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ACID-CATALYZED HYDROLYSIS OF RING-SUBSTITUTED PHENYL VINYL SULFIDES

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Abstract—The acid-catalyzed hydrolysis of phenyl vinyl sulfide and its ring-substituted derivatives has kinetically been investigated in 40% aqueous dioxane and 90% aqueous tetrahydrofuran. The observed rate constants were satisfactorily correlated with the Hammett acidity function H_0. The effect of substituents on the hydrolysis rates was found to conform to the Hammett σ constants with $\rho = -1.98$ (40% dioxane, 30°). The ρ value was compared with that found for the hydrolysis of phenyl vinyl ether in terms of the transmission efficiency of the S and O atoms.

It has been established in a previous paper[1] that the acid-catalyzed hydrolysis of alkyl vinyl sulfide proceeds through the rate-determining protonation to give acetaldehyde and mercaptan.

$$CH_2{=}CHSR + H_3O^+ \xrightarrow[\text{slow}]{} CH_3\overset{+}{C}HSR + H_2O$$

$$\xrightarrow[\text{fast}]{} CH_3CHO + RSH. \qquad (1)$$

The effect of alkyl groups on the hydrolysis rate was characterized with positive ρ^* value,[1] in contrast to the results with the oxygen homologs, alkyl vinyl ethers.[2] This difference was ascribed to the conjugation through the S atom.[1] Thus, examinations of the effect of ring substituents on the hydrolysis rate of phenyl vinyl sulfide in comparison with that of phenyl vinyl ether[3] would be useful to understand the electronic factors operating in these reactions.

EXPERIMENTAL

Materials. Phenyl vinyl sulfide (PVS) and its ring-substituted derivatives were prepared from the corresponding thiophenol and ethylene chlorohydrin.[4] Substituted thiophenols were obtained commercially or by the reduction of sulfonyl chlorides.[5] *p*-Methoxy-, *m*-methyl-, and *m*- and *p*-chlorobenzenesulfonyl chlorides were prepared by the modified Sandmeyer reaction from anilines.[6] *p*-Fluorobenzenesulfonyl chloride was synthesized by the sulfonation of fluorobenzene, followed by the chlorination with PCl_5.[7] Fluorobenzene was obtained by the Schiemann fluorination of aniline.[8] Physical and analytical data of vinyl sulfides are summarized in Table 1. NMR spectral data were reported previously.[9]

Dioxane, tetrahydrofuran and tetralin of reagent grade were distilled. Inorganic materials of analytical grade were used without further purification.

Kinetics. The rate constants of the hydrolysis were measured in 40% aqueous dioxane or 90% aqueous THF. In the former medium, the reaction was monitored spectrophotometrically at 270 nm using a Shimadzu spectrophotometer UV-200.[1] In the latter case, concentrations of PVS were determined by gas-chromatography after quenching with KOH. Tetralin was used as an internal standard.[3] A Shimadzu gaschromatograph 4APT was used.

Product analysis. A sample of PVS (5.44 g) was hydrolyzed at 60° in 100 ml of 90% aqueous THF containing 0.4 M HCl. After 4 hr reaction, most of THF was evaporated *in vacuo* at 15°. The remaining mixture was extracted with ether, washed with NaClaq and dried over Na_2SO_4. The dried ether soln was distilled. A fraction boiling at 58–60° (16 mm Hg) was obtained (2.17 g), whose properties agreed with those of thiophenol (51.5% yield). From the viscous residue (1.55 g), white needles were obtained by recrystallizations (4 times) from EtOH (0.31 g), m.p. 66.7–67.3°; NMR (CCl_4), δ 3.10 (s, 2H), 7.17 (broad, 5H). These crystallines were identified as 1,2-bis(phenylthio)ethane (m.p.[10] 66–67°).

Acetaldehyde in the mixture was separately titrated according to the literature.[11] Since thiophenol behaves as an acid, appropriate corrections have been made. About 90% of the calculated amount of acetaldehyde was titrated.

Table 1. Physical and analytical data of substituted PVS

Substituent	B.p., °C (mmHg)	n_D^{20}	Elemental analysis (Calcd) C	H	Cl
H[a]	65 – 66 (7.5)	1.5934	70.59 (70.54)	5.96 (5.92)	
p-OCH$_3$	93.0 (6.0)	1.5853	64.91 (65.02)	6.15 (6.06)	
p-CH$_3$	69 – 71 (4.0)	1.5782	71.92 (71.95)	6.65 (6.71)	
m-CH$_3$	80.0 (10)	1.5792	72.15 (71.95)	6.67 (6.71)	
p-F	62.2 (8.3)				
p-Cl	91.7 – 92.0 (7.0)	1.6024	56.33 (56.30)	4.21 (4.13)	20.85 (20.78)
m-Cl	89.0 – 89.9 (7.8)	1.6017	56.18 (56.30)	4.20 (4.13)	20.73 (20.78)

a Reported[4] b.p. 84.5 – 85° (15mmHg) and n_D^{25} 1.5878.

RESULTS

The reaction in 40% aqueous dioxane follows pseudo-first order kinetics over 90% conversion, where $[PVS]_0 \simeq 3 \times 10^{-4}$ M. However, in the hydrolysis in 90% aqueous THF with $[PVS]_0 \simeq 0.05$ M, first-order plots curved slightly downward after about 60% reaction probably due to the high concentration of PVS. A hydrolysis product, thiophenol, may not only catalyze the hydrolysis as a general acid but add to PVS as a nucleophile (eqn 3).

$$CH_2{=}CHSAr + H_2O \rightarrow CH_3CHO + ArSH \quad (2)$$

$$CH_2{=}CHSAr + ArSH \rightarrow ArSCH_2CH_2SAr. \quad (3)$$

A byproduct, 1,2-bis(phenylthio)ethane, was actually isolated from the reaction mixture. The rates were determined by the initial linear part of the first-order plots. Product analysis showed that the hydrolysis proceeds by eqn (2).

Non-linear dependence of the rate on the acid concentrations was found in both 40% dioxane and 90% THF (Table 2). The logarithmic plots of the rate constants k_1 observed for *p*-methoxy PVS against the acidity function H_0[12] and J_0[13] showed satisfactory linearity with slopes of -1.12 ± 0.05 ($r = 0.9937$) and -0.59 ± 0.02 ($r = 0.9950$), respectively (Fig. 1).

Table 2. Hydrolysis rate of *p*-methoxy-PVS in 40% aqueous dioxane at 30°

$[HClO_4]$, M	H_0[a]	J_0[b]	$10^3 k_1$, sec^{-1}
4.03	-1.66	-4.52	170
3.45	-1.26	-3.70	43.4
2.88	-0.88	-2.88	9.76
2.31	-0.51	-2.20	4.82
1.73	-0.13	-1.42	1.48
1.50	0.04	-0.08	1.40
1.15	0.31	-0.52	0.62
0.576	0.92	0.52	0.209
0.288	1.44	1.30	0.0377

[a] Ref. 12.

[b] Ref. 13.

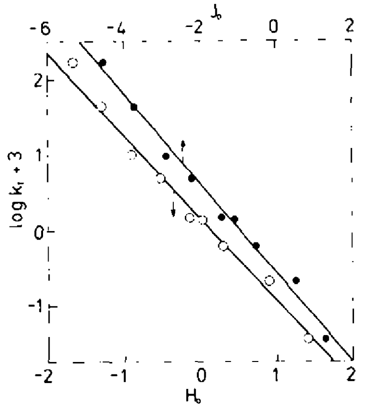

Fig. 1. Plots of log k_1 vs the acidity functions H_0 (○) and J_0 (●) for the hydrolysis of *p*-methoxy PVS in 40% aqueous dioxane at 30°

The hydrolysis rates of substituted PVS were compared in 1.5 M $HClO_4$ in 40% dioxane at 30° and in 0.4 M HCl in 90% THF at 40°. The rate constants are given in Table 3 and plotted against Hammett's σ constants of the substituents in Fig. 2. The reaction constants ρ were -1.98 ± 0.05 ($r = 0.9984$) and -1.85 ± 0.12 ($r = 0.9910$) in 40% dioxane and 90% THF, respectively.

Table 3. Hydrolysis rates of substituted PVS

Substituent	$10^4 k_1$,[a] sec^{-1}	$10^5 k_1$,[a] sec^{-1}
p-OCH_3	14.02	14.13
p-CH_3	8.78	6.38[c]
m-CH_3	5.43	4.16
H	4.09	3.58
p-F	2.69	2.74
p-Cl	1.39	1.42
m-Cl	0.78	0.762

[a] In 40% aqueous dioxane at 30.0° . $[HClO_4]$ = 1.50 M.

[b] In 90% aqueous THF at 40.0° . [HCl] = 0.398 M.

[c] $k_1 = 1.75 \times 10^{-5}$ and 12.4×10^{-5} sec^{-1} at $[HClO_4]$ = 0.599 and 0.195 M, respectively.

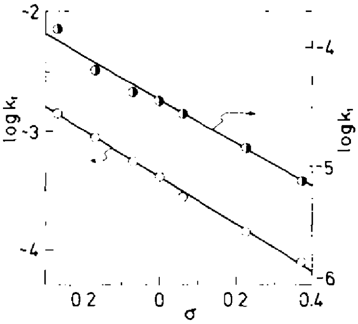

Fig. 2. The Hammett plots for the hydrolysis of substituted PVS in 40% aqueous dioxane at 30° and $[HClO_4]$ = 1.50 M (○) and in 90% aqueous THF at 40° and [HCl] = 0.398 M (◐).

DISCUSSION

Linearity of plots of log k_1 against $-H_0$ with a slope of 1.12 was found for the hydrolysis of *p*-methoxy PVS. Similar correlations were observed for the hydration of olefins[14] and 1-alkynyl sulfides,[15] which are considered to be consistent with the mechanism involving rate-determining protonation. The hydrolysis of t-butyl vinyl sulfide was examined also in 40% aqueous dioxane in the range of $[HClO_4] = 0.4$–3.2 M, to result in the linear correlation of log k_1 vs $-H_0$ with a slope near unity.[16] Furthermore, the Bunnett correlation of (log $k_1 + H_0$) vs log a_w[17] gave $w \simeq -0.3$, which is in the range of magnitude found for the hydration of acetylenic sulfides.[15] In conclusion, the hydrolysis of aryl vinyl sulfides as well as that of alkyl vinyl sulfides proceeds through the rate-determining protonation in the same way as that of the oxygen homologs, vinyl ethers.[2,3]

The logarithms of rate constants k_1 for substituted PVS correlate linearly with Hammett's σ constants. Similarly the substituent effects observed in the hydrolysis of phenyl vinyl ether (PVE) derivatives conform to Hammett's σ values.[3] The latter relationship has been rationalized from the viewpoint of the molecular orbital theory.[3]

The reaction constant for the PVS hydrolysis ($\rho = -1.98$ in 40% dioxane at 30°) is slightly smaller in magnitude than that for the PVE hydrolysis ($\rho = -2.14$ at 25° in 80% aqueous dioxane).[3] The relative sensitivities of the rates to substituents are in contrast to the results found for NMR chemical shifts of the ethylenic ^{13}C as well as ^{1}H atoms in PVS and PVE.[9,18] In these ground-state properties, the magnitudes of ρ values are greater for PVS than for PVE. Ionization equilibria of phenoxyacrylic acid and its sulfur homolog also showed the same tendency.[19] The greater efficiency of the sulfur atom in transmitting the electronic effect of ring substituents was ascribed to the conjugation through its 3d orbitals.[20] It has been shown that the through-conjugative contribution of the S atom is important only when it intervenes between two unsaturated systems.[9,18–20]

The reactivity of PVS as well as PVE in hydrolysis should depend mainly on the stability of an intermediate carbonium ion,

$$CH_3\text{-}\overset{+}{C}H\text{-}\ddot{Y}\text{-}Ar$$
$$(Y = S \text{ or } O).$$

In this electron-deficient system, the through-conjugative effect of the sulfur atom, if any, would have little importance. The observed lesser efficiency of the sulfur atom in transmitting the substituent effects must be a consequence of the irrelevance of its 3d orbitals to the carbonium ion stability. In fact, PVS is far less amenable to acid-catalyzed hydrolysis than PVE. The different sentitivities observed would be an indication that the 3p orbitals of sulfur transmits the electronic effects of substituents less efficiently than does the 2p orbitals of oxygen.

The above view can well be justified according to our previous theoretical treatments.[3,21] Thus, the change in the π-electronic energy of a reactant on protonation ΔE_π is, by a perturbation theory,[3] equal to the π-energy difference $\Delta E_\pi{}^0$ between $CH_3\overset{+}{C}H\text{-}\ddot{Y}\text{-}$ and $CH_2{=}CH\text{-}\ddot{Y}\text{-}$ *minus* the delocalization energy difference ΔDE between the π-extended systems $CH_3\overset{+}{C}H\text{-}\ddot{Y}\text{----}Ar$ and $CH_2{=}CH\text{-}\ddot{Y}\text{----}Ar$.

$$\Delta E_\pi = \Delta E_\pi{}^0 - \Delta DE. \tag{4}$$

Because of the longer C–S distance, the resonance integral γ for the Y---Ar π-bond, which has been regarded as the perturbation, is smaller in magnitude for the sulfur system (Y = S) than in the oxygen case (Y = O). Further, since the S atom is less electronegative than the O atom, the π-orbitals in both $CH_3\overset{+}{C}H\text{–}S\text{–}$ and $CH_2{=}CH\text{–}S\text{–}$ are higher lying than those in $CH_3\overset{+}{C}H\text{–}O\text{–}$ and $CH_2{=}CH\text{–}O\text{–}$. Both these effects make the delocalization term ΔDE for the sulfur system uniformly smaller and, concurrently, less sensitive to the variation in structure of the Ar identity.[21] The π-electronic energy change ΔE_π in question should, therefore, be not only larger in magnitude but also less sensitive to the substituent effects in the case of sulfides. The theoretical inference remains unaltered when the $\Delta E_\pi{}^0$ term is also taken into account. On all these grounds it can be concluded that the β-protonation of PVS should in itself be a less favorable reaction and, at the same time, be less subject to the electronic effects of ring substituents as compared with that of PVE, in accord with the experimental results.

The through-conjugation by the S atom thus appears to be hardly important in the positively charged systems. The anomalous order of reactivity previously found for the hydrolysis of alkyl vinyl sulfides[1] would have to be ascribed to other possible causes, e.g. conformational effect.

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