The kinetics and the mechanism of oxidative decarboxylation of benzilic acid by acidic permanganate (stopped-flow technique) — An autocatalytic study

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Abstract: The kinetics of the oxidation of benzilic acid by potassium permanganate in an acidic medium were studied spectrophotometrically. The reaction followed a two-stage process, wherein both stages of the reaction followed first-order kinetics with respect to permanganate ion and benzilic acid. The rate of the reaction increased with an increase in acid concentration. Autocatalysis was observed by one of the products, i.e., manganese(II). A composite mechanism involving autocatalysis has been proposed. The activation parameters of the reaction were calculated and discussed and the reaction constants involved in the mechanisms were calculated. There is a good agreement between the observed and calculated rate constants under different experimental conditions.

Key words: oxidation, autocatalysis, benzilic acid, two-stage kinetics.

Résumé : Faisant appel à la spectrophotométrie, on a étudié la cinétique de l'oxydation de l'acide benzilique par le permanganate de potassium en milieu acide. La réaction se produit en deux étapes et chacune d'elles est du premier ordre par rapport aux concentrations de l'ion permanganate et de l'acide benzilique. La vitesse de la réaction augmente avec une élévation de la concentration d'acide. On a observé de l'autocatalyse par l'un des produits, soit le manganèse(II). On propose un mécanisme composé impliquant de l'autocatalyse. On a calculé et on discute des paramètres d'activation de la réaction; on a aussi calculé les constantes de réaction impliquées dans les mécanismes. On a observé un bon accord entre les constantes de vitesses observées et calculées dans différentes conditions expérimentales.

Mots clés : oxydation, autocatalyse, acide benzilique; cinétique à deux étapes.

[Traduit par la Rédaction]

Introduction

It is evident that manganese(VII) is reduced to various oxidation states in acidic, alkaline, and neutral media during oxidation by permanganate. Out of the six oxidation states of manganese (1), from 2^+ to 7^+, permanganate Mn(VII), is the most powerful oxidant in a dilute acid medium with reduction potentials of 1.69 V for the Mn(VII)/Mn(IV) couple and 1.51 V for the Mn(VII)/Mn(II) couple.

Oxidations by permanganate ion are applied extensively in organic syntheses (2–8), especially since the advent of phase-transfer catalysis (4, 5, 7). Kinetic studies are important sources of mechanistic information on the reactions, as demonstrated by the results for unsaturated acids both in aqueous (2, 4, 8) and nonaqueous media (9).

Furthermore, the mechanism by which this multivalent oxidant oxidizes a substrate depends not only on the substrate but also on the medium (10, 11) used for the study. In some cases the mechanistic approach is based on the intermediate complex formation, and in others, the results are interpreted by a free radical mechanism. The mechanisms suggested by various authors are not uniform, indicating that a wide variety of mechanisms are possible depending on the nature of the reactive species of permanganate as well as the substrate.

Several studies have been reported on the oxidation of benzilic acid by other oxidants such as cerium(IV) (12, 13), ferricyanide (14), chromic acid (15), thallium(III) (16), persulphate (17), and *N*-bromosacharin (18). Even though the oxidation product of benzilic acid is the same in both acidic and alkaline media, the reactions differ in many kinetic parameters. Interest in kinetic studies, in particular of α-hydroxy acids (19), has developed and no attempts have been made to correlate the rate data with the structural differences in these acids.

In view of the lack of reports in the literature on the oxidation of benzilic acid by acidic $KMnO_4$, we have selected it as a substrate for study. The present study deals with the ki-

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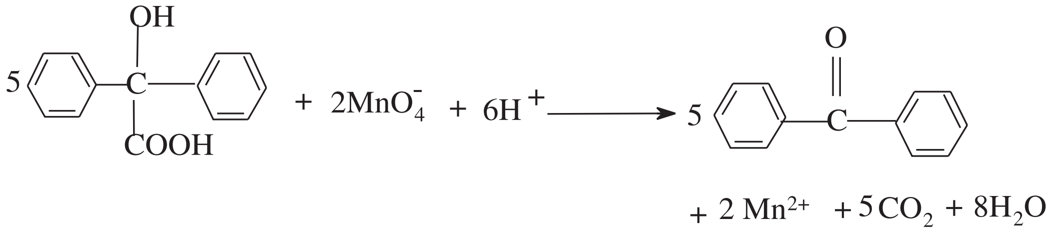


netics of the oxidation of benzilic acid by $KMnO_4$ in an acidic medium to arrive at a plausible mechanism and to determine the active species of permanganate in such media.

Experimental

Since the initial reaction was too fast to monitor by the usual method, kinetic measurements were performed on a Hitachi 150-20 spectrophotometer connected to a rapid kinetic accessory (HI-TECH SFA-12).

Materials and methods

All chemicals used were of BDH Analar specifications. Potassium permanganate (BDH) was prepared in doubly distilled water and its strength was ascertained (20*a*) by titrating against standard $H_2(CO_2)_2$ solution in hot acidic medium. The solubility of benzilic acid (Merck) (BA) is low and it was prepared in water by warming. Perchloric acid (Merck) and sodium perchlorate (BDH) were used to provide the required acidity and ionic strength, respectively. Mn(II) was prepared by dissolving manganese(II) sulphate (Riedel). Doubly distilled conductivity water was used to prepare all the solutions.

The optical density vs. concentration plot for acidified permanganate ion showed that Beer's law, under the reaction conditions in 6.0×10^{-5} to 2.0×10^{-4} mol dm^{-3} in 0.01 mol dm^{-3} $HClO_4$, was obeyed at a wavelength of 526 nm and the molar absorptivity of permanganate was found to be 2300 ± 50 dm^3 mol^{-1} cm^{-1}, which was in good agreement with previous results (21, 22).

Kinetic measurements

All kinetic measurements were performed under pseudo-first-order conditions where [benzilic acid] was always in excess over [MnO_4^-] at a constant ionic strength of 5.0×10^{-3} mol dm^{-3} in acidic medium at a constant temperature of 21 ± 0.1 °C.

The progress of the reaction was followed by monitoring the decrease in MnO_4^- in a 1 cm quartz cell of a Hitachi model 150-20 spectrophotometer at its absorption maximum (526 nm) as a function of time. Earlier, it was verified that there is negligible interference from other reaction species at this wavelength. The pseudo-first-order rate constants were obtained from the plots of log $(A_t - A_\infty)$ vs. time and the plot of log $[(A_t - A_\infty) - (A_{t'} - A_\infty)]$ vs. time, where A_t and A_∞ represent the absorbance at time t and ∞, respectively. $A_{t'}$ represents the absorbance for the extrapolated point at time t'. The plots of log $(A_t - A_\infty)$ vs. time and of log $[(A_t - A_\infty) - (A_{t'} - A_\infty)]$ vs. time indicate that there was a two-stage process and that both stages were linear. In the first slow process, the linearity was observed up to 60% completion of the reaction and in the second fast process, linearity was observed from 60% to 80% completion of the reaction. k_{obs} values were reproducible within ±5%, where the first slow stage is followed by a second fast stage process (Fig. 1). This type of two-stage process has been observed in a few cases (23, 24). During the progress of the reaction, the colour of the solution changed from violet to colourless, indicating the formation of Mn(II), which was verified by a spot test (20 *b*). The formation of Mn(II) is shown spectrally in Fig. 2.

Results

Stoichiometry and product analysis

Different sets of reaction mixtures containing excess [MnO_4^-] over [benzilic acid] were mixed in the presence of 1.0×10^{-3} mol dm^{-3} perchloric acid, adjusted to an ionic strength of 5.0×10^{-3} mol dm^{-3}, and kept for 12 h in an inert atmosphere at 21 °C. After completion of the reaction, the remaining permanganate was then determined spectrophotometrically. The results indicated that 5 mol of benzilic acid were consumed by 2 mol of permanganate as in eq. [1].

The main oxidation products were identified as benzophenone, CO_2, and manganese(II). The product, manganese(II) in acid medium, was analyzed using EDTA solution with Erichrome black-T as the indicator (20*b*). The formation of benzophenone was confirmed by its IR and NMR spectra (25). Further, the yield was quantitatively estimated to ca. 85%, evidence for which is provided by isolation of its 2,4-DNP derivative (26), with a mp of 236 °C. Benzophenone did not undergo further oxidation under the stated kinetic conditions. The test for the probable oxidation product of the ketone, i.e., benzoic acid, was negative.

Reaction orders

The reaction order for benzilic acid and perchloric acid was investigated by varying one of these concentrations while keeping all other concentrations and conditions constant and studying the effect of its concentration on the rate of the reaction.

Kinetic data were collected for initial [MnO_4^-] in the $(0.40–4.0) \times 10^{-4}$ mol dm^{-3} range. In an acid medium, the reaction followed a two-stage process (Fig. 1). All the experiments exhibited an identical pattern, with the initial slow reaction followed by a faster one. The plots of log $(A_t - A_\infty)$ vs. time and log $[(A_t - A_\infty) - (A_{t'} - A_\infty)]$ vs. time ($r > 0.9355$, $s \le 0.0144$ for stage 1, $r > 0.9951$, $s \le 0.4480$ for stage 2) for different initial concentrations of MnO_4^- exhibit two distinct straight lines for the slow and fast stages of the reaction (Fig. 1). The fairly constant k_s (s^{-1}) values for the slow stage and k_f (s^{-1}) values for the fast stage confirms that slow and fast depletions in MnO_4^- follow first-order kinetics. The concentration of benzilic acid was varied in the range of $(0.40–4.0) \times 10^{-3}$ mol dm^{-3}, keeping all other reactant con-

Fig. 1. Plot of (*a*) $\log(A_t - A_\infty)$ vs. time and (*b*) $\log[(A_t - A_\infty) - (A_{t'} - A_\infty)]$ vs. time in an acidic medium ($[MnO_4^-] = 2 \times 10^{-4}$ mol dm^{-3}, [BA] = 2×10^{-3} mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, and $I = 5.0 \times 10^{-3}$ mol dm^{-3}.

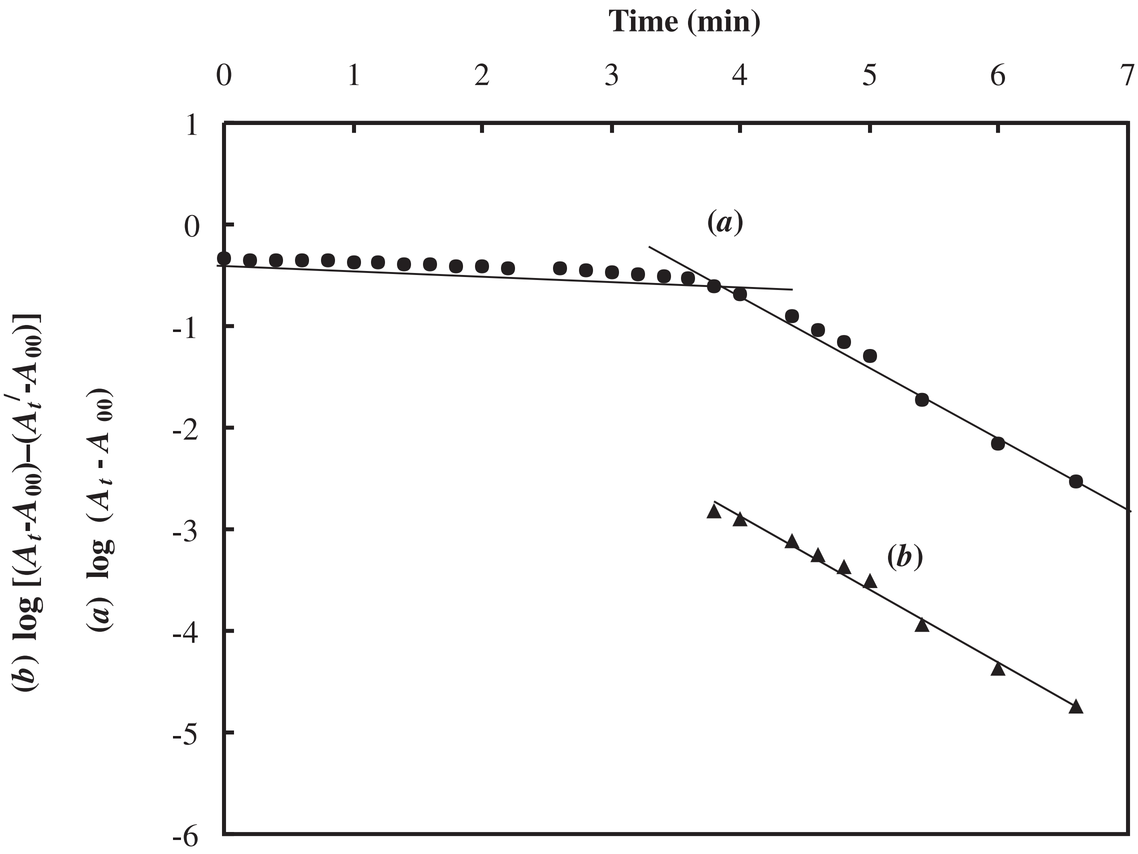
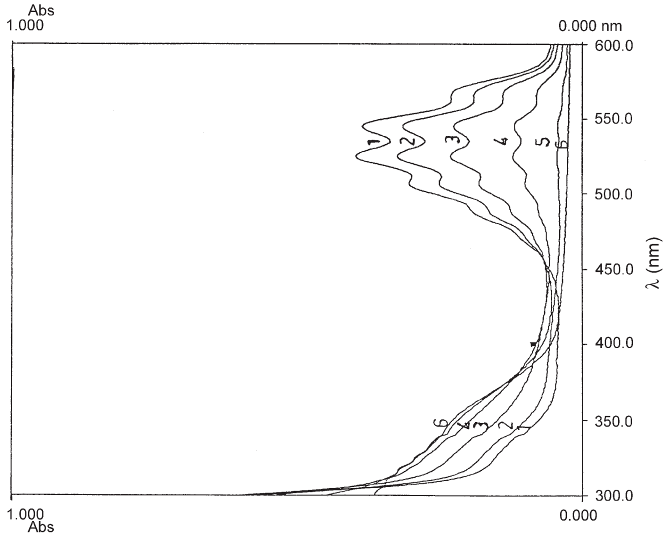


Fig. 2. Spectroscopic changes occurring in the oxidation of benzilic acid by permanganate with $[MnO_4^-] = 2.0 \times 10^{-4}$ mol dm^{-3}, [BA] = 2.0×10^{-3} mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, and $I = 5.0 \times 10^{-3}$ mol dm^{-3} at 21 °C (scanning time interval = 1 min).



centrations and conditions constant. In an acidic medium, the k_s and k_f values (Table 1) increased with increasing concentration of benzilic acid indicating first-order dependence on the [substrate] in both the stages. To study the effect of $[H^+]$ on the rate of the reaction, the $[H^+]$ was varied from $(0.50–5.0) \times 10^{-2}$ mol dm^{-3} at a constant concentration of MnO_4^- and benzilic acid, maintaining a constant ionic strength of 5.0×10^{-3} mol dm^{-3}. It was found that in both stages the rate increased with an increase of $[H^+]$. The order in both stages was less than unity (Table 1). It was found that the ionic strength and dielectric constant of the medium have no significant effect on the rate of reaction.

Effect of added products

The addition of the product benzophenone did not show any significant effect on the rate of the reaction. However, the initial addition of the product Mn(II) in the range of $(0.20–2.0) \times 10^{-4}$ mol dm^{-3}, keeping other conditions constant, had an appreciable increasing effect on the rate of the reaction. As the initial concentration of Mn(II) was increased, the rate progressively increased at an order of around 0.62 and 0.26 in the slow and fast stages, respectively. This illustrates the autocatalytic nature of the product (Table 2), which is also evident from the concentration vs. time plot (Fig. 3) and the linear plot of k_{obs} vs. k_{cal} for manganese(II) variation (Fig. 3, inset), as observed in earlier cases (27).

Polymerization study

To test for free radical intervention, the reaction mixture containing $[MnO_4^-] = 2 \times 10^{-4}$ mol dm^{-3} and [BA] = 2×10^{-3} mol dm^{-3} were taken, and the pH of the solution was adjusted to 3.0 The solution was then degassed with nitrogen

Table 1. Effect of [benzilic acid], [MnO_4^-], and [H^+] on the oxidation of benzilic acid by acidified permanganate at 21 °C, $I = 5.0 \times 10^{-3}$ mol dm^{-3}.

[BA] ($\times 10^3$ mol dm^{-3})	[MnO_4^-] ($\times 10^4$ mol dm^{-3})	[H^+] ($\times 10^3$ mol dm^{-3})	k_s ($\times 10^3$ s^{-1}) (Expt.)	k_s ($\times 10^3$ s^{-1}) (Calcd.)	k_f ($\times 10^3$ s^{-1}) (Expt.)	k_f ($\times 10^3$ s^{-1}) (Calcd.)
0.4	2.0	1.0	0.41	0.42	5.21	5.01
1.0	2.0	1.0	1.12	1.05	13.2	12.5
2.0	2.0	1.0	2.07	2.10	27.5	25.1
3.0	2.0	1.0	3.10	3.16	37.2	37.6
4.0	2.0	1.0	4.23	4.22	51.3	50.1
2.0	0.4	1.0	2.08	2.10	27.3	25.1
2.0	1.0	1.0	2.03	2.10	27.5	25.1
2.0	2.0	1.0	2.07	2.10	27.5	25.1
2.0	3.0	1.0	2.16	2.10	27.9	25.1
2.0	4.0	1.0	2.12	2.10	28.0	25.1
2.0	2.0	0.5	1.15	1.16	14.3	14.5
2.0	2.0	0.8	1.81	1.75	21.0	21.2
2.0	2.0	1.0	2.07	2.10	27.5	25.1
2.0	2.0	2.0	3.60	3.57	36.4	39.0
2.0	2.0	5.0	5.85	6.11	60.2	60.2

Table 2. Effect of product Mn(II) on the oxidation of benzilic acid by acidified $KMnO_4$ at 294 K ([BA] = 2.0×10^{-3} mol dm^{-3}, [MnO_4^-] = 2.0×10^{-4} mol dm^{-3}, [H^+] = 1.0×10^{-3} mol dm^{-3}, and $I = 5.0 \times 10^{-3}$ mol dm^{-3}).

[Mn(II)] ($\times 10^4$ mol dm^{-3})	k_s ($\times 10^3$ s^{-1})	k_f ($\times 10^3$ s^{-1})
0.0	2.07	27.5
0.2	2.75	28.4
0.6	6.13	34.0
1.0	8.11	43.4
1.5	10.2	48.3
2.0	11.3	49.1

and acrylonitrile (5 mL, 20% v/v) was added to the solution at room temperature and was kept for 24 h. On diluting the reaction mixture with methanol, no precipitate resulted indicating no polymerization of acrylonitrile. This observation indicates that the oxidation of benzilic acid by acidic potassium permanganate proceeds through the absence of polymer formation and, as well, any intervention of free radicals. There is evidence of polymerization with acrylonitrile in the earlier studies (28).

Effect of temperature

The effect of temperature on the reaction was studied at four different temperatures. The rate increased with an increase in temperature. The $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values were obtained from a $\log(k_{obs}/T)$ vs. $1/T$ plot ($r > 0.9719$, $s \le 0.01298$ for stage 1, $r > 0.9839$, $s \le 0.07748$ for stage 2). The activation parameters $\Delta H^\ddagger$ (kJ mol^{-1}), $\Delta S^\ddagger$ (J K^{-1} mol^{-1}), and $\Delta G^\ddagger$ (kJ mol^{-1}) were found to be 64 ± 2, –79 ± 6, and 87 ± 4 for stage 1 and 28 ± 2, –181 ± 16, and 81 ± 4 for stage 2, respectively.

Discussion

Oxidation of benzilic acid by permanganate in a $HClO_4$ medium is a noncomplementary reaction in which the oxidant undergoes five equivalent changes. In this experiment, the reaction between benzilic acid and MnO_4^- had a stoichiometry of 5:2 with first-order dependence on [MnO_4^-] and [BA] and fractional order dependence on both [H^+] and [Mn(II)]. Stoichiometric studies revealed 5-equivalent changes in Mn(VII). Hence, the formation of Mn(IV) as a reduced product of Mn(VII) in the reaction was excluded, although formation of Mn(IV) had been observed in earlier studies (29, 30). The strong reducing character of benzilic acid was evident in the reduction of Mn(VII) to Mn(II) in the $HClO_4$ medium.

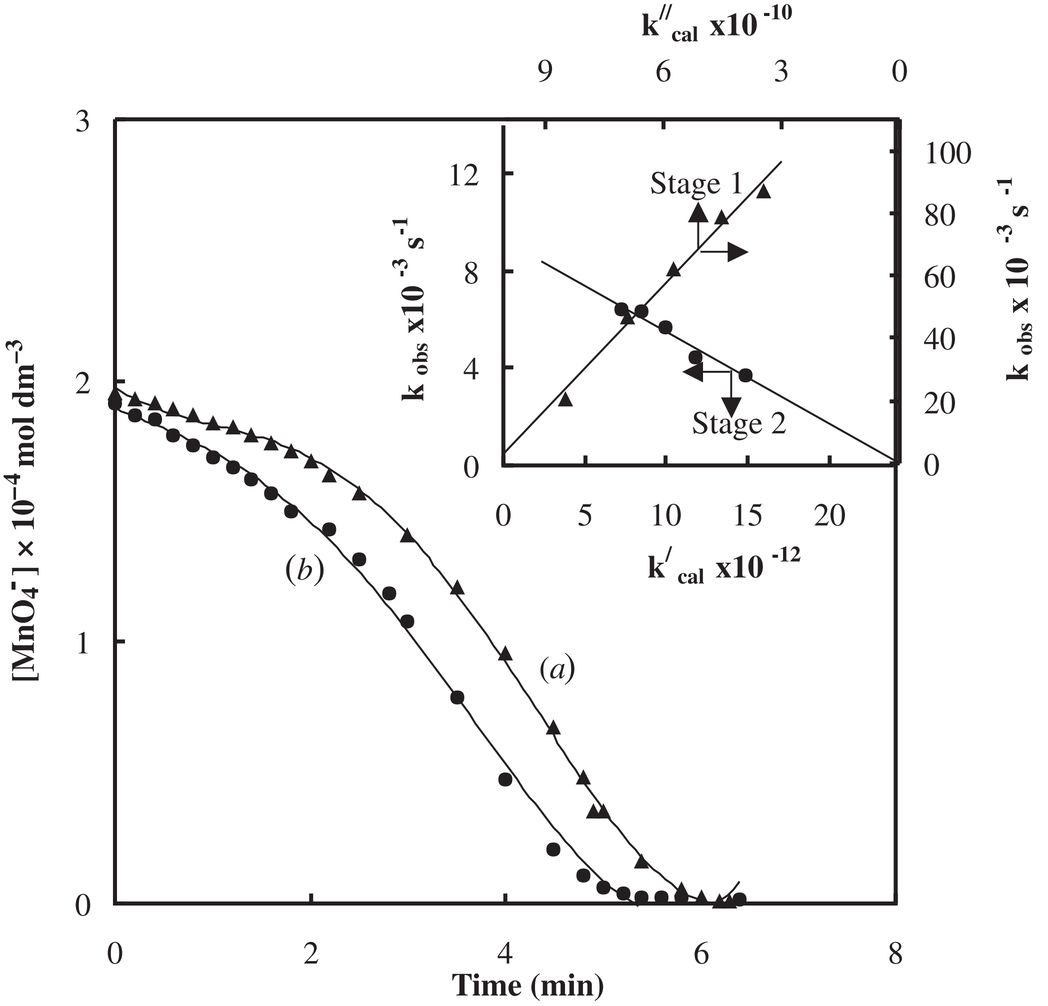
The active species of permanganate in an aqueous acid medium may be deduced from the dependence of the rate on [H^+] in the reaction medium. The apparent order of less than unity in [H^+] may be an indication of the permanganate species as permanganic acid. In an acidic medium, permanganic acid ($HMnO_4$) is a more efficient oxidant species of manganese(VII) than permanganate ion (29–31). In addition, it was observed that the reaction rate increased with an increase in [H^+] and tended to attain a limiting value at high acidities. The plot of k_{obs} vs. [H^+] in an acidic medium is a curve of decreasing slope (convex to the rate axis) and passing through the origin (Fig. 4) from which it can be inferred (32) that a rapid equilibrium between the protonated and unprotonated form is involved. At higher acidities protonation is almost complete, leading to the limiting rate, which indicates that only the protonated form is active. The negligible ionic strength effect on the rate of the reaction also confirms $HMnO_4$ as the active species of MnO_4^-. Thus, the acid permanganate equilibrium is represented as

$$[2] \qquad H^+ + MnO_4^- \overset{K_1}{\rightleftharpoons} HMnO_4$$

where K_1 is the formation constant of $HMnO_4$.

Based on the experimental results, the following mechanism can be proposed in which all the observed orders with respect to each constituent such as [oxidant], [reductant], and [H^+] may be well accommodated. The results suggest the formation of a protonated form of permanganate as the

Fig. 3. Concentration vs. time plots to show autocatalysis. (*a*) [BA] = 2.0×10^{-3} mol dm^{-3}, [MnO_4^-] = 2.0×10^{-4} mol dm^{-3}, [H^+] = 1.0×10^{-3} mol dm^{-3}, $I = 5.0 \times 10^{-3}$ mol dm^{-3} (*b*) [BA] = 3.0×10^{-3} mol dm^{-3}, [MnO_4^-] = 2.0×10^{-4} mol dm^{-3}, [H^+] = 1.0×10^{-3} mol dm^{-3}, $I = 5.0 \times 10^{-3}$ mol dm^{-3}. Inset: plot of k_{expt} vs $k'_{\mathrm{cal}} = [\mathrm{BA}]^1[\mathrm{Mn(II)}]^{0.62}[\mathrm{H^+}]^{0.70}[\mathrm{MnO_4^-}]^1$ for stage 1 and $k''_{\mathrm{cal}} = [\mathrm{BA}]^1[\mathrm{Mn(II)}]^{0.26}[\mathrm{H^+}]^{0.6}[\mathrm{MnO_4^-}]^1$ for stage 2 for the variation of manganese(II) (Table 2).



active species of MnO_4^- in a prior equilibrium, which reacts with 1 mol of benzilic acid in a rate-determining step to give a complex (C_1) that further decomposes in a fast step to give benzophenone and the intermediate Mn(V). The intermediate Mn(V), being unstable in an acidic medium, reacts with another mol of benzilic acid in a fast step to Mn(III), which is subsequently reduced to the end product Mn(II) in further fast steps satisfying stoichiometric observations. The spectral evidence for the formation of complex C_1 was obtained from UV–vis spectra of both benzilic acid and the mixture of benzilic acid and permanganic acid, which indicated a bathochromic shift from 325 to 347 nm. The steps proposed are shown in Scheme 1.

Since none of the intermediates of Mn(VII) could be detected, Scheme 1 is only one of the possible mechanisms for the reaction in the absence of free radicals. Attempts were made to allow spectrophotometric detection (in terms of wavelengths) of Mn^{5+} and Mn^{3+} intermediates as the reaction proceeded in the oxidation of benzilic acid by $HMnO_4$. Unfortunately, the low concentration of Mn^{3+} and Mn^{5+} intermediates obtained under our experimental conditions made the detection unsuccessful. However, there are reports of their existence in the earlier literature (33, 34). Scheme 1 leads to the rate law (eq. [3] that explains all the observed orders except autocatalysis.

$$[3] \qquad -\frac{\mathrm{d[Mn(VII)]}}{\mathrm{d}t} = \frac{k_1K_1[\mathrm{H^+}]_\mathrm{T}[\mathrm{Mn(VII)}]_\mathrm{T}[\mathrm{BA}]}{(1 + K_1[\mathrm{H^+}])(1 + K_1[\mathrm{Mn(VII)}])}$$

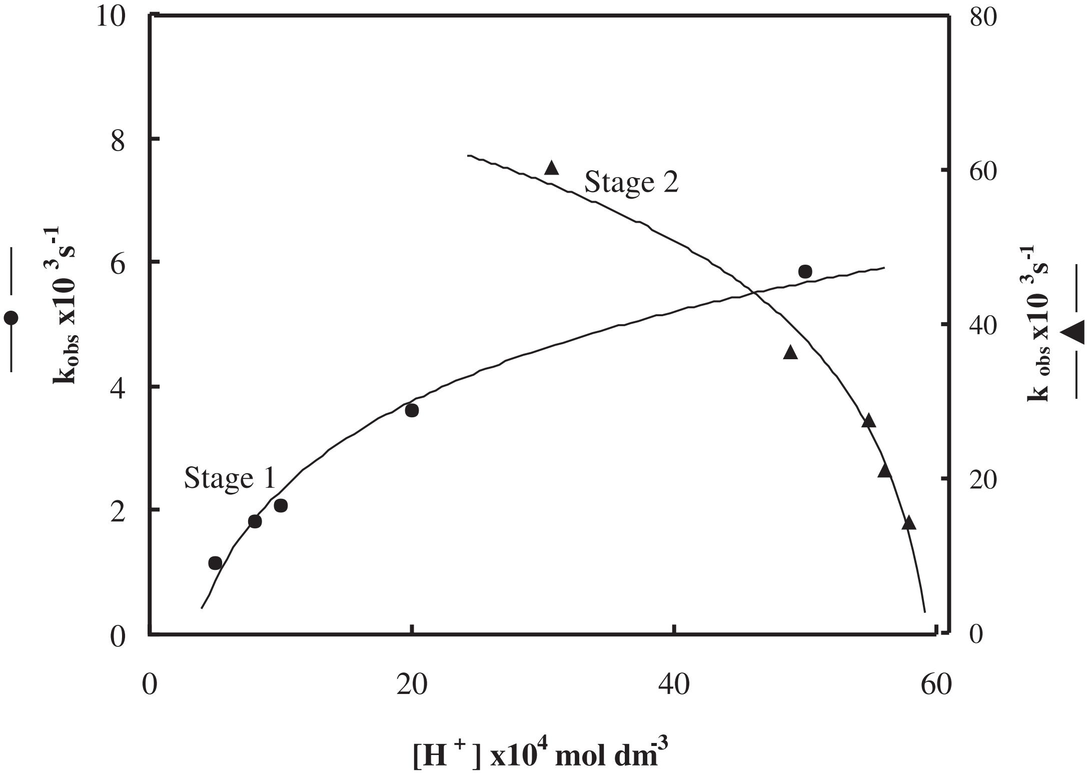
$$[4] \qquad = \frac{k_1K_1[\mathrm{H^+}][\mathrm{BA}][\mathrm{Mn(VII)}]}{1 + K_1[\mathrm{H^+}] + K_1[\mathrm{Mn(VII)}]) + K_1^2[\mathrm{H^+}][\mathrm{Mn(VII)}]}$$

The terms such as K_1[Mn(VII)] and K_1^2[H^+][Mn(VII)] in the denominator of eq. [4] are negligibly small compared with unity, in view of the low concentration of [Mn(VII)] used in the experiments. Hence, eq. [4] becomes eq. [5]

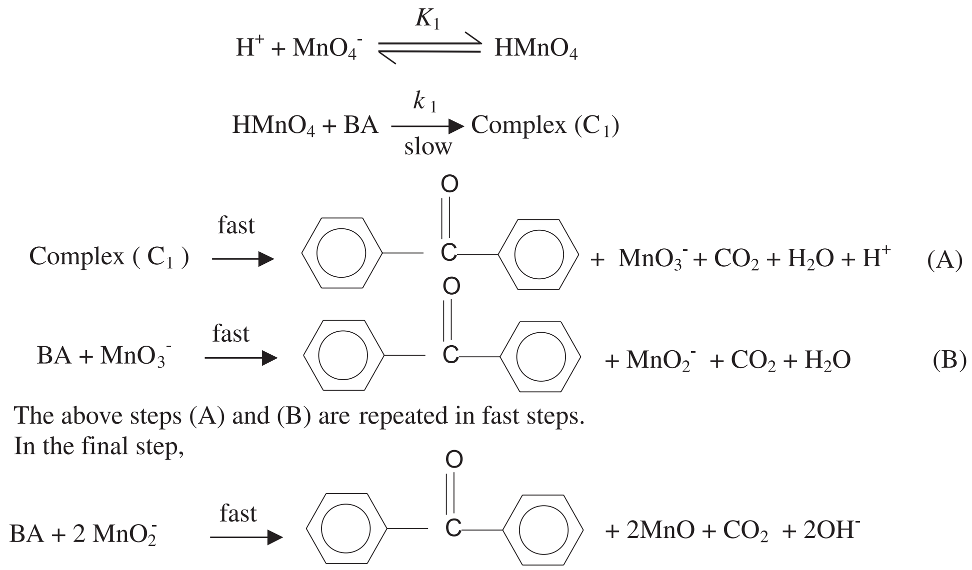
$$[5] \qquad k_{\mathrm{obs}} = \frac{\mathrm{Rate}}{[\mathrm{Mn(VII)}]} = \frac{k_1K_1[\mathrm{H^+}][\mathrm{BA}]}{1 + K_1[\mathrm{H^+}]}$$

The mechanism of Scheme 1 and rate law (eq. [3]) may be verified by rearranging to the form

Fig. 4. The plot of k_{obs} vs. $[H^+]$ (a curve of decreasing slope (convex to the rate axis)).



Scheme 1.

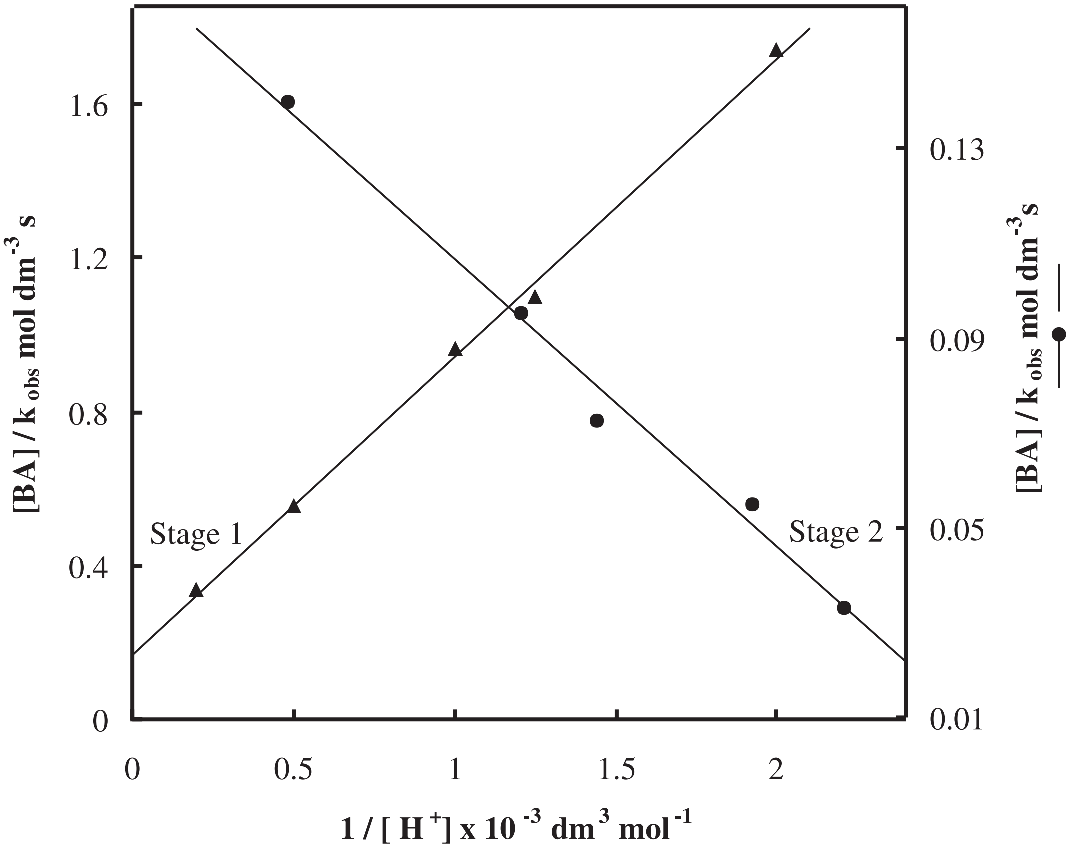


The above steps (A) and (B) are repeated in fast steps.
In the final step,

$$\frac{[BA]}{k_{obs}} = \frac{1}{k_1 K_1 [H^+]} + \frac{1}{k_1} \qquad [6]$$

where k_{obs} is first-order rate constant. According to eq. [6], the plot of $[BA]/k_{obs}$ vs. $1/[H^+]$ ($r > 0.999$, $s \leq 0.06990$ for stage 1, $r > 0.9946$, $s \leq 0.06993$ for stage 2) is expected to be linear, which is verified in Fig. 5. The slope and intercept of this plot lead to values of K_1 and k_1 at 21 °C of 221 ± 9 dm^3 mol^{-1}, 5.8 ± 0.3 dm^3 mol^{-1} s^{-1} for stage 1 and 371 ± 13 dm^3 mol^{-1}, 46 ± 2 dm^3 mol^{-1} s^{-1} for the fast stage 2, respectively. The experimental rate constants can be computed for both stages using these values. There is a reasonable agreement between the calculated and experimental rate constants (Table 1). The negligible effect of ionic strength

Fig. 5. The plot of [BA]/k_{obs} vs. 1/[H^+] (verification of rate law (eq. [3])).

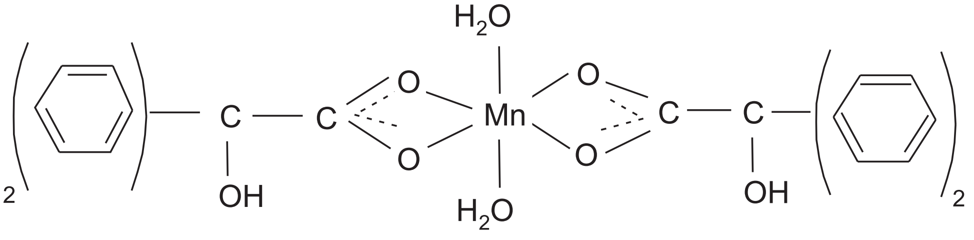


Scheme 2.

$$\mathrm{Mn(II)} + 2\mathrm{BA} \underset{}{\overset{K_2}{\rightleftharpoons}} \text{Complex } (C_2)$$

$$\mathrm{C2} + \mathrm{HMnO_4} \xrightarrow[\text{slow}]{k_2} \text{Products}$$

The probable structure of the complex (C_2) is given below



and relative permitivity on rate is qualitatively consistent with the reaction between two neutral molecules as in Scheme 1.

Autocatalysis by Mn(II) in an acidic medium

The autocatalysis by one of the products (Mn(II)) is interesting. The effect of Mn(II) as a catalyst in the case of the oxidation of permanganate is well-known (35–37). In the present case, Mn(II) was found to catalyse the rate of oxidation of benzilic acid (Table 2).

The apparent order of less than unity with respect to the Mn(II) ion may be attributed to a complex formation between benzilic acid and Mn(II). The complex (C_2) is then subsequently involved in the interaction with $HMnO_4$. These steps shown in Scheme 2 will form a part of Scheme 1.

The evidence for complex formation (C_2) was obtained from UV–vis spectra of both benzilic acid and mixtures of benzilic acid and Mn(II), which indicated a hypsochromic shift of about 4 nm from 338 to 334 nm and a new band appeared at 372 nm. Indeed, such complex formation between substrates such as styrene and Mn(II) has been observed in the literature (38, 39).

Thus, when Mn(II) is initially present, a composite scheme involving all the steps of Schemes 1 and 2 operates and the rate law becomes

$$k_{\text{gross}} = k_{\text{obs}} + k_{\text{autocat}}$$

$$[7] \qquad k_{\text{gross}} = \frac{k_1K_1[\text{BA}][\text{H}^+]}{1 + K_1[\text{H}^+]} + \frac{k_2K_2[\text{Mn(II)}][\text{BA}]^2}{\{1 + K_2[\text{BA}]^2\}\{1 + K_2[\text{Mn(II)}][\text{BA}]\}^2}$$

$$k_{\text{autocat}} = k_{\text{gross}} - k_{\text{obs}}$$

$$[8] \qquad k_{\text{autocat}} = \frac{k_2K_2[\text{Mn(II)}][\text{BA}]^2}{\{1 + K_2[\text{BA}]^2\}\{1 + K_2[\text{Mn(II)}][\text{BA}]\}^2}$$

where k_{gross} and k_{autocat} refer to the rate paths of the overall and autocatalytic paths, respectively. At constant concentrations of oxidant and substrate, a plot of $[\text{BA}]^2/k_{\text{autocat}}$ in eq. [8] vs. 1/[Mn(II)] ($r > 0.9987$, $s \leq 0.1566$ for stage 1, $r > 0.9596$, $s \leq 0.1574$ for stage 2) for both stages was found to be linear. Indeed, it is to be noted that the plot shows an intercept that is in agreement with the complex formation as shown in Scheme 2. The high negative values of $\Delta S^{\ddagger}$ indicate that complex (C_1) is more ordered than the reactants (40).

Reason for the two stages

Details regarding the occurrence of two successive stages, slow and fast, might be due to the creation of an optimum concentration of some intermediates (41–43). It might be possible that up to a certain range of MnO_4^- concentration (first slow stage), the active species of the oxidant (i.e., the protonated form of MnO_4^- ($HMnO_4$) is reactive) while in the second stage of the reaction, autocatalysis due to one of the products (Mn(II)) is operative. The product Mn^{2+} ions formed in the first slow stage, after achieving an optimum concentration, start reducing MnO_4^- ions to Mn^{3+} and or Mn^{4+} ions (44), ($MnO_4^- + 3Mn^{2+} + 8H^+ = 3Mn^{3+} + Mn^{4+} + 4H_2O$) indicating that the intermediate manganese ions are the active oxidizing species. On addition of Mn^{2+}, the acceleration of rate is due to the existence of Mn^{3+} or Mn^{4+} as the principal reactive species in the second fast stage. But the oxidation of benzilic acid by Mn(III), as well as the continuous increase in the oxidation rate with increasing Mn^{2+} added to the MnO_4^- – benzilic acid reaction mixture, indicates that Mn^{3+}, but not Mn^{4+}, is the sole oxidant throughout the auto acceleration stage.

Conclusions

In an acidic medium, the reaction exhibits an autocatalytic nature and follows two stages, as one of the products (Mn(II)) enhances the rate of the reaction. Mn(II) as the reduced product of Mn(VII) in the reaction may suggest that benzilic acid shows a strong reducing character in a $HClO_4$ medium. The overall mechanistic sequences described in the media are consistent with product, mechanistic, and kinetic studies.

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Appendix

According to Scheme 1,

$$[\mathrm{A1}]\quad \text{Rate} = k_1[\mathrm{HMnO_4}][\mathrm{BA}] = k_1K_1[\mathrm{Mn(VII)}]_\mathrm{f}[\mathrm{BA}]_\mathrm{f}[\mathrm{H^+}]_\mathrm{f}$$

The total concentration of $\mathrm{MnO_4^-}$ is given by (where "T" and "f "stand for total and free)

$$[\mathrm{Mn(VII)}]_\mathrm{T} = [\mathrm{Mn(VII)}]_\mathrm{f} + [\mathrm{HMnO_4}] = [\mathrm{Mn(VII)}]_\mathrm{f}(1 + K_1[\mathrm{H^+}])$$

Therefore,

$$[\mathrm{A1}a]\quad [\mathrm{Mn(VII)}]_\mathrm{f} = [\mathrm{MnO_4^-}]_\mathrm{T}/1 + K_1[\mathrm{H^+}]$$

Similarly,

$$[\mathrm{A1}b]\quad [\mathrm{H^+}]_\mathrm{f} = [\mathrm{H^+}]_\mathrm{T}/1 + K_1[\mathrm{Mn(VII)}]$$

Substituting eqs. [A1*a*]and [A1*b*] in eq. [A1]

$$[\mathrm{A1}c]\quad \text{Rate} = -\mathrm{d}[\mathrm{Mn(VII)}]/\mathrm{d}t = \frac{k_1K_1[\mathrm{H^+}][\mathrm{BA}][\mathrm{Mn(VII)}]_\mathrm{T}}{(1 + K_1[\mathrm{H^+}])\,(1 + K_1[\mathrm{Mn(VII)}])}$$

The term (1 + K_1[Mn(VII)]) in the denominator of eq. [A1*c*] approximates unity in view of the low concentration of Mn(VII) used.

Autocatalysis

According to Scheme 2,

$$[\mathrm{A1}d]\quad \text{Rate} = k_2[\mathrm{C_2}][\mathrm{HMnO_4}] = k_2K_2[\mathrm{Mn(II)}]_\mathrm{f}[\mathrm{BA}]_\mathrm{f}^2[\mathrm{HMnO_4}]$$

$$[\mathrm{Mn(II)}]_\mathrm{T} = [\mathrm{Mn(II)}]_\mathrm{f} + [\mathrm{C_2}] = [\mathrm{Mn(II)}]_\mathrm{f}(1 + K_2[\mathrm{BA}]^2)$$

Therefore,

$$[\mathrm{A1}e]\quad [\mathrm{Mn(II)}]_\mathrm{f} = [\mathrm{Mn(II)}]_\mathrm{T}/1 + K_2[\mathrm{BA}]^2$$

Similarly,

$$[\mathrm{A1}f]\quad [\mathrm{BA}]_\mathrm{f} = [\mathrm{BA}]_\mathrm{T}/1 + K_2[\mathrm{Mn(II)}][\mathrm{BA}]$$

Substituting eqs. [A1*e*] and [A1*f*] in eq. [A1*d*]

$$[\mathrm{A1}g]\quad \text{Rate} = \frac{k_2K_2[\mathrm{Mn(II)}][\mathrm{BA}]^2[\mathrm{HMnO_4}]}{\{1 + K_2[\mathrm{BA}]^2\}\{1 + K_2[\mathrm{Mn(II)}][\mathrm{BA}]\}^2}$$