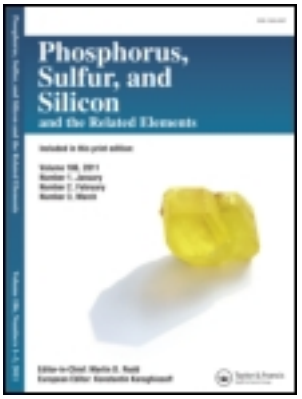

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HYDROLYSIS OF *N*-PHENYLALKANESULFINAMIDES IN AQUEOUS MINERAL ACIDS

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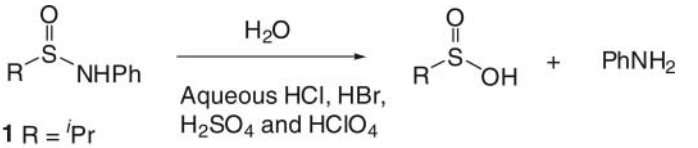
GRAPHICAL ABSTRACT



1 R = ^{i}Pr
2 R = ^{t}Bu
3 R = 1-adamantyl

Abstract *The acid-catalyzed hydrolysis of N-phenylalkanesulfinamides (RSONHPh; **1**, R = ^{i}Pr; **2**, R = ^{t}Bu; **3**, R = 1-adamantyl) has been studied in aqueous mineral acids. Hydrolysis was found to proceed via a slow spontaneous (uncatalyzed) pathway, an A-2 (bimolecular) acid-catalysis pathway, and an acid-dependent nucleophilic catalysis pathway, the last of which predominates in hydrobromic and hydrochloric acid solutions. A mechanistic switch over from A-2 to A-1 was detected for compounds **2** and **3** in concentrated sulfuric acid. Order of catalytic activity, effect of added salts, Arrhenius parameters, kinetic solvent isotope, and solvent effects are all consistent with the proposed mechanisms.*

Keywords Acid-catalyzed hydrolysis; acid-dependent nucleophilic catalysis; alkanesulfinamides; reaction mechanism

INTRODUCTION

Nucleophilic substitution at sulfur has been observed for a number of sulfinyl compounds, hydrolysis being typical of these reactions.[1] Both acid-catalyzed and hydrogen ion–dependent, nucleophile-catalyzed hydrolysis and related reactions have been reported for sulfoxides,[2,3] sulfite esters,[4,5] sulfinyl sulfones,[6] sulfinates,[7] and arenesulfinamides.[8–10]

Wagner et al. compared the rates of neutral (spontaneous) hydrolysis of a series of cyclic sulfinamides with that of *N,N*-dimethylmethanesulfinamide at pD 7.7 in D_2O.[11] The

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latter was unexpectedly more reactive than its cyclic counterparts, and its rate of hydrolysis was too fast to measure in all but mildly acid conditions.

For the hydrolysis of *N*-arylarenesulfinamides in aqueous solutions of hydrochloric and hydrobromic acids, parallel acid–catalyzed and acid-dependent nucleophilic mechanisms were proposed as the principal pathways.[8] In perchloric and sulfuric acids, the mechanism was considered to be of the A-2 type, while in halogen acid solutions, the rate-limiting step involves formation of a reactive sulfinyl intermediate, which rapidly decomposes to the products. While no spontaneous reaction could be detected at 25°C, at higher temperatures a minor nucleophilic-catalyzed spontaneous reaction was detected.

To date, however, apart from the brief study of *N*,*N*-dialkylalkanesufinamides,[11] there is no detailed account of the acid-catalyzed hydrolysis of alkanesulfinamides in the literature. We now report on the hydrolysis of *N*-phenylalkanesulfinamides (**1**–**3**) (RSONHPh; **1**, R = ^{i}Pr; **2**, R = ^{t}Bu; **3**, R = 1-adamantyl) in aqueous solutions of mineral acids.

RESULTS AND DISCUSSION

Figure 1 shows the kinetic profile of alkanesulfinamide **1**, while Table 1 displays the *pseudo* first-order rate constants (k_1) for the hydrolysis of **2** and **3** in aqueous mineral acids of different concentrations. All three compounds show similar kinetic profiles, which are broadly similar to those observed previously for the hydrolysis of *N*-arylarenesulfinamides, at relatively low acid concentration.[8]

However, there are several distinct differences. First, compounds **1**–**3** are less reactive toward aqueous mineral acids than the *N*-arylarenesulfinamides,[8] whose rates of hydrolysis at 25°C had to be studied by a stopped-flow spectrophotometric method. Even so, in our study, the hydrolysis of *N*-phenylisopropanesulfinamide (**1**) in acid solution is so fast that rate data was only obtained at very low concentrations of mineral acids. Simpler *N*-phenylalkanesulfinamides (R = Me or Et) are even more reactive, and their reactions in aqueous mineral acids could not be followed by conventional methods.

Second, unlike their arene counterparts, **1**–**3** exhibit slow, but significant, spontaneous reaction in pure water. Although a spontaneous reaction was previously observed by Wagner et al. for the hydrolysis of $MeSONMe_2$ in D_2O,[11] compounds **1**–**3** are somewhat more

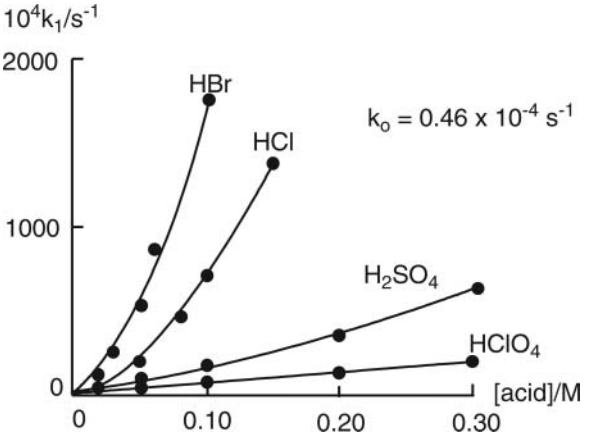


Figure 1 Pseudo first-order rate constant/acid concentration profile for the hydrolysis of **1** at 44.8°C.

Table 1 Values of 10^4 k_1 (s^{-1}) for the hydrolysis of **2** and **3** at 44.8°C

[Acid]/M	1.00	2.00	3.00	4.00	5.00	6.00
2, $HClO_4$	2.71	—	14.0	23.9	43.4	66.8
2, H_2SO_4	7.95	23.3	58.7	118	203	321
3, $HClO_4$	1.70	4.80	8.33	16.2	28.8	—
3, H_2SO_4	4.70*	14.0	34.3	63.4	107	158
[Acid]/M	7.00	8.00	9.00	10.00	11.00	12.00
2, H_2SO_4	433	462	450	455	507	692
3, H_2SO_4	188	200	193	209	275	362
[Acid]/M	0.200	0.300	0.400	0.500	0.600	0.800
2, HCl	7.71	—	—	45.3	—	112
2, HBr	24.5	49.3	88.8	—	418	—
3, HCl	5.15	—	—	29.2	—	83.3
3, HBr	20.0	41.4	72	—	184	330

10^4 k_o (s^{-1}) values are: 0.41 (**2**) and 0.38 (**3**).
*In D_2SO_4/D_2O, $10^4k_1 = 8.11$ s^{-1}.

reactive than this compound [10^4k_o (s^{-1}) for **1**, **2**, and **3** is 0.46, 0.41, and 0.38 at 44.8°C in H_2O, respectively, compared to 0.28 for $MeSONMe_2$ at 55.5°C in D_2O].

Third, the plots of k_1 versus acid concentration for the hydrolysis of **2** and **3** in H_2SO_4 are both characterized by a rate maximum occurring at ~7.5 M-H_2SO_4, followed by a minimum and then a final increase.

The catalytic order of acids for the hydrolysis of **1**–**3**, namely HBr > HCl >> H_2SO_4 > $HClO_4$, clearly reflects the relatively high nucleophilicity of Br^- and Cl^-. This was confirmed by observing the pronounced effect of added LiBr and LiCl on the rate of hydrolysis of **2** and **3** in 1.00 M $HClO_4$ (Table 2). By comparison, added $LiClO_4$ resulted in only minor increases in rate, as can be seen from Table 2. Also, the relative order and magnitude of the nucleophilic attack at sulfinyl sulfur for the hydrolysis of **2** and **3** in aqueous HBr and HCl ($k(Br^-)/k(Cl^-)$ ~ 4.0 for **2** and ~ 3.0 for **3** are similar to those observed for *N*-arylarenesulfinamides (~4.8)[8] and sulfinyl sulfones (~5.0).[6]

The order of catalytic power is typical of hydrolysis reactions that proceed via a bimolecular rate-limiting step, in sharp contrast to A-1 type reactions, such as the ring-opening hydrolysis of aromatic cyclic sulfamates,[12] where the catalytic order is $HClO_4$ > H_2SO_4. Additionally, sulfuric acid is typically a better catalyst for A-2 reactions than

Table 2 Effect of added salts on the rate of hydrolysis (10^4k_1 s^{-1}) of **2** and **3** in 1.00 M $HClO_4$ at 44.8°C

	[Salt]/M					
Substrate	0.05M-LiBr	0.10 M-LiBr	0.10 M-LiCl	0.20 M-LiCl	0.50 M-LiCl	1.00 M-$LiClO_4$
2*	39.6	74.7	23.6	40.3	113.4	3.95
3#	33.8	63.9	—	32.4	89.1	2.91

*10^4k_1 (s^{-1}) in 1.00 $HClO_4$ = 2.71.
#10^4k_1 (s^{-1}) in 1.00 $HClO_4$ = 1.70.

perchloric acid. Such behavior has been attributed by Bunton et al. to the differential stabilization of initial states and transition states by hydrogen sulfate and perchlorate anions.[13,14]

Asefi and Tillett[8] suggested a general rate equation for the hydrolysis of *N*-arylarenesulfinamides in acidic solutions containing halide ions (Eq. 1).

$$k_1 = k_o + k'_o[X^-] + k_{H+}[H^+] + k_{HX}[H^+][X^-] \quad (1)$$

Here, the terms represent (a) spontaneous (or uncatalyzed) reaction of the neutral species with water, (b) a nucleophile-catalyzed spontaneous reaction, (c) an acid-catalyzed reaction, and (d) hydrogen ion-dependent nucleophilic catalysis, respectively. Each term could be subject to a specific salt effect.

The effect of added lithium salts on the spontaneous reaction of **3** ($k_o = 0.38 \times 10^{-4}$ s^{-1}) was very slight. Thus, the pseudo first order rate constants for the spontaneous reaction were 0.43×10^{-4} s^{-1} and 0.45×10^{-4} s^{-1} with added 0.25 M $LiClO_4$ and 0.50 M $LiClO_4$, respectively, and 0.46×10^{-4} s^{-1} and 0.50×10^{-4} s^{-1} with added 0.25 M LiCl and 0.50 M LiCl, respectively. The differences between these rate constants are of the same order as the uncertainty of measurement ($\pm 0.05 \times 10^{-4}$ s^{-1}), and hence for the hydrolysis of **1**–**3**, the second term can be considered as being unimportant.

Of the other terms of Eq. (1), k_o makes only a minor contribution: except at very low acid concentrations, k_{H+} is prominent for hydrolysis in $HClO_4$ and H_2SO_4, and k_{HX} dominates hydrolysis in HBr and HCl solutions (as supported by the data in Table 2), especially at higher acid concentrations.

Figure 2 shows a plot of k_1 versus acid concentration for the hydrolysis of **2** in HCl at constant chloride ion concentration (1.50 M, achieved by the presence of LiCl), superimposed on data from Table 1. The linear plot at constant chloride ion concentration confirms the contribution of acid-catalysis (k_{H+}) to the overall pseudo first order rate constant for this compound in HCl.

Another distinct feature is the rate maximum observed in the plots of k_1 versus acid concentration for the hydrolysis of each of **2** and **3** in sulfuric acid, as shown in Table 1 and Figure 3. Similar behavior has been reported for the hydrolysis of many carboxylic acid derivatives, such as amides[15] and esters.[16,17] Such maxima can arise for a variety of

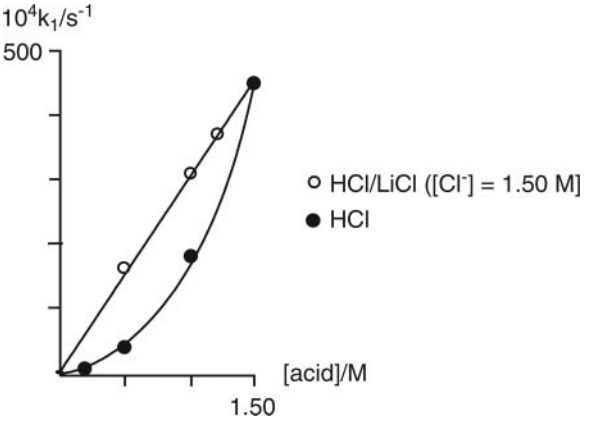


Figure 2 Hydrolysis of **2** at 44.8°C in HCl at constant chloride concentration ($[Cl^-] = 1.50$ M).

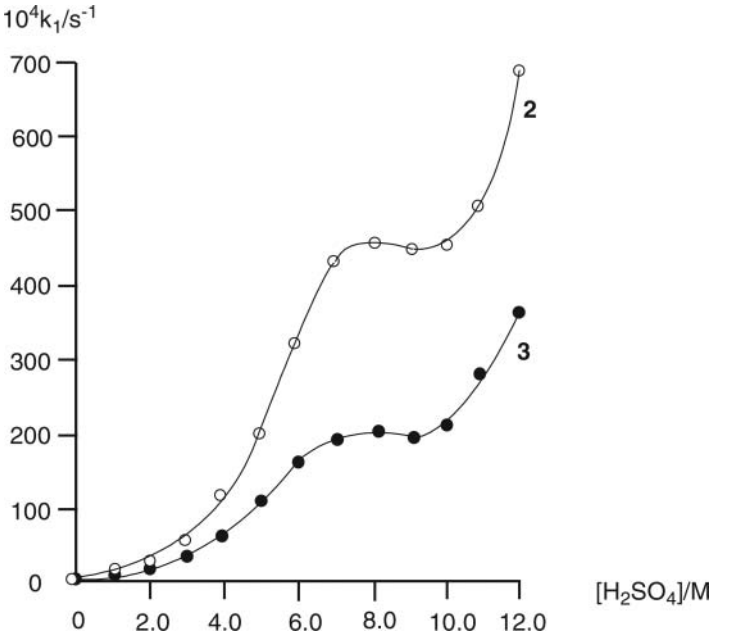


Figure 3 Rate profiles for hydrolysis of **2** and **3** in sulfuric acid at 44.8°C.

reasons, including decrease in the activity of water or superposition of a negative salt effect on an acid-catalyzed reaction or by extensive conversion of the substrate into its conjugate acid ("extensive substrate protonation").[15] Since the UV spectra of **3** (at 28.0°C) in aqueous 1.00 M and 9.00 M H_2SO_4 were found to be very similar (allowing for spectral changes caused by the significant reaction in the 9.00 M medium, even at this temperature), then the latter effect is unlikely to be the cause of this maximum.

Further confirmation of the A-2–like character of the hydrolysis of *N*-phenylalkanesulfinamides in dilute sulfuric acid comes from the entropy of activation of **3** in 3.00 M H_2SO_4 (-48 J K^{-1} mol^{-1}) (Tables 3 and 4), which falls within the range usually associated with a bimolecular mechanism.[18] The value of the kinetic solvent isotope effect $k_1(D_2O)/k_1(H_2O)$ in 1.00 M D_2SO_4/H_2SO_4 for **3** (1.72) also supports this view.[19]

Table 5 compares the pseudo first-order rate constants (k_1) for the hydrolysis of **3** in aqueous acid and in corresponding acidified 50% acetonitrile/water (v:v). The lower value of k_1 for hydrolysis in $HClO_4$ in the partially organic solvent is consistent with a bimolecular A-2 type mechanism, reflecting the lower activity of water in the rate-limiting step in partially organic solvent. On the other hand, the higher values of k_1 in 50% MeCN/water

Table 3 Values of 10^4k_1 (s^{-1}) for the hydrolysis of **3** at different temperatures

[Acid]/M	39.8°C	44.8°C	51.0°C	58.3°C
3.00 M H_2SO_4	20.2	34.3	59.6	108
[Acid]/M	34.2°C	39.6°C	44.8°C	50.5°C
11.0 M H_2SO_4	77.3	159	275	596

Table 4 Arrhenius parameters of the hydrolysis of **3**

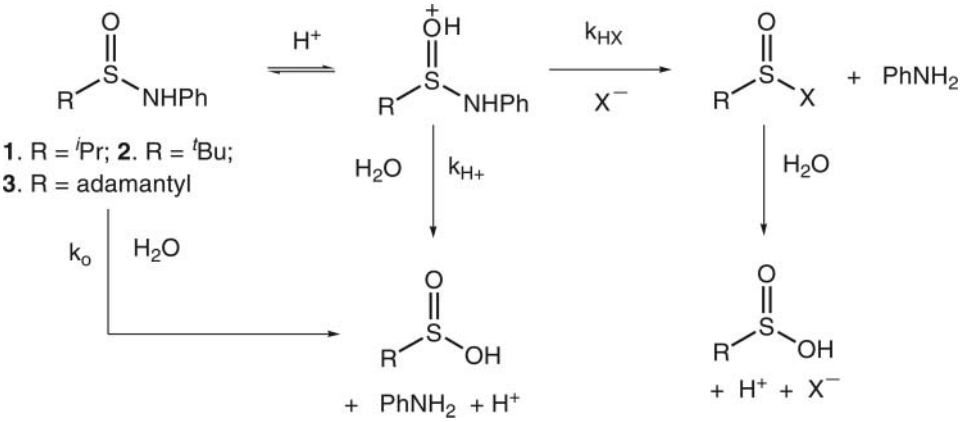
Compound	Acid	[Acid]/M	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J K^{-1} mol^{-1}
3	H_2SO_4	3.00	75 ± 3	-48 ± 7
3	H_2SO_4	11.00	99 ± 4	$+46 \pm 12$

solutions of HBr and HCl are likewise consistent with a bimolecular halide ion catalysis mechanism, reflecting the higher nucleophilicity of halide ions in partially organic solvent.

In acidic solutions, the most important hydrolysis pathways for **1**–**3** involve attack of water or nucleophile on the conjugate acid. Protonation can occur on either oxygen or nitrogen. NMR evidence for the site of protonation is equivocal,[20,21] while related alkylation and X-ray studies suggest *O*-protonation.[22,23] We therefore adopt *O*-protonation for the dominant form, although this must be in equilibrium with the minor *N*-protonated form to enable the reaction to occur (Schemes 1 and 2).

The key question regarding nucleophilic substitution at sulfur continues to be whether the reaction occurs via a classic S_N2-type (direct displacement) mechanism involving a trigonal bipyramidal transition state or via a two-step addition-followed-by-elimination mechanism, involving a discrete trigonal bipyramidal intermediate. An earlier attempt to detect the latter by ^{18}O-exchange during the alkaline hydrolysis of arenesulfinamides was unsuccessful.[23] More recently, however, Okuyama et al. have reported ^{18}O-exchange and a break in the pH-rate profile for the hydrolysis of *N*-arylbenzenesulfinamides in very dilute perchloric acid, which they suggest can be accounted for by an intermediate that can undergo pseudorotation.[9] To date, however, no direct evidence has been reported to distinguish between these possibilities for the hydrolysis of alkanesulfinamides.

The present data can be accommodated by a modified version (Scheme 1) of an earlier scheme.[8]

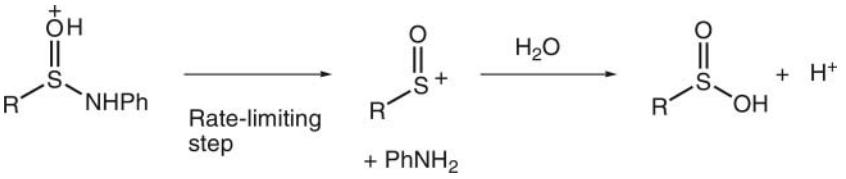


Scheme 1

The final rate increase observed for the hydrolyses of **2** and **3** in concentrated sulfuric acid (see Table 1 and Figure 3) is similar to that observed for the hydrolysis of certain carboxylate esters, where it is typically associated with a changeover from an A-2 to an A-1 mechanism.[17] This suggests that, in high concentrations of sulfuric acid, where the

Table 5 Values of $10^4 k_1$ (s^{-1}) for the hydrolysis of **3** in water and 50% acetonitrile/water (v:v) media at 44.8°C

	1.00 M-$HClO_4$	0.50 M-HCl	0.60 M-HBr
Water	1.70	29.2	184
50% MeCN/water (v:v)	0.67	60.0	422



Scheme 2

activity of water is considerably diminished, an additional reaction pathway is available to the conjugate acids of **2** and **3** (Scheme 2). Here, rate-limiting decomposition of the conjugate acid occurs to give a cationic species that is stabilized by the high polarity of the concentrated sulfuric acid medium.

From these preliminary results, we propose a mechanistic switch from A-2 to A-1 for the hydrolysis of **2** and **3** in concentrated H_2SO_4 solutions, which is supported by the much more positive value of entropy of activation ($\Delta S^{\neq} = +46$ J K^{-1} mol^{-1}) for the hydrolysis of **3** in 11.0 M H_2SO_4) (Table 4). Recently, a similar mechanistic changeover has been suggested for the hydrolysis of arenesulfinamides with a phthalimido leaving group.[10]

EXPERIMENTAL

Synthesis of Compounds 1–3: General Procedure

Tertiarybutanesulfinyl chloride was obtained from Sigma Aldrich, whereas adamantanesulfinyl chloride and isopropanesulfinyl chloride were prepared by the methods of Stetter et al.[25] and Youn and Herrmann,[26] respectively.

Compounds **1–3** were prepared by the method of Stetter et al.,[25] using alkanesulfinyl chloride (5 mmol) and aniline (10 mmol) in anhydrous ether or dry chloroform (30 mL). After completion of the reaction (monitored using TLC), the white amine salt was filtered off and the solvent was removed under reduced pressure. Column chromatography (silica gel; dichloromethane or ethyl acetate:dichloromethane, 1:9) was used to purify the residue.

***N*-Phenylpropane-2-sulfinamide (1).** White crystals. Yield: 95%. Mp: 57–59°C. FTIR (KBr) (cm^{-1}) 3021, 1601, 1541, 1520, 1497, 1467, 1374, 1275, 1246, 1236, 1192, 1073, 1027, 867. ^{1}H NMR (400 MHz, $CDCl_3$, ppm with respect to TMS) δ 7.24–7.19 (m, 2H), 7.00–6.95 (m, 3H), 6.44 (bs, 1H), 3.05–2.98 (m, 1H), 1.33 (d, J = 6.9 Hz, 3H), 1.29 (J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, p.p.m. with respect to TMS) δ 141.7, 129.3, 122.9, 118.2, 54.5, 15.8, 15.4. EIMS m/z (%) 183 (M^+, 49), 141 (93), 140 (M^+—^{i}Pr, 33), 93 (MH^+—^{i}PrSO, 100), 92 (88), 91 (11), 78 (83).

2-Methyl-*N*-phenylpropane-2-sulfinamide (2). White crystals. Yield: 96%. Mp: 103–104°C. FTIR (KBr) (cm^{-1}) 3015, 2599, 2330, 1496, 1469, 1420, 1370, 1274, 1068, 1026, 888, 859. ^{1}H NMR (400 MHz, $CDCl_3$, ppm with respect to TMS) δ 7.62–7.22 (m, 2H), 7.00–6.98 (m, 3H), 5.48 (bs, 1H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm

with respect to TMS) δ 142.0, 129.4, 123.0, 118.4, 56.5, 22.4. EIMS m/z (%) 197 (M^+, 18), 141 (100), 140 (M^+—^{t}Bu, 28), 105 (M^+—PhNH, 86), 92 (M^+—^{t}BuSO, 72), 78 (77), 57 (93).

The structure of **2** was confirmed by X-ray crystallography, using a crystal produced by evaporation of solvent at room temperature from a dichloromethane solution.[27]

***N*-Phenyladamantane-1-sulfinamide (3).** White crystals. Yield: 97%. Mp: 154–155°C. FTIR (KBr) (cm^{-1}) 3179, 2908, 2851, 1595, 1488, 1450, 1285, 1228, 1175, 1063, 1034, 877. ^{1}H NMR (400 MHz, $CDCl_3$, ppm with respect to TMS) δ 7.26–7.22 (m, 2H), 7.01–6.97 (m, 3H), 5.43 (bs, 1H), 2.18 (s, 3H), 1.92 (dd, J = 11.8, 22.8 Hz, 6H), 1.74 (dd, J = 12.2, 23.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm with respect to TMS) δ 142.4, 129.2, 122.4, 117.9, 58.2, 36.3, 34.6, 28.5. EIMS m/z (%) 276 (MH^+, 39), 275 (M^+, 85), 259 (M^+—16), 228 (18), 227 (M^+—SO, 75), 136 (59), 135 (M^+—PhNHSO, 100), 107 (28), 93 (MH^+—adamantaneSO, 66), 79 (61).

The structure of **3** was confirmed by X-ray crystallography, using a crystal produced by evaporation of solvent at room temperature from a dichloromethane solution.[28]

Product Authentication

Identification of hydrolysis reaction products of *N*-arylarenesulfinamides, namely sulfinic acid and amine, has been demonstrated previously by Biasotti and Andersen[24] (alkaline hydrolysis) and by Kutuk et al.[10] (acid hydrolysis).

In this article, however, the authentic alkanesulfinic acids were unavailable for comparison, and in any case they will have λ_{max} of around 200 nm, making them difficult to distinguish from the anilinium salt by UV spectroscopy. Hence we decided to check the presence of aniline in the product mixture by TLC. Compound **3** (20 mg) was dissolved in a 40% methanol/water solution of 2.0 M-HCl (5.0 mL) and kept at 44.8°C for 18 h. After cooling to room temperature, the solution was neutralized with aqueous 10.0 M-NaOH (1.0 mL). TLC analysis (silica gel, CH_2Cl_2, with UV visualization) confirmed the presence of aniline ($R_f = 0.38$). Compound **2** gave a similar result.

Kinetic Measurements

The rates of hydrolysis of **1**–**3** were measured by following the change in absorbance at 230 nm, corresponding to disappearance of the substrate, using a JASCO V-530 UV/visible spectrophotometer with a thermostatted cell holder, held at 44.8 ± 0.1°C, unless stated otherwise. All determinations were carried at least in duplicate. For all compounds, 0.1 M stock solutions in spectroscopic grade methanol were prepared. An aliquot (4 μL) of the relevant stock solution was added by syringe to 4.0 mL of the reaction solution contained in a cuvette and already equilibrated at the desired temperature. The reactions were monitored over at least three half-lives, and "infinity" values were measured in all cases, except for the slowest reactions. Pseudo first-order rate constants were calculated from plots of $\ln(A - A\infty)$ against time, where A is absorbance at time t and $A\infty$ is the absorbance at "infinity," except for the slowest reactions, in which case the method of Guggenheim was used.[29] All acid reaction solutions were prepared from analytical grade concentrated acids, using deionized water. Acetonitrile was of HPLC quality and all salts were of analytical grade quality.

The linearities of pseudo first-order plots were good, with R^2 better than 0.999, except for slower and spontaneous reactions (R^2 better than 0.995). Reproducibility, measured as

% relative standard deviation (%RSD) for n = 3, was better than 1.5%, except for slower and spontaneous reactions (better than 5%).

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