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# THE KINETICS OF METHYLENE BLUE – ASCORBIC ACID REACTION

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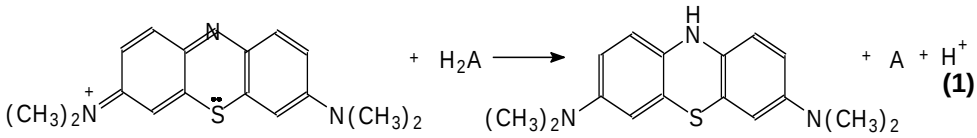
***ABSTRACT.*** The clock reaction between methylene blue and ascorbic acid has been investigated over a large variety of experimental conditions. Kinetic parameters are reported. The overall rate equation has been obtained and the Arrhenius activation energy is calculated. The effect of dielectric constant on the rate is explained. A reaction sequence is suggested and discussed in relation to previous studies.

## INTRODUCTION

The reduction of methylene blue, a basic thiazinic dye used as a redox indicator, may be performed with different reducing agents. L-ascorbic acid, vitamin C - a biologically important compound is among them. Snehalatha, Rajanna and Saiprakash [1] have demonstrated a clock reaction involving methylene blue (MB) and ascorbic acid ($H_2A$). Many advanced concepts of chemical kinetics could be explained by this clock reaction, having the stoechiometry:




**(1)**

Blue colored Colorless

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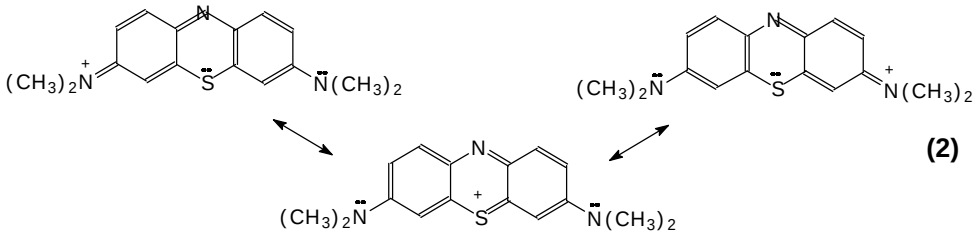
The colored cation can exist in three mezomeric forms:



**(2)**

having para quinoid structure of extended conjugation.

A biequivalent reduction of the cation, which formally means the attachment of a hydride to the central nitrogen atom, breaks the conjugation and a neutral leuco-compound is formed. Half-reduction, when a neutral free radical is formed, yields also to a colored species [2] with the formation of a colorless reduced compound and dehydroascorbic acid (A).

Such clock reaction studies have been undertaken with Landolt-type reactions [3], bromate-bromide [4], persulfate-iodide [5], bromination of phenols [6], hydrogen peroxide – bromide [7] or iodide [8] systems, to achieve kinetic or analytical.

It seems that Snehalatha and his co-workers [1] made some misinterpretation concerning the methylene blue - ascorbic acid reaction, in both the rate equation and rate-determining steps in their proposed mechanism.

In the present work, this reaction has been studied in a wide condition range of reactants and hydrogen ion concentrations, choosing those conditions that ensure time measurements less affected by the experimental errors.

## EXPERIMENTAL

Aqueous or 1,4-dioxane-water and acetone-water solutions of the reagents were freshly prepared before each set of measurements. Analytical grade reagents were used without further purification. Methylene blue chloride and sodium ascorbate (Merck) were weighted, dissolved with twice distilled water and made up to the mark in volumetric flasks of 250 ml. Hydrocloric, sulfuric and phosphoric acids were used as sources for hydrogen ions. The solutions were standardized by usual procedures.

Two solutions were prepared for each kinetic experiment, so that after mixing the total volume was 25 ml. One solution contained ascorbic acid, HCl (or other) and KCl while the other contained methylene blue. Solutions were kept at controlled temperature, the first one in a double wall glass vessel connected to a precision circulation bath. It was placed on a magnetic stirrer. The solution of methylene blue was added to the first one under stirring and a stop-watch was started. The reaction time (t) for blue color to change colorless was recorded.

Three to four replicate runs were carried out for the same experimental conditions. Time measurements do not differ with more than ± 1.5 %.

Free radical involvement was checked by the polymerization of vinyl-acetate.

## RESULTS AND DISCUSSION

The effect of reactants and hydrogen ion concentrations as well as the effect of ionic strength, solvent composition and temperature on the reaction rate are presented in tables 1 - 6.

**Table 1.**

The effect of ascorbic acid concentration on the reaction rate at T = 293 K, $[MB]_o = 1.78 \bullet 10^{-5}$ mole.l$^{-1}$, $[KCl]_o = 0.12$ mole.l$^{-1}$, in aqueous solution.

| Medium | $10^3$ $[H_2A]_o$ (mole.l$^{-1}$) | t (s) | $t_{mean}$ (s) | $10^7$ r (mole.l$^{-1}$.s$^{-1}$) |
|---|---|---|---|---|
| HCl<br>$[H^+]_o = 0.75$ mole.l$^{-1}$<br>j = 0.87 mole.l$^{-1}$ | 2 | 408, 408, 411, 412 | 410 | 0.43 |
| | 4 | 216, 215, 219, 215 | 216 | 0.82 |
| | 6 | 147, 150, 147, 148 | 148 | 1.20 |
| | 8 | 119, 120, 120, 118 | 119 | 1.49 |
| | 10 | 100, 100, 101, 101 | 100 | 1.78 |
| | 12 | 81, 81, 81, 82 | 81 | 2.19 |
| | 13 | 68, 68, 68 | 68 | 2.61 |
| $H_2SO_4$<br>$[H^+]_o = 0.44$ mole.l$^{-1}$<br>j = 0.65 mole.l$^{-1}$ | 2 | 448, 450, 447, 449, | 448.5 | 0.39 |
| | 4 | 233, 234, 230, 229 | 231.5 | 0.76 |
| | 6 | 157, 160, 158, 156 | 158 | 1.12 |
| | 8 | 125, 126, 125, 125 | 125 | 1.42 |
| | 10 | 99, 99, 102, 101 | 100 | 1.78 |
| | 12 | 82, 84, 83, 85 | 83.5 | 2.13 |
| | 13 | 70, 71 | 70.5 | 2.52 |
| $H_3PO_4$<br>$[H^+]_o = 0.04$ mole.l$^{-1}$<br>j = 0.16 mole.l$^{-1}$ | 2 | 892, 891, 888 | 890 | 0.20 |
| | 4 | 541, 542, 543 | 542 | 0.32 |
| | 6 | 387, 385, 388 | 387 | 0.45 |
| | 8 | 332, 333, 333 | 333 | 0.53 |
| | 10 | 256, 259, 258 | 258 | 0.68 |
| | 12 | 242, 243, 245 | 243 | 0.73 |
| | 13 | 226, 228 | 227 | 0.78 |

**Table 2.**

The effect of methylene blue concentration on the reaction rate at T = 293 K, $[H_2A]_o = 6 \bullet 10^{-3}$ mole.l$^{-1}$, $[KCl]_o = 0.12$ mole.l$^{-1}$, in aqueous solution.

| Medium | $10^5$ $[MB]_o$ (mole.l$^{-1}$) | $t_{mean}$ (s) | $10^7$ r (mole.l$^{-1}$.s$^{-1}$) |
|---|---|---|---|
| HCl<br>$[H^+]_o = 0.75$ mole.l$^{-1}$<br>j = 0.87 mole.l$^{-1}$ | 0.36 | 59 | 0.61 |
| | 1.07 | 110 | 0.97 |
| | 1.78 | 148 | 1.20 |
| | 2.49 | 164 | 1.51 |
| | 3.20 | 184 | 1.73 |
| | 3.91 | 199 | 1.96 |
| $H_2SO_4$<br>$[H^+]_o = 0.44$ mole.l$^{-1}$<br>j = 0.65 mole.l$^{-1}$ | 0.36 | 59 | 0.61 |
| | 1.07 | 112 | 0.95 |
| | 1.78 | 157 | 1.13 |
| | 2.49 | 180.5 | 1.37 |
| | 3.20 | 106.5 | 1.54 |
| | 3.91 | 220 | 1.77 |
| $H_3PO_4$<br>$[H^+]_o = 0.04$ mole.l$^{-1}$<br>j = 0.16 mole.l$^{-1}$ | 0.36 | 172 | 0.20 |
| | 1.07 | 288 | 0.37 |
| | 1.78 | 386 | 0.46 |
| | 2.49 | 511 | 0.49 |
| | 3.20 | 550 | 0.58 |
| | 3.91 | 619 | 0.63 |

**Reaction orders:**

Using a differential method for determining the reaction order with respect to various species, the following conclusions were drawn:

a.) The process obeys first-order dependence with respect to ascorbic acid for all experimental conditions employed. The plots of *lg (r)* versus *lg ($[H_2A]_o$)* were linear with slopes of 1.00 ± 0.03. Figure 1 presents the dependence of rate on $[H_2A]_o$. Points lie on the line, with good correlation coefficients (0.9956 – 0.9982). Slopes in figure 1 are different because of different hydrogen ion concentrations when using HCl, $H_2SO_4$ or $H_3PO_4$.

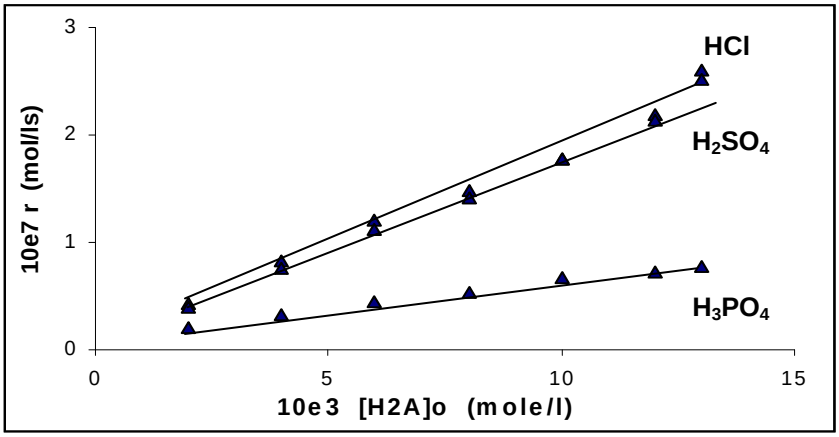



***Figure 1.*** Reaction rate versus ascorbic acid initial concentration at T = 293 K, $[MB]_o = 1.78 \bullet 10^{-5}$ mole.l$^{-1}$, $[KCl]_o = 0.12$ mole.l$^{-1}$, in aqueous solution.

b.) The process obeys a 0.5 order with respect to methylene blue as shown in figure 2 which presents the rate versus $[MB]_o^{1/2}$. Points lie on lines with good correlation coefficients (0.9925 – 0.9957) irrespective of the acid used. The slopes vary because of the same reasons as explained above.

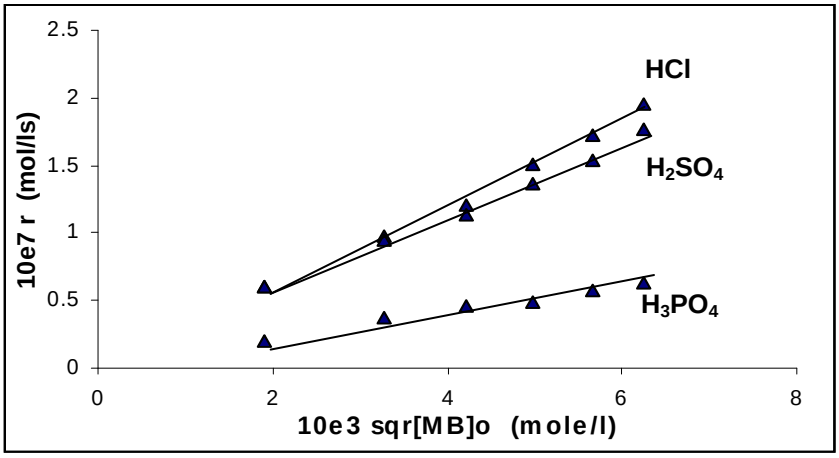



***Figure 2.*** Reaction rate versus the square root of initial methylene blue concentration at T = 293 K, $[H_2A]_o = 6 \bullet 10^{-3}$ mole.l$^{-1}$, $[KCl]_o = 0.12$ mole.l$^{-1}$, in aqueous solution.

c.) The fractional order on $H^+$ ion found by Snehalatha and his co-workers [1], was confirmed by us by plotting *lg (r)* versus *lg ($[H^+]_o$)*. Lines with good correlation coefficients, 0.9938 and 0.9898 were found. Orders of 0.47 and 0.5 were calculated in HCl and $H_2SO_4$ respectively. These values are comparable with the ones reported previously [1], of 0.68 and 0.76.

From the above-presented findings, it may be concluded that for a constant $H^+$ concentration, the rate law is:

$$r = \frac{[MB]_o}{t} = -\frac{d\,[MB]}{dt} = k_{obs}\,[H_2A]\,[MB]^{1/2} \qquad (3)$$

Using the above relationship, rate coefficients $k_{obs}$, expressed in $l^{1/2}.mole^{-1/2}.s^{-1}$, were calculated for various hydrogen ion concentrations and presented in table 3.
\

**Table 3.**

The effect of hydrogen ion concentration on the reaction rate and observed rate coefficient at T = 293 K, $[H_2A]_o = 6\bullet10^{-3}$ mole.$l^{-1}$, $[MB]_o = 1.78\bullet10^{-5}$ mole.$l^{-1}$, $[KCl]_o$ = 0.12 mole.$l^{-1}$, in aqueous solution.

| Medium | $[H^+]_o$ (mole.$l^{-1}$) | $t_{mean}$ (s) | $10^7$ r (mole.$l^{-1}.s^{-1}$) | $10^3$ $k_{obs}$ ($l^{1/2}.mole^{-1/2}.s^{-1}$) |
|---|---|---|---|---|
| HCl | 0.15 | 325 | 0.54 | 2.14 |
| | 0.45 | 178 | 1.00 | 3.96 |
| | 0.75 | 146 | 1.21 | 4.79 |
| | 1.05 | 123 | 1.44 | 5.70 |
| | 1.35 | 118 | 1.50 | 5.94 |
| $H_2SO_4$ | 0.10 | 354 | 0.50 | 1.98 |
| | 0.27 | 230 | 0.77 | 3.05 |
| | 0.44 | 157 | 1.13 | 4.47 |
| | 0.60 | 140 | 1.27 | 4.03 |
| | 0.76 | 135 | 1.31 | 5.19 |

Observed rate constants depend upon hydrogen ion concentration, with a fractional and less than unity order. A trend to level off is also observed. This can be described by the following equation:

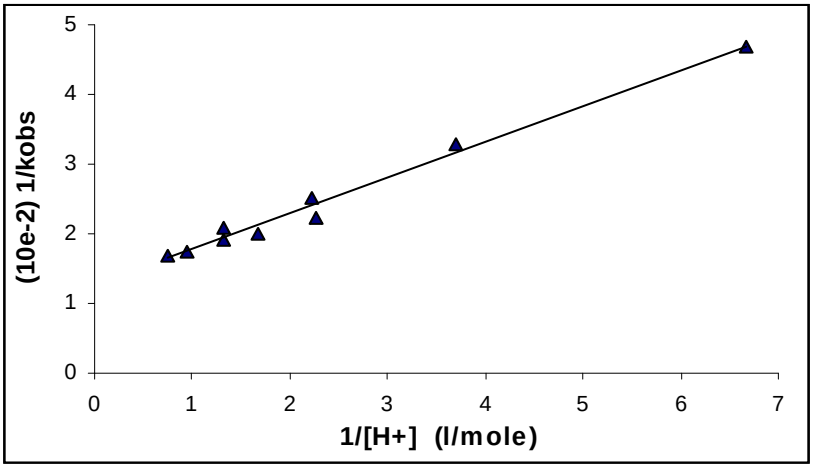
$$k_{obs} = \frac{a\,[H^+]}{1 + b\,[H^+]} \qquad (4)$$

To obtain parameters a and b, a linear, double reciprocal, form of equation (4) could be used:

$$\frac{1}{k_{obs}} = \frac{b}{a} + \frac{1}{a} \bullet \frac{1}{[H^+]} \qquad (5)$$

The linearity (correlation coefficient of 0.9930) holds with all the data obtained with hydrochloric and sulfuric acid. It is presented in figure 3. From the intercept and the slope b/a = 127.0 ± 7.0 $mole^{1/2}.l^{-1/2}.s$ and 1/a = 51.5 ± 2.3 $mole^{3/2}.l^{-3/2}.s$ were calculated.

***Figure 3.*** The plot $1/k_{obs}$ versus $1/[H^+]$ at T = 293 K, $[H_2A]_o = 6 \bullet 10^{-3}$ $mole.l^{-1}$, $[KCl]_o = 0.12$ $mole.l^{-1}$, in aqueous solution.




Finally, the rate law including all the species involved is:

$$r = \frac{[MB]_o}{t} = -\frac{d\,[MB]}{dt} = \frac{a\,[H_2A]\,[MB]^{1/2}\,[H^+]}{1 + b\,[H^+]} \qquad (6)$$

**Effect of ionic strength**

Using constant acidity and initial concentrations of reagents, but varying the concentration of potassium chloride, it was found that salt did not affect the reaction rate. Its value is practically unmodified over a large range of ionic strength, as one can conclude from table 4.

**Table 4.**

The effect of ionic strength on the reaction rate at T = 293 K, $[H_2A]_o = 6 \bullet 10^{-3}$ mole.l$^{-1}$, $[MB]_o = 1.78 \bullet 10^{-5}$ mole.l$^{-1}$, $[H^+]_o = 0.45$ mole.l$^{-1}$, aqueous solution.

| Medium | j (mole.l$^{-1}$) | t (s) | $t_{mean}$ (s) | $10^7$ r (mole.l$^{-1}$.s$^{-1}$) |
|---|---|---|---|---|
| HCl | 0.45 | 174, 173, 170 | 172 | 1.03 |
| | 0.57 | 173, 174, 174, 172 | 173 | 1.02 |
| | 0.69 | 170, 170, 171 | 170 | 1.04 |
| | 0.93 | 170, 171, 170 | 170 | 1.04 |

This indicates either compensation of primary salt effect by the secondary one, if two ions are concerned, or the interaction of an uncharged species with an ion (an ion-dipole interaction).

### Effect of solvent

Binary solvent mixtures of water-acetone and water-1,4 dioxane were used to search for the effect of dielectric constant on the rate. The reaction was performed in mixtures containing 8 - 32 % vol acetone and 8 – 24 % vol 1,4-dioxane. The kinetic results presented in table 5 indicate that, the higher the contents of organic solvent, the slower the reaction rate. Figures 4.a and 4.b present the plot of *lg ($k_{obs}$)* versus *1/D* [9], characteristic to ion-dipole interaction, and the plot of *lg ($k_{obs}$)* versus *(D-1)/(2D+1)*, characteristic to interaction between polar molecules [10], respectively.

**Table 5.**

The effect of dielectric constant (D) on the reaction rate and observed rate coefficient at T = 293 K, $[MB]_o = 1.78 \bullet 10^{-5}$ mole.l$^{-1}$, $[H^+]_o = 1.93$ mole.l$^{-1}$ (source HCl), $[KCl]_o = 0.12$ mole.l$^{-1}$, j = 2.05 mole.l$^{-1}$.

| Medium | D | $t_{mean}$ (s) | $10^8$ r (mole.l$^{-1}$.s$^{-1}$) | $10^3$ $k_{obs}$ (l$^{1/2}$.mole$^{-1/2}$.s$^{-1}$) |
|---|---|---|---|---|
| water $[H_2A]_o = 4 \bullet 10^{-3}$ mole.l$^{-1}$ | 78.5 | 231 | 7.72 | 4.57 |
| water – acetone mixture $[H_2A]_o = 4 \bullet 10^{-3}$ mole.l$^{-1}$ | 30.1 | 307 | 5.80 | 3.44 |
| | 16.95 | 440 | 4.09 | 2.42 |
| | 12.62 | 605 | 2.97 | 1.76 |
| | 8.28 | 882 | 2.04 | 1.21 |
| water – 1,4 dioxane mixture $[H_2A]_o = 6 \bullet 10^{-3}$ mole.l$^{-1}$ | 30.95 | 389.5 | 4.62 | 1.83 |
| | 18.32 | 478 | 3.76 | 1.49 |
| | 13.09 | 626.5 | 2.87 | 1.13 |

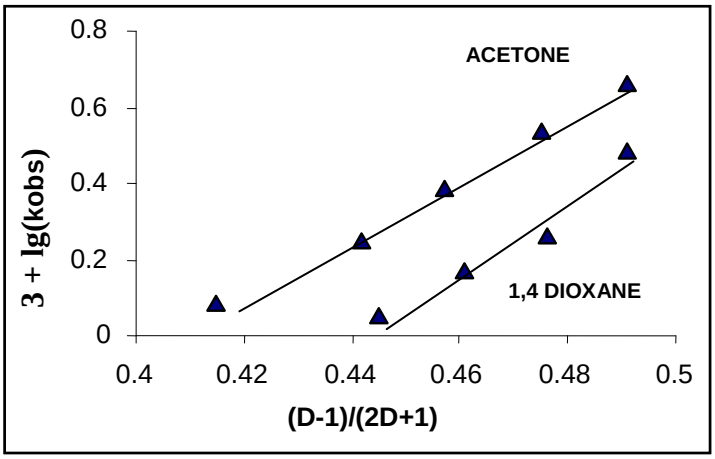



*Figure 4.a.*

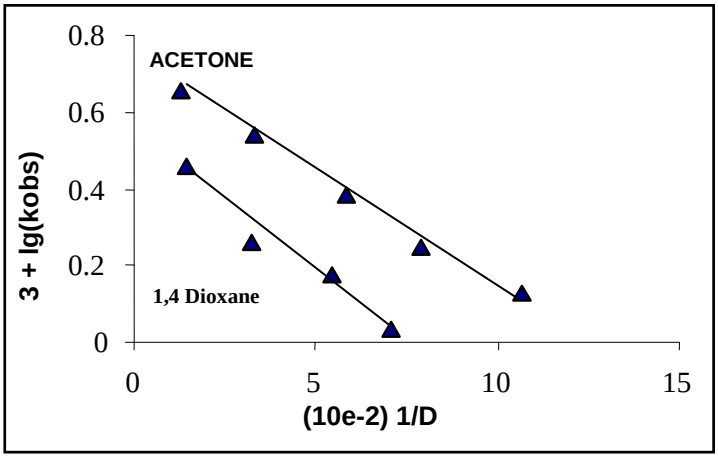



*Figure 4.b.*

***Figure 4.*** The effect of dielectric constant (D) on the observed rate coefficient at T = 293 K, $[MB]_o = 1.78 \bullet 10^{-5}$ mole.l$^{-1}$, $[H^+]_o = 1.93$ mole.l$^{-1}$ (source HCl), $[KCl]_o = 0.12$ mole.l$^{-1}$, j = 2.05 mole.l$^{-1}$, in a.) water - acetone and b.) water – 1,4 dioxane mixtures.

Points lie on lines for both plots. If the rate-determining step consists of an ion-polar molecule interaction, the attraction, assuming correct orientation of the dipole, will be somewhat greater and the rate of reaction should be larger in a medium of lower dielectric constant. The experimental results show the reverse. On the other hand, the substrate is a cationic dye, and the validity of a relation applying to interaction between polar molecules is fortuitous.

These equivocal findings show that the effect of the solvent is mainly determined by the influence on the pre-equilibrium, rather than on the rate-determining step.

**Free radical involvement**

The system MB – $H_2A$ was used to initiate polymerization of vinyl-acetate. The reaction was performed in a small calorimeter and the increase of temperature was measured. Significant difference was noticed in the presence of monomer as compared to the initial mixture, due to the cumulative thermal effect of radical polymerization.

**Effect of temperature**

Various temperatures in the range of 289.4 – 303.6 K were used to determine experimental activation energy. Table 6 contains rate data and observed rate coefficients. A value of $E_a$ = 45.4 ± 6.7 KJ.mole$^{-1}$ was obtained, in good agreement with the one previously determined [1].

**Table 6.**

The effect of temperature (T) on the reaction rate and observed rate coefficient at $[H_2A]_o = 6 \bullet 10^{-3}$ mole.l$^{-1}$, $[MB]_o = 1.78 \bullet 10^{-5}$ mole.l$^{-1}$, $[H^+]_o$ = 0.75 mole.l$^{-1}$ (source HCl), $[KCl]_o$ = 0.12 mole.l$^{-1}$, j = 0.87 mole.l$^{-1}$, in aqueous solution.

| T (K) | $t_{mean}$ (s) | $10^7$ r (mole.l$^{-1}$.s$^{-1}$) | $10^3$ $k_{obs}$ (l$^{1/2}$.mole$^{-1/2}$.s$^{-1}$) |
|---|---|---|---|
| 289.4 | 185 | 0.96 | 3.79 |
| 293 | 146 | 1.21 | 4.78 |
| 297.5 | 96 | 1.85 | 7.31 |
| 303.6 | 79 | 2.25 | 8.89 |

If the rate determining step were the interaction $HB^+$ - $H_3A^+$ as suggested by Snehalatha [1] (who omitted the charge on the cationic dye in explaining the mechanism), the activation energy should be larger because of charge repulsion.

**Reaction mechanism**

In the acid medium used (pH far less than $pK_1$), ascorbic acid exists as undissociated species $H_2A$ [11]. The redox indicator methylene blue presents a dimerisation equilibrium [11]:

$$(MB^+)_2 \Leftrightarrow 2\ MB^+ \qquad (K_1) \qquad (7)$$

which should be considered as a pre-equilibrium.

First-order dependence on $H_2A$, square root dependence on methylene blue and fractional-order dependence on hydrogen ion, in connection with the effect of ionic strength and dielectric constant on the rate are consistent with the following mechanism:

$MB^+ + H^+ \Leftrightarrow MBH^{2+}$ ($K_2$) (8)

$MBH^{2+} + H_2A \rightarrow MBH^+\bullet + HA\bullet + 2\,H^+$ ($k_1$) (9)

$MBH^{2+} + H_2A \rightarrow MBH + A + 2\,H^+$ ($k_2$) (10)

$MBH^+\bullet + HA\bullet \rightarrow MBH + A + H^+$ ($k_3$, fast) (11)

The species $MBH^+\bullet$ and $HA\bullet$ stand for protonated half-reduced and half-oxidized free radicals respectively, MBH for the reduced and colorless form of MB and A for dehydroascorbic acid.

Steps (9) and (11) should be taken into consideration for the redox process, because of the involvement of some free radicals, proved by the initialization of polymerization of vinyl-acetate. Snehalatha reported the same finding [1].

On the other hand we consider that the proton attaches to methylene blue cation which bears basic positions, rather than to ascorbic acid, which should loose protons during the oxidation. Such a process has been proposed [1] as an alternative mechanism, but the dimerization equilibrium was misinterpreted. Since the free radical $MBH^+\bullet$ is a reactive species, process (11) should proceed with the rate of process (9). Free radical $MBH^+\bullet$ is also a colored species as the dimeric $(MB^+)_2$ and monomeric $MB^+$ species. The rate was measured by the decay of the mixture's color and process (11) has here a certain contribution. Discrimination between the two redox processes could not be made with the data available. Therefore only their sum is taken into consideration.

The slower rate in the presence of an organic solvent in the reaction mixture as compared to the one in aqueous media can be explained by favoring equilibrium (7) towards the dimeric species, at lower dielectric constants of the environment.

The imperceptible influence of the ionic strength is obvious by the involvement of an ion-dipole interaction in the rate-determining step.

From the above mechanism, the rate law could be derived as:

$$r = -\frac{d\,[MB]}{dt} = (k_1 + k_2)\,[MBH^{2+}]\,[H_2A] = k\,[MBH^{2+}]\,[H_2A] \qquad (12)$$

Taking into account the protonation pre-equilibrium, the material balance for the monomeric species is:

$$[MB^+]_{total} = [MB^+]_{free} + [MBH^{2+}] = [MB^+]_{free}\left\{1 + K_2[H^+]\right\} \quad (13)$$

A correlation between dimeric and monomeric species is done by means of the dimerization equilibrium (7) so that the concentration of the protonated species is:

$$[MBH^{2+}] = \frac{K_1^{1/2} K_2 [(MB^+)_2]^{1/2} [H^+]}{1 + K_2[H^+]} \qquad (14)$$

Therefore, the rate law becomes:

$$r = -\frac{d\,[MB]}{dt} = \frac{kK_1^{1/2}K_2[(MB^+)_2]^{1/2}[H^+][H_2A]}{1+K_2[H^+]} \qquad (15)$$

of the form (6).

The observed rate constant ($l^{1/2}.mole^{-1/2}.s^{-1}$) is

$$k_{obs} = \frac{kK_1^{1/2}K_2\,[H^+]}{1+K_2\,[H^+]} \qquad (16)$$

showing the trend to level off with the hydrogen ion concentration. Its linear form is

$$\frac{1}{k_{obs}} = \frac{1}{kK_1^{1/2}} + \frac{1}{kK_1^{1/2}K_2} \bullet \frac{1}{[H^+]} \qquad (17)$$

with $b/a = (k\,K_1^{1/2})^{-1}$ and $a = k\,K_1^{1/2}K_2$. Thus, the following values could be calculated:

$k\,K_1^{1/2} = (7.9 \pm 0.4) \bullet 10^{-3}\ l^{1/2}.mole^{-1/2}.s^{-1}$ and $K_2 = 2.5 \pm 0.5\ l.mole^{-1}$.

The rate law deduced from the suggested mechanism is in accordance with all observed kinetic features. The effect of ionic strength and dielectric constant are also explained by the proposed mechanism, giving us confidence that it is operative.

## REFERENCES


1. T. Snehalatha, K.C. Rajanna, P.K. Saiprakash, *J. Chem Educ.*, ***1997***, *74(2)*, 228.
2. M. Avram, *Chimie Organica*, Ed. Zecasin, Bucuresti, ***1995***, 201-202, 441-442.
3. I.Bognar, O. Jettinec, *Mikrochim. Acta. (* Wien), ***1970***, 1017.
4. I.Bognar, L. Sipos, *Z. Physik. Chem. (Leipzig)*, ***1969***, *55*, 99.
5. B.P. Levitt, *Findlay's Practical Physical Chemistry*, Longman, London, ***1983***, 351.
6. J.R. Clarcke, *J. Chem. Educ.*, ***1970***, *47*, 775.
7. A.E. Burges, J.L. Latham, *Analyst*, ***1966***, *91*, 343.
8. K.B. Iatsimiskii, L.P. Raizman, *Zhur. Neorg. Khim.*, ***1960***, *5*, 593.
9. W.F.K. Wynne-Jones, H. Ehring, *J. Chem. Phys.*, ***1935***, *3*, 492; K.J. Leidler, H. Eyring, *Ann. N.Y. Acad. Sci.*, ***1940***, *39*, 303.
10. J.G. Kirkwood, *J. Chem. Phys.*, ***1934***, *2*, 351; J.W. More, R.G. Pearson, *Kinetics and Mechanism*, Jon Wiley and Sons, New York, 1981, 258-268.
11. W.J. Blaedel, V.W. Meloche, *Elementary Quantitative Analysis, Theory and Practice*, 2nd ed., Harper & Row, New York, ***1963***, 447 and 883; T. Snehalatha, K.C. Rajanna, P.K. Saiprakash, *J. Chem Educ.*, ***1997***, *74(2)*, 228.