

# Effect Of Cationic Micelles Of [Ctab] On Reaction Of Hydroxide Ions With Tri-2,5-Dimethyl Phenyl Phosphate ;

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Submitted: 10-11-2021

Revised: 24-11-2021

Accepted: 27-11-2021

**ABSTRACT;** Micellar effect upon substitution reactions between hydroxide ions OH<sup>-</sup> and tri 2,5-dimethyl phenyl phosphate in the presence of cetyltrimethylammonium bromide (CTABr) has been examined in buffer medium (at pH 8-10). The first order rate constant (K) are increased with the concentration of the surfactant can be analysed in terms of Br<sup>-</sup> ions in micellar pseudophases, which occur readily.

**Keywords;** Micellar, CTABr, DMPP, nucleophilic attack.

## INTRODUCTION;

The phosphate esters are compounds with interesting biological and pharmacological properties and are widely used as pesticides, drugs and nerve gases. Their accumulation and their effect in the environment are of paramount importance<sup>1,2</sup>. Interaction of phenols, aryl amines and their derivatives with orthophosphoric acid (tri-basic) to form a series of organophosphate esters. Organophosphate is a term that can be used to describe all chemical compounds in which a phosphate group or phosphate derivative, is part of an organic (i.e. carbon – containing) molecule. In practice, and more specifically, it is used to refer those organophosphorus compounds which inhibit the enzyme acetylcholine sterase. This is the

definition used for organic phosphates through out this report and it is these compounds upon which the working group focused its attention.

Material and methods;

The reaction of hydroxide ion at constant ionic strength with tri-2,5-DMPP in presence and absence of 10<sup>-5</sup> [CTAB] in 30% aqueous dioxin at 45±0.2°C has been determined at different detergent concentrations of CTAB, which strongly catalyze the reaction. Summarizes the effect of micellar catalysis of cationic micelles on the rate at constant hydroxide ion concentration with tri-2,5-DMPP, the pseudo first order rate constants have been compared with those in absence of detergent [CTAB] with the increasing detergent concentration the rate increase to a maximum value 16.72×10<sup>-5</sup>s<sup>-1</sup> at 1.6×10 mol. dm<sup>-3</sup> [CTAB] at pH 9.0, these maximum rates have been shown in the plot of rate constants against detergent concentration.

## RESULT AND DISCUSSION;

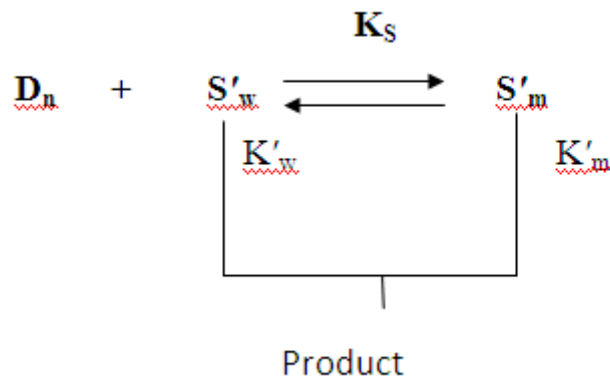
TABLE-REACTION OF [5×10<sup>-4</sup>] mol.dm.<sup>-3</sup> TRI-2,5-DIMETHYL PHENYL PHOSPHATE WITH CONSTANT [OH<sup>-</sup>] IN PRESENCE OF DIFFERENT 10<sup>-3</sup> [CTAB] AT pH 9.0 AND 45±0.2°C.

S.N.	10 <sup>3</sup> [CTAB] mol.dm. <sup>-3</sup>	K <sub>p</sub> ×10 <sup>-5</sup> sec <sup>-1</sup>
1	0.2	2.79
2	0.4	3.82
3	0.6	5.19
4	0.8	6.87
5	1.0	9.75
6	1.2	13.14
7	1.4	14.58
8	1.6	16.72
9	1.8	12.16
10	2.0	08.94

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The relation between the observed pseudo first order rate constant  $K_{\Psi}$  and surfactant concentration  $[D_n]$  for a spontaneous dephosphorylation of tri-2,5-DMPP may be shown in the following scheme-III. Where  $S'_w$  and

$S'_m$  are substrate in aqueous and micellar pseudophases respectively.  $K'_m$  and  $K'_w$  are the related first order rate constants and  $K_s$  is the binding constant.



The concentration of micellised surfactant  $D_n$  is that of total surfactant concentration less than that of monomeric surfactant concentration, which is assumed to be given by critical micelle

concentration (cmc), provided that equilibrium is maintained between substrate in micelle and water. Hence Scheme –III leads to:

$$K_{\Psi} = \frac{K'_w + K'_m K'_s [D_n - cmc]}{1 + K_s (D_n - cmc)} \quad \dots(1)$$

The value of  $K'_m$  can be obtained by analysis of the variation of  $K_s$  with  $D_n$  or by choosing conditions such that substrate is essentially fully micellar bound. Where  $D_n$  is the

micellised surfactant, is given by the following relation:

$$D_n = C_D - cmc.$$

Where  $C_D$  is the total concentration of the surfactant.

$$K_{\Psi} = \frac{K'_w + K'_m (K'_s / N) [D_n - cmc]}{1 + (K'_s / N) [D_n - cmc]} \quad \dots(2)$$

Where  $C_D$ ,  $N$  and  $K'_s$ , are the respective values of detergent concentration, the aggregation number and binding constant. The eq. (1) can be written as:

$$\frac{1}{K_\Psi - K'_w} = \frac{1}{K'_m - K'_w} + \frac{1}{K'_m - K'_w} \left\{ \frac{N}{K_s (C_D - cmc)} \right\} \dots(3)$$

Table XXXIV summarizes the estimated values of

$$\frac{1}{K_\Psi - K'_w} \quad \text{and} \quad \frac{1}{(C_D - cmc)}$$

allows the determination of the value of the rate constant in micelle ( $K'_m$ ) and the binding constant ( $K_s$ ) for the reaction of tri-2,5-DMPP with

[OH]. The value of aggregation number 'N' = 61 is taken from literature.).

**TABLE-** RELATION BETWEEN REACTION RATE AND MICELLAR CONCENTRATION IN BORATE BUFFER FOR  $[5 \times 10^{-3}]$  mol.dm.<sup>-3</sup> TRI-2,5-DIMETHYL PHENYL PHOSPHATE AT pH 9.0 AND TEMP  $45 \pm 0.2^\circ\text{C}$ .

$C_D$ mol.dm. <sup>-3</sup> $10^3$	$10^5 K_\Psi$ s <sup>-1</sup>	$10^5(C_D - cmc)$ mol.dm. <sup>-3</sup>	$\frac{10^{-5}}{(C_D - cmc)}$ mol.dm. <sup>-3</sup>	$10^5 (K_\Psi - K'_w)$ s <sup>-1</sup>	$\frac{10^{-5}}{(K_\Psi - K'_w)} \text{s}^{-1}$
100	09.75	20	0.050	7.77	0.128
120	13.14	40	0.025	11.16	0.089
140	14.58	60	0.017	12.60	0.072
160	16.72	80	0.012	14.74	0.067

$$K'_w = 1.98 \times 10^{-5} \text{ S}^{-1}, \quad cmc = 80 \times 10^{-5} \text{ mol.dm.}^{-3} \quad N = 61$$

**TABLE-** CALCULATED VALUES OF BINDING CONSTANT ' $K'_s$ ' AND ' $K'_m$ ' FOR THE REACTION OF TRI-2,5-DIMETHYL PHENYL PHOSPHATE WITH [OH] AT 9.0 AND  $45 \pm 0.2^\circ\text{C}$ .

Slope mol.dm. <sup>-3</sup>	$10^{-5}(K'_m - K'_w)$ s <sup>1</sup> (obsd).	$10^{-5} \frac{(K'_m - K'_w)}{(C_D - cmc)}$ (obsd).	$K_s = \frac{N \times \text{slope}}{(K'_m - K'_w) \times 10^{-5} \text{mol.}^{-3} \text{dm.}^{-3}}$	Intercept $10^{-5} K'_m$ mol.dm. <sup>-3</sup>	$10^5 K'_m$ s <sup>-1</sup> (cald)
1.50	19.23	0.052	4.76	0.052	21.18

**TABLE-IV**

RELATION BETWEEN REACTION RATE AND MICELLAR CONCENTRATION OF  $[20.8 \times 10^{-3}]$  mol.dm.<sup>-3</sup> [OH<sup>-</sup>] WITH  $[5 \times 10^{-4}]$  mol.dm.<sup>-3</sup> TRI-2,5-DMPP TEMPERATURE  $45 \pm 0.2^\circ\text{C}$ .

S.N.	$10^3 C_D$ mol.dm.	$10^5 K_\Psi$ S <sup>-1</sup>	$(K'_m - K'_w)$ S <sup>-1</sup>	$(K'_m - K'_w)$ S <sup>-1</sup>	$\frac{k_\Psi - K'_w}{K'_m - K'_w}$
1	0.2	2.79	0.81	19.23	0.042
2	0.4	3.82	1.84	19.23	0.095
3	0.6	5.19	3.21	19.23	0.166
4	0.8	6.67	4.69	19.23	0.243
5	1.0	9.75	7.77	19.23	0.404
6	1.2	13.14	11.16	19.23	0.580
7	1.4	14.58	12.60	19.23	0.655
8	1.6	16.72	14.74	19.23	0.766

$$K'_w = 1.98 \times 10^{-5} \text{ s}^{-1}, \text{cmc} = 80 \times 10^{-5} \text{ mol.dm.}^{-3}$$

**QUANTITATIVE TREATMENT OF MICELLAR CATALYSIS OF TRI-2,5-DMPP:**

The micellar catalyzed hydrolysis of tri-2,5-DMPP has been represented previously by scheme (I). section (I) part (A) where rate constants in equilibrium represented by eq.(5) and the ion exchange equilibrium represented by eq.(6) and (7) while the eq.(8) and (9) are used to convert the first order rate constants  $K'_s$  and  $K'_m$  into second order rate constants  $K^2_w$

and  $K^2_m$  respectively and the use of eqs.(10) to (15) of the previous section allows the determination of ion exchange parameters.

The plot of  $(K_\Psi - K'_w)/(m^{s_{OH}} - [D_n])$  Vs  $[-K_w / m^{s_{OH}}]$  for runs of different [CTAB] with [OH<sup>-</sup>] are linear and yield values of the binding constant  $K_s, m^{s_{OH}}$ , and  $K'_m$  at  $[20.8 \times 10^{-3}]$  mol.dm.<sup>-3</sup> [OH<sup>-</sup>]. The estimated value of  $(K_\Psi - K'_w)/(m^{s_{OH}} - [D_n])$  and  $[-K_w / m^{s_{OH}}]$  has been summarized in

**TABLE**

RELATION BETWEEN  $(K_\Psi - K'_w)/(m^{s_{OH}} - [D_n])$  AGAINST  $[-K_w/m^{s_{OH}}]$  OF TRI-2,5-DIMETHYL PHENYL PHOSPHATE IN BORATE BUFFER AND AT TEMPERATURE  $45 \pm 0.2^\circ\text{C}$ .

S.No.	$K_\Psi 10^{-5} \text{ s}^{-1}$	$K_\Psi - k'_w \times 10^{-5} \text{ s}^{-1}$	$\frac{K_\Psi - K'_w}{m^{s_{OH}} - [D_n]}$	$\frac{-K_w}{m^{s_{OH}}}$

1				4.84
2				7.34
3	2.79	0.81	2.46	10.68
4	3.82	1.84	5.60	14.28
5	5.19	3.21	9.78	21.77
6	6.67	4.69	14.29	30.02
7	9.75	7.77	23.68	33.52
8	13.14	11.16	34.02	38.73
	14.58	12.60	38.41	
	16.72	14.74	43.41	

$$m^s_{OH} = 0.464 \quad [D_n] = 0.8 \times 10^{-3} \text{ mol. dm}^{-3}, k_w = 1.98 \times 10^{-5} \text{ s}^{-1}$$

In borate buffer Estimated values have been summarized. These result suggest that pseudophase ion exchange modal can be applied as a first approximation to reactions of dianion of tri-2,5-DMPP with  $[OH^-]$  in [CTAB] micelles. Bimolecular reactions of hydrophilic nucleophilies  $[OH^-]$  by hydroxylic solvent, that strongly bind the hydrogen atom. Concentration of anions at the surface of cationic micelles in the stern layer

have been calculated from the above equations as :

$$[OH^-_m] = 3.61 \times 10^{-4} \text{ mol.dm}^{-3}$$

$$[Br^-_m] = 2.14 \times 10^{-4} \text{ mol.dm}^{-3}$$

$$K^{OH}_{Br} = 10$$

Which allows the determination of reaction substrate concentration of dianions of tri-2,5-DMPP in aqueous and micellar pseudophase.

**TABLE-**

ION EXCHGE PARAMETERS AND SECOND ORDER RATE CONSTANTS FOR THE REACTION OF TRI-2,5-DMPP WITH  $[OH^-]$  IN MICELLAR PSEUDOPHASE AT pH-9.0 AND TEMP.  $45 \pm 0.2^\circ\text{C}$ .

$K^{OH}_{Br}$	$10^3 [OH^-_T]$ mol $\text{dm}^{-3}$	$10^4 [OH^-_m]$ mol $\text{dm}^{-3}$	$10^3 [OH^-_w]$ mol $\text{dm}^{-3}$	$m^s_{OH}$	$10^4 [K'_m]$ $\text{s}^{-1}$	$10^5 K'_w$ mol $\text{dm}^{-3}$	$10^5 K^2_m$ mol $\text{dm}^{-3}$ $\text{s}^{-1}$	$\beta$
10	20.80	3.61	20.04	0.411	20.41	1.18	1.82	0.75

### EFFECT OF TEMPERATURE

**TABLE-ARRHENIUS PARAMETERS FOR THE HYDROLYSIS OF TRI-2,5-DIMETHYL PHENYL PHOSPHATE**

Ester	$\Delta E$ K.Cal/mol	$-\Delta S^\ddagger$ (e.u.)
Absence of [CTAB]	11.45	59.31
Present of [CTAB]	08.70	55.12

**EFFECT OF ELECTROLYTES:**

The reaction of tri-2,5-DMPP with  $[20.8 \times 10^{-3}]$  mol.dm.  $[\text{OH}^-]$  ion in presence of CTAB has been studied to see the effect of added electrolytes NaCl, NaBr and KCl at pH-9.0 It has been found that nucleophilic participation contributed by anions of these salts which are in competition with hydroxyl ion in micellar stern layer. Consequently, these anions reduce the

concentration of nucleophile  $[\text{OH}^-]$  at the surface of the micelle hence the rates are reduced by adding salts, Some anions like sulphate carbonate, NaOH and phosphate<sup>88</sup> of high charge density have been found to enhance the rates due to organizing water molecules about them. So it has been noted that ions can change the dynamic basicity of water.

**TABLE-**  
EFFECT OF INHIBITING SALTS UPON THE REACTION OF TRI-2,5-DIMETHYL PHENYL PHOSPHATE WITH  $[20.8 \times 10^{-3}]$  mol.dm.<sup>-3</sup> NaOH IN  $[5 \times 10^{-2}]$  mol.dm.<sup>-3</sup> BORATE BUFFER IN PRESENCE OF  $1.6 \times 10^{-3}$  AT pH 9.0 AND  $45 \pm 0.2^\circ\text{C}$ .

S.N.	10 <sup>3</sup> Salt mol.dm. <sup>-3</sup>	Rate Constant $K_{\Psi} 10^5 \text{ s}^{-1}$		
		KCl	NaCl	NaBr
1	0.1	10.63	8.33	6.58
2	0.2	9.21	7.67	5.78
3	0.3	8.30	6.43	5.12
4	0.4	7.12	5.98	4.29
5	0.5	6.75	4.82	3.54
6	0.6	5.44	4.06	3.02
7	0.7	4.42	3.47	2.45
8	0.8	3.38	2.70	1.92

**EFFECT OF SUBST**