

The rate expression (4) is in accordance with the experimental observations.

References

- HOUSE, D. A., *Chem. Rev.*, **62** (1962), 185.
- WILMARTH, W. H. & HARIM, A., *Mechanism of oxidation by peroxydisulphate ions in peroxide reaction mechanism*, edited by J. O. Edwards (John Wiley, New York), 1962, 175.
- SABESAN, A. & VENKATASUBRAMANIAN, N., *Indian J. Chem.*, **9** (1971), 942.
- SABESAN, A. & VENKATASUBRAMANIAN, N., *Indian J. Chem.*, **8** (1970), 251.
- SRIVASTAVA, S. P., MAHESWARI, G. L. & SINGHAL, S. K., *J. Indian chem. Soc.*, **49** (1972), 235.
- SRIVASTAVA, S. P. & SINGHAL, S. K., *J. Indian chem. Soc.*, **46** (1969), 705.
- SANTAPPA, M. & PADMA, S., *Proc. Indian Acad. Sci.*, (1969), 7.
- RADHAKRISHNA MURTI, P. S. & SWAMY, B. R. K., *Indian J. Chem.*, (in press).
- GUPTA, Y. K. & SENGAR, H. G. S., *J. Indian chem. Soc.*, **44** (1967), 769.

Kinetics & Mechanism of Ag⁺-catalysed Oxidation of Glyoxal & Glyoxalic Acid by Peroxydisulphate in Aqueous Medium

R. N. SINGH, L. N. SINGH* & H. S. SINGH

Department of Chemistry, University of Allahabad
Allahabad

Received 16 February 1977; accepted 21 June 1977

Silver(I) ion-catalysed peroxydisulphate oxidations of glyoxal and glyoxalic acid follow first order kinetics with respect to peroxydisulphate and zero order with respect to each substrate. A direct proportionality of the reaction velocity on [Ag⁺] is observed. The addition of some inorganic salts decreases the reaction rate. On the basis of the results, a probable mechanism has been proposed.

THE kinetics of Ag⁺-catalysed peroxydisulphate oxidations of several organic substrates have been extensively investigated¹⁻⁹. The kinetic results pertaining to the Ag(I)-catalysed oxidation of glyoxal and glyoxalic acid by peroxydisulphate, hitherto not reported, are presented in this note and a mechanism for the oxidation reaction has been proposed.

All the chemicals except glyoxal (40% solution, Riedel) were of either AR (BDH) or GR (E. Merck) grade. Their solutions were prepared in redistilled water. The stock solution of peroxydisulphate was always prepared fresh.

The kinetics was followed¹⁰ by estimating the amount of unconsumed peroxydisulphate at definite intervals of time iodometrically¹¹. Self-decomposition of peroxydisulphate in the presence of silver(I) ion and absence of the substrate has also been observed.

The reaction is first order with respect to [peroxydisulphate] (Table 1). In Table 1 k_a represents first order velocity constant, k_d gives the first order velocity constant for the decomposition of peroxy-

disulphate itself and $k = (k_a - k_d)$ represents the velocity constant for the oxidation process. The first order velocity constants were calculated from the slope of the plots made between logarithm of the volume of thiosulphate solution consumed (which is proportional to the concentration of S₂O₈²⁻) and time.

A close examination of the data in Table 2 clearly substantiates the direct proportionality of the reaction rate on [Ag(I)]. The rate constant is independent of the concentrations of glyoxal and glyoxalic acid (Table 3).

The kinetic study has also been performed at different temperatures and the energy of activation (E_a) for the oxidation of glyoxal (14.6 kcal mole⁻¹) and glyoxalic acid (12.3 kcal mole⁻¹) have also been calculated from the slope of the Arrhenius plot.

The addition of inorganic salts such as KNO₃ and K₂SO₄ into the reaction vessel decreases the rate of reaction (negative salt effect).

Mechanism—Thus on the basis of the observed kinetic results, the rate law (1) is suggested for the

TABLE 1—EFFECT OF VARYING THE CONCENTRATION OF PEROXYDISULPHATE IN THE Ag(I)-CATALYSED OXIDATION OF GLYOXAL AND GLYOXALIC ACID

| [S ₂ O ₈ ²⁻] × 10 ² M | k_a × 10 ² min ⁻¹ | k_d × 10 ³ min ⁻¹ | k × 10 ² min ⁻¹ |
|--|--|--|--|
| [GA] = 0.048M; [Ag ⁺] = 1.0 × 10 ⁻³ M; TEMP. = 35° ± 0.1° | | | |
| 0.50 | 4.61 | 1.33 | 4.48 |
| 0.75 | 3.76 | 1.28 | 3.63 |
| 1.00 | 4.35 | 1.21 | 4.23 |
| 1.50 | 4.08 | 1.07 | 3.97 |
| 2.00 | 4.30 | 0.97 | 4.20 |
| [G] = 0.03M; [Ag ⁺] = 1.0 × 10 ⁻³ M; TEMP. = 35° ± 0.1° | | | |
| 0.50 | 3.21 | 1.33 | 3.08 |
| 0.70 | 2.93 | 1.28 | 2.80 |
| 1.00 | 3.06 | 1.21 | 2.94 |
| 1.50 | 3.02 | 1.07 | 2.91 |
| 2.00 | 2.88 | 0.97 | 2.78 |

GA = glyoxalic acid; and G = glyoxal.

TABLE 2—EFFECT OF VARYING [Ag⁺] ON THE RATE CONSTANT FOR THE OXIDATION OF GLYOXAL AND GLYOXALIC ACID BY PEROXYDISULPHATE

| [Ag ⁺] × 10 ³ M | k_a × 10 ² min ⁻¹ | k_d × 10 ³ min ⁻¹ | k × 10 ² min ⁻¹ | $k/[Ag^+]$ M ⁻¹ min ⁻¹ |
|--|--|--|--|---|
| [S ₂ O ₈ ²⁻] = 0.01M; temp. = 35° ± 0.1° | | | | |
| [GA] = 0.048M | | | | |
| 0.25 | 1.42 | 0.32 | 1.39 | 5.55 |
| 0.50 | 2.28 | 0.67 | 2.21 | 4.43 |
| 0.75 | 2.98 | 0.92 | 2.89 | 3.85 |
| 1.00 | 4.35 | 1.21 | 4.23 | 4.23 |
| 1.50 | 6.35 | 1.82 | 6.17 | 4.11 |
| [G] = 0.03M | | | | |
| 0.50 | 2.19 | 0.67 | 2.12 | 4.25 |
| 1.00 | 3.06 | 1.21 | 2.94 | 2.94 |
| 1.25 | 3.68 | 1.54 | 3.53 | 2.82 |
| 1.50 | 4.67 | 1.82 | 4.49 | 2.99 |
| 1.75 | 5.30 | 2.16 | 5.08 | 2.90 |
| 2.00 | 5.76 | 2.57 | 5.50 | 2.75 |

*Present address: Department of Chemistry, Varanasi 221005.

TABLE 3 — EFFECT OF VARYING [SUBSTRATE] ON THE RATE CONSTANT FOR THE OXIDATION OF GLYOXAL AND GLYOXALIC ACID BY PEROXYDISULPHATE

{[S₂O₈²⁻] = 0.01M; [Ag⁺] = 1.0 × 10⁻³M; temp. = 35° ± 0.1°}

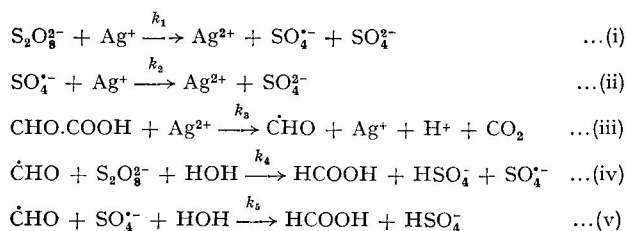
| [Glyoxalic acid] × 10 ² M | k _a × 10 ² min ⁻¹ | [Glyoxal] × 10 ² M | k _a × 10 ² min ⁻¹ |
|---|---|----------------------------------|---|
| 0.80 | 4.57 | 1.0 | 3.23 |
| 1.60 | 5.20 | 2.0 | 3.12 |
| 3.20 | 4.41 | 3.0 | 3.06 |
| 4.00 | 4.17 | 4.0 | 3.11 |
| 4.80 | 4.35 | 6.0 | 2.90 |
| 5.60 | 4.17 | 8.0 | 3.07 |

oxidation of both glyoxal and glyoxalic acid

$$-\frac{d[S_2O_8^{2-}]}{dt} = k_r [Ag^+][S_2O_8^{2-}] \quad \dots(1)$$

where k_r is specific rate constant which is equal to $k/[Ag^+]M^{-1} \text{ min}^{-1}$. The rate law (1) suggests that rate determining step between S₂O₈²⁻ and Ag⁺ ion yields one or more intermediates which subsequently oxidizes the substrate in fast steps. The negative salt effect also indicates that the interaction of two oppositely charged species might take place in the rate determining step¹².

In order to explain the rate law (1), the mechanism shown in Scheme 1 is suggested. This is valid for both the organic substrates.



Scheme 1

The evidence for the existence of Ag²⁺ and SO₄^{·-} as the reactive intermediates in the peroxydisulphate oxidations have been given by several workers¹³⁻¹⁵.

Thus, the rate of disappearance of peroxydisulphate might be given by Eq. (2)

$$-\frac{d[S_2O_8^{2-}]}{dt} = k_1 [Ag^+][S_2O_8^{2-}] + k_4 [\dot{C}HO][S_2O_8^{2-}] \quad \dots(2)$$

Considering the steady state conditions, one obtains the relationship

$$[\dot{C}HO] = \left(\frac{k_1 k_2}{k_4 k_5}\right)^{\frac{1}{2}} [Ag^+] \quad \dots(3)$$

From Eqs. (2) and (3), the rate law becomes

$$-\frac{d[S_2O_8^{2-}]}{dt} = k_r [S_2O_8^{2-}][Ag^+] \quad \dots(4)$$

where $k_r = k_1 + k_4 \left(\frac{k_1 k_2}{k_4 k_5}\right)^{\frac{1}{2}}$.

Thus derived, rate law (4) clearly explains the observed kinetics.

The formic acid was identified¹⁶ as the final reaction product in the oxidation of glyoxal and glyoxalic acid both.

Further, on comparing the rate constant values (Table 2) and also the value of Arrhenius energy of activation, one can easily conclude that the rates of oxidation of glyoxalic acid and glyoxal follow the order glyoxalic acid > glyoxal. The higher rate with glyoxalic acid might be due to the carboxylic group which would ease the formation of CHO radical.

One of the authors (R.N.S.) is very grateful to the UGC, New Delhi, for financial support.

References

- SABESAN, A. & VENKATASUBRAMANIAN, N., *Indian J. Chem.*, **9** (1971), 942.
- GUPTA, Y. K. & GHOSH, S., *Proc. nat. Acad. Sci.*, **27** (1958), 258.
- SENGAR, H. G. S. & GUPTA, Y. K., *Indian J. Chem.*, **6** (1968), 119.
- GUPTA, Y. K. & NIGAM, R. K., *J. Indian chem. Soc.*, **37** (1960), 125.
- PRASAD, B. N., SINGH, R. N. & SINGH, N. P., *J. scient. Res. BHU*, **XXIV** (1973), 6.
- SRIVASTAVA, S. P., MAHESWARI, G. L. & SINGHAL, S. K., *J. Indian chem. Soc.*, **49** (1972), 235.
- SRIVASTAVA, S. P. & SINGHAL, S. K., *J. Indian chem. Soc.*, **46** (1969), 705.
- KHANDUAL, N. C. & NAYAK, P. L., *J. Indian chem. Soc.*, **50** (1973), 194.
- KHANDUAL, N. C. & NAYAK, P. L., *J. Indian chem. Soc.*, **50** (1973), 786.
- SINGH, R. N., SINGH, L. N. & SINGH, H. S., *Indian J. Chem.*, **15A** (1977), 40.
- KOLTHOF, I. M. & CARR, E. M., *Analyt. Chem.*, **25** (1953), 298.
- LAIDLER, KEITH J., *Chemical kinetics* (Tata-McGraw-Hill, India), 1965, 220.
- BAWN, C. R. H. & MARGERISON, D., *Trans. Faraday Soc.*, **51** (1955), 925.
- HIGGINSON, W. C. & MARSHALL, J. W., *J. chem. Soc.*, (1957), 447.
- MENGHANI, G. D. & BAKORE, G. V., *Indian J. Chem.*, **7** (1969), 786.
- FRITZ FEIGL, *Spot tests: Organic applications*, Vol. 3 (Elsevier, New York), 1954, 245.

Cerimetric Determination of Boron as Borotartrate

B. MADHAVA RAO

Department of Chemistry
Sardar Vallabhbhai Regional College of
Engineering & Technology, Surat 395007

Received 18 December 1976; accepted 27 June 1977

An indirect cerimetric method for the estimation of boron is developed. Boron is precipitated as barium borotartrate complex in which boron to tartaric acid ratio is 1 : 2. The amount of Ce(IV) consumed by the complex gives a measure of tartrate ion and indirectly furnishes the boron content.

RECENTLY Gopala Rao *et al.*¹ have developed an accurate method for the determination of tartaric acid using ammonium hexanitratocerate(IV) as an oxidizing agent. This procedure has been extended for the determination of tartrate ion complexed as borotartrate, since conditions have