Asian Journal of Chemistry Vol. 16, No. 1 (2004), 85–88

Kinetics of the Reaction Between Peroxodisulphate(VI) and Iodide Ions

PONNADURAI RAMASAMI*, D.N. MOOTHOOSAMY and R. GOOJHA
Department of Chemistry, University of Mauritius, Réduit, Mauritius
E-mail: p.ramasami@uom.ac.mu

The reaction between peroxodisulphate(VI) and iodide ions is being investigated at different temperatures with a view to obtain the activation energy. Further, the effect of different catalysts on the reaction is studied. The results have been interpreted using concepts of kinetics and the Arrhenius equation has been used to calculate the activation energy. The effect of the different catalysts is explained on the basis of the mechanism by which these catalysts work.

Key Words: Kinetics, Peroxodisulphate(VI), Iodide ions.

INTRODUCTION

The reaction between peroxodisulphate(VI) and iodide ions and their kinetic investigations have been known for quite a long time[1–5]. The popularity of this reaction may be associated for it being inexpensive, safe and easy to prepare and perform. Also the reaction has sudden and vivid colour changes. The reaction has a standard redox potential of +2.55 V and the chemical equation for the reaction may be represented as

$$2KI_{(aq)} + K_2S_2O_{8(aq)} \rightarrow I_{2(aq)} + 2K_2SO_{4(aq)} \qquad (1)$$

This reaction occurs uncatalyzed as the two anions have enough energy to overcome the forces of repulsion among them. However, the rate of reaction may be increased by using transition metals ions, as catalyst.

This paper reports the investigation of the catalyzed and uncatalyzed reactions between peroxodisulphate(VI) and iodide ions. The reaction has been studied at different temperatures[6] in the presence of different catalysts and the activation energy has also been calculated[7]. The salts used to investigate catalysis effect are silver nitrate[8], iron(II) sulphate and mercury(II) chloride[9]. The activation energies, electrode potentials and the collision theory have been used for analysis of the results.

EXPERIMENTAL

All chemicals used for this work were of analytical reagent grade and were purchased from BDH and they were used without further purifications.

For study of the uncatalysed reaction

Aqueous potasium peroxodisulphate(VI) (0.05 mol/dm^3, 100 cm^3), was taken in a conical flask and aqueous potassium iodide (0.1 mol/dm^3, 100 cm^3) and ethanoic acid (2.0 mol/dm^3, 10 cm^3) were taken in another conical flask. These flasks were loosely corked and placed in a water bath set at a given temperature. When the two reactants attained the temperature of the thermostat, the aqueous potassium iodide solution was poured into the flask containing aqueous potassium peroxodisulphate(VI). A stopwatch was started simultaneously and the flask was shaken from time to time. The reaction mixture (10 cm^3) was withdrawn and transferred into a conical flask containing ice-cold water (50 cm^3) to freeze the reaction. The iodine liberated was quickly titrated against standard sodium thiosulphate (0.100 mol/dm^3) using starch indicator. Further, the reaction mixture (40 cm^3) was transferred into a flask and solid potassium iodide was added. This mixture was kept overnight at room temperature; 10.0 cm^3 of this mixture was then titrated with sodium thiosulphate. Each set of experiment was repeated thrice.

For study of the catalyzed reaction

The procedure was the same as described for the uncatalyzed reaction except that 0.200 mol/dm^3 aqueous potassium iodide was used rather than 0.100 mol/dm^3. Also 10 cm^3 of aqueous solution (0.100 mol/dm^3) containing the catalyst under investigation was added and after equilibration at the given temperature, aqueous potassium iodide and aqueous potassium peroxodisulphate(VI) were mixed. Each set of experiments was repeated thrice.

RESULTS AND DISCUSSION

Uncatalyzed reaction

The reaction between aqueous potassium peroxodisulphate(VI) and potassium iodide is known to be second order. The rate constant K mol^{-1} dm^3 s^{-1} was obtained by regression for each set. The average rate constants obtained from the three sets are reported for the three different temperatures as given in Table-1.

TABLE-1
RATE CONSTANTS OF THE UNCATALYZED REACTION AT DIFFERENT TEMPERATURES

Temperature (K)	Rate constant (mol^{-1}dm^3 s^{-1})
293.15	1.10×10^{-6} (0.02×10^{-6})*
303.15	2.26×10^{-6} (0.01×10^{-6})*
313.15	3.52×10^{-6} (0.59×10^{-6})*
323.15	6.34×10^{-6} (0.39×10^{-6})*

*Values within brackets correspond to standard error.

The Arrhenius equation, $K = Ae^{-\frac{E_a}{RT}}$, is used to evaluate the activation energy of the uncatalyzed reaction: A graph of ln K is plotted against 1/T and a linear graph with $R^2 = 0.994$ is obtained as illustrated in Fig. 1.

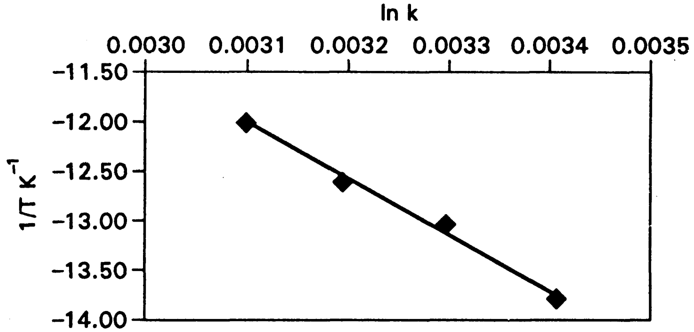

Fig. 1. Plot of ln K against 1/T.

The activation energy (E_a) is found to be 44.9 kJ/mol (2.4 kJ/mol as the standard error). This uncatalyzed reaction (1) has high activation energy due to single collision between ions of the same charge.

Catalyzed reaction

The average rate constants calculated as for the catalyzed reaction at different temperatures for the different catalysts silver nitrate, iron(II) sulphate and mercury(II) chloride are reported in Table-2.

TABLE-2
RATE CONSTANTS OF THE CATALYZED REACTION FOR DIFFERENT CATALYSTS AT DIFFERENT TEMPERATURES

Catalyst	Temperature (K)	Rate constant ($mol^{-1}dm^3 s^{-1}$)	Activation energy ($kJ mol^{-1}$)
Silver Nitrate	293.15	3.21×10^{-6} (0.50×10^{-6})*	25.2 (1.7)
	303.15	4.12×10^{-6} (0.23×10^{-6})	
	313.15	5.98×10^{-6} (0.31×10^{-6})	
	323.15	8.24×10^{-6} (0.66×10^{-6})	
Iron(II) sulphate	293.15	2.34×10^{-6} (0.09×10^{-6})*	31.5 (1.4)
	303.15	2.98×10^{-6} (0.92×10^{-6})	
	313.15	3.62×10^{-6} (0.52×10^{-6})	
	323.15	5.24×10^{-6} (0.54×10^{-6})	
Mercury(II) chloride	293.15	1.37×10^{-6} (0.07×10^{-6})*	21.7 (1.4)
	303.15	1.95×10^{-6} (0.20×10^{-6})	
	313.15	1.99×10^{-6} (0.15×10^{-6})	
	323.15	2.97×10^{-6} (0.22×10^{-6})	

*Values in brackets correspond to standard error.

Thus it can be found that these salts have increased the rate constants and decreased the activation energy for the reaction and hence serve as catalysts. In fact these catalysts work through chain reactions involving collisions of oppositely charged ions compared to the single collision between the two anions in the uncatalyzed reaction. The chain reactions can be decided using the redox potentials for the half-cell reactions. These chain reactions, if aqueous iron(II) sulphate is used, are as given by (2) and (3).

$$2Fe^{2+}_{(aq)} + S_2O^{2-}_{8(aq)} \rightarrow 2Fe^{3+}_{(aq)} + 2SO^{2-}_{4(aq)} \quad (2)$$

$$2Fe^{3+}_{(aq)} + 2I^{-}_{(aq)} \rightarrow I_{2(aq)} + 2Fe^{2+}_{(aq)} \quad (3)$$

It can be concluded that silver nitrate and mercury(II) chloride are better catalysts than iron(II) sulphate, from the results of Table-2 and this may be explained on the basis that ferrous ions have to be oxidized to the ferric state by peroxodisulphate(VI) ions first and the ferric ion can oxidize the iodide to iodine. Thus iodine is produced in the second step compared to the other two catalysts. These may be understood on the basis of standard electrode potentials.

Conclusion

The uncatalyzed reaction between peroxodisulphate(VI) and iodide ions has been investigated at different temperatures to obtain the activation energy. Also, the effect of three different catalysts namely silver nitrate, iron(II) sulphate and mercury(II) chloride has been investigated. The experimental data support the positive catalytic effect of the salts used, as the activation energy of the reaction between peroxodisulphate(VI) and iodide ions has decreased.

REFERENCES

1. A.M.G. Vasilarou and C.A. Georgiou, *J. Chem. Educ.*, **77**, 1327 (2000).
2. W.C. Boring and E. McMillan, *J. Chem. Educ.*, **61**, 744 (1984).
3. A. Lombardo, *J. Chem. Educ.*, **59**, 887 (1982).
4. A. Evenson, *J. Chem. Educ.*, **79**, 822 (2002).
5. M.P. Sah, M.D. Jha, A.K. Pathak, K.B. Lal and S.K. Sinha, *Asian J. Chem.*, **12**, 9 (2000).
6. R.E. Huie and C.L. Clifton, *J. Phys. Chem.*, **94**, 8561 (1990).
7. H. Iloukhani, N. Rashidi and M. Moghadasi, *Asian J. Chem.*, **12**, 1209 (2000).
8. B. Gupta, *J. Chem. Soc. Dalton Trans.*, **9**, 1873 (1984).
9. V. Butkovic, A. Bakac and J.H. Espenson, *Croat. Chem. Acta*, **74**, 735 (2001).

(*Received*: 4 March 2003; *Accepted*: 20 August 2003) AJC-3147