KINETIC STUDY OF THE OXIDATION OF GLYCINE BY PERMANGANATE IONS IN ACID MEDIUM

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The oxidation of glycine by permanganate ions was studied in a buffered solution at pH 2.2. An autocatalytic reaction was observed, autocatalyzed by a soluble form of Mn(IV). Autocatalytic S-shaped kinetic curves were obtained by the spectrophotometric method and characterized by the time t_i vs concentration in the inflection point.
Key words: Permanganate Oxidation; Glycine; Autocatalysis; Intermediate Mn(IV).

Several works[1–4] indicate that the oxidation of glycine by permanganate ions in neutral aqueous solutions is autocatalytic. The product emerging from this oxidation has been identified as a soluble form of colloidal manganese dioxide. The oxidation of glycine by permanganate ions has been studied[5] in a strongly acid medium (perchloric or sulfuric acid). In a study of the reaction in a buffered acid medium[6], an autocatalytic effect has been observed and attributed to Mn^{2+} ions formed during the reaction.

We have studied the permanganate oxidation of L-alanine in a buffered acid medium[7] and suggested that the autocatalyst is a soluble Mn(IV) species. The aim of the present work was to extend this study to the permanganate oxidation of glycine, to examine whether this process is autocatalyzed as well, and seek what species is responsible for the autocatalytic effect.

EXPERIMENTAL

The solvent used in all the experiments was thrice distilled water. The oxidant was potassium permanganate (Merck), its concentrations ranged from 3 to 8 . 10^{-4} mol dm^{-3}. The reductant was glycine (Merck) at concentrations of 3 to 7 . 10^{-2} mol dm^{-3}. A H_3PO_4–H_2KPO_4 (Panreac) buffer (ionic strength 0.05 mol dm^{-3}) was used to keep the pH of medium constant at 2.2. Potassium chloride (Panreac) in 0.1 to 0.4 mol dm^{-3} concentrations was used to study the salt effect. The experiments were carried out at temperatures from 31 to 46 °C.

Kinetic measurements. The reaction was followed by monitoring the absorbance changes at 525 and 418 nm, using a Spectronic 1201 spectrophotometer (200–800 nm) provided with a thermostated cell holder (pathlength 1 cm). The pH was checked with a Radiometer 51 instrument.

The reaction rate is characterized by the negative derivative of the absorption at 525 nm with respect to time. A simple procedure was applied to calculate the values at several moments. If three consecutive time–absorption pairs of data, designed as (t_1, A_1), (t_2, A_2) and (t_3, A_3), are fitted by the first three terms of the Taylor series expansion $A = x + yt + zt^2$, the rate value corresponding to the middle point is $v_2 = -y - 2zt_2$. By substituting the three pairs of values in the equation and taking into consideration the fact that the difference in time between two consecutive points is constant, Δt, it is easy to derive the approximate expression $v_2 = (A_1 - A_3)/2\Delta t$ for the reaction rate at time t_2. The error of the reaction rates so obtained never exceeded 5%.

Stoichiometry. The reaction mixtures containing glycine and permanganate ions in different ratios were prepared by mixing the components in the presence of buffer solutions adjusted to a constant ionic strength of 0.05 mol dm^{-3}. Estimation of the amount of the unreacted MnO_4^- showed that 1 mol of MnO_4^- was consumed per 2.5 ± 0.1 mol of the amino acid. The presence of both acetaldehyde and ammonia was confirmed by a simple qualitative analysis[8,9] of the products. The corresponding stoichiometric equation is

$$2\,MnO_4^- + 5\,H_3N^+CH_2COOH + 6\,H^+ \rightleftharpoons 2\,Mn^{2+} + 5\,CH_2O + 5\,NH_4^+ + 5\,CO_2 + 3\,H_2O \quad . \quad (A)$$

RESULTS AND DISCUSSION

The UV spectra of the mixtures (Figs 1 and 2) recorded during the oxidation show a decrease of absorbance at 525 nm (henceforth denoted as A_{525}) which is characteristic of the Mn(VII) species. The A_{525} vs time curves (Fig. 3) were S-shaped, indicating that the reaction is autocatalytic[10].

The absorbance at 418 nm, however, increases first, falls later on, and finally tends to become zero (Fig. 4, curve *1*). It is well known that absorbance at this wavelength can be used to measure the concentration of the Mn(IV) species generated during the

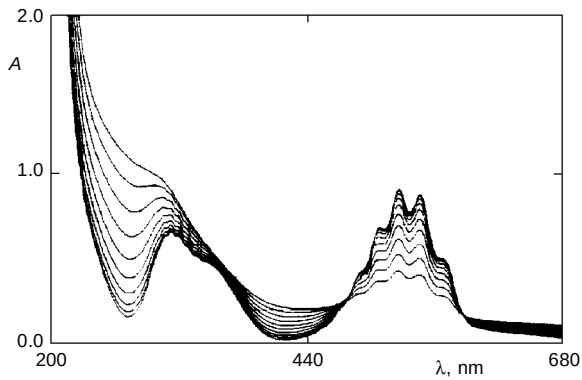

FIG. 1
Successive scans at 8-min intervals for the reduction of permanganate ion (4 . 10^{-4} mol dm^{-3}) by glycine (0.05 mol dm^{-3}) at 40 °C, pH 2.2 and at ionic strength 0.05 mol dm^{-3}

reaction[11,12]; the final reaction products do not interfere. In fact, the "ex situ" spectra of $MnSO_4$ at 4.0 . 10^{-4} mol dm^{-3} give evidence that the Mn(II) species (product of the reaction) is completely transparent at 418 nm as well as 525 nm. In Fig. 1, the background at 680 nm (when the reaction is not finished) is due to the Mn(IV) species which is not completely transparent at that wavelength. On the other hand, plots of ln A_{418} vs time or A_{523} vs A_{418} are not linear, which indicates that Mn(IV) is not an end product.

For that reason we consider Mn(IV) to be an intermediate species which is formed in measurable amounts during the reaction. The other intermediate species include Mn(VI) (ref.[13]) with maximum absorptions at 603 and 435 nm, Mn(V) (ref.[14]) at 670

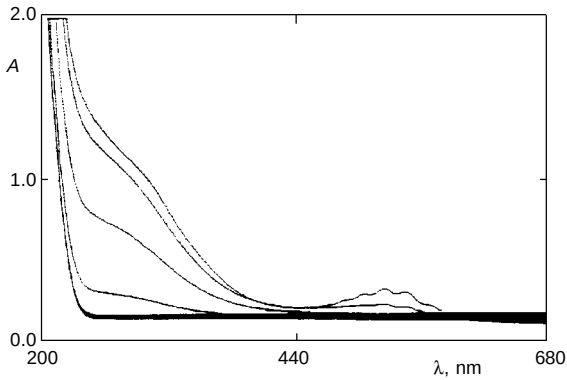

FIG. 2
Successive scans at the end of the reduction of the permanganate ion by glycine. Conditions as in Fig. 1

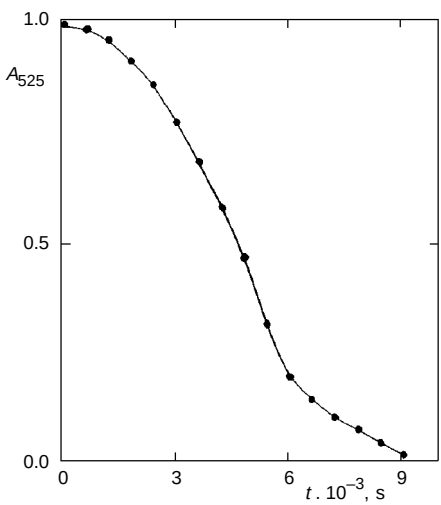

FIG. 3
Absorbance at 525 nm (A_{525}) vs time t (s) for the oxidation of glycine (0.05 mol dm^{-3}) by permanganate ion (4 . 10^{-4} mol dm^{-3}) at 40 °C, pH 2.2 and ionic strength 0.05 mol dm^{-3}

and 325 nm, and Mn(III) (ref.[15]) at 470 nm. A number of findings bear out the presence of Mn(IV) as an intermediate product. Stoichiometric considerations, on the other hand, indicate that an Mn(II) species is the reaction product. Oxidation state changes from Mn(VII) to Mn(II) only are possible by one-electron or, alternatively, two-electron steps. In the formulation of the non-catalyzed reaction, only one-electron steps are proposed, viz. the hydrolysis of the Mn(VI) species giving Mn(V) species. However, for the catalyzed process the postulated intermediates are in the sequence: Mn(VII) → Mn(VI) → Mn(IV). In spite of the fact that the presence of Mn(VI), Mn(V) and Mn(III) species has not been actually detected because the conventional technique employed did not enable that, evidence exists indicating their participation in the reaction runs.

First, two isosbestic points were identified at 478 and 582 nm. The existence of isosbestic points gives evidence that the system changes monotonously, which is consistent with the existence of a few intermediate species facilitating the changes in the oxidation state of manganese from seven to two.

Furthermore, the occurrence of the first isosbestic point at 478 nm is consistent with the increase in both the absorbance of Mn(IV) at 418 nm and the concentration of the Mn(III) species (whose characteristic band lies at 470 nm) together with the decrease in the absorbance of the Mn(VII) species at 525 nm. The latter also agrees with the location at 582 nm of the second isosbestic point because of an increase in absorbance of the Mn(VI) species at 603 nm.

On the other hand, it must be borne in mind that the existence and structure of a number of inorganic compounds are deduced from mechanistic studies, in contrast to organic compounds.

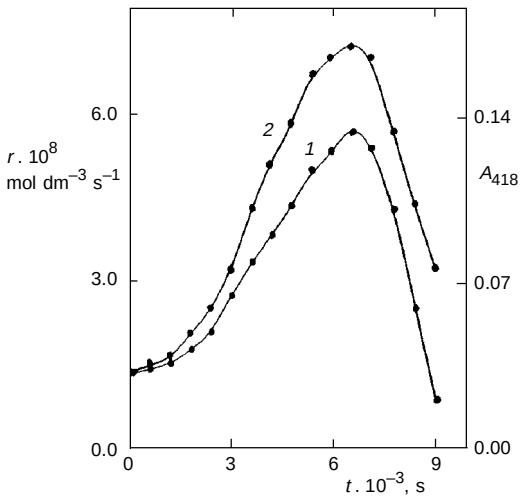

FIG. 4
Absorbance at 418 nm, A_{418} (*1*) and reaction rate, r (*2*) vs time, t (s). $[MnO_4^-] = 4 \cdot 10^{-4}$ mol dm^{-3}, [glycine] = 0.05 mol dm^{-3}, 40 °C, pH 2.2 and ionic strength 0.05 mol dm^{-3}

As illustrated by Fig. 4, curve *2*, all the reaction rate vs time plots are bell-shaped, which is consistent with the autocatalytic nature of the process. Curve *2* in Fig. 4 indicates that there exists an induction period, and curve *1* documents that the absorbance at 418 nm is constant during the induction period. The rate of oxidation increases in parallel to the absorbance A_{418}, and then both drop.

Figure 5 indicates that the induction period is very sensitive to changes in the H_2KPO_4–H_3PO_4 buffer concentration. If the total phosphate concentration is increased, the induction period extends. This is a consequence of the role of phosphate conditioning the appearance of the Mn(IV) species. At a higher buffer concentration, the Mn(IV) species appears later and its concentration is lower (as reflected by a decrease in absorbance at 418 nm). A similar effect has also[16,17] been observed at pH 6–8. In this medium the Mn(IV) soluble species remains as the final product of the reaction. At pH 2.2, however, the Mn(IV) species is a transient intermediate which acts as a catalyst of the reaction but is finally reduced to give the Mn(II) species, the actual end product of the reaction.

At the maximum absorbance at 418 nm, the log absorbance vs log wavelength plot is linear with a slope near –4 (–3.89), as predicted by the Rayleigh law for colloidal solutions[18,19]. This value differs from that found for the permanganic oxidation of glycine[2] at pH 6–9 (–4.66) where colloid flocculation occurs. These facts are in agreement with the colloidal nature of the Mn(IV) species which transforms during the reaction into a transparent Mn(II) species. Such a form of colloidal Mn(IV) has already been postulated[20–26] as an intermediate. On the other hand, the reduction of Mn(IV) to Mn(II) is favoured by solvent acidity[27]. Therefore, the fact that the colloidal Mn(IV) species converts to Mn(II) at pH 2.2 only implies that the reduction of Mn(IV) in this solvent is faster than its flocculation.

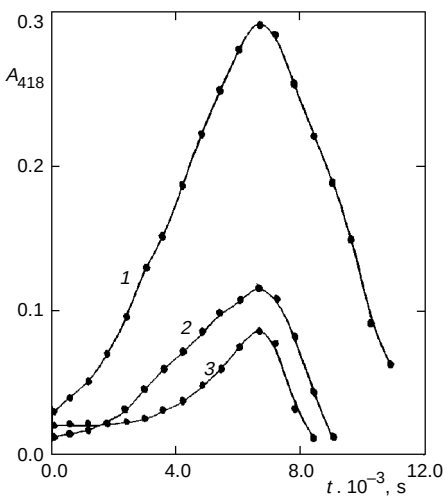

FIG. 5
Absorbance at 418 nm vs time for the oxidation of glycine (0.05 mol dm^{-3}) by permanganate ion ($4 \cdot 10^{-4}$ mol dm^{-3}) at 40 °C, pH 2.2. Ionic strength: *1* 0.01 mol dm^{-3}, *2* 0.05 mol dm^{-3}, *3* 0.10 mol dm^{-3}

In view of the existence of the induction period, an alternative treatment proposed by Bazsa et al. was used[28–30] to analyze the kinetic data. Two parallel reaction pathways were assumed, one of them autocatalytic. The time of the inflection point, t_i, in the absorbance vs time plots (which evidently corresponds to the maximum reaction rate) is given by

$$t_i = \frac{p}{k_1 + k_2[\mathrm{Mn(IV)}]_0} \quad , \tag{1}$$

where k_1 (s^{-1}) and k_2 ($mol^{-1}\ dm^3\ s^{-1}$) are the rates of the specific non-catalytic and catalytic reactions, respectively, $[Mn(IV)]_0$ is the initial catalyst concentration, and p is a parameter. From our data, $k_1/k_2 = 1.63 \cdot 10^{-3}$.

The inflection time is longer when a higher initial permanganate concentration is used. A linear relation exists between log t_i and log $[MnO_4^-]$ ($r_{xy} = 0.9987$), with a slope of 0.48 (Eq. (*2*)):

$$\log t_i = 3.65 + 0.48 \log [\mathrm{MnO_4^-}] \quad . \tag{2}$$

With increasing glycine concentration, however, the inflection time decreses. Equation (*3*) indicates that the slope of log t_i vs log [glycine] is –0.88 ($r_{xy} = 0.9997$):

$$\log t_i = 0.98 - 0.88 \log [\mathrm{glycine}] \quad . \tag{3}$$

The salt effect in the oxidation of glycine by permanganate ions as reflected by changes in the inflection time at ($[MnO_4^-] = 4 \cdot 10^{-4}$ mol dm^{-3}; [glycine] = 0.05 mol dm^{-3}; pH 2.2; 40 °C; ionic strength 0.05 + [KCl]) is as follows:

[KCl], mol dm^{-3}	0.0	0.1	0.2	0.3	0.4
t_i, min	111	127	140	154	169

These data show that the t_i values increase with increasing potassium chloride concentration. This is due to the well-known capacity of electrolytes for increasing the rate of flocculation of colloids[31]. So, higher KCl concentrations bring about decrease in the effective value of $[Mn(IV)]_0$. The increase in the t_i values can be explained in terms of Eq. (*1*).

Equation (*4*) is a form of the Arrhenius relation ($r_{xy} = 0.9998$, $E_a = 68.46$ kJ mol^{-1}).

$$\ln t_i = -22.69 + 8\,757.43\ 1/T \tag{4}$$

MECHANISM

The experimental rate equation indicates that the oxidation of glycine involves two parallel reactions[12,26,32], only one of which produces Mn(IV) that acts as the catalyst. Both mechanisms lead to a first-order rate dependence on glycine concentration.

In analogy to the permanganate oxidation of L-alanine[7], two parallel mechanisms are considered as interdependent, viz.

$$H_3N^+CH_2CO_2H + H_3N^+CH_2CO_2H \overset{K_1}{\rightleftharpoons} D \qquad (B)$$

$$D + Mn(VII) \xrightarrow{k_3} \underset{C_1}{Mn(VII)H_3N^+CH_2CO_2H{-}CO_2HCH_2H_3N^+} \qquad (C)$$

Reaction (*B*) giving rise to the glycine dimer D is to be regarded as an Arrhenius pre-equilibrium condition (actually an pseudo-equilibrium in the mechanism context); hence, the glycine dimer D is a transient compound rather than a genuine chemical compound.

The carboxylic group is a part of the molecule which is very rich in "electrons" (π-bonds, lone electron pairs). Hence, it is reasonable to expect ionic interactions between the carboxylic group and the protonated amino group of two distinct molecules, which accounts for the dimer structure.

It has been suggested that amino acids form a complex with the Mn(VII) species[33]. The permanganate attack to the dimer (D) can be explained in terms of an ionic interaction between the two molecules, which implies that Mn(VII) must be formulated as linked to the protonated amino group. Hence, the C–C bond is not broken in Eq. (*C*).

The irreversible decomposition of this complex should lead to the reaction products through the following steps.

Non-Catalyzed Oxidation

$$Mn(VII)H_3N^+CH_2CO_2H{-}CO_2HCH_2H_3N^+ + Mn(VII) \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} 2\,H_2Mn(VI)H_2NCH_2CO_2^{\bullet} \quad (D)$$

$$H_2Mn(VI)H_2NCH_2CO_2^{\bullet} \xrightarrow[\text{slow}]{k_5} H_2Mn(VI) + H_2NCH_2^{\bullet} + CO_2 \qquad (E)$$

$$H_2NCH_2^{\bullet} + Mn(VII) \xrightarrow{k_6} CH_2{=}{}^+NH_2 + Mn(VI) \qquad (F)$$

$$CH_2{=}^{+}NH_2 + H_2O \xrightarrow{k_7} CH_2O + NH_4^+ \qquad (G)$$

$$[H_2Mn(VI)] + H_2O \xrightarrow[\text{fast}]{k_8} [H_3Mn(V)OH] \qquad (H)$$

$$[H_3Mn(V)] + H_3N^+CH_2CO_2H \xrightarrow{\text{fast}} \ldots \longrightarrow Mn(III) + \ldots \qquad (I)$$

$$Mn(III) + H_3N^+CH_2CO_2H \xrightarrow{\text{fast}} \ldots \longrightarrow Mn(II) + \ldots \qquad (J)$$

The role of the Mn(VII) species is essential for understanding reaction (*D*). Effectively, the attack of the second Mn(VII) molecule must be at the protonated amino group of the second glycine molecule which is linked to the carboxylic group of the first molecule in the dimer.

Hence, in view of the fact that there is no steric hindrance, the removal of an electron from the carboxylic group appears to be more probable (one has to take into account the fact that the carboxylic group is a part of the molecule which is very rich in electrons) than from the protonated amino group. This can explain the nature of products in reaction (*D*).

This mechanism is borne out by the fact that carbon dioxide, aldehydes and ammonium ion are known to be products of the permanganate oxidation of amino acids[34–36]. These compounds may be formed as indicated in steps (*E*) and (*G*).

According to the above considerations, the rate of the reaction is $r = k_5[H_2Mn(VI)H_2NCH_2CO_2^{\bullet}]$. On the other hand, this assumption also indicates that k_5 is smaller than k_{-4}. Moreover, the existence of different isosbestic points warrants the assumption that the whole reaction proceeds uniformly in the steady-state conditions. By applying this approximation to the $[H_2Mn(VI)H_2NCH_2CO_2^{\bullet}]$ species, it was found that its corresponding concentration is the square root of $(k_4/k_{-4})[C_1][Mn(VII)]$.

Moreover, from the application of the steady-state approximation to the C_1 compound it was found that:

$$[C_1] = k_3K_1\,[H_3N^+CH_2CO_2H]^2\,[Mn(VII)]\ . \qquad (5)$$

Hence, the theoretical rate equation for the non-catalyzed mechanism is $r = k_5(k_3K_1/k_{-4})^{1/2}\ [H_3N^+CH_2CO_2H][Mn(VII)]^{1/2}$, in agreement with the experimental values of the kinetic orders.

Catalyzed Oxidation

$$[HMn(VI)] + H_3N^+CH_2CO_2H \longrightarrow H_3N^+CH_2[H_2Mn(IV)]CO_2 \qquad (K)$$

$$H_3N^+CH_2[H_2Mn(IV)]CO_2 + H_2O \longrightarrow \ldots \longrightarrow Mn(IV) + \ldots \qquad (L)$$

Two important features of the catalyzed reaction are noteworthy. First, the reaction rate shows a first-order dependence on the Mn(IV) concentration, and second, the reaction order with respect to glycine and the Mn(VII) species is the same as that for the non-catalyzed reaction.

In order to define the reaction rate corresponding to the catalyzed process, some things must be clarified. First, it is necessary to specify whether permanganate, glycine or both are adsorbed on the colloidal Mn(IV) particles. From literature dealing with the adsorption of ions on oxy-hydrates of Mn(IV) it can be deduced that the protonated species C_1 has a higher tendency to adsorption than the Mn(VII) species. Moreover, the solution bulk contains the former species in a great excess over the latter. So, it is reasonable to assume that the majority of active sites on the surface of the colloid beads will be occupied by the C_1 species. In view of the fact that the Mn(IV) species is a strong oxidant, it is necessary to decide whether the C_1 species, once adsorbed, is oxidized by Mn(VII) or by Mn(IV). In this respect, the slow rate of the N_2H_4/MnO_2 reaction[37] gives indirect evidence that the oxidation by the Mn(IV) species is irrelevant. Hence, we suggest that the process includes a heterogeneous reaction involving the C_1 species adsorbed on the colloid beads and Mn(VII), which comes from the bulk solution.

To determine the adsorbate concentration, the adsorption of the C_1 species on the colloidal Mn(IV) was assumed[38] to obey the Freundlich isotherm (Eq. (*6*)),

$$[\text{adsorbate}] = M\,[Mn(IV)]\,a\,[C_1]^b \ , \qquad (6)$$

where M is the mean molar weight of the colloidal adsorbent under the experimental conditions and a and b (whose values are 1) are parameters.

The rate of the catalyzed reaction exhibits the same dependences on the glycine and permanganate concentrations as that for the non-catalyzed oxidation. Therefore, it can be concluded that once the adsorbate formation is complete, the catalyzed oxidation involves a similar sequence of steps as the homogeneous process.

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