

The Influence of the Solvent on Reaction Velocity

XLII. The Kinetics of the Decomposition of Peroxydisulphate in Dimethyl Sulphoxide-Water Mixtures

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The kinetics of the decomposition of peroxydisulphate was studied in water and in dimethyl sulphoxide-water mixtures at several temperatures. DMSO accelerates the reaction markedly; at low DMSO concentrations the rate constant varies linearly with the DMSO concentration. The silver ion-catalysed decomposition was also studied.

The decomposition of potassium peroxydisulphate in water has been thoroughly discussed by Hakoila.¹ He noted that the reaction is catalysed by hydrogen ion and thus autocatalytic and that the first-order rate constant increases almost linearly with time. In pure water the reaction is slow; *e.g.*, at 25° the first-order rate constant is $1.97 \times 10^{-8} \text{ sec}^{-1}$ when the initial peroxydisulphate ion concentration is 0.05 M.

When we tried to study the reaction $\text{S}_2\text{O}_8^{2-} + 2\text{I}^- \rightarrow 2\text{SO}_4^{2-} + \text{I}_2$ in dimethyl sulphoxide (DMSO)-water mixtures, we found that this reaction did not go to completion but stopped after a few per cent of iodide ion had been consumed. Obviously this was due to a fast reaction between peroxydisulphate ion and water that rapidly consumed all the peroxydisulphate ions. This reaction was found to proceed according to the first-order rate law also in DMSO-water mixtures. The results of these studies are reported in the present paper.

The influence of organic solvents on the decomposition of peroxydisulphate in water has been studied by several workers.^{*cf.* 1,4} These studies have shown that many organic compounds enhance the rate of this reaction, the order of the reaction either changing or remaining constant. Larson² found that the rate of the reaction varies with the concentration of the sulphur compound when a sulphide or a mercaptide is present and shows a maximum or a limiting value. When they studied the same reaction in methanol-water mixtures, Eager and Winkler³ and Bartlett and Gotman⁴ found that methanol in 1 M solution increased the rate of decomposition 25-fold. We found in the present study that, *e.g.*, at 50° the reaction proceeds

75 times faster in a 22 wt. % DMSO-water mixture than in water. In buffered aqueous-alcoholic solutions of constant ionic strength the above mentioned authors^{3,4} found the reaction to be of 3/2 order with respect to the peroxydisulphate ion and of order 1/2 with respect to the alcohol. On the other hand, Howard and Lewitt⁵ found that the order of reaction with respect to peroxydisulphate ion remained unity after addition of diphenyl, thiodiglycol, or diethyl sulphoxide; the rate did not vary with the concentration of the sulphur compound. As atmospheric oxygen did not influence the reaction, they concluded that the reaction proceeds by a free radical mechanism that includes both the reaction with water and the oxidation of sulphoxides. Also Bartlett and Gotman⁴ discussed this reaction in water-methanol mixtures in terms of a chain mechanism.

EXPERIMENTAL

Reagents. The water was triply distilled (the first time from potassium permanganate solution, the second time from calcium hydroxide solution, and the last time without added chemicals). DMSO (Nationales Petroles, France) was distilled in a vacuum and fractionally frozen several times until the melting point was at least 18.50°. The purity of peroxydisulphate (E. Merck AG, Darmstadt) was checked according to Hakoila.¹ The sodium hydroxide solution was prepared from Titrisol ampoules (E. Merck AG, Darmstadt).

Kinetic measurements. The initial concentration of the peroxydisulphate was 0.05 M in most of the experiments. The solvents were prepared by weighing in volumetric flasks. The reaction was started by adding 50 ml of the thermostated solvent to a weighed amount of the peroxydisulphate in a volumetric flask of 100-ml capacity and shaking vigorously until the salt dissolved. The solubility of potassium peroxydisulphate is low in solvents of high DMSO content; in a 50 wt. % DMSO-water mixture the concentration is only 0.01 M. In experiments where silver nitrate was used, it was dissolved beforehand in the DMSO-water mixtures. The reaction was followed (usually from 20 to 50 % completion) by taking eight 5 ml samples at intervals and delivering them into titration vessels cooled with ice water. The samples were titrated with 0.02 M sodium hydroxide solution using cresol red as indicator. In the experiments at the highest temperatures aliquots of the reaction mixture were sealed in ampoules of 5 ml capacity.

The rate constants computed from the first-order rate law showed excellent constancy in most cases. The parameters of the Arrhenius equation were evaluated by the method of least squares. The catalytic constant k' of the silver ion was evaluated (when not otherwise mentioned) from the equation $k_{\text{obs}} = k_0 + k'[\text{Ag}]$, where k_0 is the rate constant of the uncatalysed reaction. The expansion of the solvent with temperature was taken into consideration when the catalytic constants were computed. At low DMSO contents the rate constant of the uncatalysed reaction varied linearly with the DMSO concentration of the solvent; the catalytic constant of DMSO at 40° was also computed.

RESULTS AND DISCUSSION

The experimental results are given in Tables 1–3 and plotted in Figs. 1–2. As seen from Fig. 1 and Table 1, the rate constant of the uncatalysed reaction increases initially rapidly with increasing DMSO concentration to a maximum at about 3 M DMSO. On the other hand, E and $\log A$ decrease initially very steeply with increasing DMSO content of the solvent and pass through minima.

According to Parker,⁶ basic anions are greatly destabilised because of decreased solvation when the polar hydrogen-bonding solvent water is

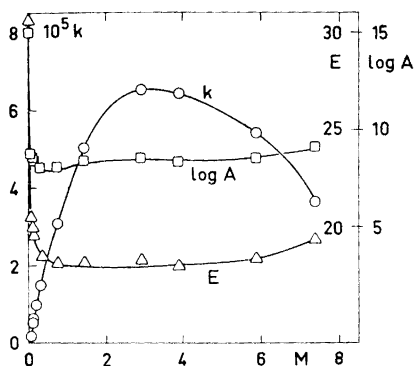


Fig. 1. Plots of k (40°), E , and $\log A$ for the reaction of peroxydisulphate ion with water against the molar concentration of DMSO.

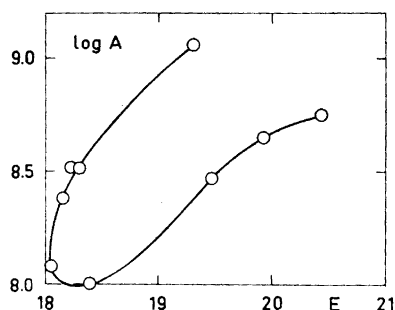


Fig. 2. Plot of $\log A$ against E .

Table 1. The decomposition of potassium peroxydisulphate in DMSO-water mixtures. The initial concentration of $K_2S_2O_8$ was 0.05 M.

DMSO		$10^5 k$ (sec $^{-1}$)					E	$\log A$	ΔS^*	ΔG^*
M	Wt. %	15.00°	25.00°	40.00°	50.00°	60.00°	kcal/mole		EU, 40°	40°
0	0		5.91 ^a	0.0408	0.189	0.761	30.64	15.00	+8.01	33.77
0.00806				0.122						
0.0248				0.183						
0.05	~0.4		0.0556	0.300	0.890		20.44	8.75	-20.60	26.27
0.1	~0.8		0.110	0.522	1.53		19.93	8.65	-21.05	25.90
0.2				0.977						
0.137	1.07	0.0527	0.153	0.726	2.00	4.80	19.48	8.47	-21.85	25.70
0.305	2.44	0.117	0.325	1.48	3.62		18.40	8.01	-23.95	24.28
0.750	5.84	0.246	0.662	3.16	7.25		18.06	8.08	-23.63	24.83
1.44	11.18	0.405	1.126	5.01	12.6		18.16	8.38	-22.27	24.51
2.94	22.41	0.489	1.38	6.51	15.1		18.23	8.52	-21.62	24.38
3.90	29.28		1.43	6.43	15.0		17.94	8.32		
5.89	43.51	0.416	1.20	5.40	13.3		18.31	8.51	-21.68	24.48
7.38	53.65		0.799	3.63	10.2		19.31	9.06	-19.17	24.69

^a at 75.00°.

replaced with the polar, but aprotic DMSO. As an example we may take the reaction between iodine and formate ion in DMSO-water mixtures. Hiller and Krueger⁷ found that the rate of this reaction increases with increasing DMSO content of the solvent. On the other hand, the desolvation of the reactants increases both the energy and the entropy of activation. It seems that this effect predominates in the reaction of peroxydisulphate with water at high DMSO contents and causes the rate constant to decrease.

Some experiments were made in which the concentration of peroxydisulphate ion was varied to study its influence on the rate. The following results were obtained at a 0.2 M DMSO concentration at 40°:

molarity of $K_2S_2O_8$	0.01	0.02	0.05	0.1	0.2
$10^5 k, \text{sec}^{-1}$	1.057	1.091	0.977	0.937	0.861

The rate constant thus decreases linearly with increasing peroxydisulphate ion concentration. A similar trend was found by Agrawal and Mushran⁸ when studying the oxidation of urea by peroxydisulphate. They explained it as due to an inhibiting action of the potassium ion; this has been found to be the case also when other organic compounds have been oxidised with peroxydisulphate.^{9,4}

The plots (not shown) of the experimental rate constant k against silver nitrate concentration were linear. The following mean values of the catalytic

Table 2. The silver ion-catalysed decomposition of potassium peroxydisulphate in DMSO-water mixtures.

DMSO M	AgNO ₃ M	10 ⁵ k (sec ⁻¹)					
		20.00°	25.00°	40.00°	50.00°	60.45°	75.00°
0.1	0			0.522			
0.1	0.0001			0.827			
0.1	0.0002	0.236	0.346	1.14	2.99		
0.1	0.0005			2.12			
0.1	0.001	0.853	1.24	3.74			
0	0			0.0408			
0	0.0002			0.509	1.21	2.85	10.93
0	0.0005			1.27			
0	0.0008			1.88			
0	0.001		0.627	2.30	4.82	10.4	
0.2	0.0005			2.63			

Table 3. Computed values of the catalytic coefficient k' of the silver ion and the derived quantities.

DMSO M	AgNO ₃ M	10 ⁵ k' (sec ⁻¹)						E kcal mole	log A
		20.00°	25.00°	40.00°	50.00°	60.45°	75.00°		
0.1	0.0002	847	1180	3110	7410			14.77	8.88
0.1	0.001	791	1130	3240				13.22	7.52
0	0.0002			2360	5180	10300	26400	14.80	8.72
0	0.001		627	2280	4700	9750		15.22	8.97

constants of the silver ion at 40° were computed from the slopes of the plots: At zero DMSO concentration: $k' = 2.34 \times 10^{-2} \text{ l mole}^{-1} \text{ sec}^{-1}$. At 0.1 M DMSO concentration: $k' = 3.14 \times 10^{-2} \text{ l mole}^{-1} \text{ sec}^{-1}$. The catalytic constant of DMSO at 40° and zero silver nitrate concentration is $4.93 \times 10^{-5} \text{ l mole}^{-1} \text{ sec}^{-1}$.

Gupta and Ghosh⁹ postulated a mechanism for silver ion-catalysed oxidations by peroxydisulphate ion in which free radicals and Ag^{2+} or Ag^{3+} are formed as intermediates. The mechanism involving the Ag^{2+} ion is the more likely one, because the transfer of one electron is more probable in an oxidation-reduction system that, like the one in question here, occurs between a transition metal ion and an ion derived from a non-transition element. It seems that DMSO to some extent helps the silver(I) ion to give up an electron, because, according to Table 3, the catalytic action of the silver(I) ion is somewhat greater in DMSO-water mixtures than in pure water.

The oxidation of organic sulphides to sulphones by peroxyacids is well known,^{11,5} and also the oxidation of DMSO by potassium peroxydisulphate to dimethyl sulphone: $(\text{CH}_3)_2\text{S}=\text{O} + \text{O} \rightarrow (\text{CH}_3)_2\text{SO}_2$.¹² We might think that the catalytic action of DMSO on the decomposition of peroxydisulphate in water is based on the oxidation of DMSO. We would then ask why the rate constants in DMSO— H_2O mixtures do not increase as the reaction proceeds, as they do because of the autocatalytic action of hydrogen ion when pure water is the solvent. On the other hand, if DMSO is consumed during the reaction, the first-order rate constants should decrease with time at low DMSO contents. It seems that these effects compensate each other. We computed the decrease of the rate constants caused by the decrease of the DMSO concentration at low DMSO contents at 40° assuming that the decrease of the molar concentration of DMSO is proportional to the extent of the reaction. From the linear plot of k against DMSO content we get: $\Delta k = 4.5\Delta[\text{DMSO}]$. If we now add this Δk to the original rate constants, we get rate constants that increase slightly and monotonously like the rate constants in pure water.

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