KINETICS AND MECHANISM OF THE REDUCTION OF METHYLENE BLUE BY Sn(II) CATALYZED BY TECHNETIUM

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Summary

The reduction of methylene blue by Sn(II) in acid media is catalyzed by traces of technetium. A reaction mechanism has been developed which is in agreement with the experimental orders found and which satisfactorily accounts for all experimental findings. The results of this study support the postulate that the catalyst action is due to the ability of the technetium(V) to bind with the reagent, forming an intermediate complex. The rate constants and Arrhenius parameters have been investigated.

Introduction

Technetium chemistry is a relatively new field of activity, and remains underdeveloped. Technetium was first isolated in 1937 [1, 2]; although larger quantities became available in 1960, its price remained prohibitive. The recent production of appreciable quantities of technetium in radiochemical processing plants (especially by fission of uranium, which leads to an approximately 6% yield of Tc-99) has allowed initiation of the study of its chemical behaviour [3 - 5]. Thus, during the last few years there has been a notable increase in technetium chemistry research, largely due to the interest of inorganic chemists in obtaining a better insight into the coordination chemistry of this relatively unstudied element.

Interest has been shown in the use of Tc-99m as a reagent for diagnostic nuclear medicine. Significant advances in this applied field will depend upon basic research into the inorganic chemistry of technetium. For this reason, technetium chemistry and technetium radiopharmaceuticals are intertwined subjects. A considerable number of complexes of this element have been studied, containing Tc in different oxidation states, and in some cases solid state structures have even been determined [6]. However, general knowledge

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of the behaviour of this element in solution is still lacking in many respects; thus we have begun a program for the study of technetium chemistry in solution [7 - 9]. We have found that technetium acts as a catalyst in the reduction of methylene blue by the Sn(II) ion [9]. The purpose of the present paper was to find a mechanism for this catalyzed reaction, and to determine the main kinetic parameters. We emphasize here that this is the first literature report of a mechanism in which technetium clearly acts as a catalyst in homogeneous medium.

Experimental

Reagents, solutions and apparatus

A solution of technetium 99 as ammonium pertechnetate was obtained from Amersham/Searle Corp., Arlington Heights, IL. A technetium solution of 119 ppm was prepared by dilution of the original standard with water.

A 0.117 g l^{-1} (3.67 × 10⁻⁴ M) ethanolic solution was prepared from methylene blue supplied by Merck.

A Zeiss DMR 11 spectrophotometer with 1.0 cm cells was used to register and follow the kinetics. The temperature was maintained at a constant value (± 0.01 °C) by use of a Heto Frig cryostat.

Procedure

The discoloration of the blue oxidized form of methylene blue was initiated by adding a $SnCl_2$ solution to the cell containing the organic reagent, water, a HCl solution and a technetium solution. A continuous reading of absorbance *vs.* time was obtained on the recorder. The wavelength employed was 665 nm, at which the maximum absorbance for the blue compound was found.

Results and discussion

The influence of HCl on the reduction of methylene blue has been previously studied [9], and it was found that, whereas in the presence of the catalyst the initial rate first increases, then reaches a maximum and finally decreases, in its absence it always increases. The influence of the Sn(II) concentration in such reactions is also studied, and its behaviour is similar to that of HCl. In the absence of technetium the reaction is first order with respect to Sn(II), as shown in Fig. 1. These measurements indicate that at low concentrations HCl and Sn(II) favour the catalytic reaction, but that at higher concentrations their presence inhibits the catalytic reaction, while favouring the uncatalyzed one. On the other hand, as can be seen in Fig. 2, the catalyzed reaction was found to be first order with respect to technetium.



Fig. 1. Logarithmic plot of the initial rate vs. $SnCl_2$ concentration in absence of technetium; [methylene blue] = 7.6×10^{-6} M, [ethanol] = 2%, [HCl] = 0.07 M.

Fig. 2. Logarithmic plot of the initial rate vs. technetium concentration; [methylene blue] = 7.6×10^{-6} M, [ethanol] = 2%, [SnCl₂] = 2.1×10^{-3} M, [HCl] = 0.07 M.



Fig. 3. Logarithmic plot of the initial rate vs. methylene blue concentration; (a) [ethanol] = 2%, $[SnCl_2] = 2.1 \times 10^{-3}$ M, [HCl] = 0.07 M, [Tc] = 0.5 ppm; (b) the same as (a) without Tc.

The influence of the reagent concentration in the presence of catalyst is shown in Fig. 3. As can be seen, the initial rate first increases and then reaches a maximum, whereas in the absence of technetium it was found to be first order with respect to methylene blue (Fig. 3). These findings indicate that, whereas methylene blue participates directly in its own reduction in the presence of technetium, it is not directly implied in such a process when technetium is absent, and probably forms an intermediate complex with this element. This observation is in keeping with the known tendency of technetium to form complexes with sulphur-containing ligands [5].

When formulating a working hypothesis for an interpretation of our measurements, we made use of some literature data referring to the reduction of methylene blue [10]. Thus the mechanism of the uncatalyzed reaction can be formulated as follows, and is in agreement with the experimental data:

 $MB_{ox} + Sn(II) \longrightarrow MB_{red} + Sn(IV)$

$$\mathsf{MB}_{\mathsf{OX}} \equiv (\mathsf{CH}_3)_2^{\mathsf{N}} \xrightarrow{\mathsf{N}}_{\mathsf{N}} (\mathsf{CH}_3)_2, \ \mathsf{MB}_{\mathsf{red}} \equiv (\mathsf{CH}_3)_2^{\mathsf{N}} \xrightarrow{\mathsf{NH}}_{\mathsf{N}} \underbrace{\mathsf{O}}_{\mathsf{N}} \xrightarrow{\mathsf{H}}_{\mathsf{NH}} (\mathsf{CH}_3)_2$$

Consequently, the overall rate must be expressed as

$$v_{\rm o} = k[{\rm Sn(II)}][{\rm MB}_{\rm ox}] \tag{1}$$

In accordance with the literature and with our experimental results, various interpretations could accommodate the full rate law, but, in accordance with the actual scanty knowledge of technetium chemistry in solution, we believe that the following mechanism is probable:

$$Tc(VII) + Sn(II) \xrightarrow{k_1} Tc(V) + Sn(IV)$$
 (2)

$$Tc(V) + MB_{ox} \xrightarrow[k_{-2}]{k_{-2}} MB_{ox} - Tc(V)$$
(3)

$$MB_{ox} - Tc(V) + Sn(II) \xrightarrow{R_3} MB_{red} - Tc(V) + Sn(IV)$$
(4)

$$MB_{ox} - Tc(V) \xrightarrow{k_4} Tc(VII) + MB_{red}$$
(5)

$$MB_{red} - Tc(V) \xrightarrow{R_5} MB_{red} + Tc(V)$$
(6)

$$Tc(V) + Cl_4 Sn^{2-} \xrightarrow{R_6} Cl_4 Sn^- + TcO_2$$
(7)

$$Tc(V) + Cl_4 Sn^- \xrightarrow{k_7} TcO_2 + Cl_4 Sn$$
(8)

A steady-rate treatment of the concentrations of Tc(V), MB_{ox} -Tc(V), MB_{red} -Tc(V) and Cl_4Sn^- in reactions (2) - (8) leads to:

$$[MB_{ox}-Tc(V)] = \frac{k_2[Tc(V)][MB_{ox}]}{k_4 + k_{-2} + k_3[Sn(II)]}$$
(9)

and

[Tc(V)]

$$= \frac{k_1[\text{Tc(VII)}][\text{Sn(II)}]}{[\text{MB}_{\text{ox}}]\left(k_2 - \frac{k_{-2}k_2}{k_4 + k_{-2} + k_3(\text{Sn(II)})} - \frac{k_3k_2[\text{Sn(II)}]}{k_4 + k_{-2} + k_3(\text{Sn(II)})}\right) + 2k_6[\text{Cl}_4\text{Sn}^{-2}]$$

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(1	0)

On the other hand, the reaction rate will be given through the disappearance of the blue MB_{ox} species.

$$v = -\frac{\mathrm{d}[\mathrm{MB}_{\mathrm{ox}}]}{\mathrm{d}t} = k_2[\mathrm{Tc}(\mathrm{V})][\mathrm{MB}_{\mathrm{ox}}] - k_{-2}[\mathrm{MB}_{\mathrm{ox}}-\mathrm{Tc}(\mathrm{V})]$$
(11)

Combining eqns. (9), (10) and (11) leads to:

$$v = k_{2}[\text{Tc}(\text{VII})] \left(1 - \frac{k_{2}}{k_{4} + k_{-2} + k_{3}[\text{Sn}(\text{II})]}\right) \times \left(\frac{k_{1}[\text{Sn}(\text{II})][\text{MB}_{\text{ox}}]}{[\text{MB}_{\text{ox}}] \left(k_{2} - \frac{k_{-2}k_{2}}{k_{4} + k_{-2} + k_{3}(\text{Sn}(\text{II}))} - \frac{k_{3}k_{2}[\text{Sn}(\text{II})]}{k_{4} + k_{-2} + k_{3}[\text{Sn}(\text{II})]}\right) + 2k_{6}[\text{Cl}_{4}\text{Sn}^{2-}]\right)$$
(12)

This expression is in qualitative agreement with the experimental data obtained. The catalytic activity of technetium should be directly related to its ability to form colloidal TcO_2 , in such a manner that an increase in its formation implies a decrease in the catalytic activity. Moreover, a notable increase in HCl concentration favours Tc(V) reduction by $SnCl_4^{2-}$ or $SnCl_4^{-}$. A large increase in $SnCl_2$ concentration also increases the amount of chloride complexes, due to the covalent character of the tin compounds, and consequently favours rapid Tc(V) reduction. The suggested formation of Sn(III) species $(SnCl_4^{-})$, when Sn(II) acts as a reducing agent in acidic media, is supported by the results obtained in other reduction processes in which Fe(III) or Cu(II) participates as oxidant [11 - 13].

For fixed reagent, $SnCl_2$ and HCl concentrations, the overall rate must be expressed as:

$$-\frac{\mathrm{d}[\mathrm{MB}_{\mathrm{ox}}]}{\mathrm{d}t} = k_{\mathrm{obs}}[\mathrm{Tc}(\mathrm{VII})]$$

 k_{obs} has been calculated for diverse conditions, and the results obtained are summarized in Table 1. The activation energy can be obtained from 'modified' Arrhenius plots of the variation of the initial rate with respect to the inverse of temperature. The results obtained are shown in Fig. 4. A value of $E_a = 30.3$ kJ mol⁻¹ was obtained.

For the uncatalyzed reaction, as has been pointed out, the overall rate must be expressed as in eqn. (1), and k has been obtained under various conditions. The results obtained are summarized in Table 2. The activation energy obtained from the 'modified' Arrhenius plots (Fig. 4) is $E_a = 37.3$ kJ mol⁻¹.

Concentration (M)			k _{obs}
Methylene blue (×10 ⁶)	Cl ₂ Sn (×10 ³)	Tc(VII) (×10 ⁶)	(min ⁻¹)
7.6	2.1	5	0.39
15.2	2.1	5	0.43
7.6	2.1	10	0.34
11.4	2.1	5	0.48
11.4	2.1	10	0.61
7.6	4.2	5	0.44
7.6	8.3	5	0.55

Kinetic study of the catalyzed reaction^a

^aIn all experiments HCl concentration (0.07 mol l^{-1}) and temperature (25 °C) were kept constant.



Fig. 4. Modified Arrhenius plots. (a) Uncatalyzed reaction: (I) [methylene blue] = 7.6×10^{-6} M, [SnCl₂] = 8.3×10^{-3} M, [HCl] = 0.07 M; (II) [methylene blue] = 7.6×10^{-6} M, [SnCl₂] = 4.1×10^{-3} M, [HCl] = 0.07 M. (b) Catalyzed reaction: (I) [methylene blue] = 7.6×10^{-6} M, [HCl] = 0.07 M. [SnCl₂] = 2.1×10^{-3} M, [Tc] = 0.5 ppm; (II) [methylene blue] = 7.6×10^{-6} M, [SnCl₂] = 2.1×10^{-3} M, [Tc] = 0.07 M.

TABLE 2

Kinetic study	' of the	uncatalyzed	reaction ^a
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Concentration (M)		k	
Methylene blue (×10 ⁶)	SnCl ₂ (×10 ³)	$(l \text{ mol}^{-1} \text{ min}^{-1})$	
7.6	8.3	3.0	
3.8	8.3	2.9	
11.4	8.3	2.9	
15.2	8.3	3.0	

^a In all experiments HCl concentration (0.07 mol l^{-1}) and temperature (22.3 °C) were kept constant.

TABLE 1

Conclusion

Technetium is a relatively recently studied element and few reports concerning its catalytic activity are found in the literature to date. In this paper, the reduction of methylene blue catalyzed by technetium is studied, and is attributed to the complexing activity of Tc(V), in such a manner that formation of Tc(IV), in the stable TcO_2 form, implies a decrease in the catalytic activity. In addition, we have found that technetium in the form of Tc(V)seems also to catalyze the reduction of other organic compounds, such as tetrahydroxy-1,4-quinone [14] or 1-amino-4-hydroxyanthraquinone [15] through the formation of the corresponding Tc(V) complexes. The high tendency of Tc(V) to capture electrons (and transform into Tc(IV)) explains the catalytic activity of Tc(V) in reduction processes through complex formation, although when Tc(IV) is formed, due to the thermodynamic stability of TcO_2 , Tc(V) disappears and catalytic activity decreases.

Acknowledgements

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