

Kinetics and correlation analysis of reactivity in oxidation of organic sulfides by hexamethylenetetramine–bromine

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Received 21 September 1999; revised 9 December 1999; accepted 25 January 2000

ABSTRACT: The oxidation of organic sulfides by hexamethylenetetramine–bromine (HABR) to the corresponding sulfoxides is first order with respect to HABR. Michaelis–Menten-type kinetics were observed with respect to the sulfide. It is proposed that HABR itself is the oxidizing species. Correlation analyses of the rate of the oxidation of 34 sulfides were performed in terms of various single and multiparametric equations. The best correlation was obtained with Charton's LDR and LDRS equations, the polar regression coefficients being negative. The oxidation of alkyl phenyl sulfides exhibited a very good correlation in terms of the Pavelich–Taft equation. A mechanism involving the formation of a halosulfonium cation in the slow step is proposed. Copyright © 2000 John Wiley & Sons, Ltd.

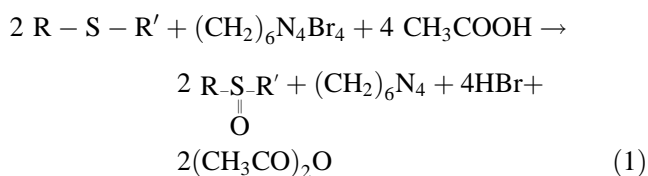
KEYWORDS: kinetics; mechanism; sulfides; oxidation; correlation analysis; polyhalide

INTRODUCTION

Hexamethylenetetramine–bromine (HABR) was reported as a synthetic reagent for the oxidation of alcohols to carbonyl compounds in 1994.¹ We have initiated a study of kinetics and mechanism of oxidations by HABR and few reports have been emanated from our laboratory on the mechanistic aspects of the oxidation of hydroxy compounds and aldehydes.^{2,3} In this paper, the kinetics of the oxidation of 34 organic sulfides by HABR in glacial acetic acid are reported. Attempts were made to correlate the structure and reactivity in the oxidation process. A suitable mechanism is proposed.

RESULTS

The oxidation of organic sulfides by HABR resulted in the formation of the corresponding sulfoxides. The overall reaction can be represented by



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Rate laws

The reactions were found to be first order with respect to HABR. In individual kinetic runs, plots of $\log [\text{HABR}]$ versus time were linear ($r^2 > 0.995$). Further, it was found that the observed rate constant, k_{obs} , does not depend on the initial concentration of HABR when the sulfide is in large excess over HABR. The order with respect to sulfide was < 1 (Table 1). A plot of $1/k_{\text{obs}}$ versus $1/[\text{sulfide}]$ was linear with an intercept on the rate ordinate.

Table 1. Rate constants for the oxidation of methyl phenyl sulfide by HABR at 298 K

| [MeSPh] (mol dm ⁻³) | 10 ³ [HABR] (mol dm ⁻³) | 10 ⁴ k_{obs} (s ⁻¹) |
|------------------------------------|---|--|
| 0.01 | 1.0 | 0.76 |
| 0.02 | 1.0 | 1.44 |
| 0.03 | 1.0 | 2.00 |
| 0.05 | 1.0 | 3.21 |
| 0.10 | 1.0 | 5.15 |
| 0.15 | 1.0 | 6.60 |
| 0.20 | 1.0 | 7.74 |
| 0.20 | 2.0 | 7.66 |
| 0.20 | 4.0 | 7.82 |
| 0.20 | 6.0 | 7.70 |
| 0.20 | 8.0 | 7.61 |
| 0.20 | 1.0 | 7.78 ^a |
| 0.20 | 1.0 | 7.70 ^b |
| 0.20 | 1.0 | 7.81 ^c |

^a Contains 0.005 mol dm⁻³ acrylonitrile.

^b Contains 0.02 mol dm⁻³ HXA.

^c Contains 0.02 mol dm⁻³ sodium bromide.

Table 2. Formation constants and thermodynamic parameters of sulfide–HABR complexes

| Substituent | K (dm ³ mol ⁻¹) | | | | ΔH (kJ mol ⁻¹) | ΔS (J mol ⁻¹ K ⁻¹) | ΔG (kJ mol ⁻¹) |
|------------------------------|--|-------|-------|-------|---------------------------------------|--|---------------------------------------|
| | 288 K | 298 K | 308 K | 318 K | | | |
| (i) Aryl methyl sulfides | | | | | | | |
| H | 7.15 | 5.54 | 4.23 | 3.28 | -22.3 ± 0.2 | -53 ± 1 | -6.7 ± 0.2 |
| <i>p</i> -Me | 5.75 | 4.50 | 3.55 | 2.80 | -20.7 ± 0.2 | -49 ± 1 | -6.2 ± 0.2 |
| <i>p</i> -OMe | 9.23 | 6.61 | 4.68 | 3.37 | -28.1 ± 0.3 | -71 ± 1 | -7.1 ± 0.3 |
| <i>p</i> -F | 8.41 | 5.92 | 4.22 | 3.00 | -28.6 ± 0.3 | -73 ± 1 | -6.8 ± 0.2 |
| <i>p</i> -Cl | 6.99 | 5.20 | 3.91 | 3.10 | -23.3 ± 0.3 | -56 ± 1 | -6.5 ± 0.2 |
| <i>p</i> -Br | 7.39 | 5.45 | 4.01 | 2.96 | -25.7 ± 0.3 | -64 ± 1 | -6.6 ± 0.3 |
| <i>p</i> -NO ₂ | 8.70 | 6.10 | 4.20 | 2.91 | -30.3 ± 0.5 | -79 ± 2 | -6.9 ± 0.4 |
| <i>p</i> -COMe | 5.90 | 4.61 | 3.55 | 2.80 | -21.5 ± 0.2 | -52 ± 1 | -6.2 ± 0.2 |
| <i>p</i> -CO ₂ Me | 6.49 | 5.00 | 3.86 | 3.00 | -22.1 ± 0.2 | -53 ± 1 | -6.4 ± 0.2 |
| <i>p</i> -NHAc | 7.88 | 5.67 | 4.15 | 2.91 | -27.6 ± 0.6 | -70 ± 2 | -6.7 ± 0.5 |
| <i>p</i> -NH ₂ | 7.18 | 5.22 | 3.91 | 2.96 | -24.9 ± 0.1 | -62 ± 1 | -6.6 ± 0.1 |
| <i>m</i> -Me | 8.20 | 6.07 | 4.53 | 3.46 | -24.4 ± 0.1 | -59 ± 1 | -7.0 ± 0.1 |
| <i>m</i> -Ome | 6.31 | 4.78 | 3.62 | 2.85 | -22.8 ± 0.2 | -56 ± 1 | -6.3 ± 0.1 |
| <i>m</i> -Cl | 5.78 | 4.51 | 3.42 | 2.67 | -22.2 ± 0.3 | -54 ± 1 | -6.1 ± 0.3 |
| <i>m</i> -Br | 9.10 | 6.61 | 4.71 | 3.49 | -27.0 ± 0.3 | -67 ± 3 | -7.1 ± 0.2 |
| <i>m</i> -I | 8.75 | 6.22 | 4.51 | 3.22 | -27.8 ± 0.3 | -70 ± 1 | -7.0 ± 0.3 |
| <i>m</i> -NO ₂ | 6.33 | 4.92 | 3.81 | 3.00 | -21.5 ± 0.2 | -51 ± 1 | -6.4 ± 0.1 |
| <i>m</i> -CO ₂ Me | 7.15 | 5.25 | 3.90 | 2.90 | -25.4 ± 0.2 | -63 ± 1 | -6.5 ± 0.2 |
| <i>o</i> -Me | 5.75 | 4.29 | 3.33 | 2.48 | -23.6 ± 0.4 | -59 ± 1 | -6.1 ± 0.3 |
| <i>o</i> -OMe | 6.98 | 4.91 | 3.52 | 2.51 | -28.4 ± 0.3 | -74 ± 1 | -6.4 ± 0.2 |
| <i>o</i> -NO ₂ | 9.63 | 7.02 | 5.15 | 3.70 | -26.7 ± 0.5 | -66 ± 2 | -7.3 ± 0.4 |
| <i>o</i> -CO ₂ Me | 8.11 | 6.00 | 4.54 | 3.38 | -24.6 ± 0.3 | -60 ± 1 | -6.9 ± 0.2 |
| <i>o</i> -NH ₂ | 8.71 | 6.40 | 4.60 | 3.44 | -26.2 ± 0.3 | -65 ± 1 | -7.0 ± 0.2 |
| <i>o</i> -Cl | 7.43 | 5.33 | 3.71 | 2.75 | -27.9 ± 0.4 | -72 ± 1 | -6.6 ± 0.3 |
| <i>o</i> -Br | 5.88 | 4.48 | 3.31 | 2.60 | -23.4 ± 0.3 | -58 ± 1 | -6.1 ± 0.3 |
| <i>o</i> -I | 6.66 | 4.90 | 3.58 | 2.65 | -25.9 ± 0.3 | -66 ± 1 | -7.2 ± 0.3 |
| <i>o</i> -CN | 9.78 | 6.94 | 5.01 | 3.56 | -28.0 ± 0.4 | -70 ± 1 | -7.2 ± 0.3 |
| (ii) Alkyl phenyl sulfides | | | | | | | |
| Et | 6.23 | 4.80 | 3.55 | 2.84 | -22.7 ± 0.4 | -56 ± 2 | -6.3 ± 0.3 |
| Pr | 7.00 | 5.48 | 4.33 | 3.29 | -21.5 ± 0.5 | -50 ± 2 | -6.7 ± 0.4 |
| <i>i</i> -Pr | 8.70 | 6.25 | 4.55 | 3.21 | -27.7 ± 0.5 | -70 ± 2 | -7.0 ± 0.4 |
| <i>t</i> -Bu | 9.00 | 6.58 | 4.75 | 3.50 | -26.5 ± 0.3 | -66 ± 1 | -7.1 ± 0.2 |
| (iii) Other sulfides | | | | | | | |
| Me ₂ S | 5.99 | 4.60 | 3.50 | 2.92 | -21.0 ± 0.5 | -50 ± 2 | -6.3 ± 0.4 |
| Pr ₂ S | 6.01 | 4.55 | 3.52 | 2.98 | -20.5 ± 0.7 | -48 ± 2 | -6.3 ± 0.5 |
| Ph ₂ S | 5.85 | 4.50 | 3.33 | 2.62 | -23.1 ± 0.4 | -57 ± 1 | -6.2 ± 0.3 |

Thus Michaelis–Menten-type kinetics were observed with respect to substrate. This leads to the postulation of following overall mechanism and the rate law:



$$\text{rate} = k_2 K [\text{sulfide}] [\text{HABR}]_t / (1 + K [\text{sulfide}]) \quad (4)$$

where

$$[\text{HABR}]_t = [\text{HABR}] + [\text{complex}]$$

The dependence of k_{obs} on the concentration of sulfide was studied at different temperatures and the values of K and k_2 were evaluated from the double reciprocal plots. The thermodynamic parameters for the complex forma-

tion and activation parameters of the decomposition of the complexes were calculated from the values of K and k_2 , respectively, at different temperatures (Tables 2 and 3).

Spectral studies

A perusal of the UV–VIS spectra of HABR (0.001 mol dm⁻³) and an equivalent amount of bromine (0.002 mol dm⁻³), in AcOH at ~293 K, showed that the difference in the nature of the spectra of HABR and bromine was not very striking but their optical densities showed variations (Fig. 1). Hexamethylenetetramine (HXA) had no appreciable absorption in this range. Further, the spectrum of HABR did not show any change during the experimental time period (ca 2 h). When a solution of HABR in acetic acid was evaporated to dryness under reduced pressure, HABR was recovered

Table 3. Rate constants of decompositions and activation parameters of sulfide–HABR complexes

| Substituent | $10^4 k_2$ (s ⁻¹) | | | | ΔH (kJ mol ⁻¹)* | ΔS (J mol ⁻¹ K ⁻¹)* | ΔG (kJ mol ⁻¹)* |
|------------------------------|-------------------------------|-------|-------|-------|--|---|--|
| | 288 K | 298 K | 308 K | 318 K | | | |
| (i) Aryl methyl sulfides | | | | | | | |
| H | 7.19 | 14.5 | 28.9 | 59.0 | 50.8 ± 0.9 | -129 ± 3 | 89.2 ± 0.7 |
| <i>p</i> -Me | 20.1 | 37.3 | 68.5 | 135 | 45.6 ± 1.2 | -139 ± 4 | 86.8 ± 0.7 |
| <i>p</i> -OMe | 81.0 | 130 | 211 | 390 | 37.0 ± 1.7 | -157 ± 6 | 83.7 ± 1.4 |
| <i>p</i> -F | 10.5 | 19.0 | 36.8 | 72.0 | 46.4 ± 1.3 | -141 ± 4 | 88.4 ± 1.0 |
| <i>p</i> -Cl | 6.84 | 13.0 | 26.0 | 51.7 | 49.0 ± 1.1 | -136 ± 4 | 89.4 ± 0.9 |
| <i>p</i> -Br | 6.83 | 13.3 | 25.9 | 52.0 | 48.9 ± 1.0 | -136 ± 3 | 89.4 ± 0.8 |
| <i>p</i> -NO ₂ | 0.49 | 1.21 | 2.71 | 6.09 | 61.2 ± 0.4 | -115 ± 1 | 95.4 ± 0.3 |
| <i>p</i> -COMe | 1.37 | 3.20 | 6.81 | 14.8 | 57.6 ± 0.5 | -119 ± 2 | 93.0 ± 0.4 |
| <i>p</i> -CO ₂ Me | 1.74 | 3.95 | 8.35 | 18.0 | 56.5 ± 0.5 | -121 ± 2 | 92.4 ± 0.4 |
| <i>p</i> -NHAc | 33.5 | 57.7 | 100 | 190 | 41.2 ± 1.4 | -150 ± 5 | 85.7 ± 1.1 |
| <i>p</i> -NH ₂ | 375 | 529 | 868 | 1330 | 30.1 ± 1.4 | -168 ± 5 | 80.1 ± 1.0 |
| <i>m</i> -Me | 12.4 | 24.3 | 46.0 | 94.5 | 48.7 ± 1.2 | -132 ± 4 | 87.9 ± 0.9 |
| <i>m</i> -OMe | 10.1 | 20.4 | 40.0 | 82.4 | 50.5 ± 0.9 | -127 ± 3 | 88.3 ± 0.7 |
| <i>m</i> -Cl | 2.07 | 4.67 | 9.99 | 21.8 | 57.0 ± 0.6 | -118 ± 2 | 92.0 ± 0.5 |
| <i>m</i> -Br | 2.03 | 4.62 | 9.90 | 21.6 | 57.3 ± 0.6 | -117 ± 2 | 92.0 ± 0.5 |
| <i>m</i> -I | 2.61 | 5.81 | 12.3 | 26.4 | 56.0 ± 0.5 | -119 ± 2 | 91.5 ± 0.4 |
| <i>m</i> -NO ₂ | 0.34 | 0.85 | 2.14 | 4.95 | 65.7 ± 0.5 | -103 ± 3 | 96.2 ± 0.4 |
| <i>m</i> -CO ₂ Me | 1.50 | 3.38 | 7.41 | 16.1 | 57.6 ± 0.5 | -118 ± 2 | 92.8 ± 0.4 |
| <i>o</i> -Me | 3.83 | 7.87 | 16.4 | 35.3 | 53.7 ± 1.2 | -124 ± 4 | 90.6 ± 0.9 |
| <i>o</i> -OMe | 12.6 | 24.8 | 47.1 | 95.0 | 48.5 ± 0.9 | -133 ± 3 | 87.8 ± 0.8 |
| <i>o</i> -NO ₂ | 0.19 | 0.47 | 1.13 | 2.64 | 63.9 ± 0.4 | -114 ± 1 | 97.7 ± 0.3 |
| <i>o</i> -CO ₂ Me | 0.45 | 1.06 | 2.44 | 5.66 | 61.6 ± 0.8 | -115 ± 3 | 95.6 ± 0.6 |
| <i>o</i> -NH ₂ | 58.4 | 107 | 186 | 355 | 42.9 ± 1.0 | -139 ± 4 | 84.2 ± 0.9 |
| <i>o</i> -Cl | 1.00 | 2.25 | 5.15 | 11.1 | 58.7 ± 0.6 | -118 ± 2 | 93.7 ± 0.4 |
| <i>o</i> -Br | 0.76 | 1.74 | 4.00 | 9.00 | 60.2 ± 0.7 | -115 ± 2 | 94.4 ± 0.6 |
| <i>o</i> -I | 0.64 | 1.48 | 3.45 | 7.80 | 61.0 ± 0.7 | -114 ± 2 | 94.8 ± 0.6 |
| <i>o</i> -CN | 0.26 | 0.64 | 1.52 | 3.61 | 64.1 ± 0.7 | -111 ± 2 | 96.9 ± 0.5 |
| (ii) Alkyl phenyl sulfides | | | | | | | |
| Et | 12.6 | 23.8 | 44.7 | 88.0 | 47.8 ± 0.7 | -135 ± 3 | 88.0 ± 0.6 |
| Pr | 7.26 | 14.8 | 30.4 | 61.0 | 51.5 ± 0.6 | -127 ± 2 | 89.1 ± 0.5 |
| <i>i</i> -Pr | 9.42 | 18.8 | 38.9 | 77.5 | 51.1 ± 0.8 | -126 ± 3 | 88.5 ± 0.6 |
| <i>t</i> -Bu | 2.37 | 4.95 | 11.0 | 24.2 | 56.6 ± 1.3 | -119 ± 4 | 91.8 ± 1.0 |
| (iii) Other sulfides | | | | | | | |
| Me ₂ S | 17.9 | 35.2 | 69.8 | 135 | 48.8 ± 0.6 | -128 ± 2 | 87.0 ± 0.5 |
| Pr ₂ S | 27.4 | 52.0 | 96.2 | 175 | 44.5 ± 0.3 | -140 ± 1 | 86.0 ± 0.2 |
| Ph ₂ S | 3.28 | 6.62 | 13.2 | 25.7 | 49.7 ± 0.4 | -139 ± 1 | 91.1 ± 0.3 |

unchanged. This confirmed that HABR retained its integrity in acetic acid.

A perusal of the spectra of HABR and of HABR + methyl phenyl sulfide showed that there is a distinct change in the absorption spectra of HABR on the addition of methyl phenyl sulfide (Fig. 2). Further, the value of the absorbance decreases with time. This supports the postulation of the formation of an intermediate complex in a pre-equilibrium, which decomposes to give products.

Induced polymerization of acrylonitrile

The oxidation of methyl phenyl sulfide, in an atmosphere of nitrogen, failed to induce the polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on the rate of oxidation (Table 1).

Effect of hexamethylenetetramine

Addition of HXA had no effect on the rate of oxidation (Table 1).

Effect of bromide ion

The rate of oxidation of sulfide was not affected by the addition of added sodium bromide (Table 1).

Oxidation by bromine

The oxidation of methyl phenyl sulfide by bromine was studied for the purpose of comparison. It was found that the oxidation by bromine, under similar conditions, was much slower than the oxidation by HABR. Further, the

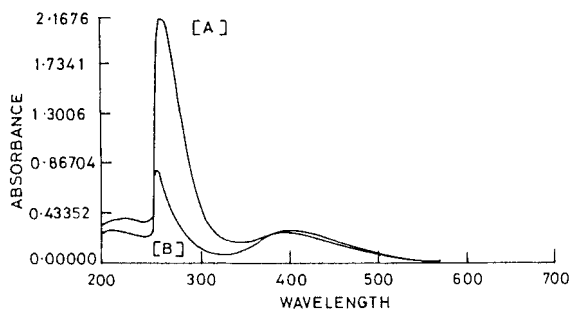


Figure 1. UV-VIS spectra of (A) 0.001 mol dm⁻³ HABR and (B) 0.002 mol dm⁻³ bromine; Temperature, 293 K; solvent, acetic acid

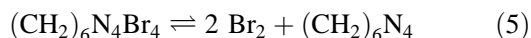
rate of oxidation by bromine is increased by the addition of bromide ion (Table 4).

To check the possibility of protonation of the amino group in the *p*- and *o*-aminophenyl methyl sulfides, we carried out some conductivity measurements. We found that the addition of the amino compounds to glacial acetic acid did not result in a noticeable increase in the conductivity of the solution. Hence a protonation of the amino group to yield an ammonium ion is unlikely.

DISCUSSION

A plot of $\log k_2$ at 288 K is linearly related to $\log k_2$ at 318 K (slope = 0.8236 ± 0.0065 ; $r^2 = 0.9990$). The value of the isokinetic temperature is 620 ± 26 K.⁴ A linear isokinetic relationship implies that all the compounds so correlated react by the same mechanism.⁴ Further, the linear relationship is also a necessary condition for the validity of linear free energy relationships.

In solutions, HABR may dissociate to form molecular bromine and HXA. HXA ($pK_A \approx 6.3$) is likely to undergo extensive protonation in acetic acid, thus resulting in a large shifting of the equilibrium (5) to the right:



The lack of any effect of added HXA or bromide ion on the rate of oxidation indicates that either the above equilibrium does not exist in acetic acid and HABR remains undissociated or the equilibrium lies far towards right and HABR acts as a source of bromine. The comparison of the rates of oxidation of the sulfide by HABR and bromine, under similar conditions, and studies of the effect of the added bromide ion on the rate, in the two reactions, rules out the latter possibility (cf. Tables 1 and 4). Therefore, it is concluded that equilibrium (5) does not exist under the reaction conditions. The spectral evidence and the isolation of unchanged HABR confirm that HABR retains its integrity in glacial acetic acid. Therefore, it is proposed that the reactive oxidizing species is HABR itself.

Table 4. Rate constants for the oxidation of methyl phenyl sulfide by bromine at 298 K

| [MeSPh] (mol dm ⁻³) | 10 ³ [Br ₂] (mol dm ⁻³) | 10 ⁵ <i>k</i> _{obs} (s ⁻¹) |
|------------------------------------|---|---|
| 0.01 | 1.0 | 1.25 |
| 0.02 | 1.0 | 2.33 |
| 0.03 | 1.0 | 3.25 |
| 0.05 | 1.0 | 4.91 |
| 0.10 | 1.0 | 7.55 |
| 0.15 | 1.0 | 9.15 |
| 0.20 | 1.0 | 10.6 |
| 0.20 | 2.0 | 11.0 |
| 0.20 | 4.0 | 9.91 |
| 0.20 | 6.0 | 9.82 |
| 0.20 | 8.0 | 10.7 |
| 0.20 | 1.0 | 16.7 ^a |
| 0.20 | 1.0 | 28.9 ^a |
| 0.20 | 1.0 | 78.0 ^c |

^a Contains 0.005 mol dm⁻³ sodium bromide.

^b Contains 0.01 mol dm⁻³ sodium bromide.

^c Contains 0.05 mol dm⁻³ sodium bromide.

Correlation analysis of reactivity

The rate constants for the oxidation of the *meta*- and *para*-compounds were correlated in terms of the Hammett⁵ equation [Eqn. (6)] but no significant correlation was obtained. We used the standard deviation (sd), the coefficient of determination (R^2 or r^2), Taft's parameter⁶ f and Exner's parameter⁷ Ψ as measures of the goodness of fit.

$$\log k_2 = -1.93 \pm 0.11\sigma - 2.58 \quad (6)$$

$$r^2 = 0.9483; \text{sd} = 0.16; n = 18; \Psi = 0.17; T = 298 \text{ K}$$

The main deviating points correspond to *para*-substituents capable of electron donation by resonance, viz. methoxy, amino and acetyl amino. Their rates are higher than those required by their Hammett σ values. This indicates that in the transition state of the reaction, there is an electron-deficient center which is stabilized by cross-conjugation with the electron-donating substituents at the *para*-position. The rate constants of *meta*- and *para*-compounds were then correlated with Brown σ^+ values⁸ to account for the cross-conjugation, but the correlation was not very good (Fig. 3).

$$\log k_2 = -1.28 \pm 0.07\sigma^+ - 3.84 \quad (7)$$

$$r^2 = 0.9608; \text{sd} = 0.14; n = 18; \Psi = 0.15; T = 298 \text{ K}$$

It has been stated⁹ that in the absence of proximity effects, the polar effects of *ortho*-substituents ought to be parallel to those of *para*-substituents. However, in the present case it was found that the rate constants of the

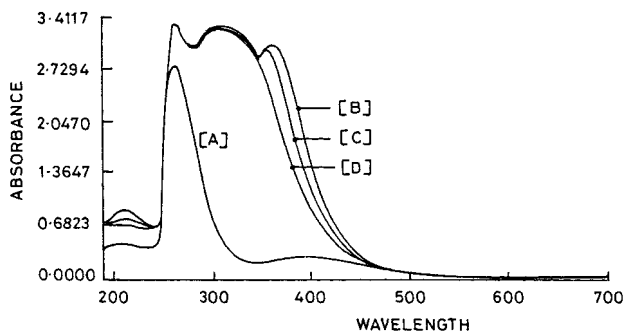


Figure 2. UV-VIS spectra of (A) $0.001 \text{ mol dm}^{-3}$ HABR; (B), (C) and (D) $0.001 \text{ mol dm}^{-3}$ HABR + 0.1 mol dm^{-3} MeSPh at 40 s, 15 min and 30 min, respectively. Temperature, 298 K; solvent, acetic acid

ortho- and *para*-substituted compounds are not linearly related. This indicated that only polar effects are not responsible for the observed effect of the *ortho*-substituents on the reaction.

$$\log k_{para} = 0.99 \pm 0.14 \log k_{ortho} - 4.40 \quad (8)$$

$$r^2 = 0.8899; \text{ sd} = 0.30; n = 8; \Psi = 0.25; T = 298 \text{ K}$$

The rate constants of the *ortho*-compounds were analysed in terms of *ortho*-substituent constant values, σ_o , of Tribble and Traynham¹⁰ also, but the correlation was not satisfactory. The unsatisfactory correlation and the fact that the value of k_2 for an *ortho*-substituted

phenyl methyl sulfide is always less than that of the corresponding *para*-compound indicate that there is a significant steric effect of the *ortho*-substituents in this reaction.

$$\log k_{ortho} = -1.05 \pm 0.10 \sigma_o - 4.93 \quad (9)$$

$$r^2 = 0.9456; \text{ sd} = 0.14; n = 8; \Psi = 0.18; T = 298 \text{ K}$$

The data for *o*-NO₂ were not included in this correlation since the σ_o value was not available.

Since the rate constants failed to yield a satisfactory correlation with any single substituent-parameter equation, the rates were analysed in terms of multiparametric equations. The rate constants for the *para*- and *meta*-substituted phenyl methyl sulfides were analysed in terms of Taft's dual substituent-parameter (DSP) equation.¹¹ In Taft's equation, $\log(k/k_0)$ were correlated with Taft's σ_1 and four different σ_R scales separately. In this set of correlation analysis, the intercept was forced through zero. The results, presented in Table 5, showed that the *meta*-substituted compounds showed a satisfactory correlation with σ_R^0 and σ_R^{BA} scales. However, the correlation for *para*-substituted compounds was poor with Taft's DSP equation. The poor correlation in the case of *para*-substituted compounds may well be due to the high sensitivity of the reaction towards the effect of substituent on the electronic demand of the active site through delocalization.

The rate constants, k_2 , were therefore analysed in terms of LDR Eqn. ((10)), introduced by Charton and Charton¹²

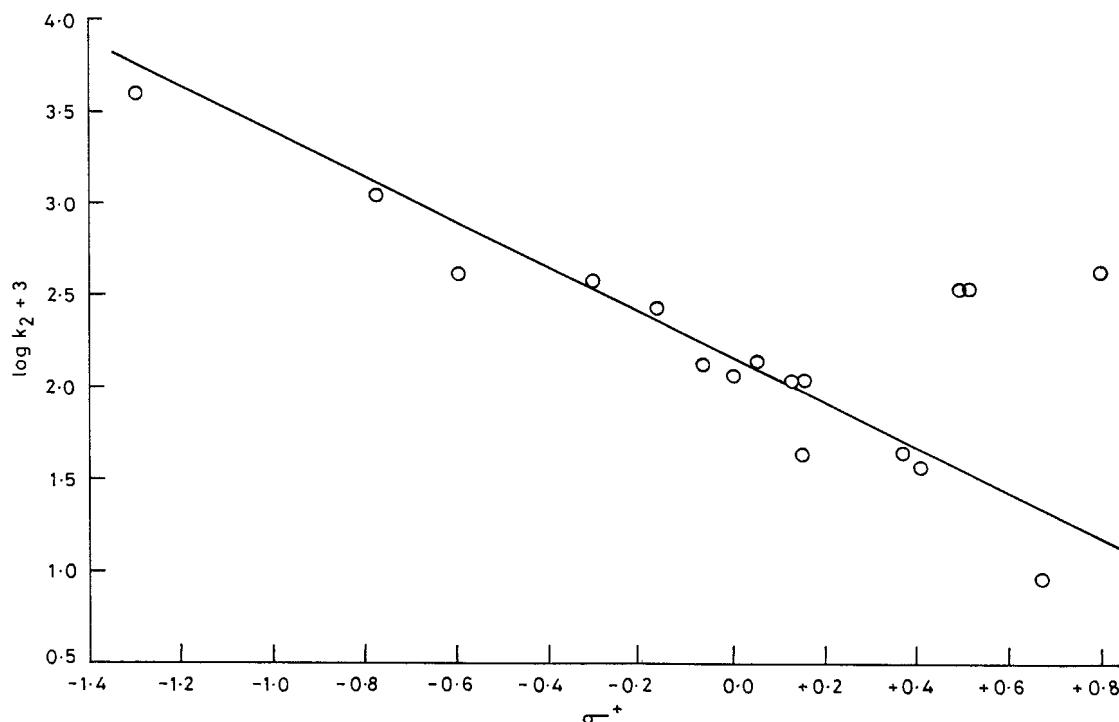


Figure 3. Plot of $\log k_2$ at 298 K vs Brown's σ^+ values

Table 5. Correlation analysis of the rates of oxidation of *meta*- and *para*-substituted organic sulfides by HABR with Taft's dual-substituent parameters at 298 K^a

| Substituent constants | ρ_I | ρ_R | R^2 | sd | f | n |
|---------------------------|------------------|------------------|--------|------|------|-----------------|
| <i>para</i> -Substituted | | | | | | |
| σ_I, σ_R^0 | -0.74 ± 0.45 | -2.76 ± 0.74 | 0.5941 | 0.51 | 0.36 | 11 |
| σ_I, σ_R^{BA} | -0.75 ± 0.48 | -2.14 ± 0.63 | 0.5503 | 0.53 | 0.37 | 11 |
| σ_I, σ_R^- | -0.16 ± 0.45 | -1.66 ± 0.53 | 0.5505 | 0.55 | 0.39 | 10 ^b |
| σ_I, σ_R^+ | -0.21 ± 0.35 | -1.13 ± 0.28 | 0.2535 | 0.38 | 0.59 | 11 |
| <i>meta</i> -Substituted | | | | | | |
| σ_I, σ_R^0 | -1.61 ± 0.03 | -1.25 ± 0.05 | 0.9972 | 0.03 | 0.04 | 8 |
| σ_I, σ_R^{BA} | -1.61 ± 0.04 | -1.02 ± 0.05 | 0.9947 | 0.04 | 0.05 | 8 |
| σ_I, σ_R^- | -1.32 ± 0.07 | -0.86 ± 0.10 | 0.9780 | 0.08 | 0.10 | 8 |
| σ_I, σ_R^+ | -1.64 ± 0.07 | -0.64 ± 0.06 | 0.9823 | 0.07 | 0.09 | 8 |

^a sd = standard deviation; $f = \text{sd}/[\text{root mean square of } \log(k/k_0)]$; R^2 = coefficient of multiple determination; n = number of data points; σ_I and σ_R values are from ref.¹¹

^b Data for NHAc were not included; σ_R^- value is not available.

in the 1980s for the quantitative description of structural effects on chemical reactivities. This equation has the advantage of not requiring a choice of parameters as the same three substituent constants are reported to cover the entire range of electrical effects of substituents.

$$\log k_2 = L\sigma_1 + D\sigma_d + R\sigma_e + h \quad (10)$$

where h is the intercept term, σ_1 is the localized (field and/or inductive) effect parameter, σ_d is the intrinsic delocalized (resonance) electrical effect parameter when the active site electronic demand is minimal and σ_e represents the sensitivity of the substituent to change in electronic demand by the active site. The last two substituent parameters are related by the equation,

$$\sigma_D = \eta\sigma_e + \sigma_d \quad (11)$$

where η represents the electronic demand of the reaction site, which is given by $\eta = R/D$, and σ_D represents the delocalized electrical parameter of the diparametric LD equation.

For *ortho*-substituted compounds, it is necessary to account for the possibility of steric effects and, therefore, the LDR equation was modified to LDRS Eqn. (12),¹² where V is the well known Charton's steric parameter based on van der Waals radii.¹³

$$\log k_2 = L\sigma_1 + D\sigma_d + R\sigma_e + SV + h \quad (12)$$

The rates of oxidation of the *ortho*-, *meta*- and *para*-substituted phenyl methyl sulfides showed excellent correlations with the LDR/LDRS equations (Table 6).

The comparison of the L and D values for the substituted sulfides showed that the oxidation of *para*- and *ortho*-substituted sulfides is more susceptible to the delocalization effect than to the localized effect. However, the oxidation of *meta*-substituted compounds exhibited a greater dependence on the field effect. In all

cases, the magnitude of the reaction constants decreases with increase in temperature, pointing to a decrease in selectivity with an increase in temperature.

All three regression coefficients, L , D and R , are negative, indicating an electron-deficient sulfur center in the transition state of the reaction. The positive value of η adds a negative increment to σ_d , increasing the donor effect of the substituent when σ_d is negative and decreasing the acceptor effect when σ_d is positive. The substituent is, therefore, better able to stabilize a cationic reaction site. This also supports the presence of an electron-deficient centre in the transition state of the rate-determining step. The large magnitude of η , which represents the electronic demand of the reaction, indicates a pronounced charge separation in the transition state and supports a mechanism involving formation of a halosulfonium ion in the rate-determining step.

The negative value of S indicates that the reaction is subjected to steric hindrance by the *ortho*-substituent. This may be due to steric hindrance of the *ortho*-substituent to the approach of the oxidizing species.

We evaluated the significance level for all the three/four independent variables by determining Student's t function for each coefficient.¹⁴ The significance level was found to be >99.9%. Hence all the parameters are required to explain the effect of structure on the reactivity in the oxidation of sulfides by HABR. There is no significant collinearity between the various substituent constants in all the three series.

The percentage contribution¹² of the delocalized effect, P_D , is given by the following equation:

$$P_D = \frac{|D| \times 100}{|L| + |D|} \quad (13)$$

Similarly, the percentage contribution of the steric parameter¹² to the total effect of the substituent, P_S ,

Table 6. Temperature dependence of the reaction constants for the oxidation of organic sulfides by HABR

| <i>T</i> (K) | <i>L</i> | <i>D</i> | <i>R</i> | <i>S</i> | η | R^2 | sd | ψ | P_D | P_S |
|---------------------------|----------------|----------------|----------------|----------------|--------|--------|------|--------|-------|-------|
| <i>para</i> -Substituted | | | | | | | | | | |
| 288 | -1.50 ±0.02 | -2.30 ±0.01 | -3.18 ±0.08 | — | 1.38 | 0.9998 | 0.01 | 0.02 | 60.5 | — |
| 298 | -1.41 ±0.02 | -2.09 ±0.01 | -3.01 ±0.09 | — | 1.44 | 0.9997 | 0.01 | 0.02 | 59.7 | — |
| 308 | -1.33 ±0.01 | -1.96 ±0.01 | -2.80 ±0.08 | — | 1.43 | 0.9999 | 0.01 | 0.01 | 59.6 | — |
| 318 | -1.28 ±0.02 | -1.84 ±0.01 | -2.53 ±0.08 | — | 1.38 | 0.9997 | 0.01 | 0.02 | 59.0 | — |
| <i>meta</i> -Substituted | | | | | | | | | | |
| 288 | -1.87 ±0.02 | -1.11 ±0.02 | -1.43 ±0.16 | — | 1.29 | 0.9997 | 0.01 | 0.02 | 37.2 | — |
| 298 | -1.72 ±0.02 | -1.05 ±0.02 | -1.29 ±0.14 | — | 1.23 | 0.9997 | 0.01 | 0.02 | 37.9 | — |
| 308 | -1.59 ±0.02 | -0.97 ±0.02 | -1.27 ±0.17 | — | 1.31 | 0.9996 | 0.01 | 0.02 | 37.9 | — |
| 318 | -1.52 ±0.03 | -0.94 ±0.02 | -1.23 ±0.20 | — | 1.31 | 0.9994 | 0.01 | 0.02 | 38.2 | — |
| <i>ortho</i> -Substituted | | | | | | | | | | |
| 288 | -1.57 ±0.02 | -1.80 ±0.02 | -2.78 ±0.12 | -1.20 ±0.02 | 1.54 | 0.9998 | 0.01 | 0.01 | 53.4 | 26.2 |
| 298 | -1.47 ±0.02 | -1.71 ±0.02 | -2.67 ±0.12 | -1.14 ±0.02 | 1.56 | 0.9998 | 0.01 | 0.01 | 53.4 | 26.4 |
| 308 | -1.38 ±0.03 | -1.61 ±0.02 | -2.37 ±0.14 | -1.05 ±0.03 | 1.47 | 0.9997 | 0.01 | 0.01 | 53.8 | 26.0 |
| 318 | -1.34 | -1.53 | -2.35 | -0.99 | 1.54 | 0.9998 | 0.01 | 0.01 | 53.3 | 25.6 |

was determined by using the equation

$$P_S = \frac{|S| \times 100}{|L| + |D| + |S|} \quad (14)$$

The values of P_D and P_S are also recorded in Table 6. The values of P_D for the oxidation of *para*- and *ortho*-substituted phenyl methyl sulfides are ca 60% and 53% respectively, whereas its value for the *meta*-substituted sulfides is ca 38%. The value of P_S shows that there is considerable steric effect on the reaction. The less pronounced resonance effect from the *ortho*-position than from the *para*-position may be due to the twisting away of the methyl sulfide group from the plane of the benzene ring.

The rates of oxidation of alkyl phenyl sulfides did not yield any significant correlation separately with Taft's σ^*

Table 7. Correlation of rate of oxidation of alkyl phenyl sulfides by HABR in terms of the Pavelich–Taft equation^a

| Temperature (K) | ρ^* | δ | R^2 | sd |
|-----------------|--------------|-------------|--------|------|
| 288 | -2.73 ± 0.09 | 0.85 ± 0.02 | 0.9996 | 0.01 |
| 298 | -2.64 ± 0.08 | 0.82 ± 0.01 | 0.9997 | 0.01 |
| 308 | -2.54 ± 0.12 | 0.77 ± 0.02 | 0.9991 | 0.01 |
| 318 | -2.34 ± 0.10 | 0.70 ± 0.02 | 0.9993 | 0.01 |

^a No. of data points = 5.

or E_s values. The rates were therefore analysed in terms of Pavelich and Taft's¹⁵ dual substituent-parameter (DSP) equation:

$$\log k_2 = \rho^* \sigma^* + \delta E_s + \log k_0 \quad (15)$$

The correlations are excellent (Table 7). Although the number of compounds is small (five) for an analysis by a DSP equation, the results can be used qualitatively. The negative polar reaction constant confirms that the electron-donating power of the alkyl group enhances the reaction rate. The steric effect plays a minor inhibitory role.

Mechanism

The absence of any effect of the radical scavenger on the reaction rate and the failure to induce polymerization of acrylonitrile point against a one-electron oxidation giving rise to free radicals.

In earlier studies, oxidation of sulfides involving a direct oxygen transfer via an electrophilic attack on the sulfide-sulfur exhibited relatively low negative reaction constants, e.g. by hydrogen peroxide (-1.13),¹⁶ permanganate (-1.52)¹⁷ and peroxydisulfate (-0.52).¹⁸ Large negative reaction constants were exhibited by oxidations involving the formation of a halosulfonium cation, e.g. by chloramine-T (-4.25),¹⁹ bromine (-3.2)²⁰ and *N*-

Table 8. Reaction constants of the oxidation of sulfides in terms of Charton's LDR/LDRS equations at 298 K

| Oxidant | <i>L</i> | <i>D</i> | <i>R</i> | η | <i>S</i> | Ref. |
|---------------------------|----------|----------|----------|--------|----------|-----------|
| <i>para</i> -Substituted | | | | | | |
| PHPB | -1.43 | -2.11 | -2.89 | 1.37 | — | 23 |
| BTMAB | -1.40 | -2.09 | -2.85 | 1.36 | — | 24 |
| BBCP ^a | -1.37 | -1.53 | -1.41 | 0.92 | — | 25 |
| HABR | -1.41 | -2.09 | -3.01 | 1.44 | — | This work |
| <i>meta</i> -Substituted | | | | | | |
| PHPB | -1.72 | -0.99 | -0.95 | 0.96 | — | 23 |
| BTMAB | -1.68 | -1.01 | -1.03 | 1.02 | — | 24 |
| BBCP ^a | -1.76 | -1.35 | -1.12 | 0.83 | — | 25 |
| HABR | -1.72 | -1.05 | -1.29 | 1.23 | — | This work |
| <i>ortho</i> -Substituted | | | | | | |
| PHPB | -1.46 | -1.66 | -2.25 | 1.36 | -1.13 | 23 |
| BTMAB | -1.42 | -1.72 | -2.10 | 1.22 | -1.15 | 24 |
| BBCP ^a | -1.41 | -1.51 | -1.45 | 0.96 | -1.12 | 25 |
| HABR | -1.47 | -1.71 | -2.67 | 1.56 | -1.14 | This work |

^a Data at 293 K.

bromoacetamide (-3.75).²¹ In the oxidation by *N*-chloroacetamide,²² the values of field (ρ_I) and resonance (ρ_R^+) reaction constants, at 298 K, are -1.3 and -1.7 respectively. We applied the LDR/LDRS equations in the oxidation of sulfides by pyridinium hydrobromide perbromide (PHPB),²³ benzyltrimethylammonium tribromide (BTMAB)²⁴ and bis (2,2'-bipyridyl)copper(II) permanganate (BBCP).²⁵ The polar constants were negative in all the three cases (Table 8). However, the magnitudes of *D* and *R*, in the oxidation of *ortho*- and *para*-benzaldehydes by BBCP, are much smaller than the values obtained in the present study. The value of η also is lower. In the oxidation of *meta*-compounds all the reaction constants in these reactions have comparable values. This may be because of the lower importance of the delocalization effect from the *meta*-position. The oxidation by BBCP was proposed to involve a direct oxygen transfer. In the oxidation by PHPB and BTMAB, where the formation of a halosulfonium cation has been proposed, the magnitude of the three polar reaction constants and η are comparable to the values obtained in the oxidation by HABR. Hence the formation of a similar intermediate, in the rate-determining step, of the present reaction is indicated.

The formation of an intermediate complex between the sulfide and HABR, in a pre-equilibrium, is confirmed by the observed kinetics, values of the thermodynamic parameters (Tables 1 and 2) and spectral studies. With the present data, nothing can be stated about the nature of the complex. However, the intermediate complex may be formed by an interaction between the non-bonded pairs of electrons of sulfur and HABR. The formation of similar complexes has been postulated in the oxidation of alcohols² and aldehydes³ by HABR involving non-bonded pairs of electrons on oxygen atoms. The negative values of *L*, *D* and *R* support an electron-deficient sulfur centre in the transition state. Further, an electrophilic

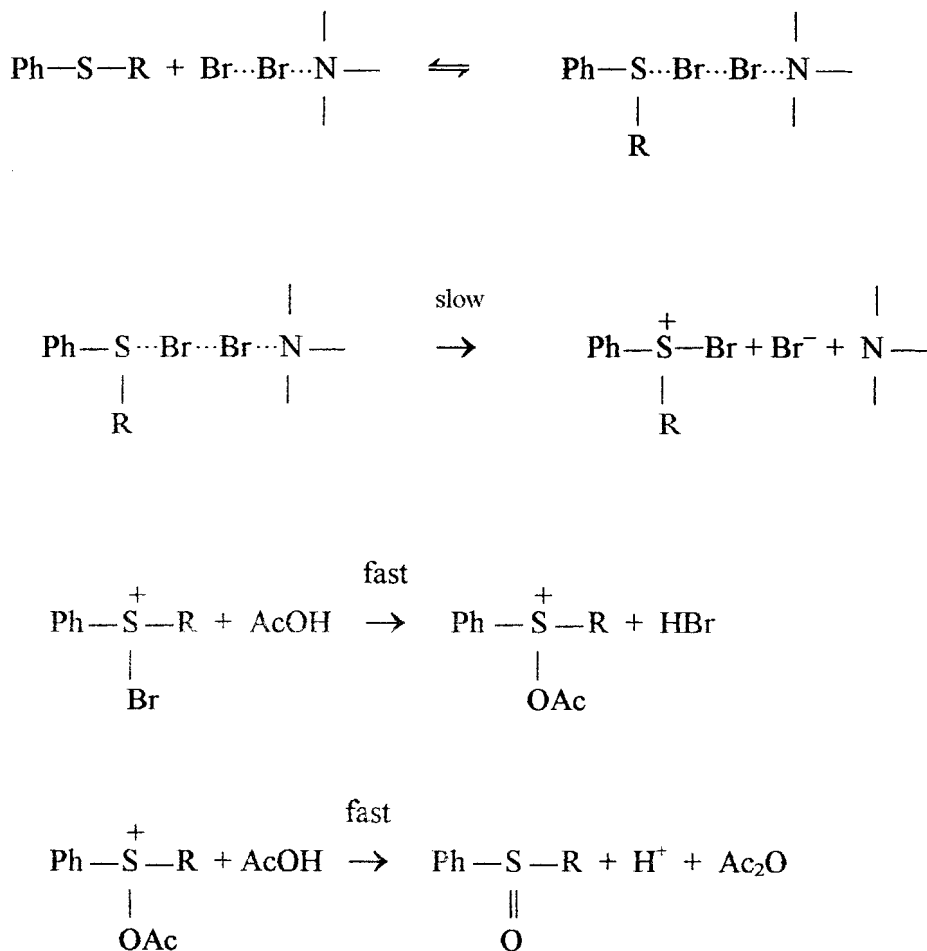
attack on the sulfide-sulfur is confirmed by the positive value of η , which indicates that the substituent is better able to stabilize a cationic or electron-deficient site. The large magnitude of η , which represents the electronic demand of the reaction, indicates a pronounced charge separation in the transition state and supports a mechanism involving formation of a halosulfonium ion in the rate-determining step (Scheme 1).

The observed negative entropy of activation supports the proposed mechanism. As the charge separation takes place in the transition state of the rate-determining step, the charged ends become highly solvated. This results in an immobilization of a large number of solvent molecules, reflected in a loss of entropy.

EXPERIMENTAL

Materials. The preparation, purification and specification of the sulfides have been described previously.²⁴ HABR was prepared by the reported method¹ and its purity was checked by an iodometric method and melting point determination. Contrary to the earlier report,¹ we found that, in acetic acid solution, the active bromine content of this complex is 2 mol per mole of the reagent. Acetic acid was refluxed with CrO₃ and acetic anhydride for 3 h and then fractionated.

Product analysis. Methyl phenyl sulfide (0.01 mol) and HABR (0.01 mol) were dissolved in glacial acetic acid (50 ml) and the mixture was allowed to stand for approximately 20 h. Most of the solvent was removed under reduced pressure. The residue was diluted with water and extracted with chloroform (3 × 50 ml). The chloroform layer was dried over anhydrous MgSO₄, the solvent was removed by evaporation and the residue was analysed by IR and ¹H NMR spectroscopy. The spectra



Scheme 1

were identical with those of MeSOPh. Peaks characteristic of MeSPh and MeSO₂Ph could not be detected. Similar experiments were performed with other aryl methyl sulfides also. In all cases, the products were the corresponding sulfoxides only.

Kinetic measurements. The reactions were studied under pseudo-first-order conditions by keeping an excess ($\times 20$ or greater) of the sulfide over HABR. The solvent was glacial acetic acid. The reactions were studied at constant temperature (± 0.1 K) and were followed by monitoring the decrease in the [HABR + complex] spectrophotometrically at 380 nm for up to 80% reaction. Beer's law was found to be valid within the concentration range used in our experiments. Pseudo-first-order rate constants, k_{obs} , were evaluated from linear plots ($r^2 > 0.995$) of \log [HABR + complex] against time. Duplicate kinetic runs showed that the rates were reproducible to within $\pm 3\%$.

Spectral analysis. UV-VIS spectra of HABR, hexamethylenetetramine (HXA) and bromine were obtained on a Hewlett-Packard diode-array rapid scanning spectrophotometer (Model 8452A) with a scanning speed of

600 nm s⁻¹. The solvent was glacial acetic acid and temperature was ~ 293 K.

UV-VIS spectra of (A) HABR (0.001 mol dm⁻³) alone and (B) of methyl phenyl sulfide (0.1 mol dm⁻³) + HABR (0.001 mol dm⁻³), at three different intervals of time, were recorded at room temperature (~ 298 K). The solvent was glacial acetic acid. For (A), the blank was the solvent and for (B) the blank was a solution of sulfide (0.1 mol dm⁻³) in acetic acid. The time gap between the preparation of (B) and the recording of the spectrum was < 10 s.

Acknowledgement

Thanks are due to the Council of Scientific and Industrial Research (India) for the financial support.

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