RESEARCH ARTICLE

KINETICS OF REDUCTION OF COLLOIDAL MnO₂ BY ACEPHATE IN AQUEOUS AND MICELLAR MEDIA

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ABSTRACT

The kinetics of the reduction of colloidal MnO₂ by acephate has been studied in an aqueous and different micellar media, viz., CTAB, SDS and TX-100. The reactions follow first order kinetics with respect to colloidal MnO₂ in both the aqueous and micellar media. It has been observed that the rate of reduction of colloidal MnO₂ by acephate increases and decreases in the presence of TX-100 (non-ionic) and SDS (anionic), respectively. However, the rate of reduction has been observed to increase up to certain concentration of cationic CTAB and beyond which it starts to decrease. The reaction rates have been discussed in the light of the different activation parameters and a mechanism for the oxidative degradation of acephate has been proposed

INTRODUCTION

Manganese is the eleventh most abundant element in the earth crust and is one of the most important micronutrients for all micro-organisms. Manganese (III, IV) oxide minerals are thermodynamically stable in the oxygenated environments. These oxide particles in earth crust and in natural water are susceptible for reduction by humic acid and organics (Barrett and McBride, 2005; Nowack and Stone, 2002; Ukrainczyk and McBride, 1993; Zhang and Huang, 2003). Thus, the humic and organic compounds are degraded into simpler molecules through the abiotic mechanisms. The oxidising and catalytic properties of manganese oxide have been limited due to its insolubility under ordinary conditions. However, in recent years, perfectly transparent water soluble manganese dioxide has been prepared by the reduction of alkaline potassium permanganate solution through γ-irradiation, and, also by the reduction of neutral or slightly acidic potassium permanganate solution by sodium thiosulphate (Aisha *et al.,* 2011; Baral *et al.,* 1985; Lume-Pereira *et al.,* 1985; Prez-Benito, 2002; Prez-Benito *et al.,* 1989, 1992, 1996). A number of organophosphorous pesticides are widely used as insecticides, germicides and even herbicides (Tomlin, 1994). Among them, O,S- dimethyl-N- acetylphosphoramidothioate (acephate) is one of the most commonly used organophosphorous insecticides. It is highly effective and low poisonous organophosphorous insecticides and commonly used for protecting crops such as cotton, rice, wheat, tea, fruit trees, vegetables and tobacco from pests. Due to its above advantages and applications acephate has recieved considerable attention in recent year (Chai *et al.,* 2008, 2010; Chuanjiang *et al.,* 2010; Kong *et al.,* 2012; Patel *et al.,* 2004; Rahman *et al.,* 2006; Sharma *et al.,* 2010). It is neither photolysed (in absence of catalyst) nor adsorbed by soil but is fortunately degraded in the soil by MnO₂ to various products. In view of the above facts it has been decided to perform a systematic study on the degradation kinetics of acephate by colloidal MnO₂. Since surfactants are widely used in pesticide formulation to increase the effectiveness of latter, it has been considered worth to study the influence of cationic CTAB (cetyl trimethyl ammonium bromide), anionic SDS (sodium dodecyl sulphate) and non-ionic TX-100 (Triton X-100) surfactants (micelles) on the degradation of acephate by MnO₂ (i.e reduction of MnO₂ by acephate).

MATERIALS AND METHODS

Chemicals

Acephate (Commercial grade, Excel Crop Care Ltd., Mumbai), potassium permanganate (ExcelaR grade, Qualigen India), sodium thiosulphate (ExcelaR grade, Qualigen, India), CTAB (AR grade, CDH, India), SDS (AR grade, CDH, India), TX-100 (98%, CDH, India), H₂SO₄ (ExcelaR grade, Qualigen, India), acetic acid (ExcelaR grade, Qualigen, India) and sodium acetate anhydrous (ExcelaR grade, Qualigen, India)

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were used as received. Doubly distilled water was used throughout the experimental work. Colloidal MnO$_2$ was prepared by mixing the standard solutions of potassium permanganate (10 ml, 0.1 mol dm^{-3}) and sodium disulphate (20 ml, 1.88x10^{-2} mol dm^{-3}) details of which have been described earlier (Aisha *et al.,* 2011). The clear and transparent solution, so prepared, was observed to be obeyed Beer's law within the range of present investigation.

Kinetic measurements

Kinetic experiments were carried out by taking the requisite amounts of aqueous solutions of acephate, colloidal manganese dioxide and surfactant in a three-necked reaction vessel. The reaction vessel was fitted with a double surface condenser to prevent evaporation. The reaction vessel was kept for sufficient time in a thermo stated water bath to attain the desired temperature ($\pm$0.5 ^{o}C). The reaction was started with the addition of colloidal MnO$_2$ solutions. The concentration in the form of absorbance was measured by means of a spectrophotometer (model: spectronic 20 D^{+}; Thermo scientific, India). The progress of the reaction was monitored by measuring the absorbance at an optimum wave length of 365 nm. Selection of the wave length is based on the fact that at this wave length colloidal MnO$_2$ solution has strong absorbance while the complexes of manganese (II) and manganese (III) have negligible absorbance. All the kinetic experiments were run under the first order reaction condition in which the concentrations of surfactants and acephate were kept in large excess over [MnO$_2$].

RESULTS AND DISCUSSION

During the preliminary experiments it has been observed that acephate quickly reduces MnO$_2$ as the brown colour of latter is faded with the addition former. It has been observed that the rate constant decreases with the increase in initial concentration of MnO$_2$. The variation of rate constant with the initial concentration of MnO$_2$ is plotted in Fig.1, at a typical concentration of acephate (5.0x10^{-3} mol dm^{-3}). The decrease in rate constant with increasing concentration of MnO$_2$ is presumably due to the aggregation of colloidal MnO$_2$ particles to form bigger colloidal particle resulting the decrease in total surface area. Fig.1 also indicates that the rate constant becomes almost independent at the higher concentration of MnO$_2$. However, interestingly, a reverse trend has been observed with the varying concentration of acephate at any fixed concentration of MnO$_2$. As shown in Fig.2, the rate constant increases sharply with the increase in initial concentration of acephate up to a certain value (1.0x10^{-3} mol dm^{-3}) beyond which it becomes independent. Thus the degradation kinetics becomes zero order with respect to acephate at its higher concentration (>1.0x10^{-3} mol dm^{-3}). In this context it is relevant to note that the reaction is more favourable in acidic medium as indicated in Fig.3 which shows the variation of rate constant with H^{+} ion concentration. In the present investigation all the experiments were performed at a fixed pH (= 6) buffered by CH$_3$COOH + CH$_3$COONa. In a similar way the studies have been extended in presence of different micellar media, viz, SDS, CTAB and TX-100. The pseudo first order rate constant (k) for the degradation of acephate by MnO$_2$ in the absence and presence of micellar media are presented in Table 1 at one typical concentration of each. This table shows that the values of rate constant for oxidative degradation of acephate increase and decrease by addition of TX-100 and CTAB, respectively in the entire temperature range of our study. However, in the presence of SDS, the values of rate constant have been observed to decrease up to the temperature of 30 ^{o}C above which they increase.

The kinetic data has further been analysed in terms of different activation parameters. The activation energy (Ea) for the degradation kinetics of acephate in the absence and presence of micellar media, as calculated from Arhenious equation are listed in Table 2. It has been inferred from Table 2 that the activation energies of the process are much lower in aqueous and non-ionic micellar media while in the presence of ionic micellar media the value are comparatively much higher. Decrease in the activation energy in presence of TX-100 further indicates the favourable role of it in the kinetics of the process.

The values of thermodynamic activation parameters ($\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$) as calculated from following Eyring equation:

$$\ln (k/T) = - (\Delta H^{\#}/R)\, 1/T + \ln (k_B/h) + (\Delta S^{\#}/R) \qquad (1)$$

are also listed in Table II. In the above equation k_B, R, h and T represent Boltzmann constant, gas constant, Planck's constant and absolute temperature, respectively. Table 2 indicates that the overall activation barrier ie $\Delta G^{\#}$ remains almost same in each case while the entropy contribution plays much significant role in aqueous and non ionic micellar media. In fact that large negative value of entropy of activation highlights the formation of highly ordered associative activated complex from the disordered species. Table 2 clearly indicates that the oxidative degradation of acephate is more prone in presence of TX-100 while it is deactivated by CTAB and SDS.

The mechanism for oxidative degradation of acephate by colloidal MnO$_2$ as proposed is given below,
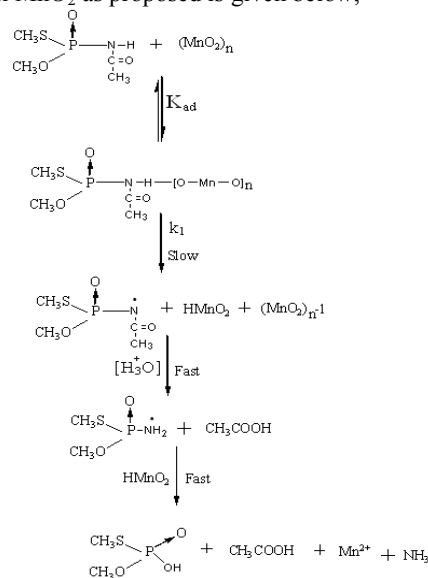
**Proposed mechanism for the oxidative degradation of acephate**

Table 1: Pseudo first order rate constant for the reduction of colloidal MnO₂ by acephate in the absence and presence of surfactants.

Temperature (^{0}C)	Aqueous media	$k \times 10^2$ (s^{-1})		
			Micellar media (Surfactant)	
		SDS	CTAB	TX-100
20	3.80	1.98	1.27	7.28
25	4.54	2.59	1.98	7.56
30	4.80	3.83	2.54	8.10
35	5.48	5.92	2.94	8.80
40	5.85	8.14	3.59	9.36
45	6.09	9.78	4.40	9.86

$[MnO_2] = 2.0 \times 10^{-4}$ mol dm^{-3}, [acephate] = 5.0×10^{-3} mol dm^{-3}, [SDS] = 1.0×10^{-4} mol dm^{-3}, [CTAB] = 2.0×10^{-4} mol dm^{-3} and [TX-100] = 5.0×10^{-3} mol dm^{-3}.

Table 2: Values of different activation parameters for the reduction of colloidal MnO₂ by acephate in the absence and presence of surfactants

Activation parameters	Aqueous media (without surfactant)	Surfactants		
		SDS	CTAB	TX-100
E_a (kJ mol-1)	14.50	52.50	36.10	9.90
$\Delta H^\#$ (kJ mol-1)	11.91	50.0	33.60	7.37
$\Delta S^\#$ (J K-1mol-1)	−231.0	−106.90	−165.3	−240.0
$\Delta G^\#$ (kJ mol-1)	81.90	82.0	83.70	80.10
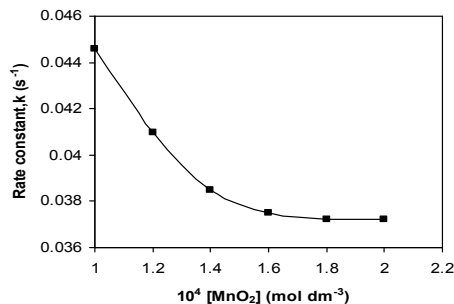
Fig. 1: Plot of dependence of rate constant vs initial concentration of [MnO₂] at a typical concentration of [acephate] (5.0×10^{-3} mol dm^{-3}), Temperature = 30 ^{0}C and pH= 6.
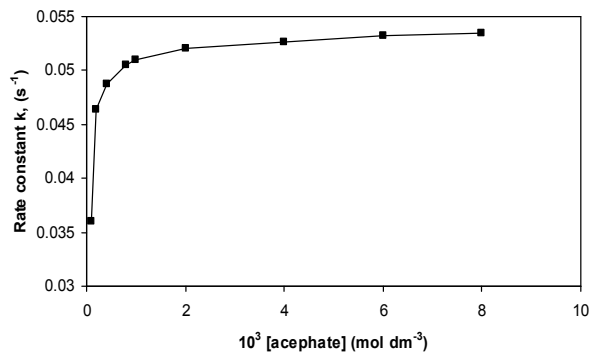
Fig. 2: Plot of dependence of rate constant on [acephate] at [MnO₂] (=2.0×10^{-4} mol dm^{-3}), Temperature = 30 ^{0}C and pH =6.
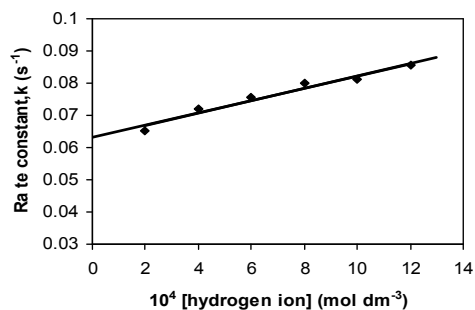
Fig. 3: Plot of rate constant versus [H⁺] at [acephate] (= 5.0×10^{-3} mol dm^{-3}), [MnO₂] (= 2.0×10^{-4} mol dm^{-3}) and Temperature = 30 ^{0}C
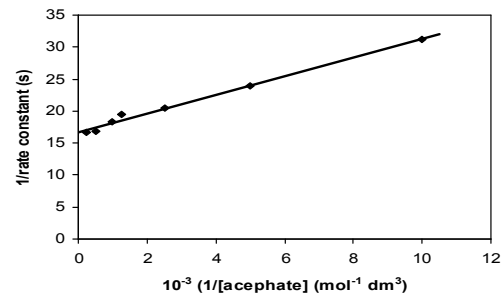
Figure 4: Plot of 1/ k_{obs} versus 1/[acephate] for [MnO₂] (=2.0×10^{-4} mol dm^{-3}), Temperature = 30 ^{0}C and pH =6.
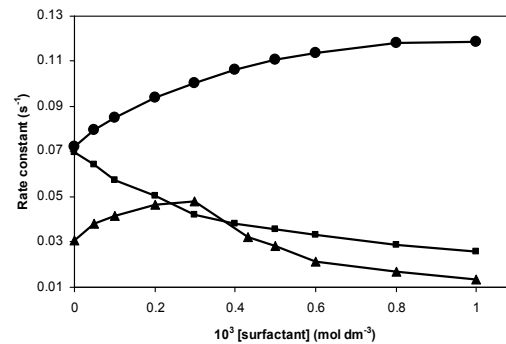
Fig. 5: Plot for the dependence of rate constant on [CTAB] (▲), [SDS] (■) and [TX-100] (●) at [MnO₂] (=2.0×10^{-4} mol dm^{-3}), [acephate] (= 5.0×10^{-3} mol dm^{-3}), Temperature = 30 ^{0}C and pH =6.

The rate of oxidation of acephate at the MnO₂ surface under the pseudo first order reaction condition is given as

$$\text{rate} = k_1 \theta [MnO_2] \qquad (2)$$

where k_1 is the rate constant and θ is the fraction of adsorption site of MnO₂ occupied and given in terms of equilibrium constant for adsorption (K_{ad}).

$$\theta = (K_{ad} [Acephate]) / (1 + K_{ad} [Acephate]) \qquad (3)$$

Thus the observed rate constant (k_{obs}) may be written as

$$k_{obs} \quad = \quad k_1 K_{ad} [Acephate] \ / \ (1+ K_{ad} [Acephate]) \quad (4)$$

Alternatively,

$$1/ k_{obs} \quad = \quad 1/(k_1 K_{ad} [Acephate]) \ + \ 1/ k_1 \quad (5)$$

Accordingly, a linear plot for $1/ k_{obs}$ vs. $1/[Acephate]$ should be obtained. Our plot of $1/ k_{obs}$ against $1/[Acephate]$ shown in Fig. 4 is linear and support the justification of the above mechanism as proposed. The effect of variation of surfactant concentration on the rate of degradation of acephate by colloidal manganese dioxide was studied at 30 ^oC by keeping the concentrations of MnO_2 and acephate constant at 2.0×10^{-4} mol dm^{-3} and 5.0×10^{-3} mol dm^{-3}, respectively. The rate of reaction has been observed to continuous increase and decrease with the increasing concentration of TX-100 and SDS, respectively in their concentration range from 0 to 1 x 10^{-3} mol dm^{-3} (Fig.5). However, very interesting result has been obtained with CTAB in which the rate of reaction increases with increasing concentration of the surfactant reaches maximum at a typical concentration of 0.3×10^{-3} mol dm^{-3} and then start to decrease on further increase of its concentration. The dependence of rate constant on $[MnO_2]$ and $[Acephate]$ in the presence of surfactants showed a similar behaviour as was observed in aqueous medium i.e. in the absence of surfactant. These observations indicate that the same mechanism is being followed in both aqueous and micellar media.

CONCLUSIONS

The kinetic studies for the reduction of colloidal MnO_2 by acephate (i.e. oxidative degradation of acephate by MnO_2) in aqueous and micellar media, namely, CTAB, SDS and TX-100 were performed. The reduction was observed to be followed first order kinetics in both aqueous and micellar media. Very interesting role of micelles has been observed. The rate of reduction of colloidal MnO_2 was found to increase and decrease non-ionic (TX-100) and anionic (SDS) micellar media, respectively. However, a little complex behaviour has been observed in cationic (CTAB) micellar media. The rate has been observed to increase up to a critical concentration of CTAB (0.3×10^{-3} mol dm^{-3}) beyond which it start to decrease. The increase in rate of reaction with TX-100 and CTAB (in limited concentration range) may be attributed due to increases in local concentration on the micellar surfaces. The kinetic data so generated has been discussed in the light of different activation parameters and a suitable mechanism for the process has been proposed.

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