

Kinetics of silver(I) catalysed peroxydisulphate oxidation of benzylphenylglycollic acids

Pranati Mishra & N C Khandual*

Department of Chemistry, Ravenshaw College, Cuttack 753 003

Received 29 September 1986; revised 25 May 1987; accepted
14 October 1988

Ag(I) catalysed peroxydisulphate oxidation of benzylphenylglycollic and substituted benzylphenylglycollic acids in acetic acid-water mixture (30% v/v) at constant ionic strength is first order each in [peroxydisulphate] and [Ag(I)] and independent of [reductant]. Addition of allyl acetate inhibits the reaction. The thermodynamic parameters have been evaluated. The $\log k_1$ values have been fitted with σ^+ values and the value of ρ^+ calculated. The rate laws have been proposed on the basis of free radical mechanism involving silver(I).

The kinetics of alkaline hexacyanoferrate(III) oxidation of benzylphenylglycollic acids have been reported by us earlier¹. Title investigation is an extension of our earlier work. Silver(I) catalysed peroxydisulphate oxidation of benzylphenylglycollic acids do not seem to have been studied so far.

Experimental

Benzylphenylglycollic acid and substituted phenylglycollic acids (BPGAs) namely, 4-OCH₃, 4-CH₃, 4-chloro and 2,4-dichloro were prepared and purified by the literature methods. Potassium peroxydisulphate (AR) was used as such. The oxidation studies were carried out in acetic acid-water mixture (30% v/v) at $\mu = 0.1 \text{ mol dm}^{-3}$ (K₂SO₄). The rate of the reaction was followed by estimating the unreacted peroxydisulphate iodometrically. The presence of oxygen²⁻⁴ or sunlight did not seem to affect the rate and all experiments were carried out under diffused room light.

The stoichiometric investigation carried out using a known excess of potassium peroxydisulphate at 35°C, showed that 1 mol of benzylphenylglycollic acid required 2 mol of peroxydisulphate to give deoxybenzoin as the final product of oxidation. The product was isolated and characterised by direct comparison (m.m.p. and co. IR) with an authentic sample.

Results and discussion

The reaction is first order in [peroxydisulphate] as shown by the linearity of the plots of [S₂O₈²⁻]_t

versus time for over 75-80% of the reaction and also by the non-variation in the rate constant values at varying [peroxydisulphate] in the range of 0.0001 mol dm⁻³ to 0.001 mol dm⁻³.

Varying [BPGA] from 1.0 × 10⁻⁴ to 10.0 × 10⁻⁴ mol dm⁻³ at 35°C did not affect the rate constant showing that the reaction is zero order in [BPGA].

The reaction rate increased with increase in [Ag(I)]. At [Ag(I)] in the range of 1.0 × 10⁻⁵ mol dm⁻³ to 10.0 × 10⁻⁵ mol dm⁻³, the plot of $\log [Ag(I)]$ versus $\log k_1$ was linear with unit slope indicating that the reaction is first order in [Ag(I)]. Further, a plot of k_1 against [Ag(I)] passed through the origin showing that the uncatalysed decomposition of peroxydisulphate was negligible.

Increase in the ionic strength decreased the rate of reaction, thus indicating negative salt effect. For example under the conditions [peroxydisulphate] = 1 × 10⁻³ mol dm⁻³, [substrate] = 5 × 10⁻⁴ mol dm⁻³, [Ag⁺] = 1 × 10⁻⁵ mol dm⁻³ and temp. = 35°C increase in ionic strength from 0.04 to 0.1 mol dm⁻³ decreased $k_1 \times 10^3$ from 1.21 to 0.52 min⁻¹ when KNO₃ was used and 1.36 to 0.67 min⁻¹ when K₂SO₄ was used.

The rate of the reaction was inhibited by added allyl acetate, an efficient scavenger for the sulphate radical ion SO₄⁻ (ref. 5). When the allyl acetate concentration was increased to 0.03 mol dm⁻³, oxidation was completely checked showing a free radical chain mechanism.

The effect of temperature on the rate of the reaction was studied at 30, 35 and 40°C and activation parameters calculated (Table 1).

The reactivities of different substituents follow the order: 4-OCH₃ > 4-CH₃ > H > 4-Cl > 2,4-dichloro. It is observed that even under conditions when the reaction shows zero order dependence on [substrate], there is considerable difference in the values of k_1 . It is also evident that electron-donating substituents on the benzene nucleus increase the rate while electron-withdrawing groups retard it. The logarithm of the rate constants at 35°C correlated well with σ^+ values⁶. A similar correlation between $\log k_1$ and σ^+ has been observed by us¹ in the alkaline hexacyanoferrate (III) oxidation of BPGAs. The above order of reactivities is in agreement with the negative values of ρ^+ (-0.5).

From the results of Table 1 it is evident that both ΔH^\ddagger and ΔS^\ddagger are important in controlling the rates of reaction, though the enthalpy factor

Table 1—Reaction rate constants and Arrhenius parameters for the peroxydisulphate oxidation of BPGA

[Peroxydisulphate] = 1×10^{-4} mol dm $^{-3}$; [substrate] = 5.0×10^{-4} mol dm $^{-3}$; [Ag(I)] = 1×10^{-5} mol dm $^{-3}$; μ = 0.1 mol dm $^{-3}$; Solvent = acetic acid-water (30%, V/V)

Substrate	$k_1 \times 10^3 \text{ min}^{-1}$			E_a kJ mol $^{-1}$	$-\Delta S^\ddagger$ J mol $^{-1}$ K $^{-1}$	ΔH^\ddagger kJ mol $^{-1}$	ΔG^\ddagger kJ mol $^{-1}$
	30	35	40°C				
4-OCH $_3$	1.25	1.58	1.99	19.98	242.71	17.41	92.16
4-CH $_3$	0.75	1.01	1.31	24.08	232.68	21.51	93.17
H	0.51	0.67	1.07	32.61	208.44	30.04	94.17
4-Cl	0.32	0.50	0.75	34.68	203.98	32.12	94.94
2,4-dichloro	0.24	0.36	0.51	38.54	194.26	35.97	95.80

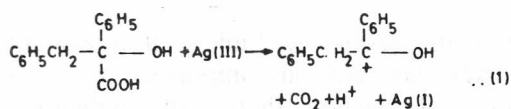
seems to be predominating. This point was also verified by calculating the isokinetic temperature (β) from the slope of the plot of ΔH^\ddagger versus ΔS^\ddagger . The value (425°K) was found to be well above the temperature range used in the present work. Constancy of calculated ΔG^\ddagger values for all BPGAs indicate that probably the same mechanism operates in all the cases. The large negative values of ΔS^\ddagger indicate that the activated complex is more rigid.

The facts that (i) the reactions proceed at rates which are considerably faster than the catalysed decomposition of peroxydisulphate, (ii) the rate of the reaction is a sensitive function of the experimental conditions, (iii) the reactions are strongly inhibited by allyl acetate, an effective captor for the sulphate radical ion $\text{SO}_4^{\cdot -}$ and (iv) ρ^+ value of -0.5 are strongly indicative of the operation of a chain mechanism involving free radicals. The nature of the silver intermediate in the oxidation by peroxydisulphate is uncertain. Both Ag^{2+} and Ag^{3+} ions have been postulated as intermediates. The nature of the silver species has been discussed by Anderson and Kochi⁷. Recent evidences in the literature point out to the fact that in aqueous acid solutions it is more likely that Ag(II) ions exist rather than Ag(III) ions⁸.

Gupta and Ghosh⁹ have proposed a mechanism involving an equilibrium which is followed by the termolecular rate-determining step.



It may be conceivable that Ag(III) is directly involved in the two equivalent oxidation of the acid (See Eq. 1).



Such a postulation has been rejected by Anderson and Kochi⁷ for it does not explain the critical role played by alkyl radicals and the catalysis of Cu(II) . Further, the value of ρ^+ (-0.5) supports the possibility of a benzylphenylmethanol radical¹⁰ and eliminates the possibility of the formation of the same cation¹¹.

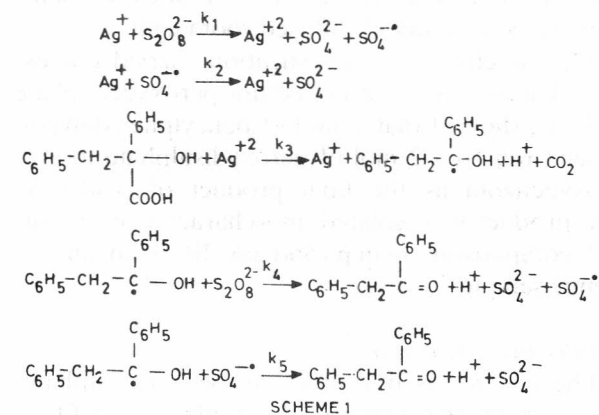
The catalytic effect of silver ions may be explained by considering Ag^{+2} and $\text{SO}_4^{\cdot -}$ as the reactive species. This is in accordance with the observations of Subbaraman and Santappa¹² and Higgenison and Marshall¹³ that one-electron transfer is more likely in oxidation-reduction system between transition metal ion and an ion derived from a non-transition element.

All the experimental evidences lead to rate law (2)

$$\frac{-d[\text{S}_2\text{O}_8^{2-}]}{dt} = k[\text{S}_2\text{O}_8^{2-}][\text{Ag}^+] \quad \dots (2)$$

The rate-determining step should not therefore involve any BPGA molecule but only $\text{S}_2\text{O}_8^{2-}$ and Ag^+ ions which yield intermediates capable of readily oxidising the substrate in subsequent fast steps. This is further supported by the negative value of ΔS^\ddagger .

On the basis of the above observations a radical chain mechanism (Scheme 1) has been proposed



SCHEME 1

Table 2—Comparison of the rates of BPGA with lactic acid and mandelic acid [Peroxydisulphate] = 1.6×10^{-4} mol dm $^{-3}$; [substrate] = 5.0×10^{-4} mol dm $^{-3}$; [Ag(I)] = 1.0×10^{-5} mol dm $^{-3}$; $\mu = 0.1$ mol dm $^{-3}$; Temperature = 35°C; Solvent = acetic acid-water (30% V/V)

Substrate	$k_1 \times 10^3$ min $^{-1}$	E_a kJ mol $^{-1}$	ΔS^\ddagger J mol $^{-1}$ K $^{-1}$
Lactic acid	0.63	34.68	-202.06
Mandelic acid	0.55	35.22	-201.46
Benzylphenylglycollic acid	0.67	32.61	-208.44

which is in agreement with the observed stoichiometry and kinetic data.

Applying the steady state condions Scheme 1 Leads to rate Law 3.

$$\begin{aligned} \text{Rate} = \frac{-d[S_2O_8^{2-}]}{dt} &= \left\{ k_1 + \sqrt{\frac{k_1 k_2 k_4}{k_5}} \right\} [Ag^+] [S_2O_8^{2-}] \\ &\approx \left[\frac{k_1 k_2 k_4}{k_5} \right]^{1/2} [Ag^+] [S_2O_8^{2-}] \\ &= k [Ag^+] [S_2O_8^{2-}] \end{aligned} \quad (3)$$

$$\text{Where } k = \left[\frac{k_1 k_2 k_4}{k_5} \right]^{1/2}$$

Results of peroxydisulphate oxidation of lactic and mandelic acids are given in Table 2. The data indicate that replacement of the methyl group in lactic acid by the phenyl group retarded the rate of oxidation. But the rate of oxidation accelerated by the introduction of a second phenyl group as in case of benzylphenylglycollic acid.

The interesting point in the present investigation is the effect of structural variation in the acid moiety on the rate and mechanism inspite of zero order dependence on reductant. The chain radical mechanism would explain this variation in rate constant, for in the proposed general mechanism, the peroxydisulphate ion is decomposed not only in the first step but also in the fourth step involving the radical $C_6H_5-CH_2-C-C_6H_5$ and this

OH

leads to the expression

$$\begin{aligned} \frac{-d[S_2O_8^{2-}]}{dt} &= k_1 [S_2O_8^{2-}] [Ag^+] \\ &+ k_4 [S_2O_8^{2-}] [C_6H_5-CH_2-C(C_6H_5)-OH] \end{aligned}$$

Although by the steady state hypothesis the concentration of $C_6H_5-CH_2-C(C_6H_5)-OH$ is a constant, this may vary from reductant to reductant giving rise to variation in the rate constant k_4 for the different variation in k_1 for

$$k = \left[\frac{k_1 k_2 k_4}{k_5} \right]^{1/2}$$

Acknowledgement

The authors are grateful to the UGC, New Delhi for financial assistance.

References

- Mishra Pranati & Khandual N C, *Indian J Chem*, 25A (1986) 902.
- Sabesan A & Venkatsubramanian N, *Indian J Chem*, 8 (1970) 251; 9 (1971) 942.
- Allen T L & Kalb A J, *J Am Chem Soc*, 86 (1964) 5107.
- Meghani G D & Bakore G V, *Indian J Chem*, 7 (1969) 786.
- Kolthoff I M, Mechan E J & Carr E M, *J Am chem Soc*, 75 (1953) 1439.
- Okamoto Y & Brown H C, *J Am chem Soc*, 80 (1958) 4979.
- Anderson M I & Kochi J K, *J Am chem Soc*, 92 (1970) 1651.
- Allen T L, Pohn & Swinhart J H, *Inorg Chem*, 7 (1968) 244.
- Gupta Y K & Ghosh S, *J inorg nucl Chem*, 1 (1959) 178.
- (a) Bartlett P B & Ruchardt C, *J Am chem Soc*, 82 (1960) 1756.
(b) Howard J A & Okamoto Y, *Canad J Chem*, 41 (1963) 1744.
- (a) Brown H C & Okamoto Y, *J org Chem*, 22 (1957) 485.
(b) Brown H C, Bernheimer R, Kim C J & Scheppele J, *J org Chem*, 89 (1967) 370.
- Subbaraman L R & Santappa M, *Z phys Chem*, Neve Folge I A II 48 (1966) 16.
- Higgenson W C & Marshall J W, *J org Chem*, (1957) 447.