ACID-CATALYZED REDUCTION OF A SULFENATE ESTER BY IODIDE

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**Abstract:** Reaction of ethyl benzenesulfenate with iodide ion in aqueous acid results in formation of diphenyl disulfide and iodine and is of first order in both acid and iodide concentrations.

Sulfenic acids and their esters are a largely unexplored class of compounds because of their instability and complexity of the reaction.<sup>1</sup> Sulfenate esters readily hydrolyze in aqueous solution, but investigations on this seemingly simple reaction are limited by its complex kinetics.

We examined the reaction of ethyl benzenesulfenate (1) in aqueous acid solution. The UV spectrum of 1 changes smoothly to that of S-phenyl benzenethiosulfinate 3 ( $\lambda_{max}$ , 275 nm;  $\varepsilon$ , 8800) with an isosbestic point at 251 nm. This change is explained by the reaction (1) which shows rapid formation of 3 from the primary hydrolysis product, benzenesulfenic acid (2). Yields of 3 is always > 90 % as determined by UV and HPLC.<sup>2</sup>

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PhSOEt + H_2O \longrightarrow PhSOH + EtOH \underline{rapid} PhS(O)SPh + EtOH (1)
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However, formation of 3 in aqueous perchloric acid ([HClO<sub>4</sub>] =  $10^{-4}$  -  $10^{-2}$  M) does not follow pseudo-first-order kinetics. The reaction is strongly catalyzed by added nucleophiles such as Cl<sup>-</sup>, Br<sup>-</sup>, R<sub>2</sub>S, and SCN<sup>-</sup>, and the substrate itself can be a good nucleophilic catalyst. The reaction (in the absence of added nucleophiles) seems to depend partially on second order of [1] even in the concentration range of 1 as low as  $10^{-5} - 10^{-3}$  M and have some induction period. The addition of nucleophiles shown above does not alter the products but makes the reaction obey good pseudo-first-order kinetics. <sup>2</sup>

However, the addition of iodide ion in aqueous acid solution of 1 completely changes the spectrum of the products<sup>3</sup> showing absorption maxima at about 285 and 350 nm which conform to spectrum of triiodide, Eq. 2. HPLC analysis of the reaction mixture shows formation of diphenyl disulfide (4).<sup>4</sup> The reduction of 1 by  $I^-$  is understandable by a reaction sequence shown by Eqs. 3-5.

$I_2 + I^- \longrightarrow I_3^-$	(2)	Table 1. Percent Yields of the products in the reaction of <b>1</b> with iodide <sup>a</sup>			
$1 + H^+ + I^- \longrightarrow PhSI + EtOH$	(3)	[I <sup>-</sup> ]/M	PhSSPh	1 <sub>2</sub>	PhS(0)SPh
PhSI + I <sup>-</sup> → PhS <sup>-</sup> + I <sub>2</sub>	(4)	0.02	90	81	6
PhS <sup>-</sup> + 1> PhSSPh + EtO <sup>-</sup>	(5)	0.01	91	86	7
4		0.005	88	80	13
$RSH + I_2 \longrightarrow RSI + HI$	(6)	0.002	68	64	26
RSI + RSH> RSSR + HI	(7)	a [HClO <sub>4</sub> ]	= 0.02 M,	[ <b>1</b> ] <sub>0</sub>	= 4.5x10 <sup>-5</sup> M.

Quantitative data for the products 4 and  $I_3^-$  analyzed by HPLC and UV spectrum, respectively, and given in Table 1 show right stoichiometry for the reduction with accompanying formation of the hydrolysis product 3. Rate measurements show that the reaction is first order in both acid and iodide, rate =  $k_3[H^+][I^-][1]$  ( $k_3 = 1.25 \times 10^3 \text{ M}^{-2} \text{s}^{-1}$  at 25 °C and the ionic strength of 0.5 maintained with  $NaClO_4$ ). The first reaction of the sequence (Eq. 3) may be rate determining and is similar to the reaction of other halide ions which results in acceleration of the hydrolysis.

Oxidation of thiol by iodine to the disulfide, which constitutes the basis for a quantitative analysis of thiols, is considered to proceed by reactions (6) and  $(7).^5$  The reaction (4) is just the reverse of the reaction (6) and seems to be incompatible. This reaction should be reversible and rapid trapping of the thiolate by the sulfenate 1 make the overall reaction be reduction. A related reduction of benzenesulfenyl chloride by iodide was actually reported.<sup>6</sup> In conclusion, RSH can be oxidized by  $I_2$  to RSSR but not to RSOH for a simple R group, and RSOH be reduced by I to RSSR but not to RSH. Iodide-iodine is a good reductantoxidant pair to obtain disulfides.

## References

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- 2. Details of the hydrolysis results will be published elsewhere.
- Reaction was carried out in the atmosphere of argon in the concentra-tion ranges [HClO<sub>4</sub>] =  $10^{-4} 2\times10^{-2}$  M and [NaI] =  $2\times10^{-3} 5\times10^{-2}$  M. The retention time and mass spectrum of the HPLC peak agree with 3. 4.
- those for 4.
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