Indian Journal of Chemistry
Vol. 16A, January 1978, pp. 43-45

Kinetics & Mechanism of Oxidation of Dimethyl Sulphoxide by Peroxydiphosphate

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Received 17 *February* 1977; *accepted* 2 *August* 1977

The kinetics of oxidation of dimethyl sulphoxide by peroxydiphosphate is found to be acid-catalysed, first order in oxidant and zero order in substrate. The experimental kinetic data are rationalized by a free-radical mechanism involving the oxidative attack of $\dot{O}H$ on sulphur. Dimethyl sulphone is identified to be the sole product of oxidation, the stoichiometric reaction being $(CH_3)_2SO+H_3P_2O_8^-+H_2O \rightarrow (CH_3)_2SO_2+2H_2PO_4^-+H^+$.

THE meagre information available concerning the mechanism of oxidation of sulphoxides makes it worthwhile to investigate the oxidation of dimethyl sulphoxide (DMSO) by a versatile oxidant like peroxydiphosphate (PP). In general, peroxyacids[1-3] are found to be effective oxidants in bringing about the oxidation of sulphides and sulphoxides. The nucleophilic attack is made by sulphur on the peroxy oxygen of the oxidant in the case of sulphides[1] and the reverse is found to be true in the case of sulphoxides[3]. The peroxyacid can afford to lose its oxygen through which the nucleophilic attack is made and actually it does so. But when the oxidant employed is of the type, peroxydisulphate or peroxydiphosphate, containing the second-row elements like sulphur and phosphorus having higher affinity towards oxygen, we cannot expect such a nucleophilic attack by the peroxy oxygen. The oxidation of sulphoxides by peroxydisulphate[4,5] has already been studied, even though the mechanism of the reaction has not been elucidated. Since P=O bond is stronger than S=O bond due to d_π-p_π bonding, we considered it desirable to choose peroxydiphosphate containing P=O bond as the oxidant and investigate the oxidation of dimethyl sulphoxide involving the formation of an S=O bond, with the expectation that the reaction should follow a different mechanism from the one proposed for the peroxyacid[3].

Materials and Methods

All the kinetic runs were performed under pseudo-first order conditions with [DMSO] > [PP] ([PP] $= 2{\cdot}5\text{-}10\times10^{-3}M$; [DMSO] $= 3\text{-}9\times10^{-2}M$) in aqueous acidic medium at constant $[H^+] = 0{\cdot}5M$ and ionic strength, $0{\cdot}85M$ in the temperature range, 30-60°. $[H^+]$ was varied from 0·1 to $0{\cdot}5M$ (by added H_2SO_4) at constant ionic strength (adjusted with $NaHSO_4$) to study the dependence of the reaction rate on $[H^+]$. $K_4P_2O_8$ (FMC Corporation, USA) was converted to the lithium salt, purification being accomplished by the method due to Chulski[6] and the lithium salt (99·1% pure) was used for the experiments. DMSO (Fluka) was used as such. The rate of peroxydiphosphate disappearance, $-d[PP]/dt$, was followed by cerimetry and the product of oxidation was characterized by IR spectra and GLC. The stoichiometry of the reaction was determined by taking a known excess concentration of PP than DMSO. The reaction was allowed to complete by keeping it overnight and the remaining PP estimated. Since dimethylsulphone was the only product identified the stoichiometry was determined from the amounts of DMSO and PP reacted. The error limits of the kinetic constants were calculated by the method of least-squares.

Results and Discussion

In the absence of H^+, peroxydiphosphate fails to oxidize DMSO and the oxidation of DMSO by PP is found to be strongly acid-catalysed, as the self-decomposition[7] of PP. It is apparent from the semi-logarithmic plots of Fig. 1 that the reaction order is unity in [PP]. The zero order in DMSO is evident from the independence of the reaction rate on [DMSO] (Table 1). The first order dependence on $[H^+]$, shown by the data of Table 2 pointed to $H_3P_2O_8^-$ as the active species* of the oxidant. The kinetic data can be better rationalized by postulating the free-radical mechanism of oxidation shown in Scheme 1.

$$H_3P_2O_8^- \xrightarrow[\text{slow}]{k_i} H_2P\dot{O}_4 + HP\dot{O}_4^-$$

$$H_2P\dot{O}_4 + H_2O \xrightarrow{k_p} H_3PO_4 + \dot{O}H$$

$$\dot{O}H + (CH_3)_2\overset{\cdot\cdot}{S}O \xrightarrow{k_3} OH^- + (CH_3)_2\overset{\cdot+}{S}O$$

$$(CH_3)_2\overset{\cdot+}{S}O + H_3P_2O_8^- \xrightarrow{k_4} (CH_3)_2\overset{++}{S}O + HP\dot{O}_4^- + H_2PO_4^-$$

$$(CH_3)_2\overset{\cdot+}{S}O + HP\dot{O}_4^- \xrightarrow{k_t} (CH_3)_2\overset{+}{\dot{S}}O + HPO_4^{2-}$$

$$(CH_3)_2\overset{++}{S}O + H_2O \longrightarrow (CH_3)_2SO_2 + 2H^+$$

Scheme 1

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*Since $[PP]_{Total} = [H_2P_2O_8^{2-}] + [H_3P_2O_8^-] + [H_4P_2O_8]$ under the present experimental conditions,

$$\frac{-d[PP]}{dt} = k_i[H_3P_2O_8^-] = \frac{k_iK_{13}[PP]_T[H^+]}{1+K_{13}[H^+]+K_{13}K_{14}[H^+]^2}$$

where K_{13} and K_{14} represent the equilibrium constants for the protonation $H_2P_2O_8^{2-}$ and $H_3P_2O_8^{2-}$ respectively. The above rate law would simplify to $-d[PP]/dt=k_iK_{13}[PP]_{Total}[H^+]$ since the second and third terms in the denominator can be neglected in comparison to unity.

The oxidative path shown in Scheme 1 on the basis of steady-state approximation would lead to the rate law (1)

$$\frac{-d[\text{PP}]}{dt} = \left(\frac{k_i k_p k_4}{k_t}\right)^{\frac{1}{2}} [H_3P_2O_8^-] = k_1[\text{PP}]_T \qquad \ldots(1)$$

in good agreement with the observed kinetics. If the nucleophilic attack is by the peroxy oxygen of PP upon sulphur as in the case of peroxyacids, the reaction would be of second order, first order in each of the reactants. The first order dependence on [PP] and zero order dependence on [DMSO] pointed to a free-radical mechanism. The formation of free radical intermediates in the reaction system was tested by adding a vinyl monomer, acrylonitrile, which got polymerized with a short induction period. The formation of (DMSO), also observed by Kitagawa[8] in the peroxydisulphate-initiated polymerization of acrylonitrile, also strengthens our conclusion. Since the decomposition of PP to give free radicals happens to be slow rate-determining step, the reaction should be acid-catalysed with first order dependence on [H^+] as the self-decomposition[7] of PP and this is actually observed (Table 2). The phosphate radical ion (or radical) produced by the decomposition of $H_3P_2O_8^-$ does not directly attack the sulphoxide, but attacks the solvent nucleophile, H_2O, giving rise to $\dot{O}H$. The hydroxyl radical thus produced makes the oxidative attack on sulphur which has to function as a nucleophile, in the sense that one of the non-bonding electrons of sulphur is taken up by $\dot{O}H$ yielding OH^- and the sulphoxide radical. The attack of $\dot{O}H$ on oxygen is also possible since DMSO is a resonance hybrid of the forms, $>S = O \longleftrightarrow \overset{+}{S}—O^-$. But, in view of the back-donation resonance of the non-bonding electrons of oxygen with the empty d-orbitals of sulphur, the availability of electrons on oxygen can be considered to be less, compared to that on sulphur. The stoichiometry of the reaction, [PP]:[DMSO] = 1:1, is also in accord with the reaction Scheme 1.

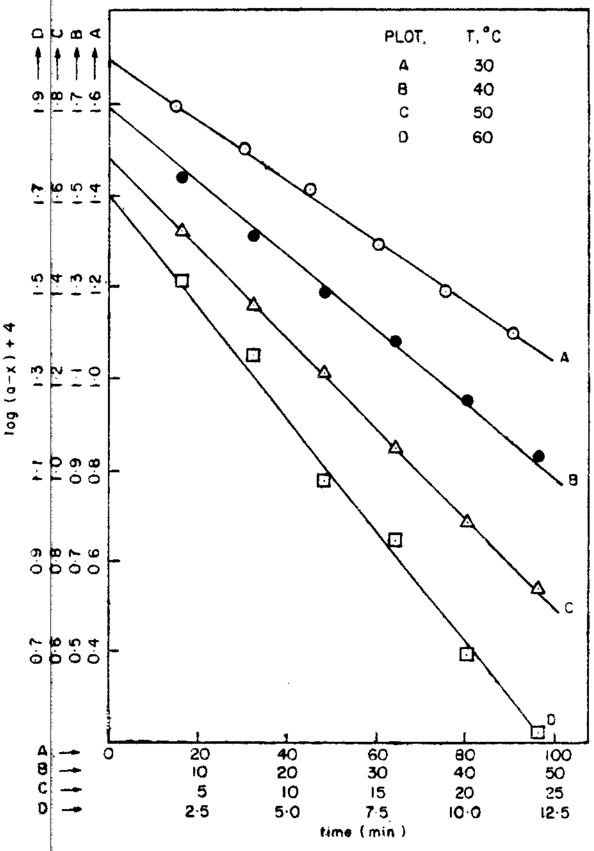

Fig. 1 — Semi-logarithmic plots at different temperatures

TABLE 1 — ZERO-ORDER DEPENDENCE ON [DMSO]

{[H^+] = 0·5M; μ = 0·85M; [PP] = 2·5-10 × $10^{-3}M$}

[DMSO] × 10^2 M	$k_1 \times 10^4$ (sec^{-1}) at 30°	40°	50°	60°
3·0	2·64	6·39	15·00	38·36
4·5	2·54	6.33	14·98	38·01
6·0	2·56	6·28	15·36	38.38
7·5	2·51	6·16	15·59	38·50
9·0	2·51	6·24	15·87	38·65

TABLE 2 — FIRST-ORDER DEPENDENCE ON [H^+]

{μ = 0·85M; [PP] = 5 × $10^{-3}M$; [DMSO] = 6·0 × $10^{-2}M$; temp. = 30°}

[H^+] M	$k_1 \times 10^5$ sec^{-1}	[H^+]	$k_1 \times 10^5$ sec^{-1}
0·1	5·62	0·4	20·26
0·2	10·23	0·5	25·60
0·3	14·87	—	—

The important characteristic of the reaction is that we have P = O bond in the oxidant stabilized by $d\pi$-$p\pi$ bonding, making the removal of oxygen more difficult. But the oxidation of sulphoxide to sulphone necessarily involves the formation of an S=O bond which will also be fairly stabilized by the same $d\pi$-$p\pi$ bonding, of course to a lesser extent than the P=O bond. Since phosphorus would not lose its oxygen, the latter has to come from some other source and that happens to be the solvent nucleophile, namely, water. Two one-electron transfer processes are brought about producing $(CH_3)_2SO^{2+}$, with the electrophilic centre on sulphur, rendering the nucleophilic attack by the oxygen of water much easier to give rise to the sulphone. The product of the reaction was identified to be dimethylsulphone, a white solid, m.p. 109°; IR: νS=O at 1310 and 1140 cm^{-1}, characteristic of sulphones. Dimethylsulphone as the exclusive product pointed to the absence of any other side reaction involving C-S bond scission. Since the reaction stoichiometry, [DMSO]/[PP] = 1, the stoichiometric reaction can be represented by Eq. (2).

$$(CH_3)_2SO + H_3P_2O_8^- + H_2O \rightarrow (CH_3)_2SO_2 + 2H_2PO_4^- + H^+ \qquad \ldots(2)$$

The activation parameters for PP-DMSO reaction are $A = (2{\cdot}69 \pm 0{\cdot}04) \times 10^9$ sec^{-1}; $E_a = 18{\cdot}09 \pm 0{\cdot}29$ kcal mol^{-1} and $\Delta S^\ddagger = -17{\cdot}60$ cal deg^{-1} mol^{-1}. It is not possible to get any insight into the nature of the transition state from a knowledge of these activation parameters since they correspond to the overall rate constants. Similar kinetic features noted by Levitt *et al.*[4] in the oxidation of sulphoxides by peroxydisulphate, like the first order kinetics in oxidant and zero order in sulphoxide, may also point to the operation of a similar free-radical mechanism as that postulated by us in the present study. Comparison with the data on the oxidation of water[7] indicated that the aprotic solvent (DMSO) is oxidized with more facility than the protic solvent (H_2O).

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