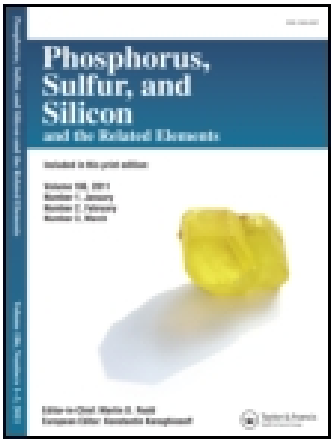

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Acid-Catalyzed Hydrolysis of Some N,N-Dibenzylalkanesulfinamides in 50% Acetonitrile-Water

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ACID-CATALYZED HYDROLYSIS OF SOME *N,N*-DIBENZYLALKANESULFINAMIDES IN 50% ACETONITRILE–WATER

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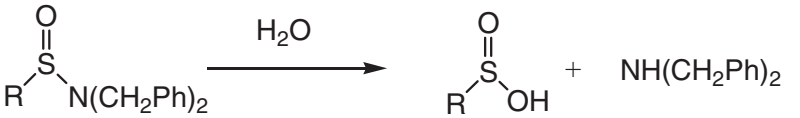
GRAPHICAL ABSTRACT



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

Abstract *The hydrolysis of some N,N-dibenzylalkanesulfinamides ($RSONH(CH_2Ph)_2$; **1**, R = Me; **2**, R = ^{i}Pr; **3**, R = ^{t}Bu; **4**, R = 1-adamantyl) has been studied in 50% (v:v) acetonitrile–water solutions of hydrobromic and hydrochloric acids, mainly at 44.8 °C, using ultraviolet (UV) spectrophotometry to determine pseudo first-order rate constants. The compounds were found to hydrolyze by concurrent bimolecular neutral, acid-catalyzed, and acid-dependent nucleophilic (halide ion) catalysis pathways. The last-named is predominant in reactions in HBr solutions, but in HCl solutions, the acid-catalyzed pathway is predominant. The results indicate that both steric and electronic effects are important in these reactions. There appears to be no mechanistic switchover in the series **1**→**4**.*

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

INTRODUCTION

Nucleophilic substitution reactions at sulfinyl sulfur (>S=O) have received considerable attention in the 1970s[1] and 1980s, including a number of mechanistic investigations.[2–5]

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The general chemistry of sulfinamides has been reviewed by Tillett,[6] where it is clear that they undergo hydrolysis under a range of conditions to the corresponding sulfinic acids and amines.

Most previous mechanistic reports on the hydrolysis of sulfinamides are on *N*-arylarenesulfinamides,[3,4,7] with the exceptions of the work of Wagner et al., which reported briefly on the neutral hydrolysis (in D_2O) of $MeSONMe_2$ (and a number of cyclic alkanesulfinamides),[8] and the report of Baltas et al., which described the alkaline hydrolysis of some *N*-aryl-β-sulfinamoyl esters.[5] More recently, Kutuk et al. have described the hydrolysis of *N*-phthalimidoarenesulfinamides in aqueous mineral acids,[9] Bozkurt and Kutuk have studied the reaction of sulfinyl phthalamides with nucleophiles in dioxane,[10] and we have reported on the hydrolysis of *N*-phenylalkanesulfinamides in aqueous mineral acids.[11]

Of the sulfinamides reported in Asefi and Tillett[3] and Datta et al.[11], *N*-arylarenesulfinamides ($Ar^1SONHAr^2$) hydrolyzed so rapidly at 25 °C that a stopped-flow spectrophotometric method had to be used.[3] In contrast, *N*-phenylalkanesulfinamides (RSONHPh) hydrolyzed more slowly at 45 °C,[11] but even here, MeSONHPh and EtSONHPh were too reactive to be studied using conventional spectrophotometric techniques, and ^{i}PrSONHPh could be studied only at low acid concentrations. The generally high reactivity of the *N*-arylsulfinamides can be ascribed, at least in part, to the efficacy of aniline (or arylamine in general) as a leaving group.

A characteristic feature of the reactions of *N*-arylsulfinamides (both $Ar^1SONHAr^2$ and RSONHAr) in aqueous HCl and HBr is the existence of acid-dependent nucleophilic catalysis, as well as bimolecular (A-2 type) acid-catalysis.[3,11] Additionally, a slow spontaneous reaction was reported for RSONHAr in water.[11]

The major aim of the present work was to synthesize a number of *N,N*-dialkylalkanesulfinamides and to study their reactions in mineral acid solutions, in the expectation that they would be less susceptible to acid-catalyzed decomposition, thus allowing study under ordinary conditions of substrates with a wider range of *S*-alkyl groups, including methyl. Another objective was to determine whether acid-dependent nucleophilic catalysis participates in the overall reaction scheme, as has been observed in the hydrolysis of *N*-arylarenesulfinamides[3] and *N*-arylalkanesulfinamides[11] in acidic media. We now report the synthesis of a series of *N*,*N*-dibenzylalkanesulfinamides (**1**–**4**) and their reactions in 50% aqueous acetonitrile (v:v) solutions of HBr and HCl. *N*,*N*-Dibenzyl derivatives were chosen to facilitate the monitoring of reaction progress using ultraviolet (UV) spectrophotometry.

RESULTS AND DISCUSSION

Most previous kinetic studies on the hydrolysis of sulfinamides have been carried out in purely aqueous or predominantly aqueous media,[3,8,9,11] except, for example, Biasotti and Andersen's work with ethanol–water medium[4] and Bozkurt and Kutuk's work with dioxane.[10] However, compounds **1**–**4** produced precipitates after partial reaction times in aqueous acids, making it difficult to use UV spectrophotometry for kinetic analysis. To overcome this problem, reactions for kinetic study were performed in 50% (v:v) aqueous acetonitrile.

Compound **4** was dissolved ($\sim 10^{-4}$ M) in a 50% aqueous acetonitrile solution of 1.00 M HCl and its UV spectrum between 225 nm and 325 nm was monitored at 3 min intervals at 58.6 °C. The results are shown in Figure 1, where it can be seen that there are

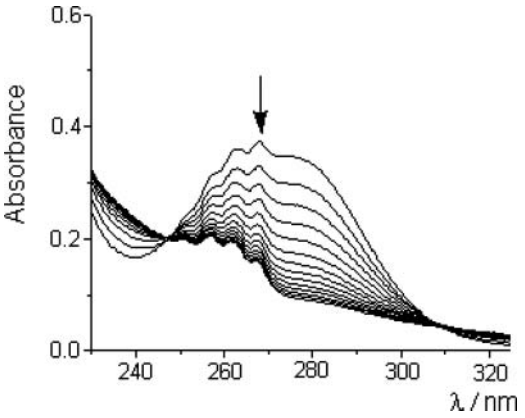


Figure 1 UV-vis spectral curves for the hydrolysis of **4** in 1.00 M HCl (50% v:v acetonitrile:water) at 58.6 ± 0.1 °C (time interval 3.00 min).

two isosbestic points (at 247 nm and 309 nm), indicating the likelihood of the reactants giving a single set of products in constant proportions.

The pseudo first-order plots for **1–3** were linear, with reasonable scatter and uncertainty, as indicated by coefficient of determination (R^2) values better than 0.990 and relative standard deviations (%RSD) for pseudo first-order rate constants (k_1) better than 5.0%. The corresponding parameters for **4** were better than 0.999 and 2.0%, respectively. Figures 2 and 3 display the variation of k_1 with acid concentration for **1–4** at 44.8 °C in 50% (v:v) acetonitrile–water solutions of HBr and HCl, respectively. Two features of these data are worthy of comment.

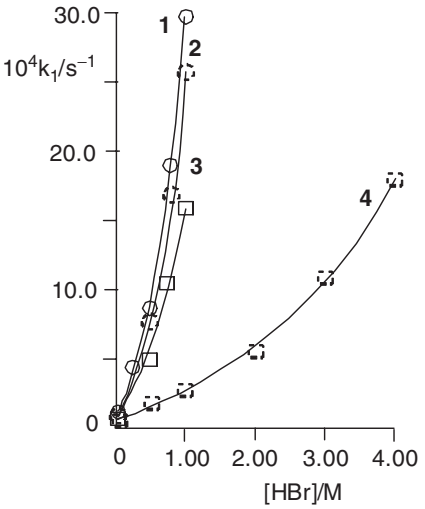


Figure 2 Pseudo first-order rate constant/acid concentration profiles of **1–4** in HBr media (50% (v:v) acetonitrile:water) at 44.8 °C. Curves drawn using OriginPro 7™ polynomial analysis tool. For k_1, %RSD ($n = 3$) for **1–3** is better than 5.0%, R^2 is better than 0.990; %RSD (n =3) for **4** is better than 2.0%, R^2 is better than 0.999.

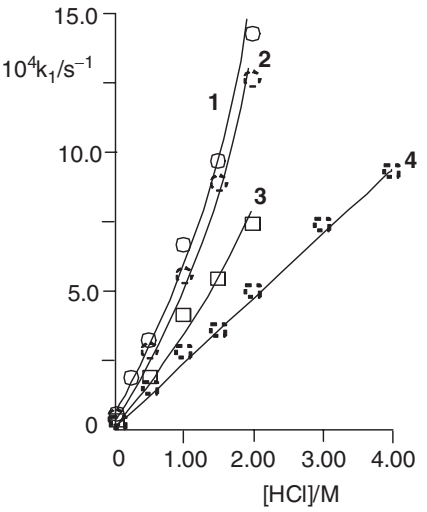


Figure 3 Pseudo first-order rate constant/acid concentration profiles of **1–4** in HCl media (50% (v:v) acetonitrile:water) at 44.8 °C. Curves drawn using OriginPro 7^{TM} polynomial analysis tool. For k_1, %RSD ($n = 3$) for **1–3** is better than 5.0%, R^2 is better than 0.990; %RSD ($n = 3$) for **4** is better than 2.0%, R^2 is better than 0.999.

First, there is a slow neutral reaction for each substrate, as observed by Wagner et al. for the hydrolysis of $MeSONMe_2$ in D_2O,[7] although **1–4** are rather more reactive than this compound (e.g., 10^4k_o (s^{-1}) for **1, 2, 3,** and **4** are 1.21, 1.15, 0.78, and 0.56, respectively, at 44.8 °C in 50% acetonitrile–water (v:v), compared with 0.28×10^{-4} s^{-1} for $MeSONMe_2$ at 55.0 °C in D_2O). Slow neutral reactions were also observed for *N*-phenylalkanesulfinamides.[11]

Second, for all the substrates (**1–4**), there is a marked dependence of k_1 on acid concentration, and especially on [HBr], suggesting the existence of specific acid-catalysis, as well as acid-dependent nucleophilic catalysis, as previously observed in the reactions of *N*-arylarenesulfinamides[3] and *N*-phenylalkanesulfinamides[11] in aqueous mineral acid solutions. It can be seen from Figures 2 and 3 that the general reactivity is in the order **1** > **2** > **3** > **4**, in both HBr and HCl, and that HBr is generally a better catalytic medium than HCl. These observations are in accord with the greater nucleophilicity of Br^- over Cl^- in aqueous media and also suggest that steric and/or electronic effects are involved in the reaction mechanism. Furthermore, reactions in $HClO_4$, whose conjugate base ClO_4^- is of very low nucleophilicity, were very slow. For example, k_1 for **1** (predicted to be the most reactive of these substrates) in 3.00 M and 5.00 M $HClO_4$ was found to be 2.33×10^{-4} and 4.01×10^{-4} s^{-1}, respectively. The considerably lower reactivity in $HClO_4$ is probably due to the absence of nucleophilic catalysis, along with extensive hydration of ClO_4^-, which reduces the catalytic activity of water required for a bimolecular rate-limiting step.

Table 1 shows the variation of k_1 with [HBr] for compound **1** at constant bromide ion concentration of 1.00 M (made up with added LiBr). Limited solubility of LiBr in the reaction medium prevented collection of data for [HBr] < 0.50 M ([LiBr] > 0.50 M). These data are consistent with the participation of both acid catalysis and acid-dependent nucleophilic catalysis in the overall reaction of **1** in HBr solutions and this conclusion can be extended to compounds **2**, **3**, and **4**, because of the observed similar kinetic behavior (see also Table 2 and discussion of Arrhenius parameters).

Table 1 Rate constants ($10^4 k_1/s^{-1}$) for hydrolysis of **1** in HBr (50% (v:v) acetonitrile:water) at 44.8 ± 0.1 °C and constant bromide ion concentration of 1.00 M

[HBr]/M	0	0.50	0.80	1.00
$10^4 k_1/s^{-1}$	1.21[a]	15.9	23.3	29.7

[a]Extrapolated value.

In order to analyze the reactions more closely, especially in terms of the relative contributions of acid-dependent nucleophilic catalysis and acid-catalysis to the overall reaction, we may write a general expression for the reactions of **1**–**4** as Equation (1),

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

as originally suggested in Ref. 3. The first specific rate constants, k_o and k_X^-, relate to the slow reactions in solutions without added acids (representing attack of H_2O and X^-, respectively, on the neutral substrate) whereas k_{H+} and k_{HX} are the rate constants for the acid-catalyzed and acid-dependent nucleophile (halide ion)-catalyzed reactions, respectively. The latter two relate to attack of water and specific nucleophile, respectively, upon the conjugate acid of **1**–**4** (protonated substrates) in the rate-determining step.

In order to check for the presence of specific nucleophilic catalysis on the neutral rate, reactions of **1** in 50% acetonitrile–water were carried out with added 0.20 M KCl and 0.20 M KBr, whence k_1 was found to be 1.22×10^{-4} s^{-1} and 1.24×10^{-4} s^{-1} ($\pm 0.06 \times 10^{-4}$ s^{-1}), respectively. Within experimental error, these values are indistinguishable from k_o, hence suggesting specific halide catalysis of the neutral reaction is insignificant, so that the second term in Equation (1) can be neglected. This is supported by the data shown in Table 1. Equation (1) thus reduces to Equation (2):

$$k_1 = k_o + k_{H+}[H^+] + k_{HX}[H^+][X^-] \quad (2)$$

In an attempt to qualitatively determine the relative contributions of acid catalysis and acid-dependent nucleophilic catalysis components of Equation (2), it is assumed that the mineral acids HX are 100% ionized, then $[HX] = [H^+]$, and $[H^+] = [X^-]$, so that Equation (2) can be written as Equation (3):

$$k_1 = k_o + k_{H+}[HX] + k_{HX}[HX]^2 \quad (3)$$

Equation (3) predicts a linear dependence of k_1 on [HX] for acid-catalysis, whereas there is a quadratic dependence for acid-dependent nucleophilic catalysis. Therefore, a distinct parabolic curvature in plots of k_1 versus [HX] is expected where the acid-dependent

Table 2 Rate constants[a] and activation parameters for the hydrolysis of **1** and **4** in 1.00 M HCl (50% (v:v) acetonitrile:water) at various temperatures

T/°C (± 0.1 °C)	44.8	51.5	51.7	53.6	57.3	59.5	59.7	67.6
$10^4 k_1/s^{-1}$ **1**[b]	6.6	13.5	—	15.1	—	24.9	—	41.6
$10^4 k_1/s^{-1}$ **4**[c]	2.9	—	6.5	8.1	11.8	—	13.2	22.5

[a]%RSD for **1** and **4** ($n = 3$); better than 5.0% and 2.0%, respectively.
[b]$\Delta H^{\neq} = 69 \pm 4$ kJ mol^{-1}; $\Delta S^{\neq} = -86 \pm 13$ J mol^{-1} K^{-1}.
[c]$\Delta H^{\neq} = 73 \pm 2$ kJ mol^{-1}; $\Delta S^{\neq} = -81 \pm 7$ J mol^{-1} K^{-1}.

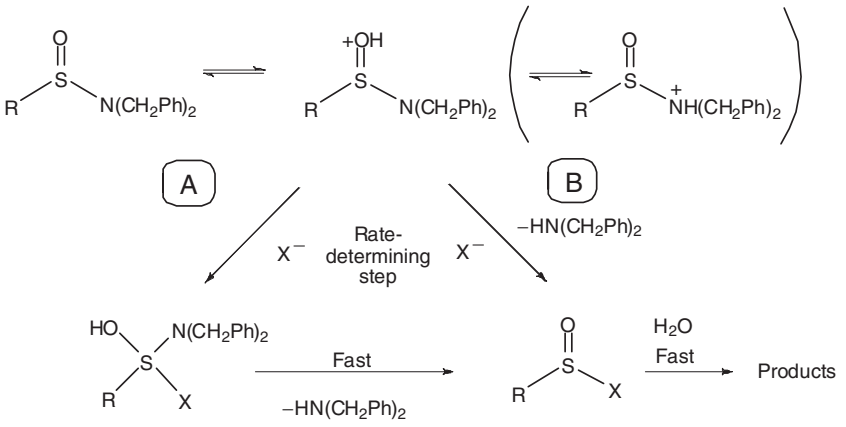
nucleophilic catalysis component is important (i.e., where $k_{HX} > k_{H+}$). Distinct curves are observed in plots of k_1 versus [HBr] for all the substrates in HBr solutions (Figure 2), reflecting the high nucleophilicity of Br^-. The degree of curvature of such plots decreases along the series **1**→**4**, suggesting a diminution of the acid-dependent nucleophilic catalysis component, in favor of the acid-catalysis component. The probable reason for this is increased steric hindrance and/or increased electronic resistance (+I effect) along the series to nucleophilic attack by Br^- (as opposed to the smaller H_2O nucleophile), on the protonated substrate in the rate-determining step. Thus for **4**, where steric hindrance and the +I effect will be greatest, $k_{HBr} \sim k_{H+}$ and the plot of k_1 versus [HBr] here has the least curvature. It can be concluded that the nucleophilicity of Br^- is sufficiently high to ensure that k_{HBr} is significant for all the substrates, particularly **1**–**3**.

On the other hand, plots of k_1 versus [HCl] show less curvature than those of k_1 versus [HBr] (Figure 3), reflecting the lower nucleophilicity of Cl^- and suggesting that the acid-dependent nucleophilic catalysis component is generally less significant in HCl media. Indeed, the plot of k_1 against [HCl] is a very shallow curve for **3** and is essentially linear for **4**, suggesting that $k_{HCl} < k_{H+}$ for both these substrates. Thus, it can be concluded that the nucleophilicity of Cl^- is insufficiently high to compete effectively with H_2O in nucleophilic attack on the protonated substrate, especially the more sterically hindered **3** and **4**.

Table 2 displays the Arrhenius parameters for **1** and **4**, in 50% aqueous acetonitrile solutions of 1.00 M HCl, along with the data that were used to determine the parameters. Given the concurrent nature of the reactions that comprise the hydrolysis of **1**–**4** (see previous discussion) and the difficulty in extracting specific rate constants at different temperatures, the thermodynamic parameters calculated from the Arrhenius equation will be composite values and, hence, cannot be compared rigorously with literature data that refer to single reactions. Nevertheless, the computed values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are similar to those reported for the acid[3] and alkaline[4] hydrolysis of *N*-arylarenesulfinamides (e.g., for *N*-*p*-tolyl-*p*-toluenesulfinamide[3] in aqueous 0.500 M-$HClO_4$, $\Delta H^{\neq} = +37.8$ kJ mol^{-1}; $\Delta S^{\neq} = -123.3$ J K^{-1} mol^{-1} and for *N*-mesyl-*p*-chlorobenzenesulfinamide[4] in 0.05 M NaOH (95% ethanol:5% water), $\Delta H^{\neq} = +83.6$ kJ mol^{-1} and $\Delta S^{\neq} = -37.2$ J K^{-1} mol^{-1}). In particular, the quite large negative values of $\Delta S^{\neq}$ are in the range generally associated with reactions that have bimolecular rate-determining steps.[12] This can be taken as evidence that the set of concurrent reactions that characterize the hydrolysis of **1** and **4** is essentially bimolecular in character. Furthermore, since compounds **1** and **4** represent the structural extremes of the series **1**–**4**, the similar values of $\Delta S^{\neq}$ for these two substrates indicate that all four compounds react by similar mechanisms and that there is no gross change in mechanism somewhere along the series.

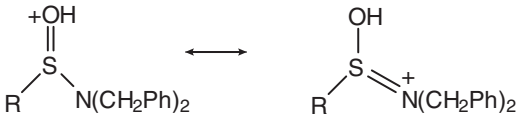
It is possible to depict the acid-catalyzed hydrolysis of sulfinamides occurring via discrete sulfurane (hypervalent) intermediates (Scheme 1, pathway A) or by direct (S_N2-like) displacement at sulfinyl S (Scheme 1, pathway B). Okuyama and coworkers have provided good evidence for the former in a study of the hydrolysis of *N*-arylarenesulfinamides in dilute aqueous acid ($HClO_4$).[8] However, it is still unclear whether protonation occurs primarily at O or N.[13,14] Our results show that specific nucleophilic species ($X^- = Br^-$ or Cl^- in Scheme 1) play an important role and are involved in the rate-determining step of a generally significant (and in certain cases predominant) acid-dependent nucleophilic catalysis route.

By comparison of our results with those for *N*-arylarenesulfinamides[3,4,7,8] and *N*-phenylalkanesulfinamides,[11] it is also clear that the order of reactivity of sulfinamides toward

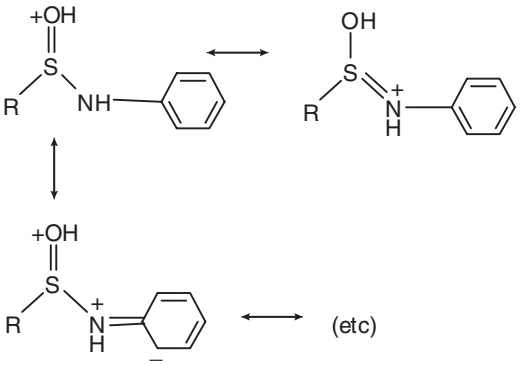


Scheme 1

hydrolysis in acidic solutions is in general, $R^1SONR_2^2 < RSONHPh < Ar^1SONHAr^2$, where R and Ar are alkyl and aryl groups, respectively. This order of reactivity can be explained partly by relative leaving group ability from the *N*-protonated conjugate acid ($ArNH_2 > R_2NH$) and partly by the different reactivities of the sulfinamide conjugate acids toward nucleophilic attack (Schemes 2 and 3), which is related to the electron density at the sulfur atom.



Scheme 2



Scheme 3

For **1**–**4**, electron delocalization of the sulfinamide system (O—S—N) is maximized (Scheme 2), whereas for *N*-arylalkanesulfinamides[11] (Scheme 3) and *N*-arylarenesulfinamides,[3] *N*-aryl delocalization competes with this, resulting in overall lower

electron density at sulfinyl sulfur, thus making it more susceptible to nucleophilic attack, thereby rendering *N*-arylsulfinamide conjugate acids more reactive than those of **1**–**4**.

Although at the present time, there is no direct evidence for *N*-aryl delocalization in *N*-arylsulfinamide conjugate acids (protonated substrate) as suggested above, existence of this feature in the solid state neutral substrate is evident from the short $N{-}C_{aryl}$ bond (1.408 Å) in 2-methyl-*N*-phenylpropane-2-sulfinamide,[15] as opposed to considerably longer $N{-}C_{alkyl}$ bonds (1.470–1.530 Å) found in *N*-alkylsulfinamides[16–18] and also in an *O*-methylated *N*-alkylarenesulfinamide.[19]

CONCLUSIONS

N,*N*-Dibenzylalkanesulfinamides (**1**–**4**) were shown to undergo hydrolysis in 50% acetonitrile–water solutions of HCl and HBr by concurrent neutral, acid-catalyzed, and acid-dependent halide ion-catalyzed pathways (all bimolecular), the last-named being the most important for reaction in HBr media and generally significant (but not predominant) for reaction in HCl media.

EXPERIMENTAL

Synthesis of Compounds 1–4: General Procedure

The general procedure is illustrated by the synthesis of *N*,*N*-dibenzylmethanesulfinamide (**1**). Methanesulfinyl chloride was prepared by the reaction of methyl disulfide and sulfuryl chloride in acetic acid, according to the method of Youn and Herrmann.[20] The general procedure for the formation of sulfinamides from the sulfinyl chloride and amine is based on that of Stetter et al.[21] To our knowledge, there are no previous data in the literature for compounds **1**, **2**, and **4**.

***N*,*N*-Dibenzylmethanesulfinamide (1).** To a solution of dibenzylamine (1.97 g, 10 mmol) in dry ether (20 mL) was added a solution of methanesulfinyl chloride (490 mg, 5 mmol) in dry ether (15 mL), dropwise, with stirring over a period of 20 min, at 0 °C. The reaction mixture was then stirred at 0 °C for 3 h. The white solid amine salt was filtered off and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (dichloromethane) to provide **1** as a white solid (1.25 g, 97%), mp 68–70 °C.

FTIR (KBr) ν_{max} (cm^{-1}): 3108, 3088, 3064, 3033, 3011, 1496, 1455, 1446, 1436, 1409, 1384, 1311, 1267, 1210, 1130, 1084, 1056, 1015, 949. ^{1}H NMR (400 MHz, $CDCl_3$, ppm with respect to TMS): δ 7.34–7.29 (m, 10H), 4.33 (s, 4H), 2.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm with respect to TMS): δ 135.4, 128.8, 128.7, 128.0, 49.8, 40.3. EIMS *m/z* (%): 259 (M^+, 12), 196 ($M^+ - CH_3SO$, 47), 184 (49), 91 (100). Anal. calcd. for $C_{15}H_{17}NOS$: C, 69.50; H, 6.56; N, 5.40; S, 12.35. Found: C, 69.46; H, 6.58; N, 5.52; S, 12.28.

***N*,*N*-Dibenzyl-2-propanesulfinamide (2).** *Iso*-propylsulfinyl chloride was prepared by the reaction of *iso*-propyldisulfide and sulfuryl chloride in acetic acid.[20] The general procedure was followed by using dibenzylamine (1.24 g, 6.34 mmol), *iso*-propylsulfinyl chloride (400 mg, 3.17 mmol), and dry ether (30 mL). The crude product was purified by silica gel column chromatography (5% ethyl acetate in hexane) to give **2** as a white solid (880 mg, 96%), mp 155–157 °C.

FTIR (KBr) ν_{max} (cm^{-1}): 3082, 3056, 1485, 1453, 1409, 1383, 1334, 1290, 1272, 1224, 1152, 1110, 1072, 1010, 950. ^{1}H NMR (400 MHz, $CDCl_3$, ppm with respect to TMS): δ 7.45–7.24 (m, 10H), 3.91 (t, $J = 5.3$ Hz, 4H), 2.86–2.80 (m, 1H), 1.22 (d, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm with respect to TMS): δ 130.5, 130.2, 129.2, 129.0, 50.9, 49.3, 17.7. EIMS *m/z* (%): 286 (M^+–H, 12), 285 (54), 208 (63), 197 (MH^+– *iso*-propylsulfinyl, 15), 167 (20), 149 (42), 141 (34), 134 (21), 106 (MH^+– dibenzyl, 88), 91 (100).

***N,N*-Dibenzyl-2-methylpropane-2-sulfinamide (3).** The general procedure was followed by using dibenzylamine (1.20 g, 6.09 mmol), *tert*-butylsulfinyl chloride (obtained from Aldrich-Sigma, 428 mg, 3.04 mmol), and CH_2Cl_2 (30 mL). The residue was purified by silica gel column chromatography (EtOAc: hexane, 1:4) to afford sulfinamide **3** as a white solid (896 mg, 98%), mp 55–57 °C (lit.[21] 54–56 °C).

^{1}H NMR (400 MHz, $CDCl_3$, ppm with respect to TMS): δ 7.31–7.22 (m, 10H), 4.27 (d, $J = 15.36$ Hz, 2H), 4.03 (d, $J = 15.36$ Hz, 2H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm with respect to TMS): δ 136.87, 128.71, 128.44, 127.40, 58.56, 51.56, 23.26. EIMS *m/z* (%): 302 (MH^+, 7), 301 (M^+, 15), 247 (44), 246 (72), 245 (MH^+– ^{t}Bu, 95), 196 (MH^+– ^{t}BuSO, 25), 195 (53), 106, (48), 91 (100).

***N,N*-Dibenzyl-1-adamantanesulfinamide (4).** 1-Adamantanesulfinyl chloride was obtained by the reaction of adamantane and thionyl chloride in the presence of $AlCl_3$.[21] The general procedure was followed by using dibenzylamine (1.20 g, 6.09 mmol), 1-adamantanesulfinyl chloride (664 mg, 3.04 mmol), and dichloromethane (30 mL). The residue was purified by silica gel column chromatography (dichloromethane-hexane, 1:1) to afford sulfinamide **4** as a viscous liquid (1.1 g, 95%).

FTIR (neat) ν_{max} (cm^{-1}): 2907, 2851, 1591, 1487, 1449, 1351, 1295, 1075, 891, 815. ^{1}H NMR (400 MHz, $CDCl_3$, ppm with respect to TMS): δ 7.31–7.22 (m, 10H), 4.27 (d, $J = 15.3$ Hz, 2H), 4.01 (d, $J = 15.3$ Hz, 2H), 2.08 (s, 3H), 1.91 (d, $J = 11.3$ Hz, 3H), 1.76–1.62 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm with respect to TMS): δ 136.87, 128.68, 128.35, 127.31, 60.31, 51.93, 36.29, 35.26, 28.41. EIMS *m/z* (%): 379 (M^+, 11), 280 (9), 253 (20), 136 (34), 135 [M^+– $(PhCH_2)_2NSO$, 100], 129 (72), 91 (50).

Authentication of Products from Kinetic Experiments

Before commencing kinetic investigations, it was necessary to confirm the product identity. The amine was chosen, since the sulfinic acid products are UV-inactive and are unavailable as standards. A larger scale reaction of **2** (40 mg) in 2.00 M HCl (50% acetonitrile:water) (10.0 mL) was investigated at 44.8 °C over a period of 12 h by TLC (silica gel, ethyl acetate, UV visualization). A new spot at $R_f \sim 0.37$ was observed after 1 h, which was identified as dibenzylamine hydrochloride by comparison with a pure authentic sample run on the same plate. Identical results were obtained for **1**, **3**, and **4**. Also, under the above TLC conditions, R_f values of **2** and dibenzylamine were found to be 0.64 and 0.80, respectively.

Kinetic Measurement

The rates of hydrolysis were measured by following the decrease in absorbance at 257 nm for compounds 1–3 and 267 nm for compound 4, using a JASCO V-530 UV/visible spectrophotometer with a thermostatted cell holder. For all compounds, 0.1 M stock solutions in methanol were prepared. Aliquots (4 μL) of the relevant stock solution were

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 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, whence the method of Guggenheim was used.[22] All acid reaction solutions were prepared from analytical grade concentrated acids, using deionized water and HPLC grade acetonitrile, making appropriate allowance for the water content of the acid. The reaction solutions were discarded after use, freshly made solutions being used for each experiment, because of the appearance of crystals in some solutions after several weeks standing at room temperature. These were identified as ammonium salts and were probably the result of slow acetonitrile hydrolysis in some of the more concentrated acid solutions.

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