J. Chem. Research (S), 2002, 451–453
J. Chem. Research (M), 2003, 0801–0821

Kinetics and mechanism of oxidative decarboxylation of benzilic acid by alkaline permanganate using the stopped-flow technique

Sairabanu A. Farokhi and Sharanappa T. Nandibewoor*
P.G. Department of studies in Chemistry, Karnatak University, Dharwad, 580003, India

A mechanism involving the formation of complex between benzilic acid and permanganate has been proposed for the title reaction and activation parameters for the slow step of reaction and reaction constants involved in the mechanism were calculated and discussed.

Keywords: benzilic acid, alkaline permanganate

The mechanism by which permanganate ion oxidises a substrate depends not only on the nature of substrate but also on the medium[9] used for the study. In strongly alkaline medium the stable reduction product[10, 11] of permanganate ion is manganate ion, MnO_4^{2-}. No mechanistic information is available to distinguish between a direct one-electron reduction to Mn (VI) (Scheme 1) and a mechanism, in which hypomanganate (Scheme 2) is formed in a two–electron reduction followed by rapid oxidation of the hypomanganate ion.[12]

$$\mathrm{Mn(VII)} + \mathrm{S} \xrightarrow{k'_1} \mathrm{Mn(VI)} + \mathrm{S}^{\cdot}$$

$$\mathrm{Mn(VII)} + \mathrm{S}^{\cdot} \xrightarrow{k'_2} \mathrm{Mn(VI)} + \text{Products}$$

$$\mathrm{S} = \text{Substrate},\ k'_2 >> k'_1$$

Scheme 1

$$\mathrm{Mn(VII)} + \mathrm{S} \xrightarrow{k'_4} \mathrm{Mn(V)} + \text{Products}$$

$$\mathrm{Mn(VII)} + \mathrm{Mn(V)} \xrightarrow{k'_3} 2\mathrm{Mn(VI)}$$

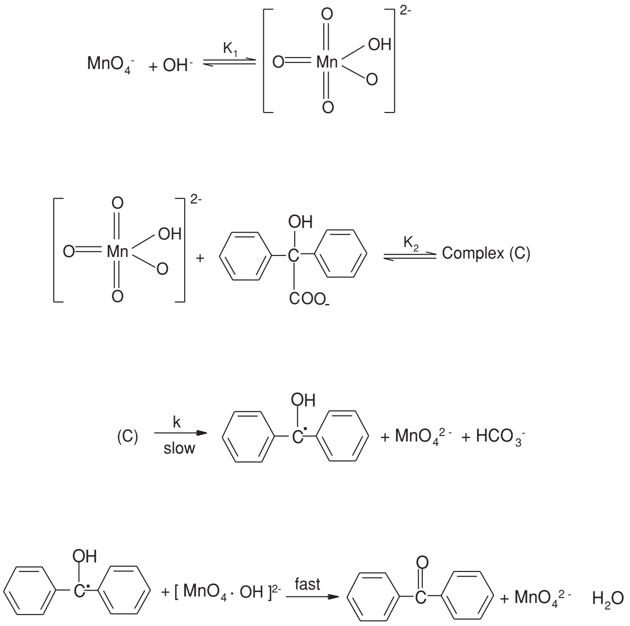
$$\mathrm{S} = \text{Substrate},\quad k'_4 >> k'_3$$

Scheme 2

The kinetics of oxidation of benzilic acid by permanganate in aqueous alkaline medium at a constant ionic strength of 0.50 mol/dm^3 was studied spectrophotometrically. The reaction is first order in permanganate and less than unit order both in benzilic acid and alkali under the experimental conditions. No significant effect was observed on the rate of the reaction by varying ionic strength and solvent polarity.

Permanganate ion, MnO_4^-, acts as an oxidising agent in aqueous alkaline medium. At pH >12 the reduction product of MnO_4^- *viz*. MnO_4^{2-}, is stable and further reduction of product MnO_4^{2-} stops.[20] Diode array rapid scan spectrophotometer (DARSS) studies have shown that at pH >12, the reduction product of MnO^-_4 is MnO_4^{2-} with no further reduction, as reported by Simandi, et al.[20] However, on prolonged standing, the reaction mixture turns brown, indicating the reduction of MnO_4^{2-} to MnO_2 under our experimental conditions. Oxidation of benzilic acid by permanganate in NaOH medium is a non-complementary reaction with oxidant undergoing one equivalent change. The reaction between benzilic acid and MnO_4^- has a stoichiometry 1:2 with first order dependence on MnO_4^-, and fractional order dependence on both BA and OH.

The active species of permanganate in aqueous alkaline medium may be deduced from the dependence of the rate on [OH^-] in the reaction medium. The apparent order of less than unity, in OH^- may be an indication of the formation of permanganate species as alkali permanganate $MnO_4.OH^{2-}$ from permanganate ion in a prior equilibrium step[21]. The formation of $MnO_4.OH^{2-}$ species in alkaline medium was further supported by the Michaelis–Menton plot (Fig. 3) which is linear with a positive intercept. It is also known that, permanganate ion in alkaline medium[22] exists as $MnO_4.OH^{2-}$. As the pK_a of benzilic acid is less than 4, it will be present largely as the carboxylate anion[23] in the present experimental conditions. Based on the experimental results, a mechanism can be proposed for which all the observed orders with respect to each constituent such as oxidant, reductant and OH^- may be well accommodated. Here the alkaline permanganate species, $MnO_4.OH^{2-}$ reacts with the carboxylate anion of substrate to give a complex C, which decomposes in a slow step to give a free radical, derived from decarboxylated benzilic acid. This radical in turn reacts with another molecule of permanganate in a fast step to yield the products. The existence of isosbestic points around 460 and 560 nm in the UV/Vis spectrum of $KMnO_4$ in an alkaline medium (Fig. 1) indicate the presence of a metastable intermediate between the reactant and product. The mechanism is proposed as in Scheme 3.

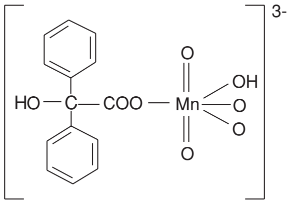


Scheme 3

---

* To receive any correspondence. E-mail: stnandibewoor@yahoo.com

The probable structure of complex C is shown below.



Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from the UV/ vis spectra of the MnO_4^- and MnO_4^- – benzilic acid mixture. A bathochromic shift of about 10 nm from 545 to 555 nm is observed and hyperchromicity is observed at 555 nm. Analogous effects upon a complex formation between a substrate and an oxidant have been observed in other investigations.[24] Further the formation of a complex is also proved kinetically by the non-zero intercept of the plot of $1/k_{obs}$ versus 1/[BA] (Fig. 3). The observed modest enthalpy of activation and a relatively low value of the entropy of activation, as well as a higher rate constant for the slow step, indicates that the oxidation presumably occurs *via* an inner-sphere mechanism. This conclusion is supported by an earlier observation.[25] Since Scheme 3 is in accordance with the generally well-accepted principle of noncomplementary oxidations taking place in sequences of one electron steps, the reaction between a substrate and oxidant would afford a radical intermediate. A free radical scavenging experiment revealed such a possibility (*vide infra*). This type of radical intermediate has also been observed in earlier work[26] on the alkaline permanganate oxidation of various organic substrates.

Scheme 3 lead to the following rate law (2)

$$\text{Rate} = -\frac{d[MnO_4^-]}{dt} = \frac{k K_1 K_2 [BA][MnO_4^-][OH^-]}{1 + K_1[OH^-] + K_1 K_2 [BA][OH^-]} \tag{2}$$

$$\times \frac{1}{(1+K_1K_2[MnO_4^-][OH^-])(1+K_1[MnO_4^-]+K_1K_2[BA][MnO_4^-])}$$

The terms $(1+ K_1 K_2 [MnO_4^-][OH^-])$ and $(1+ K_1 [MnO^-_4] + K_1 K_2 [BA][MnO^-_4])$ in the denominator of Eqn (2) approximate to unity in view of the low concentration of MnO_4^- used. Therefore Eqn (2) becomes

$$\text{Rate} = -\frac{d[MnO_4^-]}{dt} = \frac{kK_1K_2[BA][MnO_4^-][OH^-]}{1 + K_1[OH^-] + K_1K_2[BA][OH^-]} \tag{3}$$

or

$$\frac{\text{Rate}}{[MnO_4^-]} = k_{obs} = \frac{k K_1 K_2 [BA][OH^-]}{1 + K_1[OH^-] + K_1 K_2 [BA][OH^-]} \tag{4}$$

Equation (4) can be rearranged to the following form, which is used for verification of the rate law.

$$\frac{1}{k_{obs}} = \frac{1}{k K_1 K_2 [BA][OH^-]} + \frac{1}{k K_2 [BA]} + \frac{1}{k} \tag{5}$$

According to equation (5), the plots of $1/k_{obs}$ versus 1/[BA] ($r > 0.999$, $s \le 0.072$) and $1/k_{obs}$ versus $1/[OH^-]$ ($r > 0.998$, $s \le 0.096$) should be linear, as verified in Fig 2. The slopes and intercepts of such plots lead to values of, K_1, K_2 and k at 25°C as 6.1 ± 0.3 dm^3/mol, (1.05 ± 0.05) x 10^3 dm^3/mol and (1.30 ± 0.06) x 10^{-2} s^{-1}, respectively. Using these values rate constants under different experimental conditions were calculated and compared with experimental data (Table 1). There is a reasonable agreement between them. The value of K_1 is in good agreement with that derived in earlier work.[22]

The negligible effect of ionic strength and relative permitivity on rate are qualitatively consistent with the reaction between an ion and a neutral molecule as in Scheme 3. The values of $\Delta H^\#$ and $\Delta S^\#$ are consistent with an electron transfer process. The favourable enthalpy is due to release of energy on solution changes in the transition state. The value of $\Delta S^\#$, which is within the range for radical reactions, has been ascribed[27] to the nature of electron pairing and electron unpairing processes, and to the loss of degrees of freedom, formerly available to the reactions on the formation of rigid transition state. The higher negative value of $\Delta S^\#$ indicates that the complex is more ordered than the reactants.

Comparison of the oxidising capacity of $KMnO_4$ between the two media

Permanganate has a better oxidising capacity in an acid medium[28] than in an alkaline medium. The protonation of permanganate ion shifts the Mn (VII) / Mn (VI) couple to a more positive value (+1.3V), which makes $HMnO_4$ a stronger oxidising agent than MnO_4^- ion. Manganate ion, MnO_4^{2-} is stable only in an alkaline medium whereas in acid medium it is highly unstable. Hence it very rapidly disproportionates, leading to the stable reduction product, Mn^{2+} as the final product.

Techniques used: Spectrophotometer connected to a rapid kinetic accessory (HI-TECH SFA-12), FT-IR and 1HNMR by Gemini-200MHZ spectrometer with operating procedure (DOP-13) (in $CDCl^3$).

References: 28

Tables 2

Figure 1: Spectroscopic changes occurring in the oxidation of benzilic acid by permanganate

Figure 2: Order of reaction with respect to [BA] and [OH-] on the oxidation of benzilic acid by aqueous alkaline permanganate at 25°C.

Figure 3: Verification of rate law (4) in the form of (5) (Conditions as in Table 1).

Received 12 May 2003; accepted 9 July 2003
Paper 03/1902

References cited in this synopsis

9 R. Stewart in *Oxidation in Organic Chemistry*, Part A, edited by K.B. Wiberg, Academic Press, New York, 1965, K.A. Gardner, L.L. Kuehnert and J.M. Mayer, *Inorg. Chem.,* 1997, **36,** 2069.
10 L.I. Simandi, M. Jaky, C.R. Savage and Z.A. Schelly, *J. Am. Chem. Soc.,* 1985, **107,** 4220.
11 P.L.Timmanagoudar, G.A. Hiremath and S.T. Nandibewoor, *Transition Met. Chem.,* 1977, **22,** 193*;* P.L. Timmanagoudar, G.A. Hiremath and S.T. Nandibewoor *Pol. J. Chem.,* 1996, **70,** 1459; S. Nadimpalli, R. Rallabandi and L.S.A. Dikshitulu, *Transition Met. Chem.,*1993*,* **18**, 510.
12 R.G. Panari, R.B. Chougale and S.T. Nandibewoor, *Pol. J. Chem.*, 1998, **72,** 99.
20 L.I. Simandi, M. Jacky Savage and Z.A. Schelly, *J. Am. Chem. Soc.,* 1985, **107**, 4220.
21 R.G. Panari, R.B Chougale, and S.T. Nandibewoor, *J. Phys. Org. Chem.,* 1998, **11,** 448.

22 S. Vivekanandan, K. Venkatarao, M. Santappa and Sp. Shanmuganathan, *Indian J. Chem.,* 1983, **22A**, 244; N.N. Halligudi, S.M. Desai and S.T. Nandibewoor, *Transition Met. Chem.,* 2001, **26**, 28.

23 S.M. Desai, N.N. Halligudi, S.K. Mavalangi and S.T. Nandibewoor, *Z.Phys. Chem.,* 2002, **216**, 803; D.C. Bilehal, R. M. Kulkarni and S.T. Nandibewoor, *Can. J. Chem.,* 2001, **79**, 1926.

24 Devi, S. Kothari and K.K. Banerje, *Indian J.Chem.,* 1995, **34 A,** 116; S.A. Farokhi and S.T. Nandibewoor *Tetrahedron,* 2003, **59**, 7595; S.M. Tuwar, S.T. Nandibewoor and J.R. Raju, *Transition Met. Chem.,* 1991, **16,** 196.

25 F.M. Moore and K.W. Hicks *Inorg. Chem.,* 1975, **14,** 413; N.N. Halligudi, S.M. Desai and S.T. Nandibewoor, *Int. J. Chem. Kinet.,* 1999, **31**, 789.

26 K.A.K. Lott and M.C.R. Symons, *Discuss. Faraday Soc,* 1960, **29,** 105; M. Jaky, Z. Szevereny and L.I. Simandi, *Inorg. Chem. Acta.,* 1991, **186**, 33.

27 C. Walling, *Free radicals in Solution,* New York, 1957, p.38.

28 Miss S.A. Farokhi and S.T. Nandibewoor, *Can. J. Chem.,* 2003 (in press).