J. Chem. Research (S),
1999, 2–3
J. Chem. Research (M),
1999, 0219–0231

Studies on the Oxidation of some Sulfides with Pyridinium Dichromate in Acetonitrile medium

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The kinetic behaviours of oxidation of dialkyl, alkyl aryl and diphenyl sulfides are quite different with pyridinium dichromate in acetonitrile medium; studies indicate the involvement of a sulfur cation free radical intermediate in diphenyl sulfide oxidation; electron releasing and withdrawing groups retard the reactivity of aryl methyl sulfides; the observed non-linear concave downwards type Hammett plot is well explained by assuming shifts in the rate-limiting step within the same overall reaction pathway.

Chromium compounds play an important role in oxidative reactions. Pyridinium dichromate (PDC) is reported to be a neutral and mild oxidant for selective oxidation.[1] Not many reports on the kinetics of oxidation by PDC are available. The present paper deals with the kinetics and mechanism of oxidation of diethyl, diphenyl and nine *meta*- and *para*-substituted phenyl methyl sulfides with PDC in acetonitrile medium. The significance of reaction constants ρ_+ and ρ_- obtained from non-linear Hammett plots is discussed.

Pseudo-first-order conditions were maintained by keeping a large excess of sulfide over PDC. Reactions were followed by monitoring the decrease in absorption of PDC at 350 nm. Stoichiometric studies reveal that one mole of the oxidant is consumed by three moles of sulfide. Under the present experimental conditions oxidation takes place only up to sulfoxide stage. Product analysis indicates the negligible presence of sulfone in the reaction mixture.

Initial-rate methods were used to determine the order with respect to reactants in the oxidation of diethyl sulfide. Second-order dependence on *p*-toluenesulfonic acid (TsOH) and first-order each on substrate [S] and [oxidant] is observed.

$$k_{\mathrm{obs}} = k'[\mathrm{S}][\mathrm{TsOH}]^2$$

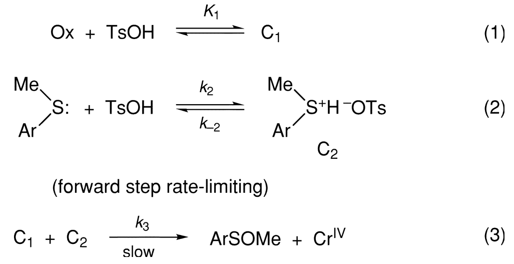
Acrylonitrile significantly retards the rate of diphenyl sulfide oxidation. Electron transfer from sulfur to $\mathrm{Cr^{VI}}$ resulting in a free radical intermediate is assumed to be the slow rate-limiting step. Sulfur cation free radicals have been suggested by various authors[3,4,6] in the oxidation of sulfides and sulfoxides.

$$k_{\mathrm{obs}} = \frac{k_2 k_1[\mathrm{S}][\mathrm{TsOH}]}{k_{-1} + k_2[\mathrm{S}]}$$

The derived rate law is in agreement with fractional order dependence on [S], and is first-order for both [oxidant] and [TsOH].

Detailed kinetic investigations have been carried out for aryl methyl sulfide oxidation with PDC. A plot of $1/k$ *versus* $1/[\mathrm{S}]$ shows an intercept on the y-axis indicating Michaelis–Menten dependence on [sulfide]. Same fractional order dependence on [sulfide] is observed for *p*-methoxy and *p*-nitrophenyl methyl sulfides. There was no significant oxidation in the absence of TsOH. The order dependence on [TsOH] is >1 and <2 throughout the entire range of acidities studied.

Interestingly the rates of *meta*- and *para*-substituted phenyl methyl sulfides are lower than for the parent (Table 4). The non-linear concave downwards type Hammett plot (Fig. 4) obtained is a composite of two straight lines, one with positive ρ value and the other with negative ρ value. A ρ_- value indicates that the nucleophilic sulfur atom is more positively charged in the transition state than in the reactant, while a ρ_+ value indicates dispersal of the positive charge. These results can be explained by invoking a mechanism having a shift in the rate-limiting step within the same overall reaction pathway (Scheme 1).



Scheme 1

Step (2) is slow and rate-limiting for electron-withdrawing groups and step (3) slow for electron-releasing groups. The linear relation between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ suggests the operation

Table 4 Rate constants and activation parameters for the oxidation of aryl methyl sulfides; $[\mathrm{PDC}] = 3.08 \times 10^{-4}$ mol dm^{-3}, $[\mathrm{S}] = 7.95 \times 10^{-3}$ mol dm^{-3}

		$10^2 k'^{a}$					
No.	Sulfide	20 °C	35 °C	45 °C	$\Delta H^\ddagger$/kJ mol^{-1}	$-\Delta S^\ddagger$/J K^{-1} mol^{-1}	$\Delta G^\ddagger$/kJ mol^{-1}
1	MPS	2.31	8.21	16.11	57.48	79.91	82.09
2	*p*-Br	1.86	7.45	15.99	64.03	59.41	82.33
3	*m*-Me	1.71	5.52	14.95	63.86	61.22	82.72
4	*m*-Cl	1.00	5.03	11.90	74.34	29.37	83.39
5	*p*-Me	1.48	6.27	15.31	69.69	42.18	82.68
6	*p*-Cl	1.68	7.01	14.69	64.80	57.60	82.54
7	*p*-OMe	0.87	4.42	11.21	76.69	22.60	83.65
8	*p*-NO_2	0.75	1.89	4.13	49.70	116.30	85.52
9	*m*-NO_2	0.81	3.95	4.95	55.16	95.74	84.65

[a] $k' = k_1/[\mathrm{S}]^n$ where n is the order wrt sulfide.

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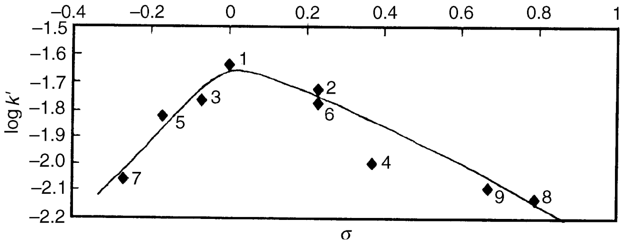

Fig. 4 Representative Hammett plot at 20 °C (for numbering see Table 4)

of a similar mechanism in all the aryl methyl sulfides;[14] $\Delta G^{\ddagger}$ values are nearly constant further confirming the above view.

Techniques used: IR, UV–VIS spectrophotometry, TLC

References: 19

Table 1: Dependence of reaction rate on acidity in the oxidation of diethyl sulfide

Table 2: Effect of acrylonitrile on the reaction rate in the oxidation of diphenyl sulfide

Table 3: Effect of [sulfide] and [TsOH] on the reaction rate in the oxidation of aryl methyl sulfide

Fig. 1: Dependence of [TsOH] on the diphenyl sulfide oxidation rate

Fig. 2: Michaelis–Menten plot for the oxidation of diphenyl sulfides

Fig. 3: Fractional order dependence on substituted phenyl methyl sulfides

Received, 15th July 1998; Accepted, 6th October 1998
Paper E/8/04504F

References cited in this synopsis

1 E. J. Corey and G. Schmidt, *Tetrahedron Lett.*, 1979, **5**, 399.
3 (*a*) K. B. Wiberg, *Oxidations in Organic Chemistry*, ed. K. B. Wiberg, Academic, New York, 1965; (*b*) K. B. Wiberg and P. A. Lepse, *J. Am. Chem. Soc.*, 1964, **86**, 2612.
4 C. Srinivasan, S. Rajagopal and A. Chellamani, *J. Chem. Soc., Perkin Trans. 2*, 1990, **2**, 1839.
6 V. Balaiah and P. V. V. Satyanarayana, *Indian J. Chem.*, 1978, **164**, 966.
14 C. Srinivasan, A. Chellamani and P. Kuthalingam, *J. Org. Chem.*, 1982, **47**, 428.