Asian Journal of Chemistry Vol. 15, Nos. 3 & 4 (2003), 1672–1676

Kinetics and Mechanism of the Reduction of Methylene Blue by Titanium(III) Sulfate

DILIP B. PATIL* and AJAY P. GANORKAR†

Department of Chemistry
Institute of Science, Nagpur-440 001, India

Kinetics of the rapid reduction of methylene blue by titanium(III) sulfate has been carried spectrophotometrically at various temperatures. From the results, kinetic parameters such as specific reaction rate, energy of activation, entropy of activation and frequency factor have been evaluated at 25°C and found to be 433 m^{-1} s^{-1}, 63.8 kJ mol^{-1}, 10.59 J K^{-1} mol^{-1} and 6.04×10^{13} mol^{-1} s^{-1} respectively. In order to speculate the most probable mechanism of the reaction, the effect of sulphuric acid concentration on specific rate has been determined.

Key Words: Kinetics and mechanism, Methylene blue, Titanium(III) sulfate.

INTRODUCTION

Dyes are coloured substances in which the relation between the colour and the chemical constitution is very important. Several types of dyes are known such as azo, nitro, nitroso, vat, azine, thiazine, etc. each with its characteristic chromophoric groups. Any reaction which alters the chromophoric group naturally affects the colour. A typical such reaction is reduction[1]. It would be interesting to study the kinetics and mechanism of the reduction of azo dyes. As a typical case methylene blue has been studied. The reduction of methylene blue has been studied by various workers[2-7] and its reduction by titanium(III) has been known since long; yet the kinetic study of the reduction has not been carried out meticulously. The reasons for this are evident: firstly the reaction is rather rapid and needs some special technique; secondly both the leucobase of methylene blue and titanium(III) are succeptible to atmospheric oxidation. Under these circumstances, the kinetics of the reaction has been studied spectrophotometrically and the most probable mechanism has been proposed.

†Department of Chemistry, K.Z.S. Science College, Kalmeshwar, Nagpur, India

EXPERIMENTAL

Analytical grade chemicals were used to prepare the solutions. The water used for the preparation of solutions was double distilled. A stock solution of methylene blue (5.0×10^{-3} M) was prepared. For kinetic study this solution was further diluted to accurately known concentration. Titanium(III) sulfate solution was prepared by the procedure recommended by Vogel[8]. The stock solution of titanium(III) was transferred to a storage bottle in which the air had been displaced. This stock solution was standardized against potassium permanganate and later was standardized against oxalic acid solution.

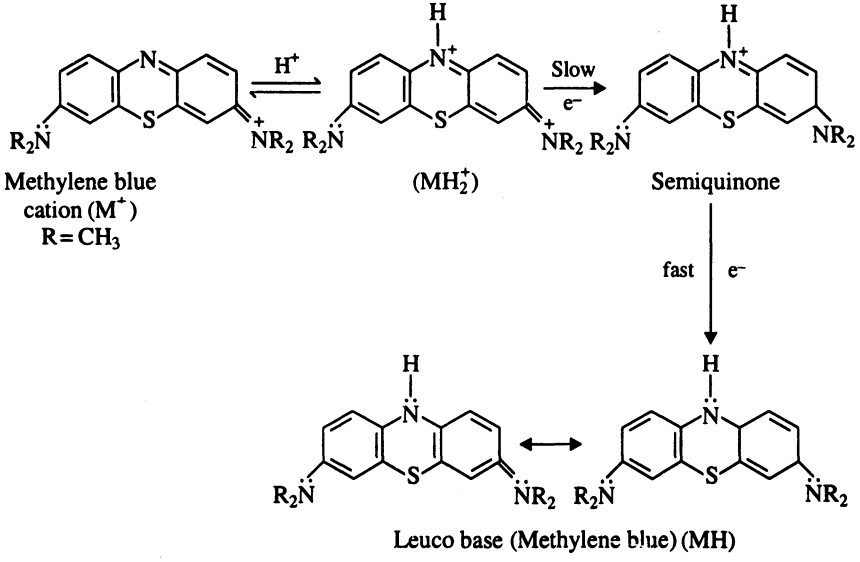

Chart-1

Kinetic Measurements

50 c.c. each of 5×10^{-4} M solution of methylene blue and 1.0×10^{-3} M solution of titanium(III) sulfate were taken in glass-stoppered bottles from which air had been displaced and both the bottles were kept in a thermostat. The water from the thermostat was circulated through the cuvette jacket of the spectrophotometer. When the solution had attained the temparature of the thermostat, equal volumes of the reactant solutions were mixed and immediately the mixture was transferred into the cuvette of the spectrophotometer, which was set at wavelength 550 nm (λ_{max}).

From the measurements of the optical density, the concentrations of methylene blue yet remaining unreacted at various time intervals were determined (Table-1).

The reciprocal of the unreacted methylene blue was plotted versus time. The

curve was a straight line showing that the reaction was of second order. The slope of the straight line was determined and half of the slope was the specific reaction rate. Repeated measurements yielded specific reaction rates agreeing within ±2%.

TABLE-1
KINETICS OF REDUCTION OF METHYLENE BLUE BY TITANIUM(III) IN AQUEOUS SOLUTION

Initial concentration of methylene blue : 2.5×10^{-4} M
Initial concentration of titanium(III) sulfate : $5.0\ 10^{-4}$ M
Concentration of sulphuric acid : 1.0 M
Temperature : 25°C

Time (sec)	Optical density	$\left[\text{Unreacted methylene blue}\right] \times 10^{-4}$ M	$\left[\frac{1}{\text{methylene blue}}\right] \times 10^{-4}\ M^{-1}$
0	1.40	2.50	0.40
3	0.76	1.55	0.65
6	0.48	1.10	0.91
9	0.33	0.85	1.18
12	0.27	0.70	1.43
15	0.21	0.60	1.67
18	0.18	0.50	2.00
21	0.16	0.45	2.22
24	0.14	0.40	2.50
27	0.12	0.35	2.86
30	0.10	0.33	3.03

From similar kinetic measurements the specific reaction rates were obtained at various temperatures and from the Arrhenious plot, the energy of activation for the reaction was obtained (Table-2) further the entropy of activation and frequency factor were also evaluated.

TABLE-2
ENERGY OF ACTIVATION FOR THE REDUCTION OF METHYLENE BLUE BY TITANIUM(III) SULFATE IN AN AQUEOUS SOLUTION

Temp (°C)	Temp. T (K)	$1/T \times 10^{-3}\ K^{-1}$	Specific reaction rate, K_2 ($m^{-1}\ s^{-1}$)	log K_2
11	284	3.52	128	2.1072
15	288	3.47	175	2.2430
20	293	3.41	293	2.4669
25	298	3.36	433	2.6365
30	303	3.30	667	2.8241

Slope of the graph of log K_2 *va.* $1/T = -3.33 \times 10^3$

$$\text{Energy of activation} = \frac{-2.303 \times 8.314 \times (-3.33 \times 10^3)}{1000} = 63.8\ \text{kJ mol}^{-1}$$

RESULTS AND DISCUSSION

The reduction of methylene blue by titanium(III) sulfate is a fast reaction and its kinetic parameters at 25°C are summarized below.

Specific reaction rate	:	433 $m^{-1}s^{-1}$
Energy of activation	:	63.8 kJ mol^{-1}
Entropy of activation	:	10.59 J K^{-1} mol^{-1}
Frequency factor	:	6.04×10^{13} mol^{-1} s^{-1}

In spite of the rapidity of the reaction, the kinetics can be readily studied by the spectrophotometric method. It is to be noted however that even with as dilute solution as 2.5×10^{-4} M, methylene blue evinces significant deviation from Beer's law[9]. Consequently the evaluation of the concentration of methylene blue from optical density measurment was carried out from an optical density *vs.* concentration plot.

The reduction of methylene blue can be represented by the equation

$$M^+ + 2e^- + H^+ \rightarrow MH$$

where M^+ is the dye cation, MH is the leuco form. Titanium(III) ion provides e^- for the reduction

$$Ti(III) \rightleftharpoons Ti(IV) + e^-$$

This shows the need of two Ti(III) ions for the reduction of every methylene blue, thus justifying the 1 : 2 ratio of the methylene to Ti(III) in the reduction reaction.

Methylene blue is an active electron acceptor and its protonated form is readily reduced. Yushina and Nikolaev[6] suggested that the site of proton transfer in a molecule of methylene blue is the N atom in a thiazine ring. This is quite reasonable, since according to Pullman and Pullman[7], this atom carries the most negative charge. An electron is probably transferred through the part of the methylene blue molecule containing the dimethyl amino group, where negative charge is the minimum.

Since proton is involved in the reduction of methylene blue, it is evident that the reduction potential would increase at higher concentration of acid. This might favour increased rate for the reduction at higher concentration of the acid. This expectation is found to be borne out from the result of experiments carried out to study the influence of acid concentration on the specific reaction rate. The sulphuric acid concentration was increased from 0.2 to 1.25 M; consequently the specific reaction rate increased from 141 to 584 m^{-1} s^{-1} (Table-3).

The marked influence of acid concentration on the rate of the reduction suggested that H^+ ion adds initially to the cation of methylene blue and doubly charged protonated methylene blue cation is produced. This then combines with an electron, in a slow rate determining step which converts the methylene blue into protonated semiquinone. Subsequent rapid addition of an electron converts the semiquinone into the leuco form of methylene blue **(Chart-1).**

TABLE-3
DEPENDENCE OF SPECIFIC REACTION RATE ON SULPHURIC ACID CONCENTRATION AT 25°C

Sulphuric acid concentration (M)	Specific reaction rate (K_2) ($m^{-1} s^{-1}$)
0.25	141
0.50	209
0.75	314
1.00	433
1.25	584

ACKNOWLEDGEMENTS

Authors thank Prof. M.N. Deshpande, Director, Institute of Science, Nagpur and Dr. M.R. Patil, Head, Department of Chemistry, Institute of Science, Nagpur for providing the facilities to carry out the present work.

REFERENCES

1. J.D. Robert and M.C. Casirio, Modern Organic Chemistry, W.A. Benjamin Inc., New York-Amsterdam, p. 696 (1967).
2. Adamcikova, L. Ubica, Pavlikoa, Katarina and S. Peter, *Int. J. Chem. Kinet.*, **31**, 463 (1999).
3. R. Agrawal and K.K. Mishra *J. Phys. Chem.*, **211**, 91 (1999).
4. J. Kiwi, N. Denisov and V. Nadtochenko, *J. Phys. Chem.* (*B*), **103**, 1941 (1999).
5. T. Tesu, T. Shinichiro, M. Tetsuya, T. Denold and A.F. Akiva, *J. Phys. Chem. (B)*, **103**, 8033 (1999).
6. V.V. Yushina and L.A. Nikolaev, *Zh. Fiz. Khim.*, **46**, 740 (1972).
7. B. Pullman and A. Pullman, Quantum Biochemistry, Izd. Mir, Moscow (1961).
8. A.I. Vogel, A Textbook of Quantitative Inorganic Analysis, 3rd Edn., English Language Book Society, p. 329 (1981).
9. L. Michaelis and S. Granik, *J. Am. Chem. Soc.*, **67**, 1212 (1945).

(*Received*: 6 February 2003; *Accepted*: 12 May 2003) AJC-3082