



Effect of CTAB reverse micelles on the kinetics of aminolysis of *p*-nitrophenyl acetate by hydrazine

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Kinetic study of the aminolysis of *p*-nitrophenyl acetate (PNPA) by hydrazine (HY) in the CTAB/chloroform/hexane reverse micelles has been carried out as a function of W ($W = [\text{H}_2\text{O}]/[\text{CTAB}]$) and CTAB concentration. The reaction obeys first order kinetics with respect to each of the reactants in both media. The rate of reaction in reverse micelles decreases with increasing the value of W and observed rate constants are always lower than those for the corresponding reactions in aqueous solution under identical experimental conditions. The kinetic behavior was interpreted by using modified Berezin pseudo phase model, taking into consideration, distribution of the reactants, PNPA and hydrazine between the three pseudo phases, i.e., water pool, interface and organic phase.

Keywords: Kinetics, *p*-nitrophenyl acetate, hydrazine, water pools, CTAB reverse micelles.

Introduction

Reverse micelles which are three component water in oil microemulsions are transparent, thermodynamically stable, isotropic systems. Reverse micelles are formed by aggregation of surfactants in organic solvents with their polar groups located in the interior or core of the aggregate while the hydrocarbon tails extended in the bulk solvent. Water is readily solubilized in the polar core forming a water pool characterized by W ($W = [\text{H}_2\text{O}]/[\text{CTAB}]$). This solubilized water exhibits special properties like lower dielectric constant, higher ionic strength (in the case of reverse micelles made of ionic surfactants) and altered nucleophilicity compared to water in the conventional aqueous media¹⁻⁵. Since the water pool has different properties compared to ordinary water the rates of reactions and mechanisms can be expected to be different. Reverse micelles are also good solvents for both hydrophobic and hydrophilic reactants and therefore, useful media for studying reactions involving different types of reactants⁶⁻¹¹.

We have earlier reported reactions taking place in the presence of reverse micelles and have given a quantitative

assessment for the change in special properties with change in W and the observed kinetic results were explained quantitatively using Berezin pseudo phase model¹²⁻¹⁴. All these reactions studied take place in the water pool or at the micellar interface. However reactions taking place in all the three pseudo phases, water pool, micellar interface and organic phase have not been studied and mathematical treatment involving reactants soluble in all the three pseudo phases has not been attempted so far.

The reactions attempted so far are electron transfer reactions of metal complexes. However, systematic kinetic studies involving the effects of reverse micelles on rates of organic reactions have been carried out by very few investigators. Garcia Rio *et al.* have studied solvolysis reactions of benzoyl halides in micro emulsions and used the pseudo phase model to explain the kinetic results¹⁵. Silber *et al.* have studied the kinetics of reaction between 1-fluoro-2,4-dinitrobenzene and piperidine in AOT reverse micelles¹⁶.

Therefore, in the present study, we have taken up an organic reaction, aminolysis of the *p*-nitrophenyl acetate by hydrazine. In this reaction, PNPA is soluble in all the three

phases while hydrazine is present in the water pool and at the interface. The results of the kinetic study of this reaction along with the kinetic model have been presented in this paper.

Experimental

Materials:

Stock solutions of PNPA (Merck, India), hydrazine (Merck, India) were prepared in double distilled water. Chloroform and hexane were distilled before use. CTAB (cetyl trimethyl ammonium bromide) purchased from Merck (India) was used to prepare stock solutions of CTAB in chloroform-hexane (3:2 v/v) mixture.

Experimental method:

0.04 ml of hydrazine solution of concentration 2.5 mol dm^{-3} was added into 10 ml of 0.1 mol dm^{-3} CTAB solution using a micro pipette. 0.02 ml of PNPA solution of concentration 0.02 mol dm^{-3} was then added to initiate the reaction. The reaction mixtures were shaken sufficiently to obtain a homogenous solution which can be regarded as a reverse micellar medium. The value of W was varied in the range 3.33 to 20.0 by varying the molar ratio of [water] to [CTAB].

Kinetic measurement:

The reaction was monitored by measuring the increase in absorbance of the product *p*-nitrophenol where it has maximum absorbance at a wave length of 400 nm, using a Shimadzu UV-1800 double beam spectrophotometer. The reaction was carried out under pseudo-first order conditions, $[\text{HY}] \gg [\text{PNPA}]$. The pseudo-first order rate constants K' were obtained from slopes of $\log(A_\infty - A_t)$ versus time. The second order rate constants, k_2 , were obtained by dividing the pseudo-first order rate constants, by the overall concentration of hydrazine. The kinetic data obtained are the averages from triplicate runs with reproducibility less than $\pm 4\%$.

Results and discussion

The kinetic investigations of the reaction have been carried out under the conditions, $\{[\text{HY}] \gg [\text{PNPA}]\}$, and plots of $\log(A_\infty - A_t)$ versus time were found to be good straight lines in the presence of CTAB reverse micelles showing first order dependence with respect to PNPA (Fig. 1). The pseudo-first order rate constant K' , is directly proportional to concentration of hydrazine showing first order kinetics with respect

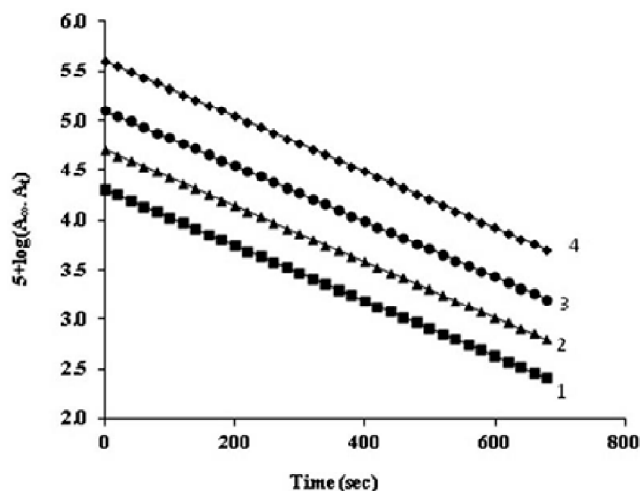


Fig. 1. Plots of $\log(A_\infty - A_t)$ vs time at different concentrations of PNPA; $[\text{CTAB}] = 0.1 \text{ mol dm}^{-3}$, $W = 6.66$; $T = 304 \pm 0.1 \text{ K}$; $[\text{HY}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$: (1) $[\text{PNPA}] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, (2) $[\text{PNPA}] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$, (3) $[\text{PNPA}] = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$; (4) $[\text{PNPA}] = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$.

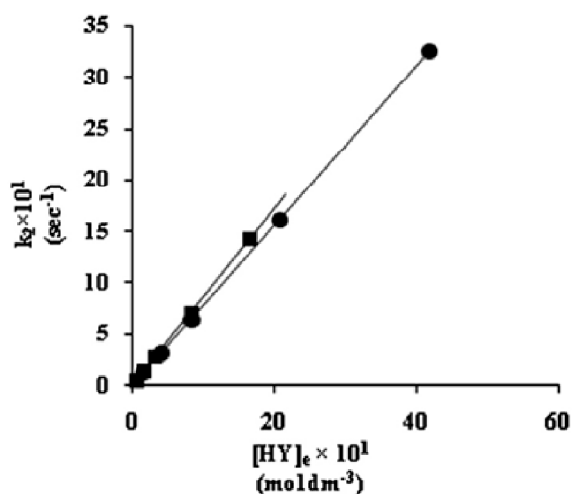


Fig. 2. Plot of K' vs $[\text{HY}]$; $[\text{PNPA}] = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$ $[\text{CTAB}] = 0.1 \text{ mol dm}^{-3}$, $T = 304 \pm 0.1 \text{ K}$: (1) $W = 16.6$, (2) $W = 6.6$.

to hydrazine (Fig. 2). The reaction has also been carried out in aqueous medium under identical conditions and similar kinetic features were observed (Table 1). The pseudo-first order rate constants determined in aqueous medium and in the reverse micelles at the same concentration of PNPA and hydrazine indicate that the reaction is much faster in the presence of aqueous medium by approximately twenty times compared to CTAB reverse micellar medium (Table 2).

Table 1. Pseudo-first order rate constants in aqueous medium at $T = 304 \pm 0.1$ K

[PNPA] $\times 10^5$ (mol dm ⁻³)	[HY] $\times 10^4$ (mol dm ⁻³)	μ (mol dm ⁻³)	$k' \times 10^3$ (s ⁻¹)
1.0	4.0	0.5	5.26
2.0	4.0	0.5	5.26
4.0	4.0	0.5	5.29
6.0	4.0	0.5	5.28
4.0	0.8	0.5	1.24
4.0	2.0	0.5	2.50
4.0	4.0	0.5	5.29
4.0	10.0	0.5	12.0
4.0	20.0	0.5	25.1
4.0	4.0	0.1	5.26
4.0	4.0	1.0	5.27
4.0	4.0	3.0	5.28
4.0	4.0	5.0	5.27

The reaction follows an S_N2 mechanism and the transition state develops a partial negative charge compared to the reactants which are neutral (Mechanism 1). Since high dielectric constant conditions favours such a transition state,

Table 2. Comparison of rate constants in the aqueous medium and in the presence of reverse micelles (0.1 mol dm⁻³ CTAB) at same ionic strength

[HY] = 4.0×10^{-4} mol dm⁻³; [PNPA] = 4.0×10^{-5} mol dm⁻³; T = 304 ± 0.1 K

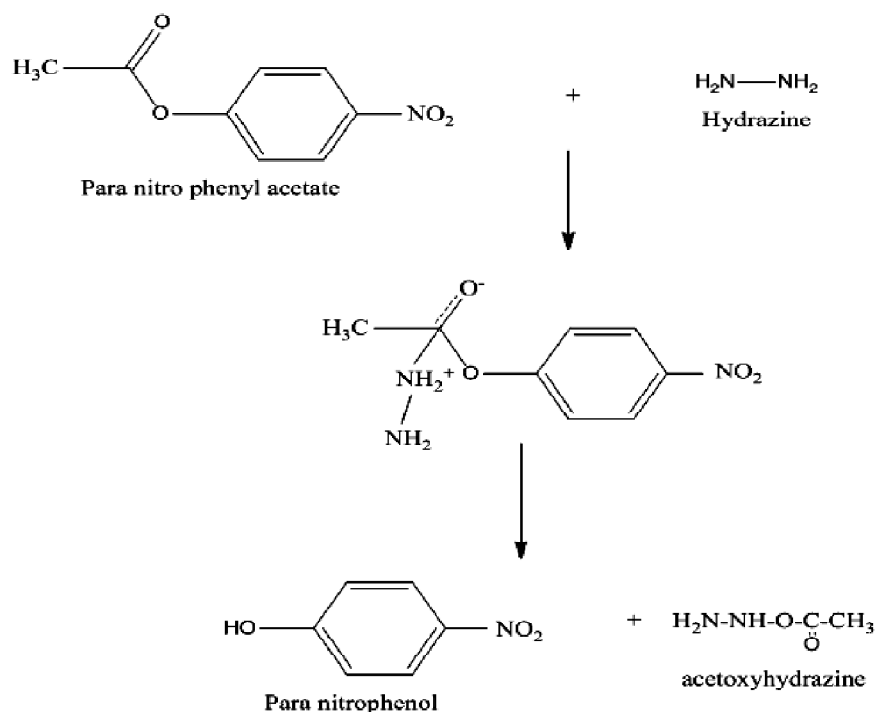
μ (mol dm ⁻³)	$k'_{\text{aq. med}} \times 10^3$ (s ⁻¹)	$k'_{\text{(rev mic)}} \times 10^4$ (s ⁻¹)
3.33	5.29	2.52
4.16	5.29	3.24

the reaction is much faster in aqueous medium compared to CTAB reversemicelles.

Effect of W on rate:

The kinetics of the reaction has been investigated at different values of *W* keeping [CTAB], [PNPA] and [HY] constant and the study has been repeated at three different concentrations of CTAB. The rate constants indicate that the pseudo-first order rate constant *k'*, decreases with increasing *W* (Table 3).

To analyse the kinetic behavior in the aminolysis of PNPA by hydrazine, it is necessary to consider the distribution model



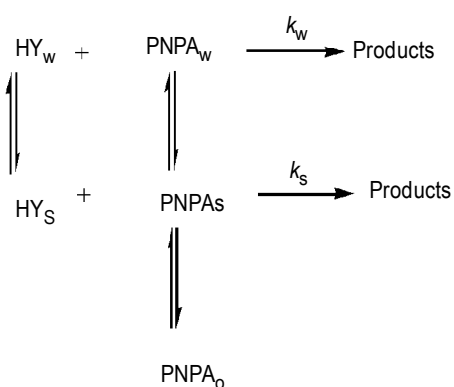
Mechanism 1

Table 3. Effect of variation of W and [CTAB]

$[\text{PNPA}]_0 = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$; $[\text{HY}]_0 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$;
 $T = 304 \pm 0.1 \text{ K}$

CTAB (mol dm ⁻³)	[Br ⁻] _e	W (mol dm ⁻³)	$k' \times 10^3$ (s ⁻¹)	$k_2 \times 10^1$ {=k'/[HY]} (mol ⁻¹ dm ³ s ⁻¹)
0.1	16.6	3.33	12.0	12.0
	12.5	4.44	8.96	8.96
	8.33	6.66	6.40	6.40
	6.25	8.88	5.37	5.37
	4.16	13.3	3.35	3.35
	3.33	16.6	2.83	2.83
	2.77	20.0	2.42	2.42
	0.2	16.6	3.33	12.4
12.5		4.44	9.01	9.01
8.33		6.66	6.42	6.42
6.25		8.88	5.40	5.40
4.16		13.3	3.61	3.61
3.33		16.6	2.89	2.89
2.77		20.0	2.48	2.48
0.3		16.6	3.33	12.9
	12.5	4.44	9.12	9.12
	8.33	6.66	6.49	6.49
	6.25	8.88	5.47	5.47
	4.16	13.3	3.49	3.49
	3.33	16.6	2.95	2.95
	2.77	20.0	2.56	2.56

for the reactants^{17,18}. Hydrazine is highly hydrophilic species which can present in the aqueous water pool and interface. PNPA is found to be distributed between the three pseudo phases. Accordingly Scheme 1 is considered.



Scheme 1

$$K_{\text{HY}} = \frac{[\text{HY}]_s}{[\text{HY}]_w}; K_{\text{PNPA}} = \frac{[\text{PNPA}]_s}{[\text{PNPA}]_w}; Q_{\text{PNPA}} = \frac{[\text{PNPA}]_o}{[\text{PNPA}]_w} \quad (1)$$

where K_{HY} and K_{PNPA} represent distribution constants between the water pool and the interface and Q_{PNPA} is the distribution constant between the water pool and the oil phase. According to the above reaction scheme, the overall concentrations of hydrazine and PNPA are related to the corresponding local concentrations in each region by the mass balance, eqs. (2) and (3).

$$[\text{HY}]_{\text{OVR}} = [\text{HY}]_w \phi_w + [\text{HY}]_s \phi_s \quad (2)$$

$$[\text{PNPA}]_{\text{OVR}} = [\text{PNPA}]_w \phi_w + [\text{PNPA}]_s \phi_s + [\text{PNPA}]_o \phi_o \quad (3)$$

$$\phi_w = 0.018[\text{CTAB}]_o W \quad (4)$$

$$\phi_s = 0.323[\text{CTAB}]_o \quad (5)$$

$$\phi_o = 1 - (\phi_w + \phi_s) \quad (6)$$

where ϕ_w , ϕ_s and ϕ_o represent the volume fractions of the aqueous droplets, the interface and the oil phase, respectively. These volume fractions can be estimated by means of eqs. (4-6) where $0.018 \text{ dm}^3 \text{ mol}^{-1}$ and $0.323 \text{ dm}^3 \text{ mol}^{-1}$ are the molar volumes of water and CTAB. It can be derived that, under the pseudo-first order conditions used ($[\text{HY}] \gg [\text{PNPA}]$), the overall second order rate constant k_2 is given by eq. (7).

$$k_2 = \frac{k'}{[\text{HY}]_{\text{OVR}}} = \frac{k_w \phi_w + k_s \phi_s K_{\text{HY}} K_{\text{PNPA}}}{(\phi_w + K_{\text{HY}} \phi_s)(\phi_w + K_{\text{PNPA}} \phi_s + Q_{\text{PNPA}} \phi_o)} \quad (7)$$

Eq. (7) can be simplified by taking into account that the hydrophobic PNPA reside preferentially in the oil phase compared to aqueous pools and that is larger than either ϕ_w and ϕ_s . As a consequence, eq. (7) is reduced, after an appropriate rearrangement and by the use of eq. (4) to eq. (8). In this the denominator involved the W which is important in determining the observed decreasing trend of k_2 with increasing molar ratio W .

$$k_2 \phi_o = \frac{1.80 \times 10^{-3} k_w W + k_s \phi_s K_{\text{HY}} K_{\text{PNPA}}}{Q_{\text{PNPA}} (1.80 \times 10^{-3} W + K_{\text{HY}} \phi_s)} \quad (8)$$

The partition coefficient of hydrazine can be assumed to be

much less than 1 since there is no exchange between hydrazine with the counter ions Br⁻ of CTAB. Since the values of W lie in the range 0.89–0.95 the term $K_{HY}\phi_s$ can be neglected.

The eq. (8) now becomes,

$$k_2\phi_0 = \frac{(1.80 \times 10^{-3} k_w / Q_{PNPA})W + k_s \phi_s K_{HY} K_{PNPA} / Q_{PNPA}}{(1.80 \times 10^{-3} W)} \quad (9)$$

According to above equation, a plot of $k_2\phi_0$ versus $1/W$ should be linear. Fig. 3, shows that the plots of $k_2\phi_0$ versus $1/W$ are good straight lines for 0.1 mol dm⁻³ of CTAB and is true for all concentrations of CTAB. The linear trend was observed at high values of W while at low values of W (3.33–4.44) small deviation from linearity was observed. This linear trend implies the absence of special properties of the water pool and their effect on the reaction rate. Since the

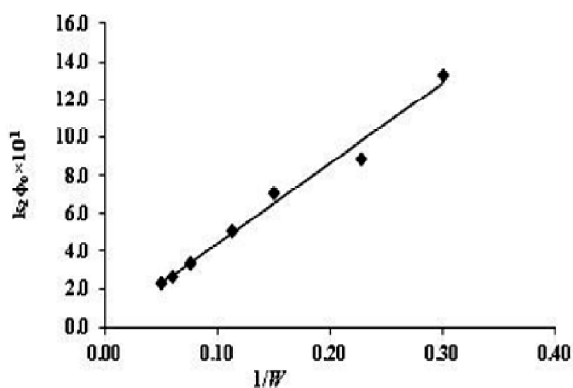


Fig. 3. Plots of $k_2\phi_0$ vs $1/W$; [CTAB] = 0.1 mol dm⁻³; [HY] = 1.0 × 10⁻² mol dm⁻³, T = 304 ± 0.1 K.

properties exist at $W < 4$, there is a deviation from linear trend at low W values.

Conclusions

The aminolysis of the PNPA by hydrazine obeys first order kinetics with respect to each of the reactants in aqueous as well as CTAB/hexane/chloroform reverse micellar medium.

The reaction occurs predominantly in the aqueous water pool of the reverse micelles and the rate constant decreases when the water content of the system increases. The effect of W on rate was interpreted by applying modified Berezine pseudo phase model. The plots of $k_2\phi_0$ versus $1/W$ are good straight lines for all concentrations of CTAB. The linear trend

was observed at high values of W implies the absence of special properties of the water pool and their effect on the reaction rate while at low values of W (3.33–4.44) small deviation from linearity was observed since the special properties exist at low values of W .

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