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Effect of sulfuric acid on reactions of peroxymonosulfate ion with sulfides and thiol esters

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ABSTRACT: Peroxymonosulfate ion, HSO_{5^-}, as Oxone in aqueous H_2SO_4, oxidizes sulfides [$MeSC_6H_4X(p)$, X = Me, H, NO_2] to sulfoxides and converts aryl thiobenzoates [$PhCOSC_6H_4X(p)$, X = Me, H] and thiol phosphorus(V) esters [Ph_2POSPh, $(EtO)_2POSPh$, Ph_2POSEt, $Ph(EtO)POSEt$] into the acids and sulfonate ions. Second-order rate constants increase with increasing concentration of H_2SO_4 (10–53 wt%), owing to the high polarity of the medium rather than to acid catalysis. The rate increases fit the Grunwald–Winstein equation based on Y_{OTs} solvent parameters derived from rate effects on S_N1 solvolyses. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: peroxymonosulfate ion; oxidation; sulfuric acid

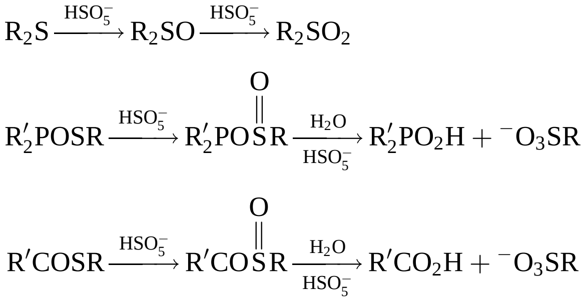
INTRODUCTION

Peroxymonosulfate ion, HSO_5^-, in the form of Oxone ($2KHSO_5$, $KHSO_4$, K_2SO_4), is a useful water-soluble oxidant of sulfides to sulfoxides and eventually to sulfones.[1,2] It decomposes thiol phosphorus(V) esters by initial oxidation at sulfur, followed by nucleophilic attack of water at the phosphorus center,[3,4] and rapidly detoxifies the nerve agent VX.[3b] It is therefore a potentially useful oxidant for the destruction of chemical weapons, both nerve and blister agents.[3]

$$EtO(Me)POSCH_2CH_2CH_2N(iPr)_2$$

VX

It also reacts with aryl thiobenzoates by initial oxidation at sulfur.[2b] The final products of the ester reactions are the corresponding acids plus sulfonate ion (Scheme 1).



$$R_2S \xrightarrow{HSO_5^-} R_2SO \xrightarrow{HSO_5^-} R_2SO_2$$

$$R'_2POSR \xrightarrow{HSO_5^-} R'_2PO\overset{\overset{\displaystyle O}{\|}}{S}R \xrightarrow[HSO_5^-]{H_2O} R'_2PO_2H + {}^-O_3SR$$

$$R'COSR \xrightarrow{HSO_5^-} R'CO\overset{\overset{\displaystyle O}{\|}}{S}R \xrightarrow[HSO_5^-]{H_2O} R'CO_2H + {}^-O_3SR$$

Scheme 1

We used model compounds that are non-toxic, but chemically similar to the agents, and whose reactions can be followed spectrophotometrically.[2–5] Model compounds used were as follows: sulfides, $MeSC_6H_4X(p)$, where X = Me, H, NO_2 (**1a**, **b** and **c** respectively) and Ph_2S (**2**); aryl thiobenzoates, $PhCOSC_6H_4X(p)$, where X = Me, H (**3a** and **b**, respectively); and thiol phosphorus(V) esters, Ph_2POSPh (**4**), $(EtO)_2POSPh$ (**5**), Ph_2POSEt (**6**) and $Ph(EtO)POSEt$ (**7**).

Rates of these reactions (Scheme 1) are modestly increased by electron-donating substituents in the phenyl groups, based on fitting to the Hammett equation, but the sulfides are much more reactive than the esters.[2,4,6] The activation enthalpies are low and activation entropies are negative,[2b,4] as seems to be general for oxygen transfers.[7,8]

An increase in solvent polarity sharply increases reaction rates, as also seems to be general for oxygen transfers.[2,4,8] For reactions in aqueous acetonitrile, solvent effects fit the Grunwald–Winstein equation:[9,10]

$$\log(k/k_0) = mY \qquad (1)$$

where Y is an indicator of solvent polarity and was originally based on the solvolysis of *tert*-butyl chloride for which $m = 1$, by definition.[9] For oxidations by HSO_5^- the m values are in the range 0.9–1.4,[2,4] i.e. some of these reactions are more sensitive to solvent polarity than typical S_N1 reactions.[9] Oxidations of sulfides by periodate ion are also speeded by polar, aqueous solvents, with fits to the Grunwald–Winstein equation.[2a,8]

For many reactions, especially those involving displacements at carbon centers, a high kinetic sensitivity to solvent polarity or water content is associated with large electronic effects, as in S_N1 reactions. Mechanistic

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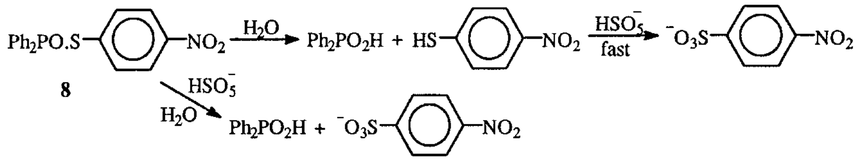

differences between these reactions and oxygen transfers, which can be regarded as nucleophilic displacements at oxygen, have been discussed.[2,6–8] It was suggested that electron transfer from sulfur to oxygen is involved in transition-state formation, and a mechanistic rationale was given for the substituent and solvent effects on reactions in aqueous media.[4]

Added salts and limited pH change do not affect rates of reactions of HSO_5^- with the sulfides and thiol esters.[2,4] However, in preliminary work we saw modest rate increases on addition of mineral acid. Reactivity could increase in more concentrated acid for several reasons. Protonation could generate H_2SO_5, a better oxidant than HSO_5^-. There is also the possibility of initial acid-catalyzed hydrolysis of the esters, followed by rapid oxidation of the thiol. We see this path in the reaction of **8** with HSO_5^-, without added acid, but it is unimportant with other esters,[2b,4] and would not apply to oxidations of the sulfides.

The high polarity of moderately concentrated mineral acids should lead to an increase in rates of oxidation at sulfur by a medium effect, in view of the sensitivity of these reactions to solvent polarity.[2,4,8] Bentley *et al.*[11] found moderately concentrated H_2SO_4 to be an excellent solvent for S_N1 reactions, and they established a Y_{OTs} polarity scale in up to 70 wt% H_2SO_4 (sulfonation becomes a problem at higher acidities). The high polarity of aqueous H_2SO_4 should make it an effective solvent for oxidations by HSO_5^-, and in that event the Y_{OTs} scale should fit the rate increases.

RESULTS AND DISCUSSION

We followed these reactions spectrophotometrically with dilute substrate [$1–8 \times 10^{-5}$ mol dm^{-3}, except for reaction of **5** where we used 4×10^{-4} mol dm^{-3}] in aqueous H_2SO_4 containing 0.4 vol.% MeCN. As found earlier for reactions in the absence of added acid reactions are overall second order, i.e. first order in each reactant.[2,3,4]

Reactions of the sulfides

First-order rate constants, k_ψ, varied linearly with $[HSO_5^-]$ (Fig. 1), consistent with earlier results.[2] Second-order rate constants of oxidations by HSO_5^- increase monotonically with increasing $[H_2SO_4]$ and $\log k_2$ increases linearly with Y_{OTs}[11] (Fig. 2). Based on second-order rate constants, k_2 (Table 1), substituent effects are similar to those without added acid.[2b]

Reactions of aryl thiobenzoates

Provided that reactions of **3a** and **b** were followed in a double-beam HP 8450 diode-array spectrophotometer, the first-order rate constants, k_ψ, varied linearly with $[HSO_5^-]$ and the plots had zero intercepts (Figs 3 and 4), as had been found earlier for reactions in the absence of added acid.[2b] However, when reactions were followed in

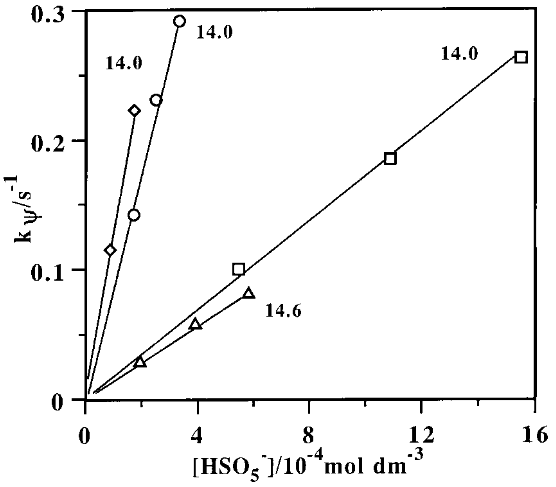

Figure 1. Sulfide oxidations by HSO_5^- at the indicated wt% H_2SO_4. ◇**1a**; ○, **1b**; □, **1c**; △, **2**

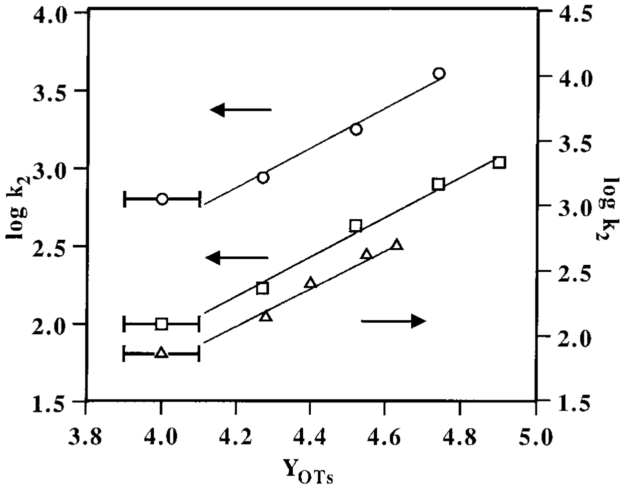

Figure 2. Dependence of second-order rate constants for sulfide oxidations on solvent polarity. ○, **1b**; □, **1c**; △, **2**

Table 1. Sulfide oxidations in aqueous H_2SO_4[a]

Substrate	H_2SO_4 (wt%)	14.0	14.6	23.2	29.6	31.3	36.3	42.5	52.5
	Y_{OTs}[b]	4.27	4.28	4.40	4.52	4.55	4.63	4.74	4.90
1a, $MeSC_6H_4OMe(p)$		1250							
1b, $MeSC_6H_5$		875			1777			4109	
1c, $MeSC_6H_4NO_2(p)$		170			429			799	1103
2, Ph_2S			137	254		413	489		

[a] Values of k_2, $dm^3\ mol^{-1}s^{-1}$ at 25.0 °C.
[b] Ref. 11.

a single-beam HP 8451 spectrophotometer, plots of k_ψ vs $[HSO_5^-]$ were linear and the slopes were similar to those obtained with the HP 8450 spectrophotometer, but we frequently saw non-zero intercepts with erratic values. We did not have this problem in the absence of H_2SO_4,[2b] so there seems to be photochemical hydrolysis, or other reactions, in aqueous H_2SO_4, if reaction is followed in a single-beam, diode-array spectrophotometer. This problem is considered in more detail in the Experimental section. Second-order rate constants, k_2, are given in Table 2.

Reactions of thiol phosphorus(V) esters

Provided that reactions of **4–6** were followed in a double-beam HP 8450 spectrophotometer first-order rate constants varied linearly with $[HSO_5^-]$ with zero intercepts (Figs 3 and 4), as found earlier for reactions in the absence of added acid.[4] For reaction of **7** there was agreement in the data from the two instruments and second-order rate constants for reactions of **4–7** over a range of $[H_2SO_4]$ are also given in Table 2.

Role of sulfuric acid

Second-order rate constants, k_2, increase monotonically with increasing concentration of H_2SO_4 (Tables 1 and 2). This increase is probably not due to acid catalysis. Except in dilute acid rates of hydrogen ion-catalyzed reactions of weakly basic substrates typically increase more rapidly than hydrogen ion concentration, largely because a decrease in hydration sharply increases protonating power. This acid catalysis is described by various acidity functions[12] or by an excess-acidity scale.[13] The sensitivity of reaction rates to these acidity scales depends on substrate structure and reaction mechanism.[12,13]

For our reactions of HSO_5^-, plots of log k_2 against Hammett's acidity function,[12a] H_0', have slopes less than **1,** and they are curved for some reactions. Other acidity functions also failed to fit the data. This behavior is atypical of hydrogen ion-catalyzed reactions not directly involving water as a nucleophile in the transition state,[12,13] and it is improbable that water is involved nucleophilically in the rate-determining steps of these oxidations. In addition, substituent effects on rate do not change significantly with added H_2SO_4.[2b,4] Such a change would be expected if the oxidant was H_2SO_5 rather than HSO_5^-. We therefore conclude that H_2SO_4 is exerting a kinetic solvent effect[11] rather than providing acid catalysis, based on the known sensitivity of these oxidations to solvent polarity.[2,3,8]

The Y_{OTs} scales are typically based on solvolyses of sulfonates[11,14] but there is uncertainty in the value of Y_{OTs} in water. It is in the range 3.9–4.1, and seems to depend on extrapolations and on the substrate used to set the scale.[10,11,14] Plots of log k_2 against Y_{OTs} are reasonably linear in aqueous H_2SO_4 (Figs 2, 5 and 6) and fit the data points for reaction in water[2b,4] within the uncertainties in Y_{OTs}. The spread of reported values of Y_{OTs} for water is indicated. The high values of m (Table 3) are typical of reactions whose rates are very sensitive to solvent polarity,[9,11] and are similar to, but slightly higher than, those for reactions in H_2O–MeCN without added H_2SO_4.[2b,4] There are similar variations of m in S_N1

Table 2. Reactions of esters in aqueous H_2SO_4[a]

Substrate	H_2SO_4 (wt%)	11.9	13.9	19.5	25.3	30.3	36.1	42.2	52.5
	Y_{OTs}[b]	4.24	4.27	4.37	4.46	4.53	4.63	4.73	4.90
3a, $PhCOSC_6H_4Me(p)$			0.121	0.183		0.327		0.650	1.46
3b, $PhCOSC_6H_5$				0.118		0.253		0.490	0.980
4, Ph_2POSPh				0.0240		0.044		0.0824	0.158
5, $(EtO)_2POSPh$				0.0119			0.0316		0.0925
6, Ph_2POSEt		0.0925			0.185		0.308		0.650
7, $Ph(EtO)POSEt$			0.236	0.347				0.720	1.05

[a] Values of k_2, $dm^3\ mol^{-1}s^{-1}$ at 25.0 °C.
[b] Ref. 11.

Table 3. Values of *m* for reactions of sulfides and esters with HSO_5^{-a}

Substrate	*m*	Substrate	*m*
1b, $MeSC_6H_5$	1.3	**4,** Ph_2POSPh	1.5
1c, $MeSC_6H_4NO_2(p)$	1.3	**5,** $(EtO)_2POSPh$	1.6
2, Ph_2S	1.4	**6,** Ph_2POSEt	1.3
3a, $PhCOSC_6H_4Me(p)$	1.6	**7,** $Ph(EtO)POSEt$	1.1
3b, $PhCOSC_6H_5$	1.5		

[a] In aqueous H_2SO_4 at 25.0 °C with values of Y_{OTs} from Ref. 11.

reactions which follow the Grunwald–Winstein equation or extensions of it.[9,11] It had been assumed that oxidation at sulfur is the rate-limiting step for reactions with HSO_5^- and that, for the esters, subsequent attack of water is fast.[2b,3b,4] As a result the low nucleophilicity of H_2O in moderately concentrated H_2SO_4[11] does not inhibit reaction, because ester hydrolysis is kinetically unimportant.[2,4]

Sulfuric acid has a higher dielectric constant than water and the value in 100% H_2SO_4 is *ca* 100, with some dependence on the method of measurement.[12b,15] This high dielectric constant favors reactions with high charge development in the transition state, e.g. S_N1 solvolyses of non-ionic substrates, as does hydrogen bonding to anionoid leaving groups.[11,14,16] These factors also influence oxidations by HSO_5^-, which are highly sensitive to solvent polarity, although electronic substituent effects are small, e.g. $\rho \approx -0.4$ to 0.6, based on $_{\mathrm{m}}$ and σ_p parameters,[2b,4] whereas for S_N1 reactions ≈ -4 based on σ^+ parameters.[17,18]

Carboxylic and phosphorus(V) esters are much less reactive towards HSO_5^- than the sulfides in both aqueous media[2,4] and in moderately concentrated H_2SO_4 (Tables 1 and 2),[2,4] and rate differences are much larger than expected based on inductive effects of acyl groups, for example.[18] Reactivities correlate with ionization potentials, and initial electron transfer from sulfur to oxygen is postulated.[2b,4] Correlations of nucleophilicity with ionization potential[19] are understandable in terms of the valence-bond, avoided-crossing, model of nucleophilic substitutions.[20]

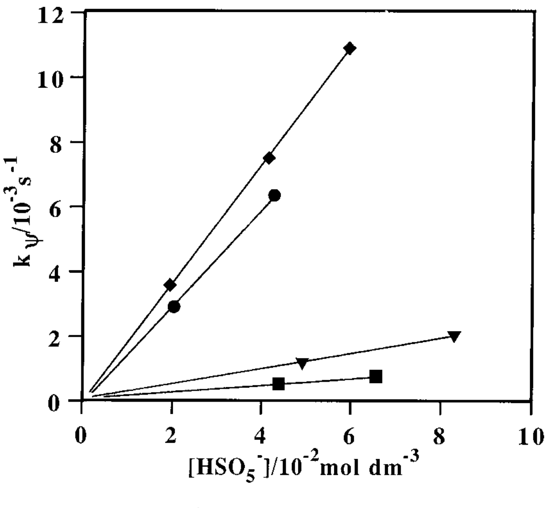

Figure 3. Oxidations of esters by HSO_5^- in 19.5 wt% H_2SO_4. ◆ **3a;** ●, **3b;** ▽, **4;** ■, **5**

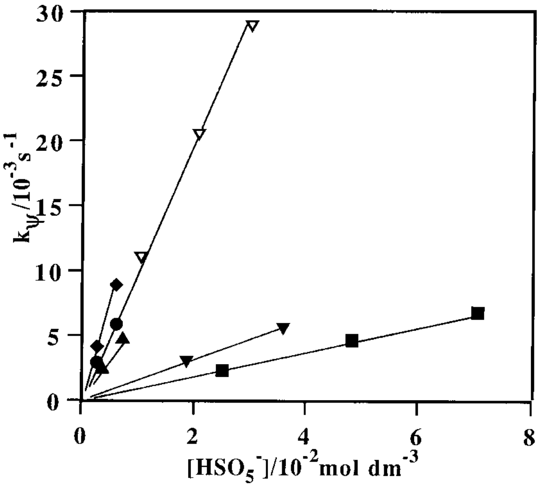

Figure 4. Oxidations of esters by HSO_5^- in 52.2 wt% H_2SO_4. ◆, **3a;** ●, **3b;** ▽, **4;** ■, **5;** △, **6;** ▽, **7**

These oxygen transfers can be regarded as nucleophilic displacements,[2,4,7,8] e.g. by sulfur on peroxy oxygen and the build-up of negative charge on oxygen should be favored by strong hydrogen-bonding donors, as are S_N1 solvolyses.[11,14,16] However, despite similar solvent effects, S_N1 solvolyses and HSO_5^- oxidations differ markedly in other mechanistic aspects as manifested by activation parameters and electronic substituent effects.[2,4,8] For example, activation enthalpies are considerably lower and entropies more negative for these oxygen transfers than for S_N1 reactions.

Although we conclude that the rate enhancements by H_2SO_4 are medium effects and not due to acid catalysis, based on correlation of log k_2 and Y_{OTs} (Figs 2, 5 and 6) and evidence against introduction of a new oxidant, we note that over limited ranges of acidities Y_{OTs} varies linearly with H_0, and plots of Y_{OTs} (or H_0) against log a_{H_2O} are approximately linear.[11] These relations cause major problems in interpreting rate data in moderately concentrated acids because acidity functions, medium polarity and water activity are not independent variables. Nonetheless, the variations of k_2 with acid concentration are not consistent with acid catalysis.

Hydrolyses of the esters

The zero intercepts in plots of k_ψ against $[HSO_5^-]$ (Figs 3 and 4 and Refs 2 and 4) show that acid-catalyzed (and spontaneous) hydrolyses are relatively slow, even though thiol esters of carboxylic and phosphorus(V) esters are more reactive towards anionic nucleophiles than the

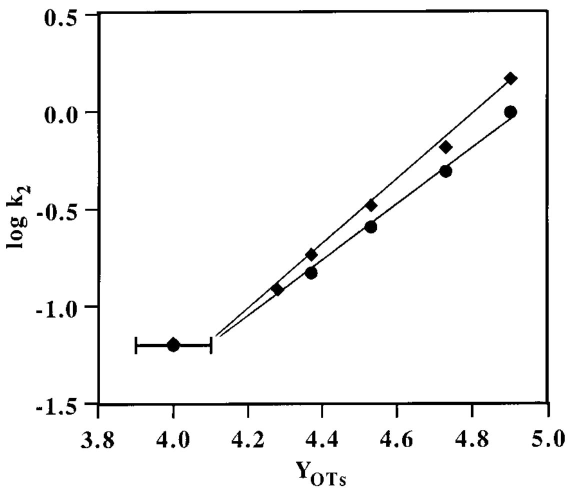

Figure 5. Dependence of second-order rate constants for reactions of the aryl thiobenzoates on solvent polarity. ◆, **3a**; ●, **3b**

corresponding alkoxy or aryloxy derivatives.[21,22] The differences arise because RS^- is a better leaving group than RO^-, and there are differences in conjugative electron release by sulfur and oxygen. These leaving-group effects are partially offset for reactions at phosphorus(V) by the higher apicophilicity of RO over RS in transition states with bipyramidal character.[23]

Acid hydrolysis requires proton transfer, usually in an equilibrium step,[12,13] and it is disfavored when oxygen is replaced by sulfur.[21] Therefore, although carboxylic esters are readily hydrolyzed in moderately concentrated H_2SO_4,[12,13] thiobenzoates are much less reactive in these conditions, unless a photochemical reaction intervenes (see Experimental section). Trialkyl and triaryl phosphates are not readily hydrolyzed in aqueous acid,[24] so acid hydrolysis of the phosphorus(V) esters should be unimportant in our dark reaction conditions.

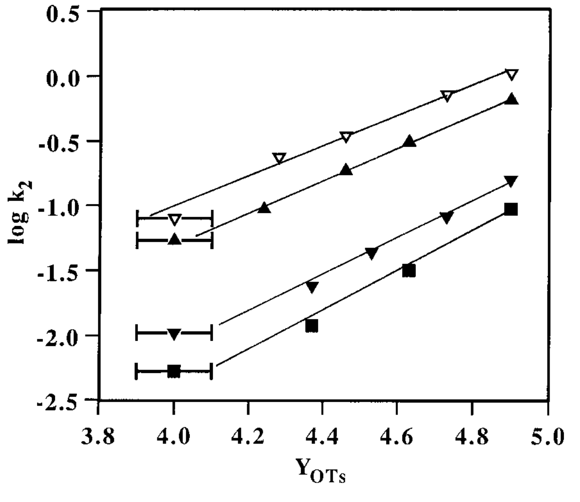

Figure 6. Dependence of second-order rate constants for reactions of phosphorus(V) esters on solvent polarity. ▽, **4**; ■, **5**; △, **6**; ▽, **7**

EXPERIMENTAL

Materials. The preparation and purification of the sulfides and esters has been described previously.[2,4,22] The HSO_5^- content of Oxone solutions was determined iodimetrically and freshly made-up solutions were used to avoid hydrolysis of HSO_5^-.

Kinetics. Reaction solutions were prepared by adding weighed amounts of pre-analyzed aqueous Oxone and H_2SO_4 to a volumetric flask and making the solution up to the mark with a weighed amount of water so that molar or weight % concentrations could be calculated. The solution was kept cool during mixing to reduce hydrolysis of HSO_5^-. Reproducible data were obtained provided that solutions were not left for several hours before use.

Oxone absorbs up to *ca* 250 nm, depending on its concentration, and its solutions were usually used as a reference, but these rate constants agreed with those measured with water as reference. Reactions were followed at 25.0 °C at the following wavelengths: **1a** and **b,** 250–265 nm; **1c,** 340 and 360 nm; and **2,** 270 and 280 nm. We saw isosbestic points at the following wavelengths: **1a,** 253; **1b,** 240; **1c,** 310; and **2,** 244 nm. Reactions of the thiobenzoates **3a** and **b** were followed at 290 and 300 nm and those of the phosphorus(V) esters at (**5** and **7**) 240 and 245 nm, (**4**) 240–260 nm and (**6**) 230–245 nm. All reactions were followed in 1 cm cuvettes and because of the absorbance by Oxone we saw isosbestic points only with reactions of the sulfides in dilute Oxone. First-order rate constants were unaffected by small changes in wavelength. Substrates were added as solutions in MeCN so that reaction solutions contained 0.4 vol.% MeCN.

We obtained agreement between rate data obtained with either a single- or a double-beam spectrophotometer for the sulfides and for Ph(EtO)POSEt (**7**). Agreement was poor for reactions of the other substrates in aqueous H_2SO_4, although we had no problems with reactions of the aryl thiobenzoates followed, without added H_2SO_4, in the single-beam spectrophotometer.[2b]

For reactions of the aryl thiobenzoates followed in aqueous H_2SO_4 on an HP 8451 single-beam spectrophotometer, plots of k_ψ vs $[HSO_5^-]$ gave finite intercepts whose values depended, irreproducibly, on $[H_2SO_4]$. The problem was reduced, but not eliminated, by using a Melles Griot WG 280 glass filter. We conclude that there was an acid-mediated photochemical reaction in the single-beam spectrophotometer, even though we used as few as 20 data points. The problem was not reduced by aspirating the reaction solution with N_2. This instrument uses a deuterium lamp to irradiate the sample over the whole wavelength range with intermittent opening of a shutter. In the HP 8450 double-beam spectrophotometer, a swinging mirror directs the beam over sample and reference cells.

Our aim was to eliminate, rather than to explain, the irreproduciblity of the results, but it appears that the high light flux in the single-beam instrument was giving photochemical hydrolysis of some of the esters in acidic solutions.

Hydrolysis of HSO_5^-. Values of k_ψ in 65 wt% H_2SO_4 decreased when solutions of Oxone and H_2SO_4 were left standing before addition of the substrate. They became constant after a time, probably because equilibrium was reached between HSO_5^- and H_2O_2. We did not have these problems with up to 52 wt% H_2SO_4, but in all conditions reactions were started as soon as possible after solutions were made up. Sufficient time was allowed for temperature equilibriation. The high viscosity of 65 wt% H_2SO_4 caused mixing problems, so it was difficult to obtain good data in these conditions, even when solutions were used promptly after being made up. In H_2SO_4 the substrates react with H_2O_2, but under the conditions of our experiments these reactions are slower than those of HSO_5^-.

Acknowledgment

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REFERENCES

1. (a) R. J. Kennedy and A. M. Stock. *J. Org. Chem.* **25,** 1901 (1960); (b) W. Zhu and W. T. Ford. *J. Org. Chem.* **56**, 7022 (1991); (c) K. S. Webb. *Tetrahedron Lett.* **35,** 3457 (1994).
2. (a) R. Bacaloglu, A. Blasko, C. A. Bunton and H. Foroudian. *J. Phys. Org. Chem.* **5,** 171 (1992); (b) C. A. Bunton, H. J. Foroudian and A. Kumar. *J. Chem. Soc., Perkin Trans.* **2,** 33 (1995).
3. (a) Y. -C. Yang, J. A. Baker and J. R. Ward. *Chem. Rev.* **92,** 1729 (1992); (b) Y. -C. Yang, L. L. Szafraniec, W. T. Beaudry and D. K. Rohrbaugh. *J. Am. Chem. Soc.* **112,** 6621 (1990); (c) Y. -C. Yang. *Chem. Ind.* (London) 334 (1995).
4. A. Blasko, C. A. Bunton and A. Kumar. *J. Phys. Org. Chem.* **10,** 427 (1997).
5. *Alternative Technologies for Destruction of Chemical Agents and Munitions.* National Academy Press, Washington, DC (1993).
6. M. D. Johnson and D. Nickerson. *Inorg. Chem.* **31,** 3971 (1992).
7. R. W. Murray. *Chem. Rev.* **89,** 1187 (1989); (b) W. Adam, C. Curci and J. O. Edwards. *Acc. Chem. Res.* **22,** 205 (1989).
8. F. Ruff and A. Kucsman. *J. Chem. Soc, Perkin Trans.* **2**, 683 (1985).
9. A. H. Fainberg and S. Winstein. *J. Am. Chem. Soc.* **78,** 2770 (1956).
10. C. A. Bunton, M. M. Mhala and J. R. Moffatt. *J. Org. Chem.* **49,** 3637 (1984).
11. T. W. Bentley, S. Jurczyk, K. Roberts and D. J. Williams. *J. Chem. Soc. Perkin Trans.* **2**, 293 (1987).
12. (a) C. H. Rochester. *Acidity Functions.* Academic Press, London (1970); (b) M. Liler. *Reaction Mechanisms in Sulphuric Acid.* Academic Press, London (1971); (c) J. F. Bunnett and F. P. Olsen. *Can. J. Chem.* **44,** 1899 (1966).
13. (a) R. A. Cox and K. Yates. *J. Am. Chem. Soc.* **100,** 3861 (1978); (b) V. Lucchini, G. Modena, G. Scorrano, R. A. Cox and K. Yates. *J. Am. Chem. Soc.* **104,** 1958 (1982).
14. (a) T. W. Bentley and P. v. R. Schleyer. *Adv. Phys. Org. Chem.* **14,** 1 (1977); (b) D. N. Kevill, S. W. Anderson and E. K. Fujimoto. in *Nucleophilicity,* Advances in Chemistry Series, No. 215, edited by J. M. Harris and S. P. McManus Chapt. 19. American Chemical Society, Washington, DC (1987).
15. R. J. Gillespie and R. F. M. White. *Trans Faraday Soc.* **54,** 1846 (1958).
16. J. M. Harris, S. P. McManus, M. R. Sedaghat-Herati, N. Neamati-Mazraeh, M. J. Kamlet, R. M. Doherty, R. W. Taft and M. H. Abraham. in *Nucleophilicity,* Advances in Chemistry Series, No. 215, edited by J. M. Harris and S. P. McManus, Chapt. 17. American Chemical Society, Washington, DC (1987).
17. H. C. Brown and Y. Okamoto. *J. Am. Chem. Soc.* **80,** 4979 (1958).
18. T. H. Lowry and K. S. Richardson. *Mechanism and Theory in Organic Chemistry*, 3rd ed., Chapt. 2.2 Harper and Row, New York (1987).
19. (a) C. D. Ritchie. *J. Am. Chem. Soc.* **105,** 7313 (1983); (b) E. Buncel, S. S. Shaik, I.-H. Um and S. Wolfe. *J. Am. Chem. Soc.* **110,** 1275 (1988).
20. (a) A. Pross. *Acc. Chem. Res.* **18,** 212 (1985); (b) S. S. Shaik. *Acta Chem. Scand.* **44,** 205 (1990).
21. (a) T. C. Bruice. *Organic Sulfur Compounds,* Chapt. 35. Pergamon Press, New York (1961); (b) B. K. Morse and D. S. Tarbell. *J. Am. Chem. Soc.* **74,** 416 (1952).
22. (a) R. D. Cook, S. Farah, L. Ghawi, A. Itani and J. Rahil. *Can. J. Chem.* **64,** 1630 (1986); (b) A. Blasko, C. A. Bunton, Y. S. Hong, M. M. Mhala, J. R. Moffatt and S. Wright. *J. Phys. Org. Chem.* **4,** 618 (1991).
23. G. R. Thatcher and R. Kluger. *Adv. Phys. Org. Chem.* **25,** 99 (1989).
24. C. A. Bunton. *Acc. Chem. Res.* **3,** 257 (1970).