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Oxidation of Organic Sulfides by Permanganate Ion

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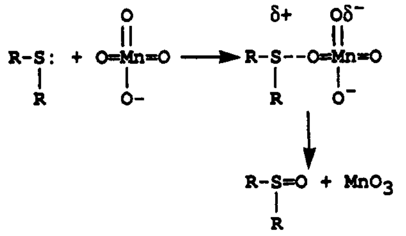
The current literature on the oxidation of sulfides by permanganate contains a suggestion that the reaction mechanism involves an electrophilic oxygen transfer in an S_N2-like mechanism. Contrary to this assumption, it is argued that the experimental facts obtained from a study of the oxidation of (arylthio)acetic acids can more reasonably be accommodated in a mechanism that is initiated by the formation of a coordinate covalent bond utilizing an unshared pair of sulfur electrons and empty manganese d-orbitals. Rearrangement of this intermediate then leads to the formation of sulfoxide and manganate(V) ion.

Introduction

The literature on the oxidation of sulfides by permanganate contains a description of the reaction mechanism that appears to be incorrect. Banerji[1] recently proposed that the reaction between permanganate and sulfides involves "a rate determining electrophilic oxygen transfer from permanganate ion to the sulfide" and compared the process to an S_N2 mechanism in which oxygen is transferred from the oxidant to the reductant as in eq 1.



$$\mathrm{R{-}\underset{\displaystyle R}{S}{:} + O{=}\underset{\displaystyle O^-}{\overset{\displaystyle O}{Mn}}{=}O \longrightarrow R{-}\underset{\displaystyle R}{\overset{\delta+}{S}}{-}{-}O{=}\underset{\displaystyle O^-}{\overset{\displaystyle O\delta^-}{Mn}}{=}O \longrightarrow R{-}\underset{\displaystyle R}{S}{=}O + MnO_3} \qquad (1)$$

This is an unrealistic assumption; in its reactions with other reductants permanganate acts as a powerful electrophile.[2] This paper presents evidence and arguments that lead to the proposal of a more plausible mechanism for the oxidation of sulfides.

Experimental Section

Materials. All reagents, including potassium permanganate, were of analytical grade. Water was purified by double distillation, the second time from basic permanganate.

(Arylthio)acetic acids were prepared from the reaction of substituted thiophenols with bromoacetic acid. In a typical preparation, a 250 mL Erlenmeyer flask was charged with thiophenol (5.00 g, 44.08 mmol), THF (20 mL), water (30 mL), and phase-transfer agent (Bu_4NBr, 100 mg). The flask was immersed in an ice–water bath, and sodium hydroxide (3.3 g, 80.30 mmol) was added slowly with stirring, followed by a solution of bromoacetic acid (6.4 g, 45.10 mmol) in 50 mL of THF. The solution was stirred for about 30 min at room temperature, acidified, and diluted with 20 mL of ether. The resulting aqueous layer was extracted with ether (3 × 50 mL). The combined etheral layers were dried over anhydrous $MgSO_4$ and evaporated on a rotary evaporator. The residue was cooled in a refrigerator followed by filtration to yield crude (phenylthio)acetic acid (7.04g, 95%).

The melting points of the products (after recrystallization from carbon tetrachloride), their elemental analysis, and spectroscopic data are consistent with the proposed structures. See supplementary materials.

Reaction Stoichiometries. Various amounts of (phenylthio)acetic acid were mixed with a constant amount of permanganate in an aqueous solution. The amount of unreacted permanganate was determined spectrophotometrically, and plots of unreacted MnO_4^- vs the amount of (phenylthio)acetic acid added then gave the reaction stoichiometries both at pH 7.4 (Figure 1) and in 1.0 M KOH (Figure 2).

Kinetic Methods. (Arylthio)acetic acids were used as substrates to ensure good solubilities in aqueous solutions. The rates were determined by following the decrease in absorbance at 546 nm using an HP8450A spectrophotometer. Plots of ln (absorbance – final absorbance) were linear, thereby indicating that the reactions are first order in permanganate. Further, the observed pseudo-first-order rate constants were directly proportional to sulfide concentration confirming that the rate of reaction is also first order in reductant.

Product Studies. Spectral studies showed that under neutral conditions (pH 7.4) the inorganic product is manganese dioxide (Figure 3), while manganate(VI) is obtained in 1.0 M KOH (Figure 4).

The organic product of this reaction, (phenylsulfonyl)acetic acid, was isolated as follows. (Phenylthio)acetic acid (1.68 g, 10 mmol) was added to 100 mL of aqueous KOH (pH 11–12), and a portion (1.89 g, 12 mmol) of finely ground potassium permanganate was added over a period of 15 min. After being stirred for 40 min at room temperature, the solution was placed in an ice bath and sodium sulfite (3.33 g, 26 mmol) introduced. Careful addition of concd HCl (40–50 mL) then reduced all of the manganese compounds to colorless manganese(II). Extraction with 4 × 50 mL of ether, followed by drying of the extracts over anhydrous $MgSO_4$ and evaporation of the solvent, gave a white solid (1.40 g, 70%). IR (Nujol): ν 2923.6 (vs); 1737.2 (s); 1454 (s); 1327.9 (s); 1153 (s). Proton NMR ($CDCl_3$): δ 4.17 (s, 2 H); 7.68 (m, 3 H); 8.00 (d, 2 H). Mp: 112–114 °C (lit.[3] mp 113–114 °C).

Results

In 1.0 M KOH the product of the reaction is manganate(VI) and the stoichiometry is 4:1 (Figure 2), thereby indicating that the reaction may be expressed as in eq 2.

$$4MnO_4^- + RSR + 4OH^- \rightarrow 4MnO_4^{2-} + RSO_2R + 2H_2O \qquad (2)$$

$$4MnO_4^- + 3RSR + 2H_2O \rightarrow 4MnO_2 + 3RSO_2R + 4OH^- \qquad (3)$$

However, under neutral conditions (pH 7.4) manganese dioxide is the product and the stoichiometry is close to 4:3 (Figure 1) in accordance with eq 3.

Under approximately neutral conditions the rate of the reaction is independent of the base concentration; however, at higher concentrations the rate is directly dependent on the basicity of the solutions (Figure 5).

The rate constants for substituted (arylthio)acetic acids correlate well with published substituent constants[4] (Figure 6) giving a Hammett ρ value of –1.25.

Studies of the effect of temperature (5–25 °C) on the rate constants for the reaction (Figure 7) gave the following

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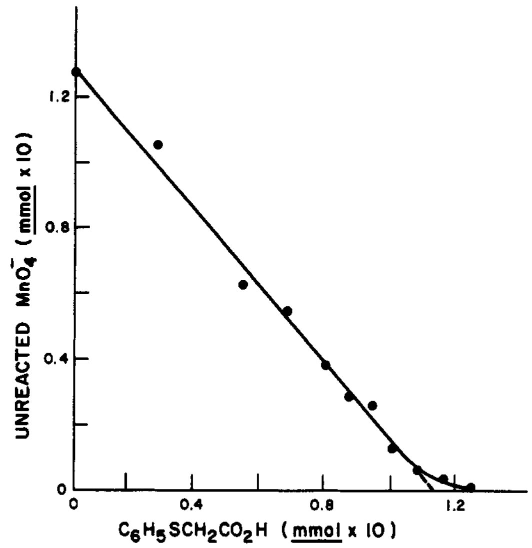


Figure 1. Determination of the stoichiometry for the oxidation of (phenylthio)acetic acid by permanganate in buffered solutions at pH 7.4.

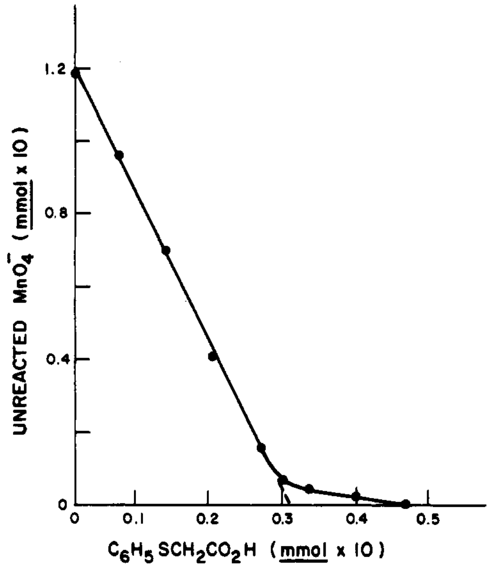


Figure 2. Determination of the stoichiometry for the oxidation of (phenylthio)acetate by permanganate in 1.0 M KOH solutions.

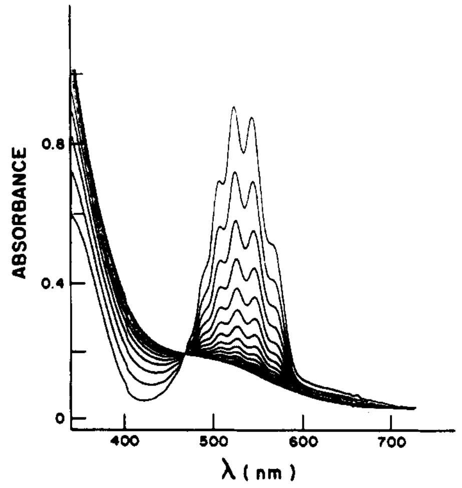


Figure 3. Successive scans obtained at intervals of 10 s during the oxidation of (phenylthio)acetic acid (4.0 × 10^{-3} M) by permanganate (3.56 × 10^{-4} M) in buffered solutions at pH 7.4 and 25.0 ± 0.1 °C. A good isosbestic point is observed at 470 nm, and the final spectrum is that of manganate(IV).

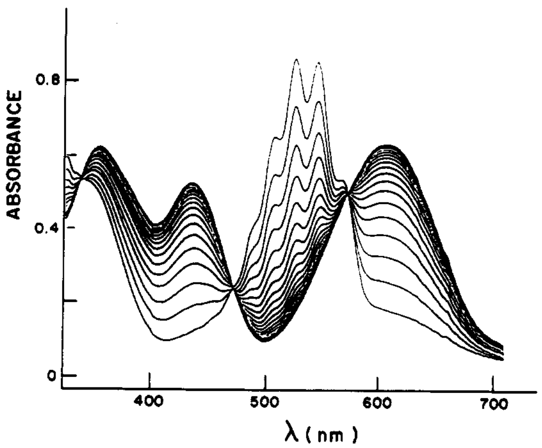


Figure 4. Successive scans obtained at intervals of 6 s during the oxidation of (phenylthio)acetate ion (4.0 × 10^{-3} M) by permanganate (3.56 × 10^{-4} M) in 1.0 M KOH solutions at 20.0 ± 0.1 °C. Good isosbestic points are observed at 335, 473, and 578 nm. The final spectrum is that of manganate(VI).

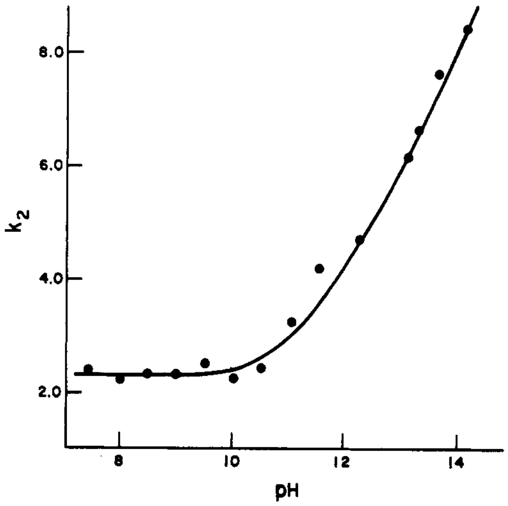


Figure 5. Dependence of the rate constants on the basicity of the solutions for the oxidation of (phenylthio)acetic acid by permanganate at 20.0 °C.

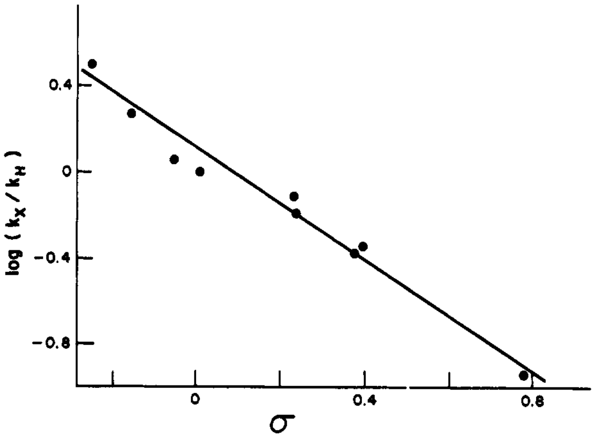


Figure 6. Hammett plot for the oxidation of substituted (phenylthio)acetic acids by permanganate in buffered solutions at pH 7.4 and 20.0 ± 0.1 °C: $\rho = -1.25 \pm 0.08$; $r = 0.984$.

activation parameters: $\Delta H^\dagger = 18 \pm 1$ kJ mol^{-1}, $-\Delta S^\dagger = 176 \pm 1$ J mol^{-1} K^{-1}.

Discussion

The negative Hammett ρ value for this reaction (−1.25) indicates that the transition state is electron deficient as

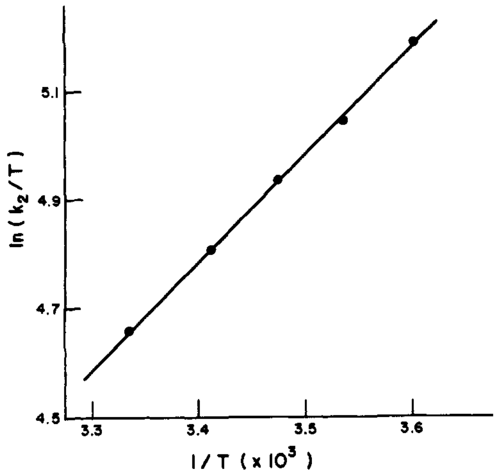
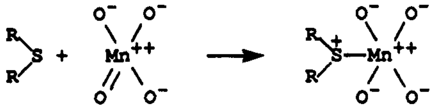


Figure 7. Plot of ln (k_2/T) vs $1/T$ for the oxidation of (phenylthio)acetic acid by permanganate: slope = 2.15 ± 0.09 K; intercept = −2.55 ± 0.31; r = 0.973.

compared to the sulfide—presumably because an unshared pair of electrons from sulfur is utilized in the formation of a coordinate covalent bond. Theoretical calculations[5] have shown that there is a substantial amount of charge transfer from the metal to the oxygens in permanganate and that the manganese is essentially dipositive as in structure 1. The most logical mode of interaction between a sulfide and permanganate would therefore be nucleophilic attack at the metal as in eq 4.



(4)

1 2

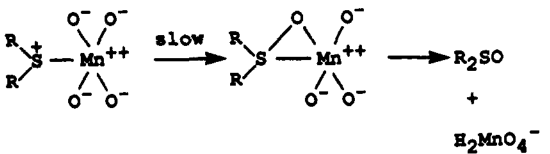
Donation of an unshared pair of electrons to an empty d-orbital on the metal would result in the formation of a coordinate covalent bond with the consequent development of a positive charge on the sulfur (in accordance with the negative Hammett ρ value). To assume, as has previously been done, that there would be an initial nucleophilic attack by the sulfur on an electron-rich oxygen seems to be quite unreasonable and would be inconsistent with the knowledge that permanganate acts as an electrophile in its reactions with alkenes and alkynes.[2]

The observation that the inorganic product is manganese dioxide in neutral solutions (Figure 3) and manganate(VI) under basic conditions (Figure 4) suggests that manganate(V) is involved; it is known to disproportionate to manganese dioxide in neutral solutions (eq 5) and to rapidly react with permanganate to form manganate(VI) in 1 M KOH (eq 6).[6]

$$3H_2MnO_4^- \rightarrow MnO_4^- + 2MnO_2 + 2H_2O + 2OH^- \quad (5)$$

$$H_2MnO_4^- + MnO_4^- \rightarrow 2HMnO_4^- \quad (6)$$

The initially formed intermediate 2 would likely undergo a further rapid reaction in which the incipient oxide and sulfonium ions bond to form a highly structured intermediate 3 that could then rearrange to give a sulfoxide and manganate(V) as in eq 7.



(7)

2 3

Formation of a highly structured intermediate in the slow step is also in agreement with the negative entropy of activation for this process. Of course, in the presence of excess permanganate the sulfoxide formed in eq 7 would be oxidized to the corresponding sulfone in agreement with the stoichiometries previously discussed.

The dependency of the rates of reaction on the basicity of the solution above pH 9 (Figure 5) may also be related to the formation of manganate(V) in the slow step of the reaction. The fact that manganate(V) is known to be more stable in highly basic solutions[7] would, according to the Hammond postulate,[8] lead to increased rates if the transition state is product-like.

An alternative explanation based on the possibility that the sulfide would be activated by loss of a proton in highly basic solutions (eq 8), as previously suggested for other reductants such as alcohols,[9] does not seem to be consistent with these results. Involvement of a thioenol would undoubtedly result in the formation of cleavage products through the reactions depicted in eqs 9 and 10.

$$PhCH_2SCH_2CO_2^- + OH^- \rightleftharpoons Ph\overset{-}{C}HSCH_2CO_2^- + H_2O \quad (8)$$

$$Ph\overset{-}{C}HSCH_2CO_2^- \leftrightarrow PhCH{=}\overset{-}{S}CH_2CO_2^- \quad (9)$$

$$PhCH{=}\overset{-}{S}CH_2CO_2^- + MnO_4^- \rightarrow PhCO_2^- + CH_2(SO_3^-)CO_2^- \quad (10)$$

Furthermore, an explanation based on ionization of the reductant cannot account for the increased rates of oxidation of substrates such as alkenes,[10] which do not contain acidic hydrogens. Because the rates of oxidation of all types of organic compounds by permanganate increase in highly basic solutions, it is most reasonable to assume that this phenomenon is associated at least partly with the oxidant rather than the reductant. Although a completely satisfying explanation is not yet available, it seems highly likely, as discussed above, that the rate increases may be a consequence of the involvement of manganate(V) in all of these reactions.[6]

Conclusions

The results obtained from a study of the oxidation of sulfides by permanganate is most consistent with a mechanism initiated by a reaction between an unshared pair of sulfur electrons with an empty d-orbital of manganese. Other features of the reaction are consistent with the involvement of manganate(V) as an intermediate in the reaction.

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Supplementary Material Available: Melting points, elemental analysis, and NMR and IR spectroscopic data for arylmercaptoacetic acids and kinetic rate plots (4 pages). Ordering information is given on any current masthead page.

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