

KINETICS OF GUYARD'S REACTION WITH REGARD TO PERMANGANATE CHEMICAL OSCILLATORS

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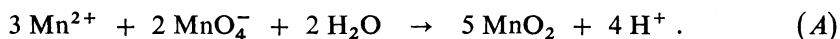
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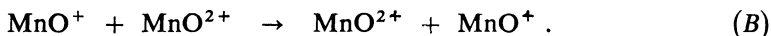
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Phosphoric acid is a necessary component of permanganate chemical oscillators. When Mn(II) ions are present in a stoichiometric excess, the reaction is of first order with respect to the concentration of MnO_4^- ions and of fractional order with respect to the concentration of Mn(II). When MnO_4^- ions are in a stoichiometric excess, the reaction is autocatalytic in nature and the inflexion time increases linearly with the concentration of H_3PO_4 ; analysis of the sigmoidal curve gave the rate constant of the non-catalytic step, k_1 , and that of the catalytic step, k_2 , which is indirectly proportional to the concentration of H_3PO_4 . The probable mechanism of the Guyard reaction involves a reversible equilibrium between Mn(IV) and colloidal MnO_2 and subsequent coagulation to form a MnO_2 suspension. Similarly to permanganate chemical oscillators, phosphoric acid or its ions play the key role, since they stabilize the colloidal MnO_2 which serves as a reservoir of Mn(IV) ions.

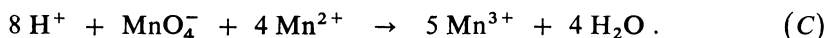
The redox reaction between MnO_4^- and Mn(II) ions in a sulfuric acid solution is often denoted as Guyard's reaction¹. Its final product is the precipitate of MnO_2 formed according to the stoichiometric reaction



As observed already by Polissar², the reaction has an induction period and is autocatalysed by the MnO_2 product. Adamson³ studied the rate of exchange reaction between Mn(II) and Mn(VII), Mn(VI) and Mn(VII), and Mn(II) and Mn(III), by using radioactive Mn; he came to the conclusion that the rate-determining step is the exchange of an electron according to



Kalra and Gosh⁴ found that the reaction between MnO_4^- and Mn(II) ions proceeds at higher H_2SO_4 concentrations stoichiometrically with the formation of Mn(III)



According to Morrow and Perlman⁵, the reaction between MnO_4^- and Mn(II) ions with the formation of Mn(III) in the medium of H_2SO_4 corresponds to the rate equation

$$\frac{d[\text{MnO}_4^-]}{dt} = \{k_0 + k_1[\text{H}^+] + k_2[\text{H}^+]^2\} [\text{Mn(II)}]^2 [\text{MnO}_4^-]. \quad (1)$$

Since the Guyard reaction is very probably involved in permanganate chemical oscillators⁶⁻⁹, we concentrated on its kinetic study in the presence of phosphoric acid as an inherent component of these oscillators. Our aim was to elucidate the role of colloidal MnO_2 both in the Guyard reaction and in the permanganate oscillators. Recently this study gained more importance since according to Orbán and Epstein¹⁰ the reaction in the medium of a $\text{KH}_2\text{PO}_4/\text{NaOH}$ buffer in a continuously stirred tank reactor represents a minimum permanganate oscillator which can form the basis of a new series of permanganate oscillators.

EXPERIMENTAL

The kinetics of the Guyard reaction was studied spectrophotometrically with a Specord M 40 type spectrophotometer (Carl Zeiss, Jena) by recording the time course of the spectrum in the visible or UV region or the absorbancy at a selected wavelength corresponding to MnO_4^- ions or to the autocatalytic MnO_2 particles. The cuvette with the reaction solution was placed in a tempered block connected to a U 10 type ultrathermostat (Medingen, G.D.R.).

When Mn(II) ions were in excess, the first-order rate constant was evaluated from the time course of the absorbancy of MnO_4^- ions at a wavelength of 522 nm according to a first-order kinetic equation. When the MnO_4^- ions were in a stoichiometric excess, the reaction having an autocatalytic course, the sigmoidal course of the MnO_2 content at $\lambda = 418$ nm was used to evaluate the rate constants of the non-catalysed, k_1 , and catalysed, k_2 , steps according to Schwartz¹¹. This was done by linearization of the autocatalytic sigmoidal curve based on subtracting pairs of values of absorbancy with equal time difference.

Stock solutions were prepared from commercial chemicals, KMnO_4 , MnSO_4 , and H_3PO_4 of reagent grade (Lachema, Brno). Stock solution of KMnO_4 was prepared according to Kolthoff et al.¹². The concentration of H_3PO_4 was checked alkalimetrically. All solutions were prepared from redistilled water.

RESULTS

When Mn(II) ions are in excess against MnO_4^- ions, the reaction between them is of the first order with respect to MnO_4^- ions (Fig. 1). The experimental rate constant of the first order (s^{-1}) is a non-linear function of the Mn(II) concentration and the corresponding reaction order, n , depends on the temperature: For the conditions given in Fig. 2, n was found to be equal to 1.87, 1.67, and 1.55 at 5, 20, and 35°C, respectively.

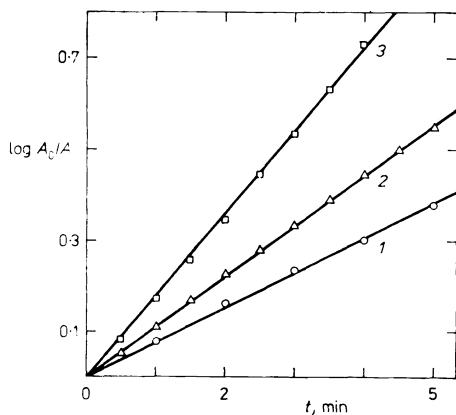


FIG. 1

First-order kinetics at a stoichiometric excess of Mn(II); $3 \cdot 10^{-4}$ M-KMnO₄, $3 \cdot 10^{-3}$ M-MnSO₄, 0.075 M-H₃PO₄, 1 5°C; 2 20°C; 3 35°C

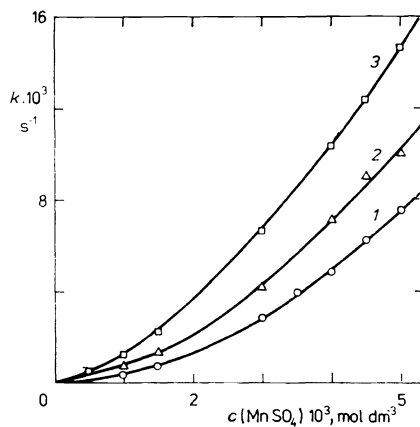


FIG. 2

Dependence of the rate constant (s^{-1}) on the concentration of Mn(II); $3 \cdot 10^{-4}$ M-KMnO₄, 0.075 M-H₃PO₄. 2 5°C; 2 20°C; 35°C

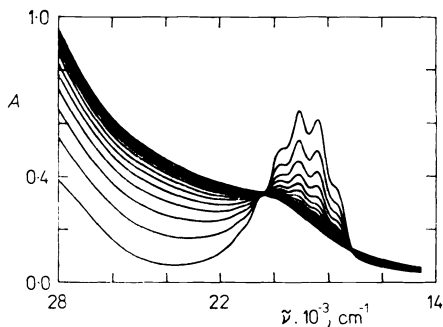


FIG. 3

Time dependence of absorption spectrum in the visible region; $3 \cdot 10^{-4}$ M-KMnO₄, $1.5 \cdot 10^{-3}$ M-MnSO₄, 0.075 M-H₃PO₄, 20°C. The values of absorbance were measured at 4 min intervals

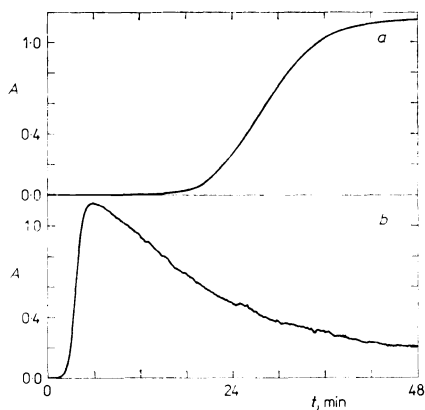


FIG. 4

Influence of H₃PO₄ on the course of the autocatalytic sigmoidal curve; $8 \cdot 10^{-4}$ M-KMnO₄, $1 \cdot 10^{-4}$ M-MnSO₄, 0.015 M-HClO₄, 35°C. a 0.015 M-H₃PO₄; b without H₃PO₄

The influence of the temperature on the reaction rate was evaluated by means of the Eyring equation and the activation parameters were determined as $\Delta H^\ddagger = 17.7 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -232 \text{ J K}^{-1} \text{ mol}^{-1}$.

Since phosphoric acid plays a key role in permanganate chemical oscillators⁶⁻⁹, we studied its effect on the Guyard reaction. If the time dependence of the absorption spectrum in the visible region is recorded at a concentration of H_3PO_4 $0.075 \text{ mol} \cdot \text{dm}^{-3}$, the absorbancy of MnO_4^- in the region of $\lambda = 490-583 \text{ nm}$ decreases and the absorbancy (light scattering) in the whole range of wavelengths increases; isosbestic points are observed at $\lambda = 490$ and 583 nm (Fig. 3).

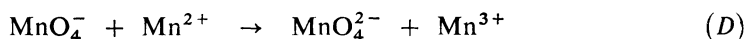
If the reaction is followed at a stoichiometric excess of MnO_4^- ions ($8 \cdot 10^{-4} \text{ M-KMnO}_4$, $1 \cdot 10^{-4} \text{ M-MnSO}_4$, $0.015 \text{ M-H}_3\text{PO}_4$, 0.015 M-HClO_4), a sigmoidal increase of absorbancy (light scattering) is observed at $\lambda = 418 \text{ nm}$ with an inflexion time of 1710 s (Fig. 4a). If this is compared with the reaction course in the absence of H_3PO_4 , precipitation of MnO_2 is observed after an inflexion time of 216 s , corresponding to a non-linear decrease of the absorbancy (Fig. 4b). Both the inflexion time and the rate constant k_2 , evaluated by the Schwartz method¹¹ from the sigmoidal curve, are practically linear functions of the concentration of phosphoric acid; the value of k_1 is constant within the limits of accuracy of the determination (Table I).

The dependence of the inflexion time on the temperature in the interval $25-40^\circ\text{C}$ has an Arrhenian character; the inflexion time at 20°C deviates from this dependence and depends on the rate of stirring (Fig. 5). The activation parameters were evaluated from the temperature dependence of the rate constants, k_2 , by using the Eyring equation as $\Delta H^\ddagger = 22.9 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = 172 \text{ J K}^{-1} \text{ mol}^{-1}$.

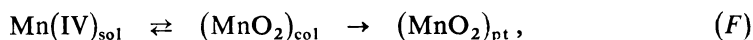
DISCUSSION

It follows from the results that the Guyard reaction has in the medium of phosphoric acid an autocatalytic course only if MnO_4^- ions are in a stoichiometric excess. This is evidenced by the sigmoidal course of the time dependence of the absorbancy (light scattering) at a wavelength of 418 nm . Analysis of the curves by the Schwartz method¹¹ gave the values of the rate constants k_1 and k_2 corresponding to the non-catalysed and catalysed reaction step, respectively.

In the non-catalysed reaction, the rate-determining step is the following:



and this is followed by dismutation of Mn^{3+} ions yielding MnO_2



where the subscript sol refers to hydrated ions, col to colloidal particles, and pt to precipitate.

The autocatalytic course of the Guyard reaction can be elucidated by the fact that the step (D) is followed by

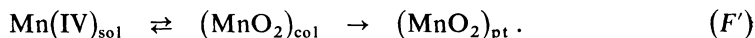


TABLE I

Dependence of the inflexion time and rate constant k_2 on the concentration of phosphoric acid. $8 \cdot 10^{-4} \text{M-KMnO}_4$, $1 \cdot 10^{-4} \text{M-MnSO}_4$, 35°C ; value of $k_1 \leq 0.02 \text{ min}^{-1}$

$[\text{H}_3\text{PO}_4] \cdot 10^2$ mol dm^{-3}	t_1 min	k_2 $\text{min}^{-1} \text{ mol}^{-1} \text{ dm}^3$
0.5	8.0	8 539
1.0	19.0	7 636
1.5	20.0	6 767
2.0	28.6	6 548
3.0	44.0	5 111
4.0	57.7	2 819
5.0	74.9	1 497

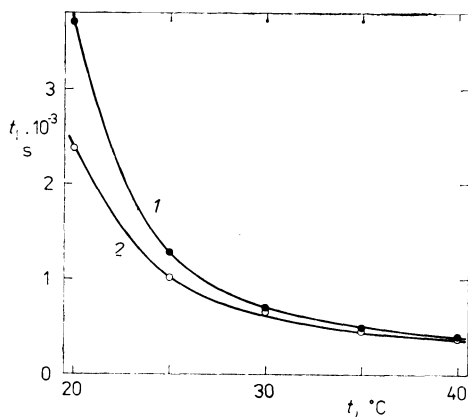


FIG. 5
Temperature dependence of the inflexion time, t_1 ; $8 \cdot 10^{-4} \text{M-KMnO}_4$, $1 \cdot 10^{-4} \text{M-MnSO}_4$, $5 \cdot 10^{-3} \text{M-H}_3\text{PO}_4$. 1 Without stirring; 2 with stirring

Here, the steps (G) and (H) represent a two-fold positive feedback: step (G) gives MnO_4^- ions and step (H) generates MnO_4^{2-} ions which enter into step (G). When the Guyard reaction proceeds at a stoichiometric excess of Mn^{2+} ions, step (D) is considerably accelerated and the reaction becomes first-order with respect to the concentration of MnO_4^- ions.

The linear increase of the inflexion time and the linear decrease of the rate constant k_2 with increasing concentration of H_3PO_4 can be elucidated as follows. At higher concentrations of the acid, the colloidal MnO_2 becomes more stable, hence also the form $\text{Mn(IV)}_{\text{sol}}$; this causes decrease of the rate of the reversible step (H) and thus of the rate constant k_2 of the autocatalytic reaction. Phosphoric acid or its ions were reported to have indeed a stabilizing effect on colloidal MnO_2 (ref.¹³).

The occurrence of isobestic points on the time dependence of the absorption spectrum, which is apparently overlapped by light scattering (Fig. 3), suggests the existence of a simple reversible equilibrium between $\text{Mn(IV)}_{\text{sol}}$ and $(\text{MnO}_2)_{\text{col}}$. This equilibrium, in which the colloid is stabilized by phosphoric acid, plays a key role also in permanganate chemical oscillators⁶⁻⁹.

It can be concluded that the Guyard reaction in the medium of phosphoric acid, its kinetics and mechanism constitute probably an essential part of the complex reaction mechanism of permanganate chemical oscillators.

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