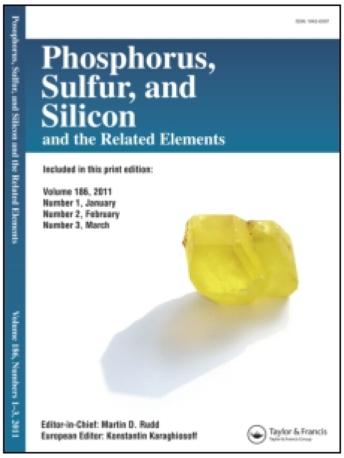

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Kutuk, Halil and Ozturk, Seyhan(2009) 'A Kinetic Study of Acid-Catalyzed Hydrolysis of Some Arylsulfonyl Phthalimides', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 2, 332 — 340
To link to this Article: DOI: 10.1080/10426500802119655
URL: http://dx.doi.org/10.1080/10426500802119655

Phosphorus, Sulfur, and Silicon, 184:332–340, 2009
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802119655

A Kinetic Study of Acid-Catalyzed Hydrolysis of Some Arylsulfonyl Phthalimides

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The acid-catalyzed hydrolysis of arylsulfonyl phthalimides was studied in aqueous solutions of sulfuric, perchloric, and hydrochloric acid at 35.0 ± 0.1°C. Analysis of the data by the excess acidity method and activation parameters, as well as substituent and solvent isotope effects, indicate hydrolysis by an A-2 mechanism at low acidity. At higher acidities, a changeover to an A-1 mechanism is observed.

Keywords Acid-catalyzed hydrolysis; arylsulfonyl phthalimides; excess acidity; mechanism

INTRODUCTION

N-alkyl and *N*-arylsulfonyl phthalimides were prepared by Heller by the reaction of potassium phthalimide with sulfonyl chlorides.[1] Earlier attempts by Evans and Dehn[2] to prepare several *N*-aryl derivatives and later by Scott and Lutz[3] to prepare several *N*-alkyl derivatives by this reaction were unsuccessful. More recently, potassium phthalimide was reported to interact with *p*-toluenesulfonyl chloride at 140°C or in dimethylformamide at 5°C to 40°C to yield *N*-(*p*-tolylsulfonyl)phthalimide.[4] The mechanisms of the acid catalyzed hydrolysis of *N*-(*p*-substituted-arylsulfinyl)phthalimides **1** have been studied in some detail in our laboratory.[5] There has been a systematic study of the acid-catalyzed hydrolysis of sulfonylphthalimides in highly acidic solutions. We now report a complementary study of the acid-catalyzed hydrolysis of a series of *N*-(*p*-substituted-arylsulfonyl)phthalimides **(2a–c)** in concentrated aqueous mineral acids.

The rate of hydrolysis of **1** in acid solution at all temperatures is much higher than that of **2** (Scheme 1).

Received 15 December 2007; accepted 8 April 2008.

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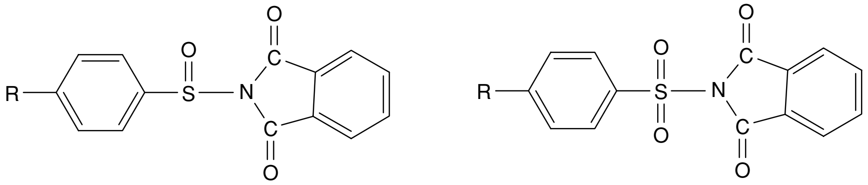


1 (R = CH_3 , H , Cl)

2 a: R = H
b: R = CH_3
c: R = Br

SCHEME 1

Compounds **2** have two oxygen atoms bonded to the sulfur atom, and a water molecule attacks the sulfur atom in the rate-determining step at low acid concentrations. When compared with compounds **1**, it is more difficult for a water molecule to attack the sulfur atom in **2** because of steric hindrance. At high acid concentrations, the sulfur atom of the sulfinylium cation is less positive than that of the sulfonium ion. Therefore, under these conditions, the more stable sulfinylium cation forms more easily than the sulfonium cation.

RESULTS AND DISCUSSION

The first-order rate coefficients, k_1, for the hydrolysis of *N*-(phenylsulfonyl)phthalimide **2a** in aqueous solutions of mineral acids are shown in Figure 1. It is evident that with increasing concentration of sulfuric and perchloric acid up to 7.00 M, the rate of hydrolysis decreases, while at acid concentrations above 8.00 M the rate increases, and there is no indication of a rate maximum even at fairly high acidity. In all cases, the rates of hydrolysis decrease continuously with increasing concentration of hydrochloric acid (Table I). Values of k_1 for the perchloric acid catalyzed hydrolysis of **2a–c** are shown in Figure 2.

The order of catalytic effectiveness of the acids observed for the hydrolysis of **2a** was $HCl \cong H_2SO_4 > HClO_4$. Similar behavior has been observed for the acid-catalyzed hydrolysis of *p*-toluenesulfinamide.[6] Bunton et al. suggested that such an order is characteristic of a bimolecular mechanism, transition states of positive character being preferentially stabilized by anions of high charge density such as Cl^-, whereas the opposite is usually the case for A-1 reactions.[7,8] The kinetic data in Table I were also analyzed by the excess acidity treatment of Cox and Yates.[9] A simplified version of their relationship for mainly unprotonated

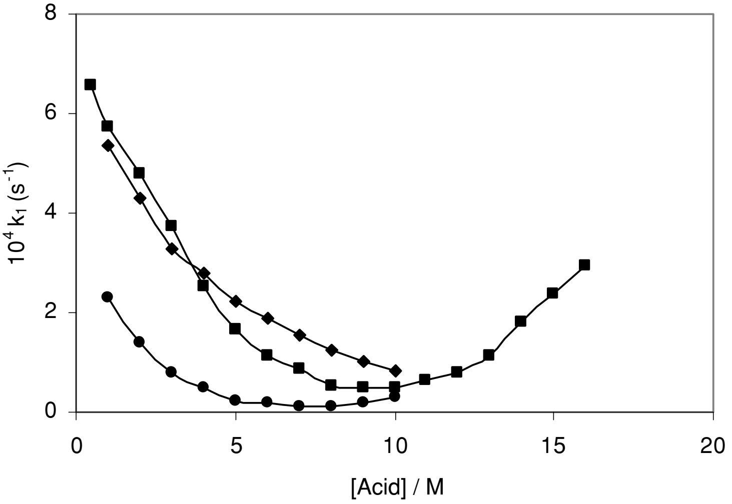


FIGURE 1 Plots of k_1 for the acid catalyzed hydrolysis of **2a** in aqueous acid solutions at 35.0°C; ■ :H_2SO_4, ♦:HCl, •:$HClO_4$.

TABLE I Values of $10^4 k_1$ (s^{-1}) for the Hydrolyses of *N*-(*p*-substitued arylsulfonyl)-phthalimides at 35.0°C

Acid (M)	**2a** H_2SO_4	**2a** $HClO_4$	**2a** HCl	**2b** H_2SO_4	**2b** $HClO_4$	**2b** HCl	**2c** H_2SO_4	**2c** $HClO_4$	**2c** HCl
0.50	6.55	—	—	—	—	—	—	—	—
1.00	5.74	2.31	5.35	10.30	1.97	7.15	—	3.07	—
2.00	5.10	1.40	4.31	6.00	1.00	5.62	—	2.15	—
3.00	3.73	0.78	3.30	4.10	0.56	3.60	—	1.30	—
4.00	2.51	0.49	2.79	2.98	0.36	2.66	—	0.57	—
5.00	1.66	0.23	2.21	1.49	0.22	1.86	—	0.30	—
6.00	1.13	0.18	1.87	1.39	0.17	1.36	—	0.23	30.3
7.00	0.87	0.10	1.53	0.80	0.15	0.98	—	0.08	5.04
8.00	0.54	0.11	1.23	0.63	0.16	0.83	17.3	0.09	2.07
9.00	0.50	0.17	1.03	0.75	0.24	0.93	3.24	0.10	1.17
10.00	0.49	0.29	0.83	1.07	0.43	1.18	0.45	0.20	1.26
11.00	0.65	—	—	1.23	—	—	0.35	—	—
12.00	0.78	—	—	1.40	—	—	0.60	—	—
13.00	1.13	—	—	1.60	—	—	1.10	—	—
14.00	1.81	—	—	2.46	—	—	1.26	—	—
15.00	2.39	—	—	—	—	—	—	—	—
16.00	2.94	—	—	—	—	—	—	—	—

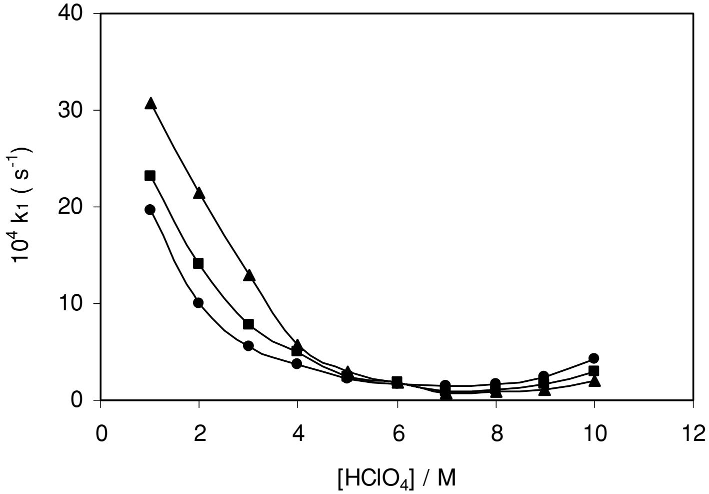


FIGURE 2 Plots of k_1 for the perchloric acid catalyzed hydrolysis of **2a–c** at 35.0°C; ●: p-CH$_3$, ■: p-H, ▲: p-Br.

substrates was used:

$$\log k_1 - \log C_{\mathrm{H+}} - \log Cs/(Cs + C_{\mathrm{SH+}})$$
$$= m^* m^{\neq} X + r \log a_{\mathrm{Nu}} + \log\ (k_0/K_{\mathrm{SH+}}) \qquad (1)$$

Because of the extremely low basicity of the sulfonyl phthalimides studied, the protonation correction term [log Cs / (Cs + C_{SH+})] can be neglected. Values of X for the aqueous solution of the acid were used.[10,11] Where m^* is obtained from protonation studies, $m^{\neq}$ is the slope parameter and characteristic of the type of reaction; $r \log a_{Nu}$ for the A-2 reaction represents the nucleophilic activity, where r is the number of water molecules involved in forming the transition state.

A plot of $\log k_1$- $\log C_H^+$ versus X is shown in Figure 3 for the hydrolysis of **2a** in sulfuric acid solution. A similar graph was observed for **2a–c** in perchloric acid solution. Initially, all such graphs for the arylsulfonyl phthalimides in the low acidity region exhibit downward curvature typical of A-2 reactions involving water.[12]

These changes with increasing acidity to an upper linear region are characteristic of an A-1 process. Similar behavior has been observed for the hydrolyses of sulfinylphthalimides,[5]a number of esters,[13] and benzohydroxamic acids.[14] This suggests that a gradual changeover in mechanism from A-2 to A-1 occurs with increasing concentration of the acid.

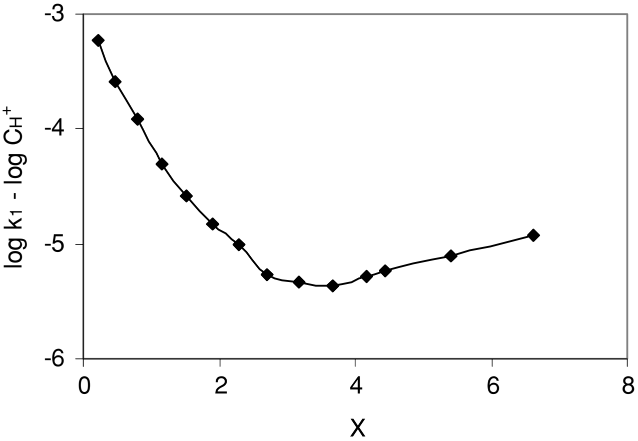


FIGURE 3 Plots of $\log k_1 - \log C_H+$ versus excess acidity for the sulfuric acid catalyzed hydrolysis of **2a** at 35.0°C.

The temperature dependence of the rate constants of the hydrolysis reaction was analyzed by a least-squares procedure using a spreadsheet program (Eyring equation). The values at different acidities are shown in Table II. Acid-catalyzed hydrolyses of esters and amides[15] proceeding by an A-1 mechanism have $\Delta S^{\neq}$ of about 0 to –41.8 JK^{-1} mol^{-1}, while those proceeding by an A-2 mechanism have $\Delta S^{\neq}$ of –62.8 to –125.5 JK^{-1} mol^{-1}. Values of $\Delta S^{\neq}$ for the acid-catalyzed hydrolysis of (*p*-methoxybenzoyl)-*p*-tolueneiminosulfonate were reported by Kutuk and Tillett[13] (–92.3 JK^{-1} mol^{-1} in 3.00 M and +17.2 JK^{-1} mol^{-1} in 8.00 M sulfuric acid, –57.8 JK^{-1} mol^{-1}in 3.00 M perchloric acid, and +9.6 $JK^{-1}mol^{-1}$ in 6.50 M perchloric acid, respectively). They suggested an A-2 mechanism at low acid concentration and an A-1 mechanism at high acid concentration. Over the range 5.00–13.00 M sulfuric acid, the values of $\Delta S^{\neq}$ changed from –76.86 to –23.67 JK^{-1} mol^{-1} for the hydrolysis of **2a**. Values in perchloric acid varied in a similar way, as expected.

The kinetic solvent isotope effect (k_D/k_H) observed for the hydrolysis of **2a** is shown in Table III. The increasing values of the kinetic solvent isotope effect with acidity [e.g., for **2a**, k_1D_2O/k_1H_2O = 1.19 (3.00 M H_2SO_4) and 2.38 (14.00 M H_2SO_4)] are also consistent with a change from A-2 to A-1.[16]

In the acidity range studied, electron-donating substituents cause the highest rate of hydrolysis (**2b** > **2c**), and the substituent effects are well correlated by a satisfactory Hammett $\rho\sigma$ plot [at 9.00 M $HClO_4$,

TABLE II Arrhenius Parameters for the Hydrolysis of *N*-(*p*-substituted arylsulfonyl)-phthalimides

	Acid	(M)	$\Delta H^{\neq}$ (kJ/mol)	$\Delta S^{\neq}$ (J/molK)	Temperature Range (°C)	r^2
2a	H_2SO_4	5.00	74.30 ± 0.95	–76.86 ± 3.10	25–40	0.9994
		9.00	87.28 ± 0.86	–44.51 ± 2.80	25–40	0.9997
		13.00	91.61 ± 1.33	–23.67 ± 4.33	25–40	0.9995
	$HClO_4$	2.00	56.98 ± 0.71	–134.34 ± 2.32	25–40	0.9995
		5.00	76.10 ± 0.68	–87.47 ± 2.17	30–45	0.9997
		9.00	82.68 ± 1.17	–68.68 ± 3.75	30–45	0.9993
2b	H_2SO_4	5.00	74.07 ± 1.28	–78.25 ± 4.18	25–40	0.9992
		9.00	81.24 ± 1.18	–60.73 ± 3.85	25–40	0.9993
		13.00	87.46 ± 0.78	–34.51 ± 2.55	25–40	0.9997
	$HClO_4$	2.00	63.75 ± 0.57	–115.39 ± 1.87	25–40	0.9997
		5.00	70.64 ± 1.10	–105.76 ± 3.55	30–45	0.9992
		9.00	80.38 ± 1.02	–73.27 ± 3.26	30–45	0.9994
2c	$HClO_4$	2.00	59.94 ± 0.76	–121.25 ± 2.47	25–40	0.9996
		5.00	72.80 ± 0.62	–95.87 ± 2.00	30–45	0.9998
		9.00	86.18 ± 1.62	–61.35 ± 5.19	30–45	0.9991

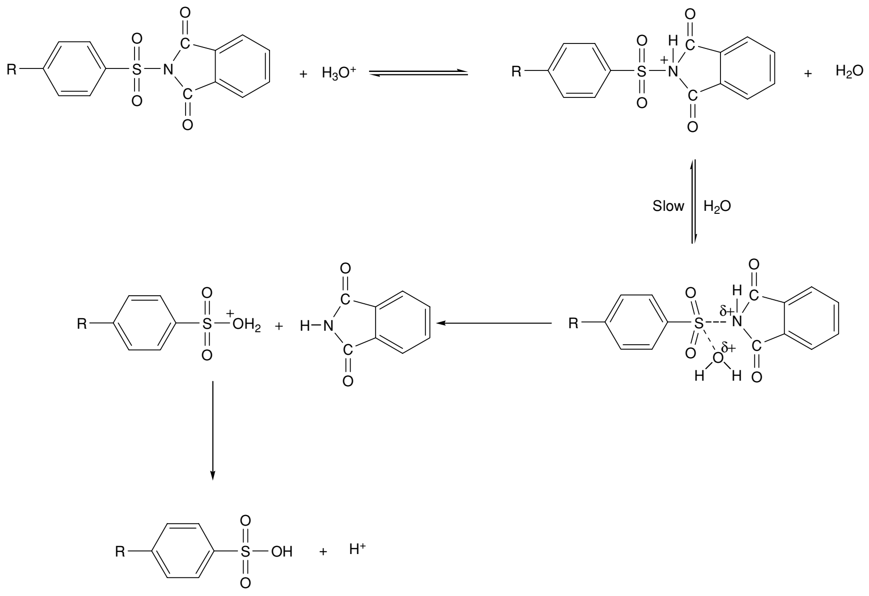
$\rho = -0.955$ (corr. 0.9959)]. Clearly at these acidities, electron-donating substituents both facilitate protonation of the substrate and stabilize the sulfonium cation in the case of an A-1 mechanism. At lower acidities, however [e.g., 2.00 M $HClO_4$, $\rho = 0.848$ (corr. 0.9997)], **2c** hydrolyzes more rapidly than **2b**, consistent with a predominantly A-2 mechanism, in which substituent effects on the protonation and slow step operate in opposite directions. There is no direct evidence concerning the site of protonation of sulfonyl phthalimides; however, protona-

TABLE III Deuterium Solvent Isotope Effect for the Hydrolysis of 2a in Sulfuric Acid Solutions at 35.0 ± 0.1°C

Acid (mol dm^{-3})	$10^4 k_1 (s^{-1})$	$10^4 k_{ave.} (s^{-1})$	k_{D2O}/k_{H2O}
3.00 M D_2SO_4	4.47 4.45	4.46	1.19
3.00 M H_2SO_4	3.74 3.72	3.73	
14.00 M D_2SO_4	4.30 4.32	4.31	2.38
14.00 M H_2SO_4	1.82 1.80	1.81	

tion of sulfinamides,[6,17]sultams,[18] and cyclic sulfamate esters[19]occurs preferentially at the nitrogen atom.

In the light of the overall evidence, we propose that the acid-catalyzed hydrolysis of arylsulfonyl phthalimides occurs according to an A-2 mechanism at lower acidities and an A-1 mechanism at higher acidities, as shown in Schemes 2 and 3, respectively.

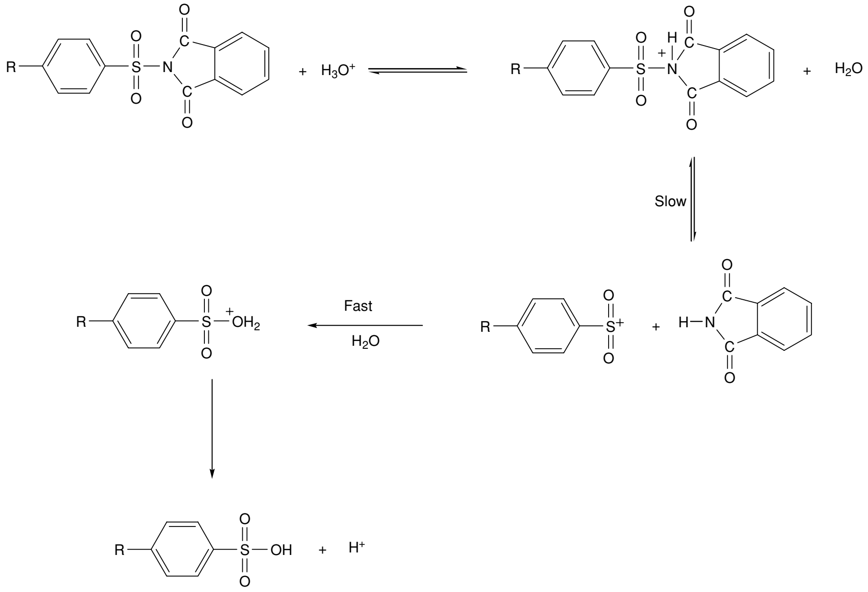


SCHEME 2

EXPERIMENTAL

Materials

Arylsulfonyl phthalimides **2a–c** were prepared from the corresponding arylsulfonyl chlorides by reaction with potassium phthalimide in refluxing acetonitrile, as described by Heller.[1] Phthalimide was obtained from Aldrich, and *p*-toluenesulfonic acid was prepared as described in the literature.[20] ^{1}H NMR spectra were recorded on a Bruker AC 200 MHz spectrometer using TMS as the internal standard. All melting points were obtained using an electrothermal digital melting point apparatus. **2a:** m.p. 202–203°C (lit.[1]202.5–203.5°C); ^{1}H NMR (d^6-DMSO): $\delta =$ 7.5–8.1 (m, 9H, arom-H); **2b:** m.p. 240–241°C (lit.[1] 239–240°C); ^{1}H NMR (d^6-DMSO): $\delta = 1.8$ (s, 3H, CH_3), 7.4–8.0 (m, 8H,



SCHEME 3

arom-H); **2c:** m.p. 249–250°C (lit.[1] 247–248°C); ^{1}H NMR (d^6-DMSO): $\delta = 7.5$–8.0 (m, 8H arom-H).

Kinetic Studies

The rates of hydrolysis of arylsulfonyl phthalimides were followed spectrophotometrically at 230–250 nm using a GBC Cintra 20 Model UV-VIS spectrometer with a thermostatted cell compartment (± 0.05°C). Good first-order behavior was observed with clean isosbestic points. Values of k_1 were calculated from the standard equation using a least-squares procedure. All kinetic measurements were duplicated and the average deviation from the mean was $<3\%$.

Product Analysis

The products of hydrolysis were determined by comparing the UV spectrum obtained after completion of the kinetic experiment with the spectrum of the expected products at the same concentration and under the same conditions. Thus for the hydrolysis of *N*-(*p*-toluenesulfonyl)phthalimide, the UV spectrum recorded at the end of the reaction was identical with that of a 1:1 mixture of phthalimide and *p*-toluenesulfonic acid.

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