concentration does not affect the process rate.

Correlation analysis of the results obtained yields eqns. (14)–(17).

$$\log k_s = -(3.97 \pm 0.03) + (2.09 \pm 0.09)\sigma;\ r\ 0.99,\ s_0\ 0.07 \quad (14)$$

$$\log k_n = -(2.78 \pm 0.03) + (0.66 \pm 0.17)\sigma;\ r\ 0.94,\ s_0\ 0.05 \quad (15)$$

$$\log k_s = -(3.96 \pm 0.05) + (1.65 \pm 0.37)\sigma_R^0 + (0.39 \pm 0.36)\sigma_R^+ \quad (16)$$
$$r\ 0.99,\ s_0\ 0.08$$

$$\log k_n = -(2.81 \pm 0.02) + (0.83 \pm 0.13)\sigma_R^0 - (0.36 \pm 0.18)\sigma_R^+ \quad (17)$$
$$r\ 0.99,\ s_0\ 0.02$$

The inductive effect of the substituents R in $RC_6H_4CH_2SO_2Cl$ upon the rate of the sulfene route is *ca.* twice as high as on the substitution route rate. In the latter case this seems to be accounted for by a weakened inductive effect due to the methylene bridge between the aromatic ring and the sulfur atom of the sulfonyl group. In both cases the contribution of the mesomeric effect is negligible and can be ignored.

To estimate the influence of the nature of the substrate leaving group upon the rate and ratio of the competing routes the kinetics of interaction of phenylmethanesulfonyl halides $PhCH_2SO_2Hal$ (Hal = F, Cl, Br, J) with phenol have been studied in the presence of pyridine in chlorobenzene (Table 3). The influence of the leaving group was estimated by the equation proposed by Litvinenko and Popov,[16] where τ_X is the

$$\log k_s = -(8.0 \pm 0.5) + (1.2 \pm 0.1)\tau_X,\ r\ 0.99,\ s_0\ 0.15 \quad (18)$$

$$\log k_n = -(4.2 \pm 0.2) + (0.33 \pm 0.06)\tau_X,\ r\ 0.98,\ s_0\ 0.22 \quad (19)$$

electron chemical characteristic of the leaving group in RSO_2Hal, which is a function of halogen inductive effect and S–Hal bond polarizability.

The sulfene route is about 3.5 times more sensitive to the halide nature in $PhCH_2SO_2Hal$ than the alternative route. In the case of phenylmethanesulfonyl fluoride, phenol sulfonylation only occurs by the route of direct substitution at the sulfur atom, and in the case of sulfonyl iodide it is only the sulfene mechanism that is realized. The use of chloro- and bromoanhydrides results in the parallel occurrence of both competing routes. The transition from phenylmethane- to methane-sulfonyl halides is accompanied by a substantial decrease in the overall reaction rate, and by a sharply decreased contribution of the sulfene route.

When considering the qualitative aspect of the problem, one may assume similar influence of the leaving group upon both competing routes. In the series I–Br–Cl–F an increase in the negative inductive halide effect should promote both reaction routes, owing to an increase in the effective positive charge on the sulfur atom of the sulfonyl group, on the one hand, and increased acidity of the α-hydrogen atom, on the other. At the same time, in this series S–Hal polarizability decreases, which should result in deceleration of both competing routes.

The results obtained prove that it is the polarizability effects of the S–Hal bond that play the dominant role, since in the transition from F to I both routes accelerate substantially.

In the case of the sulfene route the very fact that reactivity varies with a change in the leaving group of the acylating agent testifies in favour of the fact that S–Hal bond rupture occurs in the rate-limiting step of the reaction. This is an argument against an $(E1cB)_1$ mechanism, when abstraction of the α-hydrogen atom occurs in the slow step, and that of the leaving group in the fast step. Such behaviour of the system leads one to expect a mechanism close to the synchronous E2.

The low sensitivity to the nature of Hal for the route competing with the sulfene one, also indicates predominant general-base catalysis by pyridine path (ii). The influence of the medium nature upon this route may serve as additional corroboration of the above conclusion.

The Solvent Effect.—When analysing the experimental

Table 2 The effect of the structure of substituted phenylmethanesulfonyl chlorides $RC_6H_4CH_2SO_2Cl$ upon the rate of their interaction with phenol in the presence of pyridine[a]

R	k_s'[b]/10^{-4} dm^3 mol^{-1} s^{-1}	k_s/10^{-4} dm^3 mol^{-1} s^{-1}	k_n/10^{-3} dm^6 mol^{-2} s^{-1}
4-Me	0.75	0.75[c]	1.32[c]
	—	0.53	1.42
3-Me	0.80	0.79[c]	1.54[c]
	—	0.60	1.46
H	—	1.33[c]	1.55[c]
	—	1.27	1.47
4-Cl	3.55	3.55[c]	2.52[c]
	—	3.13	2.51
3-Cl	6.76	6.76[c]	negligible
	—	6.56	
4-NO_2	47.4	47.0	negligible
	—	46.2	

[a] For reactant concentrations and solvent see Table 1. [b] The values for k_s' were obtained by the method of potentiometric titration in the absence of phenol. [c] The values for k_s and k_n were obtained by the method of potentiometric titration under varying phenol concentrations.

Table 3 The influence of the leaving group (Hal) upon the rate of alkanesulfonyl halides RSO_2Hal reaction with phenol in the presence of pyridine[a]

Substrate	Hal	τ_x	k_s'[b]/10^{-6} dm^3 mol^{-1} s^{-1}	k_s/10^{-6} dm^3 mol^{-1} s^{-1}	k_n/10^{-6} dm^6 mol^{-2} s^{-1}
$PhCH_2SO_2Hal$	F	0.00	*c*	*c*	5.25
	Cl	3.40	126	82	121
	Br	4.79	2 320	2 220	176
	I	5.35	16 100	15 700	*c*
$MeSO_2Hal$	Cl	3.40	*c*	*c*	21
	Br	4.79	27	20	250

[a] For reactant concentrations and solvent see Table 1. [b] The values for k_s' have been obtained by potentiometric titration in the absence of phenol. [c] Negligible.

Table 4 The influence of medium upon the rate of alkanesulfonyl chlorides reaction with phenol catalysed by pyridine[a]

Substrate	Solvent	ε	$k_s'^{b}/10^{-5}$ dm^3 mol^{-1} s^{-1}	$k_s/10^{-5}$ dm^3 mol^{-1} s^{-1}	$k_n/10^{-4}$ dm^6 mol^{-2} s^{-1}
$PhCH_2SO_2Cl$	60% chlorobenzene + 40% benzene	4.25	5.3	6.0	4.6
	chlorobenzene	5.60	12.6	8.2	12.1
	methylenechloride	9.08	69	66	24
	60% chlorobenzene + 40% nitrobenzene	15.2	129	128	73
	nitrobenzene	34.8	420	710	76
$MeSO_2Cl$	chlorobenzene	5.60	*c*	*c*	2.1
	80% chlorobenzene + 20% nitrobenzene	10.2	*c*	*c*	17.8
	40% chlorobenzene + 60% nitrobenzene	21.1	*c*	*c*	38
	nitrobenzene	34.8	22[d]	*c*	110[d]
	nitrobenzene	—	—	2	110

[a] For reactant concentrations and solvent see Table 1. [b] The values for k_s' have been obtained by potentiometric titration in the absence of phenol. [c] Negligible. [d] The value has been obtained by the potentiometric titration method.

results as to the solvent effect upon the rate of pyridine-catalysed reaction of alkanesulfonyl chlorides with phenol (Table 4), it should be noted that when phenylmethanesulfonyl chloride is used over a broad range of medium polarity variations, both competing routes are realized. The contribution of the elimination–addition mechanism increases sharply with an increase in medium polarity, and in nitrobenzene the process proceeds almost completely by the sulfene mechanism (Fig. 2).

On changing to methanesulfonyl chloride the region of realization of the elimination–addition mechanism is sharply narrowed, which causes almost complete suppression of the latter in low-polarity solvents, and it is only in nitrobenzene that its contribution reaches *ca.* 5%. It should be mentioned that when triethylamine is used as a catalyst the reaction of mesylation of phenols in benzene proceeds only by the sulfene mechanism.[12]

Treatment of the results (Table 4) using the Kirkwood equation yields the following equations for the competing routes:

$$\log k_s = -(9.6 \pm 0.8) + (15 \pm 2)(\varepsilon - 1)/(2\varepsilon + 1),\ r\ 0.98,\ s_0\ 0.24 \quad (20)$$

$$\log k_n = -(6.5 \pm 0.4) + (9 \pm 1)(\varepsilon - 1)/(2\varepsilon + 1),\ r\ 0.98,\ s_0\ 0.11 \quad (21)$$

The nucleophilic substitution route is much less sensitive to medium polarity than the sulfene route. On changing to methanesulfonyl chloride the sensitivity of the nucleophilic substitution path to the solvent polarity rises by a factor of 1.8.

$$\log k_n = -(9.6 \pm 0.7) + (16 \pm 2)(\varepsilon - 1)/(2\varepsilon + 1),\ r\ 0.99,\ s_0\ 0.13 \quad (22)$$

These facts testify in favour of pronounced separation of charges in the transition state of the substitution route. Such behaviour of the system does not contradict the general-base catalysis mechanism (ii) with H–O bond rupture preceding S–O bond formation in the transition state.

When a nucleophilic catalysis mechanism is assumed, with sulfonylpyridinium salt (an ionic compound) participating in the transition state, one should expect at least equal (or higher) sensitivity of the rate to medium polarity as compared with the sulfene path (polar transition state). Therefore, the results obtained are in better agreement with the general-base catalysis mechanism in the substitution route.

Theoretical Study.—The reasons for the fact that route (i) makes a small contribution to the total reaction rate are likely to involve the instability of intermediate **1** in the low polarity medium, with $K_{e2} \ll 1$, *i.e.* the equilibrium of its formation is largely shifted to the initial reactants. Besides, a decrease in reactivity of **1** is promoted by additional steric and electrostatic hindrances to nucleophile attack at the sulfur atom of the sulfonyl group by the halide anion.

On the basis of the results of kinetic studies we have assumed preferential existence of sulfene (**2**) in the organic medium as compared with **1**. We were also interested to obtain theoretical results.

To determine the parameters for equilibrium geometry and the atomic charges in the molecules under investigation the MNDO semi-empirical method[17] was used, and estimation of thermochemical characteristics of the reactions was performed on the basis of the calculated formation energies.

According to the results of quantum-chemical calculations, the gas-phase reaction of mesyl chloride with pyridine with the formation of sulfene or mesylpyridinium chloride can be described by eqns. (23) and (24). Both processes are endo-

$$MeSO_2Cl + Py \rightleftharpoons CH_2{=}SO_2 + PyH^+Cl^-;\ \Delta H = +172\ \text{kJ mol}^{-1} \quad (23)$$

$$MeSO_2Cl + Py \rightleftharpoons MeSO_2Py^+Cl^-;\ \Delta H = +227\ \text{kJ mol}^{-1} \quad (24)$$

thermic, which seems to be associated with the formation of ionic compounds in both cases. However, generation of sulfene is 55 kJ mol^{-1} less disadvantageous. The solvation apparently strongly decreases the formation energy, both for sulfene and mesylpyridinium chloride. In the low polarity medium a situation may arise when the process (23) is exothermic, and (24) is endothermic, when the reaction proceeds by the sulfene mechanism. The use of high polarity media may bring about equally likely generation of both intermediates.

As far as the sulfene intermediate is concerned, its much higher reactivity as compared to methanesulfonyl chloride seems not to be associated with an increase in the positive charge of the sulfur atom, caused by its greater steric accessibility in the sulfene planar structure and enhanced nucleophilicity of the carbon atom (Table 5). The latter factor leads to intramolecular general base promotion of the nucleophile attack at the sulfur atom. All these factors are the main reasons for high sulfene reactivity in reactions with

Table 5 Results of theoretical calculations for the sulfene molecule ($H_2C{=}SO_2$)

Method	Atomic charges in a.u. H	C	S	O	E_{HOMO}/eV	E_{LUMO}/eV	$\Delta E_{(HOMO-LUMO)}$/eV
MNDO[a]	0.118	−0.309 −0.052[b]	1.092	−0.510	−10.34	−2.37	7.97
MINDO/3	0.104	−0.453	1.562	−0.659	−9.47	−1.49	7.98
CNDO/2[21]	0.12	−0.21	1.20	−0.62	−10.74	−2.33	8.41

[a] Geometrical characteristics (bond distances/Å and angles/°) of sulfene by the results of MNDO calculations, *r*(C–H) 1.08, *r*(S–O) 1.47, *r*(C–S) 1.61, ∠CSO 119.6, ∠HCS 118.9. [b] Carbon charge in mesyl chloride.

nucleophiles, in oligomerization processes[18] and for its kinetic stability only at temperatures below 120 K.[19]

The high lability of the ionic bond in mesylpyridinium halides facilitates the anion Hal^- attack at the moveable hydrogen atom of the cationic methyl group which may encourage monomolecular decomposition [eqn. (25)]. Strictly speaking,

$$MeSO_2Py^+Hal^- \longrightarrow CH_2{=}SO_2 + PyH^+Hal^- \quad (25)$$

however, non-rigidity of ion pairs is not an indispensable condition for thermal instability of mesylonium salts. Nevertheless, an assumption about conversion (25) was used in the literature[20] to account for experimental data on acylation of alcohols with mesyl chloride in the presence of organic bases.

According to the results of quantum-chemical calculations, the processes of monomolecular decomposition of mesyl derivatives can be described by the following thermochemical equations. All the reactions except the first one are exothermic,

$$MeSO_2Cl \rightleftharpoons CH_2{=}SO_2 + HCl;\ \Delta H = +69\ kJ\ mol^{-1} \quad (26)$$

$$MeSO_2Py^+ \rightleftharpoons CH_2{=}SO_2 + PyH^+;\ \Delta H = -33\ kJ\ mol^{-1} \quad (27)$$

$$MeSO_2OPy^+ \rightleftharpoons CH_2{=}SO_2 + PyOH^+;\ \Delta H = -34\ kJ\ mol^{-1} \quad (28)$$

$$MeSO_2Py^+Cl^- \rightleftharpoons CH_2{=}SO_2 + PyH^+Cl^-;\ \Delta H = +55\ kJ\ mol^{-1} \quad (29)$$

$$MeSO_2OPy^+Cl^- \rightleftharpoons CH_2{=}SO_2 + PyOH^+Cl^-;\ \Delta H = -107\ kJ\ mol^{-1} \quad (30)$$

with the conversion of mesyloxypyridinium chloride [eqn. (30)] being most favourable energetically. In an attempt to obtain the latter preparatively in the reaction of mesyl chloride with pyridine *N*-oxide in toluene we isolated a precipitate that gradually became resinous, *i.e.* mesyl-oxypyridinium chloride. This is a corroboration of the possibility of sulfene formation by reaction (30) under normal conditions.

Thermodynamic stability of ion pairs is much lower than that of the isolated cation which results from an increase in the acidity of α-hydrogen atoms under the influence of interaction with halide anions. Comparison of the thermochemical characteristics of reactions (26)–(30) with positive charge values Q_H (in a.u.) at hydrogen atoms of the methyl group yields the following linear relationship:

$$\Delta E = (280 \pm 50) - (2900 \pm 500)Q_H,\quad r\ 0.98,\ s_0\ 0.22 \quad (31)$$

Relationship (31) can be used to estimate thermochemical characteristics for reactions of monomolecular decomposition of mesyl derivatives with the formation of sulfene on the basis of the calculated values for the atomic charges.

Thus, theoretical studies corroborate predominant formation of the sulfene intermediate in low polarity media, as compared with acylonium salts. Under the conditions when intermediate **1** slowly reacts with the nucleophiles and undergoes conversion into sulfene, the general-base catalysis route competes with the sulfene route.

Conclusions

As a result of kinetic studies of the pyridine-catalysed formation of alkanesulfonyl esters in organic media the following conditions for realization of the sulfene mechanism have been determined: (*a*) the use of substrates with good leaving groups (Cl, Br, I) and electron-accepting substituents at the α-carbon atom of alkanesulfonyl halides; (*b*) the use of catalysts with pronounced basic properties; (*c*) polar reaction medium. Joint use of these conditions may result in the reaction proceeding almost completely by the sulfene mechanism.

The results of kinetic and theoretical studies prove predominantly general-base nature of the nucleophilic substitution at the sulfur atom of the sulfonyl group, competing with the sulfene path. The most probable reasons for the small contribution of the nucleophilic catalysis route (i) are steric hindrance to nucleophile attack by the halide anion and potential conversion of intermediate **1** into sulfene.

Isolation of stable sulfonylonium salts and the experimental study of the routes of their thermal conversion into sulfene is an intriguing subject of further research.

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