OXIDATION STUDIES—V

Oxidation of Light and Heavy Water by Peroxydisulphate

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Abstract

Oxidation of light and heavy water by peroxy disulphate was studied at 60–70° C. The acid independent and acid dependent rate constants and respective ΔE values were computed. An attempt is made to explain the kinetic isotopic effect observed. A probable mechanism is proposed.

Results reported on oxidation of light water by peroxydisulphate by several workers[1-7] revealed that oxidation proceeds both by (i) acid dependent as well as (ii) acid independent paths. The rate constants and Arrhenius parameters for these paths reported by Kolthoff and Miller[1] were in sharp contrast from those of Breuer and Jenkins.[7] All the mechanisms suggested both for acid catalysed and acid independent reactions lead to

$$S_2O_8^{=} + H_2O \rightarrow 2HSO_4^{-} + \tfrac{1}{2} O_2$$

as the final stoichiometric equation; (i) was assumed to proceed by homolysis of $S_2O_8^{=}$ to radical ions $SO_4^{\cdot -}$ which react with water producing HSO_4 and OH radicals which dimerise to $H_2O + \tfrac{1}{2} O_2$. (ii) involved the formation of $HS_2O_8^{-}$ which decomposes to HSO_4^{-} and SO_4 radicals, the latter reacting further in $SO_4 \rightarrow SO_3 + \tfrac{1}{2} O_2$ and $SO_3 + H_2O \rightarrow H^+ + HSO_4^-$. OH and SO_4 are therefore the precursors for O_2 from (i) and (ii) respectively. We have studied the oxidation of light water by $S_2O_8^{=}$ in the pH range 0–10 at 60–80° C. Acid dependent and acid independent rate constants and the respective ΔE values are being reported. Similar studies with heavy water were made but confined to the pH range 2–8, k_{H_2O}/k_{D_2O} values have been reported for the 'overall rate' constants as well as for 'acid catalysed' and 'acid independent' reactions. Curiously enough for the overall rate, $k_{D_2O}/k_{H_2O} > 1$ while for the latter reactions $k_{H_2O}/k_{D_2O} > 1$ were observed. The rate was found to be proportional to total acidity and not to Hammett's

H_0, thus emphasizing participation of both H^+ and H_2O in the transition state for the catalysed reaction.

EXPERIMENTAL

$K_2S_2O_8$ (E Merck; G.R.); H_2SO_4 (A.R. 36 N Basynth; India); $HClO_4$ (A.R., 60%, Mayand Baker); NaOH (G.R., E. Merck); Heavy Water (Atomic Energy, Trombay, India; 99·4% purity) were employed. Distilled water, distilled over alkaline $KMnO_4$ twice and then passed through Ion exchange resin (Biodeminrolit; Permutit Co., U.K.) was used for preparation of all solutions. Adjustments of ionic strengths were made with H_2SO_4, $HClO_4$ and NaOH solutions. pHs of solutions were measured in pH meter (Leeds and Northrup Cat. No. 7666) provided with a system of glass and calomel electrodes and standardised by potassium biphthalate (M/20; pH = 4·00 at 35° C.). All the experiments were confined to $[S_2O_8^{=}] = 0·005$ M and ~ 35% conversions of the former and for ~ 90 minutes.

The solution of $S_2O_8^{=}$ (in light or heavy water) after adjustment of pH (by the addition of H_2SO_4 or NaOH) was thermostated at the required temperature (60–80° C.) ± 0·1° C. controlled by a relay and toluene regulator. Aliquots (5 c.c.) were withdrawn at 10 min. intervals; quenched in ice-cold water (25 c.c.) containing KI (2 gm.); set aside for about 45 minutes; acidified with acetic acid (6·0 N, 2 ml.) and titrated against standard sodium thiosulphate (0·025 N). From $[S_2O_8^{=}]$ reacted, rate of $S_2O_8^{=}$ disappearance, $-R_{S_2O_8^{=}}$, was computed. Rate measurements by addition of excess standard (Fe^{+2}) to aliquots and back titration with standard $KMnO_4$ or ceric sulphate compared well with those by iodometry and the rates may be considered accurate to within ± 1%.

RESULTS AND DISCUSSION

(i) The orders with respect to $[S_2O_8^{=}]$ were observed to be unity, the log $(a - x)$ *vs.* t plots being linear in H_2O (Fig. 1, A) as well as D_2O (Fig. 1, B) at various pHs. Perchloric acid in place of H_2SO_4 for adjustments of pH in H_2O did not make any difference. The pseudo first order rate constants in light and heavy water k_{H_2O} and k_{D_2O} respectively at 60° and 70° C. at various pHs together with the respective ΔE values, etc., appear in Table I. It is seen from Table I that there is an irregular increase and decrease in ΔE values with variations in pH and the lowest value for $\Delta E = 10·7$ at pH 2·14 in H_2O was noticed. Our values are in better agreement with those of Breuer and Jenkins[7] (ΔE = 23–35) than those of Kolthoff and Miller[1]

TABLE I

Rate constants and ΔE values at various pHs

pH	0	0·5	1·0	1·5	1·9	2·0	2·14	2·31	2·49
60° C.—									
$k_{H_2O} \times 10^4$	1·33	0·89	0·5	0·77	0·97	1·6	0·8	0·31	0·23
(H_2SO_4)	..	..	..	..	(0·96)	(1·61)	(0·81)	..	(0·23)
$k_{D_2O} \times 10^4$	..	..	..	..	..	..	0·77	0·96	0·24
70° C.—									
$k_{H_2O} \times 10^4$	2·16	2·27	1·19	1·58	2·12	..	1·4	0·7	1·0
(H_2SO_4)	..	..	..	..	(2·2)	..	(1·3)	..	(1·0)
$k_{D_2O} \times 10^4$	..	..	..	..	..	..	3·7	2·2	1·4
ΔE in K.cal.—									
H_2O ..	20·2	21·4	20·7	20·1	18·70	10·00	10·7	17·0	26·9
	..	..	..	..	(18·8)	(16·00)	(10·6)	..	(26·9)
D_2O	..	..	..	..	..	..	35·7	33·0	32·0

pH	3·05	3·4	4·4	5·0	6·0	7·0	8·0	9·0	10·0
60° C.—									
$k_{H_2O} \times 10^4$ ..	0·69	1·4	1·9	2·8	3·7	1·7	1·44	0·39	0·58
(H_2SO_4) ..	(0·69)	..	..	..	..	..	..	..	..
$k_{D_2O} \times 10^4$ ..	..	..	0·74	..	..	0·64	..	..	..
70° C.—									
$k_{H_2O} \times 10^4$ ..	1·6	2·9	6·6	7·8	9·0	2·4	5·9	6·3	6·5
(H_2SO_4) ..	(1·6)	..	..	..	..	..	..	..	..
$k_{D_2O} \times 10^4$ ..	..	..	1·33	..	..	1·0	0·92	..	..
ΔE in K.cal.—									
H_2O ..	19·2 (19·2)	19·5	23·2	22·2	22·4	22·4	21·3	20·5	23·0
D_2O ..	..	..	..	..	..	..	..	..	..

Values in brackets refer to those in $HClO_4$ in H_2O.

All k_H and k_D values have dimensions $sec.^{-1}$

($\Delta E = 26–33$ K.cal./mole). All these workers confined their oxidation studies to 40–50° C. range while our investigations were carried out in the 60–70° C. range.

(ii) *Form of* H^+ (D^+) *function*: It was found that $\log k_{H_2O}$ (or k_{D_2O}) was found to be proportional to total acidity [H^+] and plots of $\log k_{H_2O}$ *vs.* H_0 were curves (Fig. 1, F).

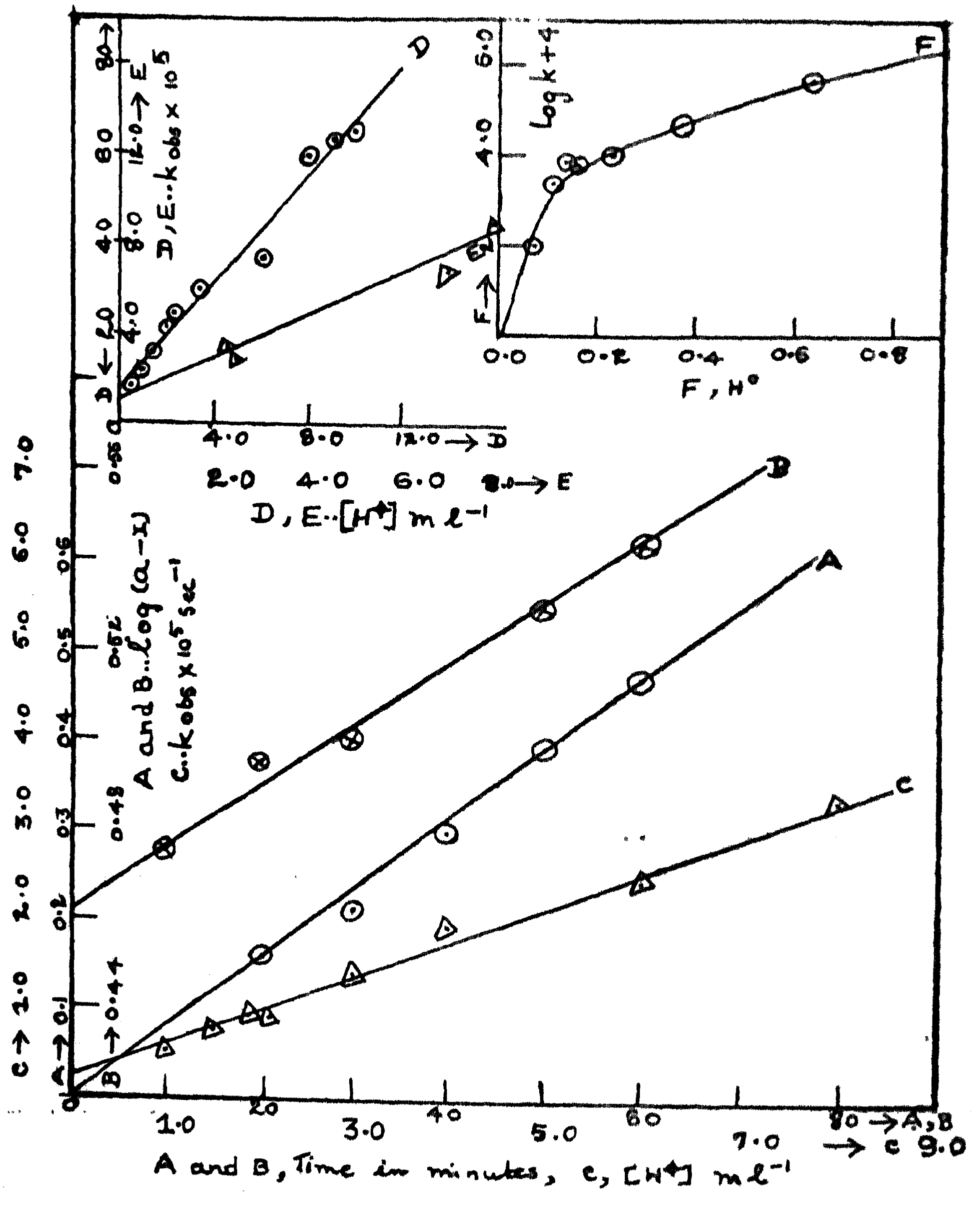

FIG. 1. Plots A and B, $\log (a - x)$ *vs.* time. [$S_2O_8^{=}$] = 0·005 M in H_2O (A), D_2O (B) at 60° C. Plot C, pseudo first order rate constant *vs.* [H^+] ml.$^{-1}$ for H_2O at 60° C. Plot D, Pseudo first order rate constant kobs *vs.* [H^+] ml.$^{-1}$ for H_2O at 60° C. Plot E, kobs *vs.* [H^+] ml.$^{-1}$ for D_2O at 60° C. Plot F, log kobs *vs.* H_0 for both H_2O and D_2O.

(iii) Separation of k_{H_2O} (k_{D_2O}) to acid independent k_{1H_2O} (k_{1D_2O}) and acid dependent k_{2H_2O} (k_{2D_2O}) terms: From the intercepts and slopes[2] of the plots $-R_{S_2O_8^{=}}$ *vs.* [H+] (Fig. 1, C, D and E) k_{1H_2O} and k_{2H_2O} respectively were evaluated at 60° and 70° C. Similarly k_{1D_2O} and k_{2D_2O} were also evaluated (Table II).

TABLE II

Acid dependent and acid independent rate constants and Arrhenius parameters in H_2O and D_2O

pH range	60° and 70° C. Rate constants				60° and 70° C. Isotopic effects		Activation parameters in K. cal./mole			
	$k_{1H} \times 10^5$	$k_{1D} \times 10^5$	$k_{2H} \times 10^3$	$k_{2D} \times 10^3$	k_{1H}/k_{1D}	k_{2H}/k_{2D}	ΔE_{1H}	ΔE_{2H}	ΔE_{1D}	ΔE_{2D}
0–13 for light water	2·2	1·65	6·3	4·9	2·05	1·27	31·6	27·2	35·5	15·2
2·2–7·9 for D_2O ..	7·0	5·0	20·0	25·00	1·41	0·82	..	..	..	..

It is seen that k_{D_2O}/k_{H_2O} are usually greater than unity (1·041, 0·98 and 0·936 at 60° C. and 3·4, 3·1 and 2·90 at 70° C. all in the pH range 2·2 to 8). The isotopic effects (k_{H_2O} and k_{D_2O} were resolved into k_{1H_2O}, k_{2H_2O}, etc.): $k_{1H_2O}/k_{1D_2O} = 2·05$ and 1·41 at 60° and 70° C. respectively and $k_{2H_2O}/k_{2D_2O} = 1·27$ and 0·82 respectively at 60° and 70° C. all in the pH range 2·2 to 8·0. It may be seen that the kinetic isotopic effect $k_{D_2O}/k_{H_2O} > 1$ and the ratio increases with increase of temperature. The opposite effects are found in the kinetic isotopic effects with the resolved constants $k_{1H_2O}/k_{1D_2O} > 1$ and $k_{2H_2O}/k_{2D_2O} > 1$ and the ratio decreases with increase of temperature. These are rather anomalous. In the case of organic substrates with C–H bonds the $k_{H_2O}/k_{D_2O} > 1$ is usually understood in terms of a proton transfer being involved in the rate-determining step; on the other hand $k_{D_2O}/k_{H_2O} > 1$ meant the equilibrium involving the substrate, $S + H^+ \rightleftharpoons SH^+$ being important. If similar arguments apply for a substrate like $S_2O_8^{=}$ (which does not involve a C–H bond) it is rather likley that acid catalysed reaction is

$$S_2O_8^{=} + H^+ \rightleftharpoons HS_2O_8^- \tag{1}$$

$$HS_2O_8^- + H_2O \xrightarrow{\text{slow}} 2HS_4^- + H^+ + \tfrac{1}{2}O_2 \tag{2}$$

This mechanism is also supported by the fact that rate is a function of total acidity and not of Hammetts function H_0. An alternative to step (2) may be 2(*a*):

$$HS_2O_8^- + H_2O \rightarrow HSO_4^- + H^+ + SO_4^{\cdot} + OH \quad (2\,a)$$

which may be important in substrate oxidations. The kinetic isotopic effects decreasing with increasing temperature are in order. Acid independent path may follow the course not involving any proton transfer:

$$S_2O_8^{=} \rightarrow 2\,SO_4^{\cdot -} \quad (3)$$

$$2\,SO_4^{\cdot -} + 2\,H_2O \rightarrow 2HSO_4^- + 2\,OH \quad (4)$$

$$2\,OH \rightarrow H_2O + \tfrac{1}{2}\,O_2 \quad (5)$$

The kinetic isotopic effect $k_{D_2O}/k_{H_2O} > 1$ is probably subject to solvent isotopic effects which are not quite clear.

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REFERENCES

1. Kolthoff, I. M. and Miller, I. K. — *J. Amer. Chem. Soc.*, 1951, **73**, 3055.
2. Bawn, C. E. H. and Margerison, E. — *Trans. Farad. Soc.*, 1955, **51**, 925.
3. Bartlett, P. D. and Cotman, J. D., Jr. — *J. Amer. Chem. Soc.*, 1949, **71**, 1419.
4. Fronaeus, S. and Ostman, C. O. — *Acta Chem. Scand.*, 1955, **9**, 902.
5. Schumh and Rittner .. *J. Amer. Chem. Soc.*, 1940, **62**, 3416.
6. Edgar Howard, Jr. and Leonard S. Levitt — *Ibid.*, 1953, **75**, 6170.
7. Breuer, M. M. and Jenkins — *Trans. Farad Soc.*, 1953, **59**, 1310.

319-68. Printed at The Bangalore Press, Bangalore City, by M. S. Narayanamurthy, Secretary and Published by B. S. Venkatachar, Editor, "Proceedings of the Indian Academy of Sciences," Bangalore