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Kinetic Investigation of Micellar Promoted Pyridine based Oximate and Hydroxamate Catalysis on Phosphotriester Pesticides

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Abstract The nucleophilic hydrolysis of paraoxon, parathion and fenitrothion by pyridine oximate ($PyOx^-$) and hydroxamate ($PyHA^-$) has been studied in aqueous and cationic micellar media. A noticeable kinetic changes has been observed at $pH > pK_a$ due to effective nucleophilicity of oximate ($–CH=NO^-$) and hydroxamate ($–CONHO^-$) functions. The Ox^- nucleophile shows large reactivity than corresponding HA^-. The reactivity of nucleophiles toward the electrophilic center of P=O and P=S bond of phosphate ester shows prominent effect in the presence of cetyltrimethylammonium bromide (CTAB) and tetradecyltrimethylammonium bromide (TTAB) micelles than aqueous media. The adjacent lone pair of electron in nitrogen atom on the nucleophile moiety of 2-PyOx and 2-PyHA helps to augment the reactivity compared to presence in remote of 4-PyOx and 4-PyHA nucleophile. The application of the pseudophase model of micellar catalysis showed that the ratio k_2^m/k_2^w is higher for the reaction of esters.

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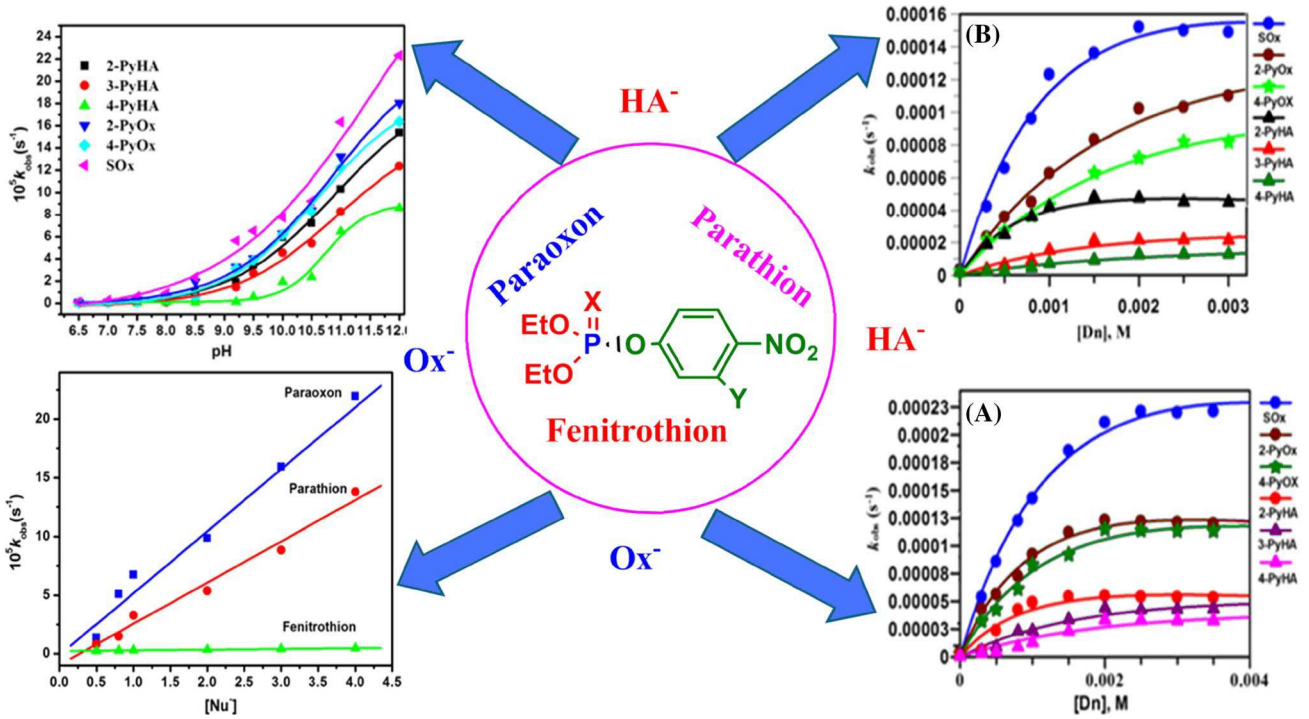
Graphical Abstract



Keywords Pesticides · Oximate · Hydroxamate ions · Micellar catalysis

1 Introduction

The tuning of oxime and hydroxamic acids has received renewed interest due to their high affinity to bind the metal ions to form metal complexes [1, 2]. Hydroxylamine is the parent compound for the three typical classes of the oxygen-containing amidoxime, oxime and hydroxamic acid. Their deprotonated –NOH functional group such as amidoximate ($–C(NH_2)=NO^-$), oximate ($–CH=NO^-$) and hydroxamate ($–CONHO^-$) plays a very essential role towards the scavenging of Fe(III) from the environment [3, 4]. The functional group of hydroxamic acids provide a better platform in numerous applications such as binding of metal ions [5], inhibitors of enzyme [6] and promising drugs for the treatment of a variety of diseases. An account of their antimalarial [7, 8], antifungal [9] and anticancer activities has been extensively studied [10–12]. Recently, Danial et al. have used salinomycine based hydroxamic acids as an effective anticancer agent [13]. The coordination chemistry of acids with metal has also been studied widely [14, 15]. The oximate (Ox^-) and hydroxamate (HA^-) ions play a fundamental role as deacylating and dephosphorylating agent towards the organophosphate esters. Organophosphate (OP) esters are widely used as pesticides, insecticides as well as a chemical warfare agent [16, 17]. These compounds are extremely potent inhibitors of acetylcholinesterase enzymes [18]. There is an immediate required to develop effective, convenient and economic method to detoxify them. A considerable amount of α-nucleophiles was reportedly investigated for hydrolysis of OP compounds, pesticides and chemical warfare agents [19–25]. Nucleophiles such as peroxides [19], hypochlorites [20], oximates [21, 22],o-iodosylcarboxylate [23] and hydroxamates [24] have been used alone or in the presence of surfactants. The study of nucleophilic reactivities of the α-effect Ox^- function led to the development of antidotes for the reactivation of organophosphate-inhibited cholinesterase enzymes [26, 27]. Nucleophilic reactivity of other nucleophiles such as monoperoxyphthalates [28], 4-*N*,*N*-dialkylaminopyridines [29], hydroxybenzotriazoles [30], 5-alkyl-1*H*-tetrazoles [31] and have been studied in physiological conditions.

Oximate (Ox^-) and hydroxamate (HA^-) ions are known to be very effective α nucleophiles and their reactivity are influenced by the basicity of the Ox^- and HA^- functions, at least in the pK_a range 7–10 [32]. The use of relatively acidic hydroxamic acids (HA) at pH close to natural pH ensures a large fraction of their highly reactive conjugate bases. The reactivities of amphiphilic [33] and aromatic *N*-substituted hydroxamate [34] ions are increased by comicellization with surfactant in water. Effective hydrolytic reactions of bis (2,4-dinitrophenyl)

phosphate (BDNPP) were also achieved with a long-chain hydroxamic acid, i.e. hydroxamate polymers [35] and desferoxamine [36]. Surprisingly, nucleophilic cleavage of OP compound has largely been studied using Ox^- ions. However, the nucleophilic reactivity of pyridine based HA^- ions towards dephosphorylation reaction of pesticides have not been claimed in previous studies. We have documented effective catalysis of HA^- and Ox^- ions towards the dephosphorylation of paraoxon, parathion and fenitrothion in CTA^+X^- cationic micelles [37] and microemulsions [38].

In the present exploration, we have examined the reaction of model OP esters such as paraoxon, parathion and fenitrothion with pyridine based Ox^- and HA^- ions (Scheme 1). The reactivity of oximate (Ox^-) and hydroxamate (HA^-) ions is described by a common Brønsted equation and believed that the main factor determining the reactivity of Ox^- and HA^- ion is their nucleophilicity. The acid-base functional groups present on some HA^- ions could exert a nucleophilic effect on reaction with P=O and P=S centers. Therefore, we have also studied the reactivity of HA^- ions, especially of those possessing acidic-basic groups ($PyHA^-$) towards phosphate and thiophosphate esters. To evaluate the factors governing the nucleophilic reactivities and strength of micelle interaction, the reactivity of structurally similar Ox^- ions ($PyHA^-$, $PyOx^-$) were also investigated in cationic alkyltrimethylammonium bromide (RTA^+Br^-; R = $C_{16}H_{33}$ and $C_{14}H_{29}$) micelles.

2 Experimental

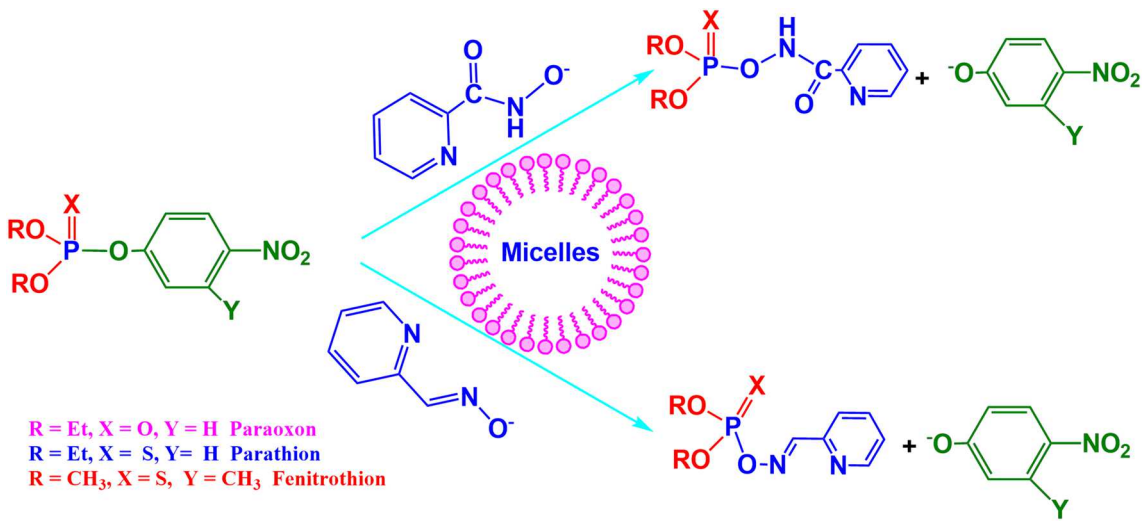
2.1 Materials and Method

Syn-2-pyridinealdoxime (2-PyOx), 4-pyridinealdoxime (4-PyOx), cetyltrimethylammonium bromide (CTAB), tetradecyltrimethylammonium bromide (TTAB), paraoxon, parathion and fenitrothion were procured from Sigma-Aldrich Chemicals Pvt. Ltd. Bangalore (India). Pyridinehydroxamic acids such as 2-pyridinehydroxamic acid (2-PyHA), 3-pyridinehydroxamic acid (3-PyHA) and 4-pyridinehydroxamic acids (4-PyHA) were prepared by reaction of esters with hydroxylamine in alkaline condition [39]. Salicylaldoxime (SOx) was prepared by the reaction of methanolic solution of salicylaldehyde and hydroxylamine hydrochloride [40]. Other chemicals used were of AR/high purity (99.0%) grade. All the solutions were prepared in triple-distilled water.

2.2 Determination of pK_a of Hydroxamic Acids

The acid dissociation constant (pK_a) values of all synthesized oximes and hydroxamic acid were determined by potentiometric titration at 27 °C (Fig. S1, a–e). Typically, 0.001 M solutions of oxime and hydroxamic acids were titrated with 0.01 M NaOH using Orion Star A-211 pH-meter. The ionic strength was maintained constant at 0.1 M by adding KCl. Under the experimental condition, the pK_a values were obtained from the measured pH values to the solution by means of Eq. 1.

$$pK_a = pH - \log \frac{[A^-]}{[HA]} \quad (1)$$



Scheme 1 Nucleophilic reaction of pyridine oximate and hydroxamate with phosphate esters

2.3 Kinetic Measurements

All reactions were performed at 27 °C with a Thermofisher Evolution 300 UV–Visible spectrophotometer equipped for temperature control (Peltier). All the kinetic runs were followed under pseudo-first-order conditions in which the concentration of nucleophiles (1.0×10^{-3} M) was at least 10 times larger than the initial concentration of substrates (1.0×10^{-4} M). The additions of nucleophile and substrate were done under thermal control at 27 °C. The cuvettes were allowed to equilibrate thermally (27 ± 0.1 °C) in the cell holder for 30 min. After temperature equilibrium, the stock solutions of each substrate were added to cuvettes, and the kinetic runs were started. The observed rate constants (k_{obs}) for the reaction of nucleophiles with ester were determined by following the increase in absorption of 4-nitrophenoxide ion at 400 nm and 3-methyl-4-nitrophenoxide ion at 398 nm (Fig. S2). All the kinetic experiments were performed at an ionic strength of 0.1 M KCl. Borate buffer was employed. For all the kinetic runs, the absorbance/time result fit the first-order rate equation very well.

$$\ln\left(A_\infty - A_t\right) = \ln\left(A_\infty - A_0\right) - kt \quad (2)$$

The values of pseudo-first-order rate constants (k_{obs}) were obtained by least squares fits. The second-order rate constants (k_2) in the aqueous medium were determined from linear plots of k_{obs} versus nucleophile concentrations. The intercept were negligible. Generally, k_{obs} values were measured at five different concentrations of each nucleophile.

3 Results and Discussion

3.1 Hydrolytic Reaction in Aqueous Media

The acidity constant (pK_a) of the oxime and hydroxamic acids were measured at 27 °C by standard potentiometric titration methods. The ionic strength was kept at 0.1 M by adding KCl as required. The pK_a values for the ionization of Ox^- and HA^- group of oximes and hydroxamic acid were independently determined in similar ways (Table 1). Pyridiniumcarbaldehyde oximes constitute the most important class of potential AChE reactivators [41]. The most efficient Ox^- reactivators are 2-PAM, TMB-4 and HI-6. These compounds have both Ox^- functionality and a positively charged moiety, which is a disadvantage in terms of penetration of biological membrane. Pyridine substituted hydroxamate α-nucleophiles may meet these requirements to be a function as hydrolytic catalyst and AChE reactivators. The pK_a of 2-PyHA$^-$ is found to be 8.73, which are ≈0.3 pK_a units greater than the pK_a values of corresponding Ox^- ion (i.e. pK_a of 2-PyOx$^-$ = 8.41). Most importantly, 4-PyHA$^-$ shows pK_a value of 7.2, which is ≈2.2 pK_a units less than corresponding Ox^- ion, 4-PyOx$^-$ (pK_a = 9.39). The pK_a value of 4-PyHA$^-$ is even less than the well-known reactivators, 2-PAM (pK_a = 7.75) and 4-PAM (pK_a = 8.27). Therefore, it is advantageous to investigate the catalytic effect of the PyHA$^-$ ions for the cleavage of environmental persistent OP pesticides, viz. paraoxon, parathion and fenitrothion.

Table 1 Second-order rate constants for the reaction of ester

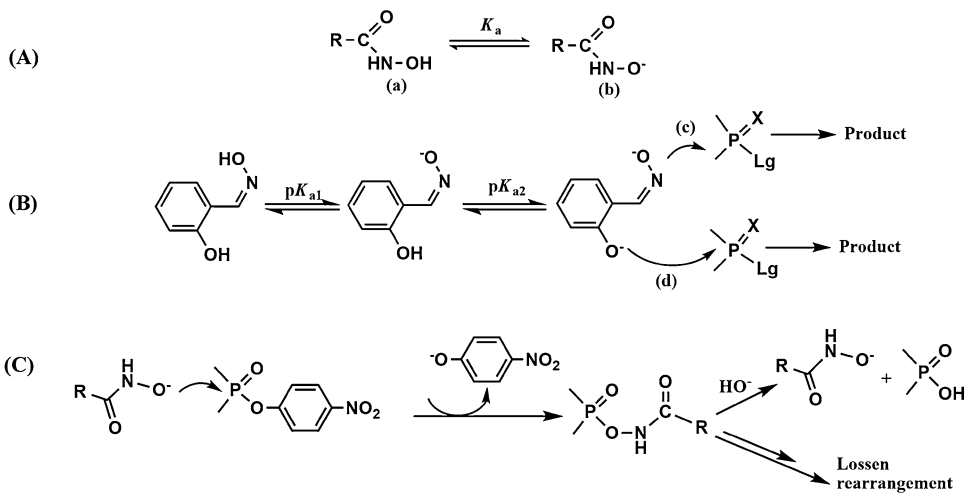
[Nu$^-$]	pK_a	$10^5 k_2$ (M^{-1} s^{-1})		
		Paraoxon	Parathion	Fenitrothion
2-PyHA$^-$	8.73 (8.2)[a]	1.64 ± 0.12	0.17 ± 0.13	0.032 ± 0.11
3-PyHA$^-$	9.10 (8.8)[a]	1.08 ± 0.11	0.11 ± 0.11	0.023 ± 0.10
4-PyHA$^-$	7.20 (7.1)[a]	0.16 ± 0.12	0.08 ± 0.11	0.020 ± 0.11
2-PyOx$^-$	8.41	4.67 ± 0.11	3.25 ± 0.12	0.043 ± 0.10
4-PyOx$^-$	9.38	3.10 ± 0.10	2.96 ± 0.12	0.031 ± 0.10
SOx$^-$	9.20	4.81 ± 0.11	3.50 ± 0.13	0.060 ± 0.11

[a]Determined under the micellar condition: [CTAB] = 5×10^{-3} M, [KCl] = 0.1 M, pH = 10, Temp. = 27 °C

3.2 Effect of pH

Studying pH effect allows us to estimate the pK_a of nucleophiles and therefore, provide situation to control the rate of reaction at preferable reaction conditions. There is a noticeable effect of pH on the reaction rates. At pH > pK_a sufficient rate enhancement may be observed due to oxime and hydroxamic acid function completely dissociated into the oximate (–CH=NO$^-$) and hydroxamate (–CONHO$^-$) ions. The relatively high acidity of hydroxamic acids (a) is one of the striking properties. A number of pK_a values for RCONHOH are reported in the literature [42, 43]. The structure of the anion is still subject to controversy. At this point, it is difficult to generalize beyond one hydroxamic acid, and the solvent systems used for the particular study. Another difficulty lies in the detection of minute fraction; this problem also hindered the tautomerism. Widespread literatures have been reported that hydroxamate anion represents a unique type of reactive α-nucleophile since it behaves as a one-cut self-destructive molecular scissor, losing its nucleophilic ability after destroying the phosphate ester (Scheme 2c) [44]. It was observed that the rate of reaction increased with the rise in pH as represented in Fig. 1a, b. A pH versus rate constant profile for the nucleophilic cleavage of paraoxon and parathion by oximate and hydroxamate ion gave the apparent pK_a value (Table 1). The higher rate constant was observed from these experiments were at pH > pK_a, due to the appearance of dissociated oxime and hydroxamic acid functionality (–CH=NO$^-$ and C(O)NHO$^-$).

Scheme 2 Ionization of hydroxamic acid and nucleophilic attack of HA^- Ion



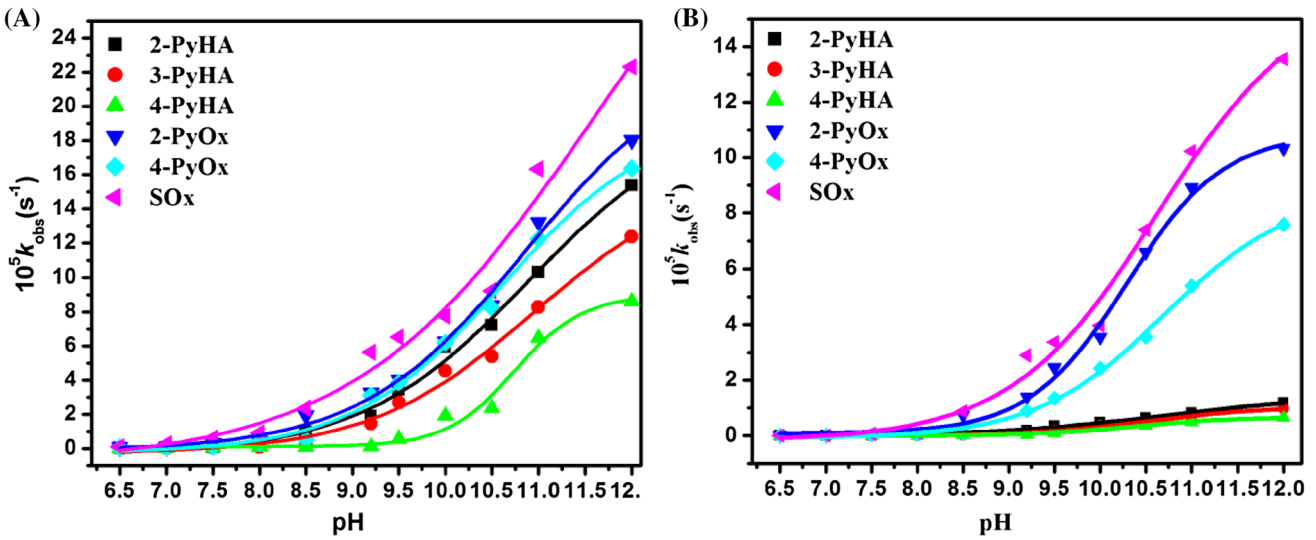


Fig. 1 pH effect of oximate and hydroxamate ions with **a** Paraoxon and **b** Parathion. Reaction condition: [Ester] = 1×10^{-4} M, [Nu^-] = 1×10^{-3} M, Temp. = 27 °C

Equation (3) describes the reaction of phosphate esters with nucleophiles; k_o defined in Eq. (4). It corresponds to the intercept in the k_{obs} versus [Nu^-] plot.

$$k_{obs} = k_o + k_2[Nu^-] \tag{3}$$

$$k_o = k_{H_2O} + k_{HO}[HO^-] \tag{4}$$

3.3 Effect of Nucleophiles

The plots of k_{obs} versus nucleophile concentration for the reactions of phosphate ester with HA^- and Ox^- anions were linear with positive intercepts k_o. This indicates that the contribution of other nucleophiles i.e. H_2O/OH^-, is negligible and hydroxamate and oximate ions are very strong nucleophiles for the hydrolysis of phosphate esters (Fig. 2). Second-order rate constants (k_2) were calculated from the slope of plots of k_{obs} versus [Nu^-] (Tables S1–S3); results for the various pyridine based nucleophiles are presented in Table 1. It can be seen that 2-$PyHA^-$, 2-$PyOx^-$ and SOx^- ions had more efficiency to attack the electrophilic center of phosphate ester than other nucleophile. We have applied two types of electrophilic model substrate, i.e. P=O (paraoxon) and P=S (parathion and fenitrothion); the more electronegativity of oxygen has more tendencies to attract the nucleophile as compared to the sulfur substituted electrophiles. Fenitrothion has extra methyl group, i.e. electron donor group which response to repulsion takes place between nucleophile and fenitrothion. All nucleophile shows more reactivity towards the P=O center than P=S center of ester. The order of reactivity for all the substrate

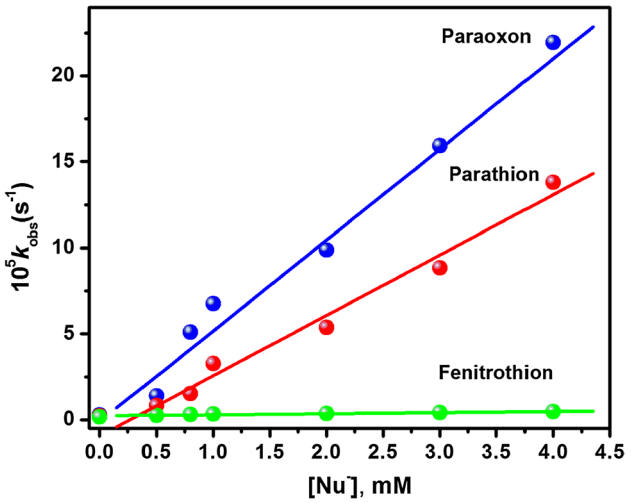
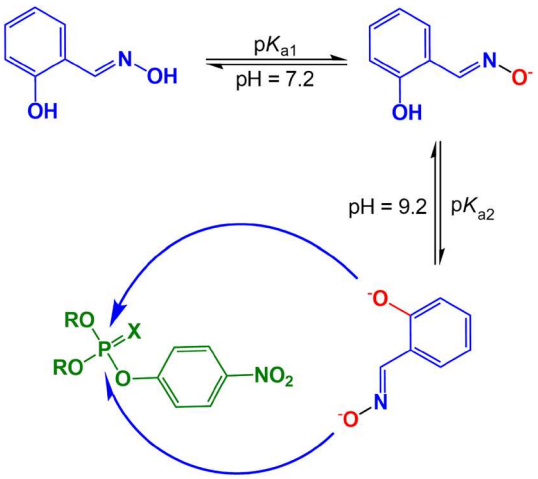


Fig. 2 Plots of k_{obs} versus [SOx$^-$] for the reaction of paraoxon, parathion and fenitrothion. Reaction condition: [Ester] = 1×10^{-4} M, pH = 10, Temp. = 27 °C



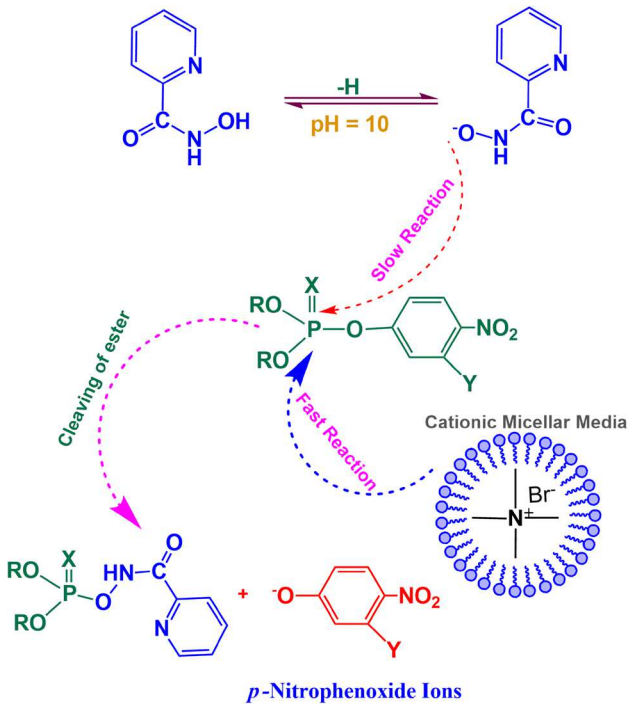
Scheme 3 Bifucntional attack of salicyladoximate ion on P=O and P=S center of ester

can be predicted as paraoxon > parathion > fenitrothion. We also compared the nucleophilicity of all pyridine based nucleophile towards the hydrolysis of phosphate ester. We observed that the 2-PyHA$^-$ and 2-PyOx$^-$ had more abilities to cleave the ester because of the presence of lone pair electron of nitrogen in ortho position to the hydroxamate and oximate function of 2-PyHA and 2-PyOx therefore, it increased the nucleophilicity compared to presence in para position of 4-PyHA and 4-PyOx; hence, it behaves as an excellent nucleophile than other pyridine based nucleophiles. Comparison of the reactivity of Ox$^-$ ions with those of HA$^-$ ions for the reaction of ester provided a reliable evidence for the large α-effect of Ox$^-$ ions. In general, Ox$^-$ ions are more reactive than HA$^-$ ions. It is interesting to note that salicylaldoximate ions may act as a bifunctional catalyst (Scheme 3) at operational pH (pH = 10) in which both of the oximate and phenolate ions attack at the P=X (O, S) center [32].

3.4 Hydrolytic Reaction in Micellar Media

The k_{obs} values for the reactions in micellar system are evaluated through k_{obs} versus surfactant concentration profiles. At fixed concentration of ester and nucleophile, under pseudo-first order conditions, with increasing the concentration of surfactant gives k_{obs} versus [surfactant] profiles which go through a maximum. This maximum corresponds to the balance point between a rate increase caused by the transfer of the nucleophile into the micellar pseudophase and a rate decrease due to dilution of nucleophile as the surfactant concentration increases. The extent of micellar catalysis is expected to be depending on the relative amount of substrate incorporated in micelles. Therefore, we describe here an examination of micellar mediated nucleophilic reactivity of model substrate, followed by their application to decomposition of OP pesticides i.e. paraoxon, parathion and fenitrothion.

The k_{obs} values for the reaction of 1.0×10^{-4} M phosphate esters with 1.0×10^{-3} M nucleophiles at pH 10 were determined under micellar conditions. All the HA$^-$ and Ox$^-$ ions showed significant catalysis for hydrolysis of esters. The results follow the typical biphasic pattern. Cationic micelles catalyzed the reaction and k_{obs} passed through maxima at the value closed to the critical micelle concentration (cmc) of the surfactants. The positions of rate maxima are independent of the type of surfactants but the magnitude of the observed rate constants depends on the types of surfactant. The variation of rate constants below the cmc is difficult to quantify due to reactant induced micellization and interaction with nonmicellized surfactants. The reactions are faster with 2-PyHA$^-$ in comparison to other nucleophiles which may be due to strong interaction with the micelles. SOx$^-$ showed significant rate acceleration for the reaction of phosphate ester due to its intrinsic nucleophilicity and effective micellar interaction at micellar stern layer. The structure of surfactant head group plays an important role towards the molecular packing of organized self-assemblies [45]. An increase in the head group size leads to an increase in the interface area, and the space between two head group is also enhanced [46]. The space between two head groups allows the α-nucleophiles to solubilize itself smoothly at the interfacial region. Because of the enhanced interfacial region, the concentration of nucleophile and substrate increased and showed higher reactivity (Scheme 4). The micellar-mediated nucleophilic reactivity of nucleophiles are strongly depends on the structure and charge of the surfactant head group. Analysis of kinetic

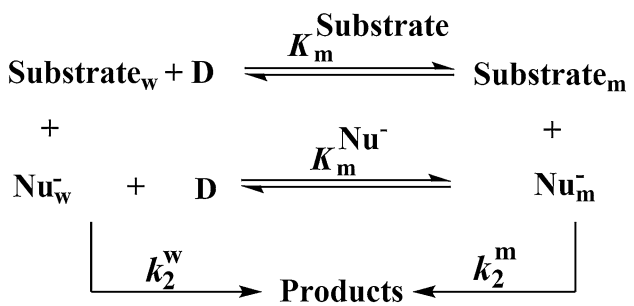


Scheme 4 Enhance the nucleophilicity of HA^- and Ox^- in cationic micellar media

data indicates that CTAB showed higher reactivity than TTAB for the reaction of paraoxon, parathion and fenitrothion. The increase of k_{obs} values with increasing chain length of the surfactant, that is, with an increasing aggregation number of micelles, is mainly due to the increase in the electrical surface potential and partially due to an increase in hydrophobicity of the palisade layer of the micelle.

3.5 Application of Pseudophase Model [PPM]

For the quantitative treatment of surfactants on the rate of bimolecular reactions are rationalized by pseudophase model [47, 48]. In this model the efficacy of nucleophiles in both pseudophase have determined towards the hydrolysis



Scheme 5 Pseudophase model

of phosphate esters. The overall reaction rate is the sum of the rate in each pseudophase and depends on the rate constants and reactant concentrations in each pseudophase [27]. The different reactivities in the aqueous and micellar pseudophases have been taken into account through the corresponding second-order rate constants: k_2^w and k_2^m. The values of k_2^w have been obtained by studying the reaction in absence of the surfactant. The Ox^- and HA^- concentration in the micellar pseudophase has been defined as the local, molar concentration within the micellar pseudo phase: $[Nu^-]_T = [Nu^-]_m/D\bar{V}$, where $\bar{V}$ is the molar volume in $dm^3\ mol^{-1}$ of the reaction region and $[D]\bar{V}$ denotes the micellar fractional volume in which the reaction occurs. We assume $\bar{V}$ equal to the partial molar volume of the interfacial reaction region in the micellar pseudophase, determined by Bunton as 0.14 $dm^3\ mol^{-1}$ [49]. Micellar binding of substrate and Nu^-, is governed by hydrophobic interactions and the equilibrium constants $K_m^{substrate}$ and K_m^{Nu} are expressed by referring these concentrations to the total volume of the observed rate constants, k_{obs}, based on Scheme 5 and on the above considerations, is given by the following equation:

$$k_{obs} = \frac{k_2^w + \frac{k_2^m}{\bar{V}} K_m^{substrate} K_m^{Nu^-}[D]}{\left(1 + K_m^{substrate}[D]\left(1 + K_m^{Nu^-}[D]\right)\right)}[Nu^-]_T \quad (5)$$

Second-order rate constants (k_2^m) at the micellar interface and association constants of the Ox^- and HA^- ions to the cationic micelles were fitted by Eq. 5 to the experimental data. Figures 3, 4 and 5 shows the rate-surfactant profiles for the reaction of paraoxon, parathion and fenitrothion with SOx^-, 2-$PyOx^-$, 4-$PyOx^-$, 2-$PyHA^-$, 3-$PyHA^-$ and 4-$PyHA^-$ in CTAB (A) and TTAB (B) cationic micellar media. It is possible to evaluate the association constant for micelle-nucleophile interaction (K_m^{Nu}) from Eq. 5. The micellar association constant of SOx, K_m^{SOx}=478.9 and 453.36 in CTAB and TTAB micelles respectively. It shows the association constants of oximate, K_m^{Ox}, is relatively higher than hydroxamate K_m^{HA} in both the cationic micelles (Tables 2, 3, 4). Larger micellar interaction of SOx^- results greater micellar catalysis ($k_2^m/\ k_2^w$) of the factor ≈118 and 37 in CTAB and TTAB micelles respectively with paraoxon. However, significant acceleration of k_{obs} values have been observed for the reaction of SOx^- in CTAB and TTAB micelles, which may be due to the cooperative intrinsic nucleophilicity of SOx^- with aggregate micelle. The N–OH groups are considerably ionized as N–O^- at operational pH and therefore, also bind to the quaternary ammonium through electrostatic interactions. 2-$PyHA^-$ showed 143- and 117-fold micellar catalysis in CTAB and TTAB respectively. The satisfactory fit obtained from these experiments supports the validity of the model

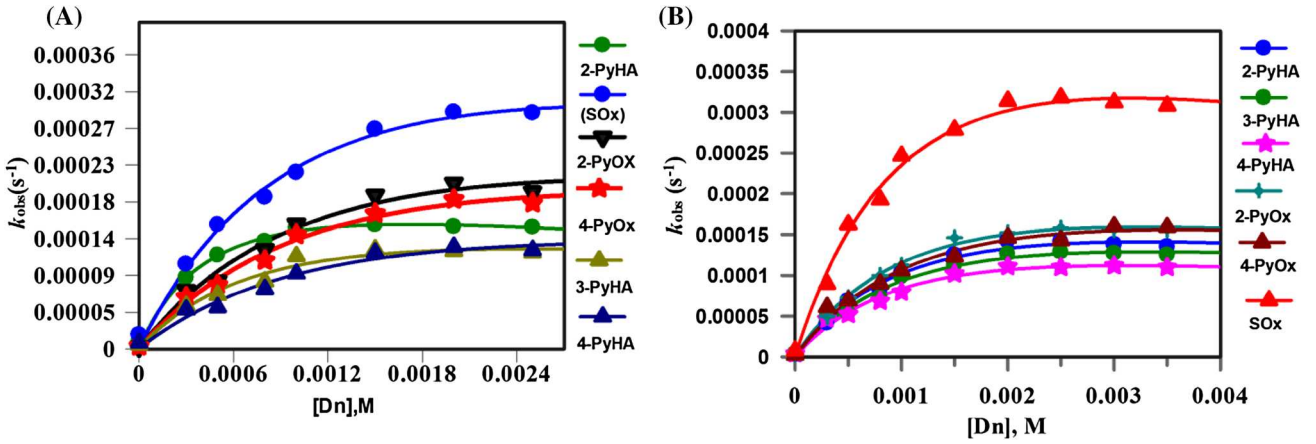


Fig. 3 Simulated rate-surfactant profile for the reaction of paraoxon with hydroxamate and oximate ions in the presence of CTAB (**a**) and TTAB (**b**). Reaction condition: [Paraoxon] = 1.0×10^{-4} M, [Nu^-] = 1.0×10^{-3} M, pH = 10, Temp. = 27 °C

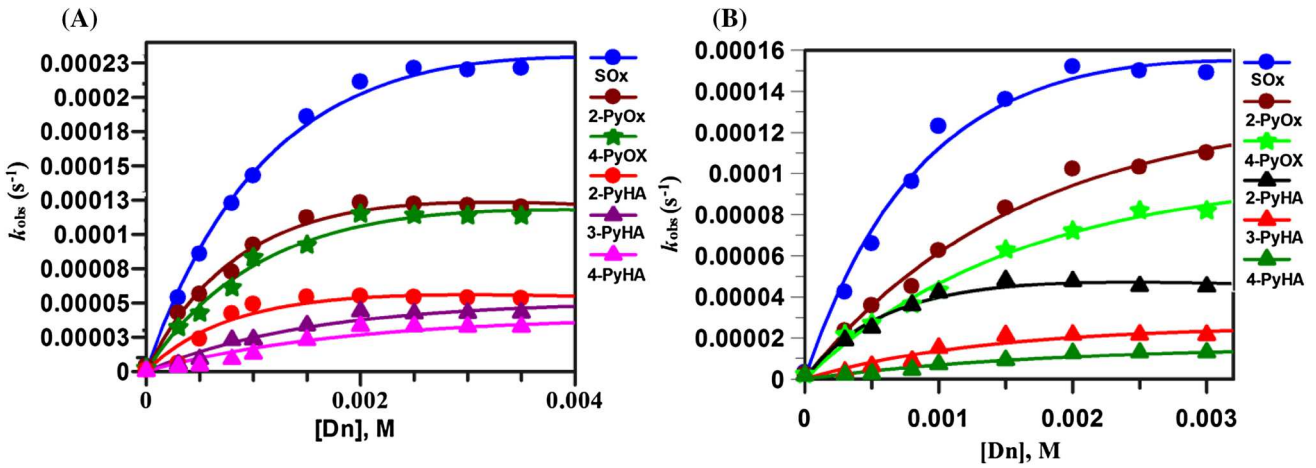


Fig. 4 Simulated rate-surfactant profile for the reaction of parathion with hydroxamate and oximate ions in the presence of CTAB (**a**) and TTAB (**b**). Reaction condition: [Parathion] = 1.0×10^{-4} M, [Nu^-] = 1.0×10^{-3} M, pH = 10, Temp. = 27 °C

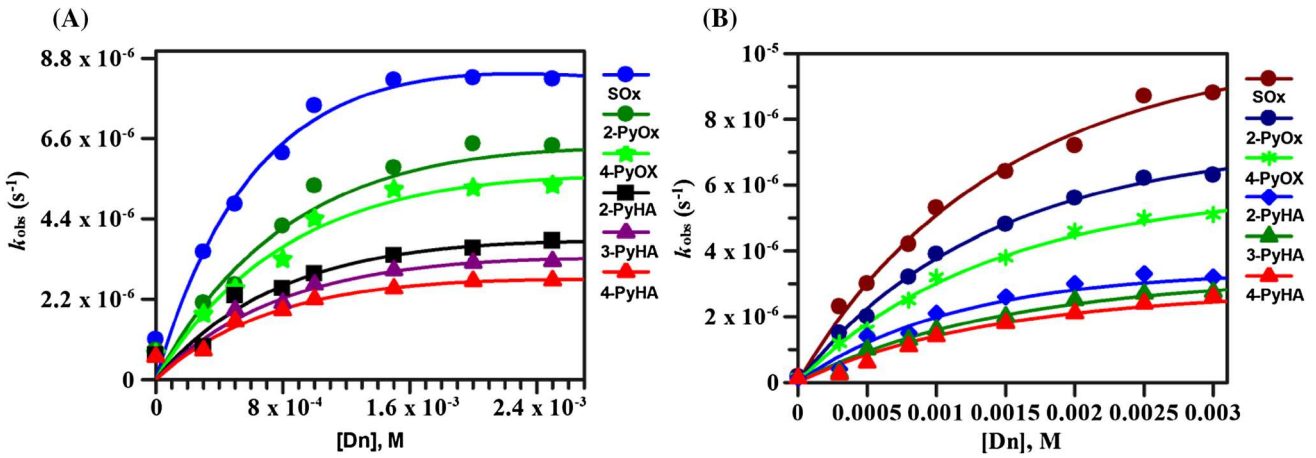


Fig. 5 Simulated rate-surfactant profile for the reaction of fenitrothion with hydroxamate and oximate ions in the presence of CTAB (**a**) and TTAB (**b**). Reaction condition: [Fenitrothion] = 1.0×10^{-4} M, [Nu^-] = 1.0×10^{-3} M, pH = 10, Temp. = 27 °C

Table 2 Kinetic parameters obtained by applying pseudophase model for the reaction of paraoxon in the presence of cationic micelles

[Nu$^-$]	$10^5k_2^w$ (M^{-1} s^{-1})	K_m^{Nu} (M^{-1})		$10^3k_2^m$ (M^{-1} s^{-1})	
		CTAB	TTAB	CTAB	TTAB
SOx	4.81 ± 0.02	478.59	453.36	5.70 ± 0.1	3.80 ± 0.1
2-PyOx	4.67 ± 0.01	467.35	434.53	3.20 ± 0.1	2.10 ± 0.1
4-PyOx	3.10 ± 0.01	415.63	447.36	2.70 ± 0.1	1.95 ± 0.1
2-PyHA	1.64 ± 0.01	389.96	381.54	2.35 ± 0.1	1.92 ± 0.1
3-PyHA	1.08 ± 0.01	385.63	361.44	1.40 ± 0.1	1.53 ± 0.1
4-PyHA	0.16 ± 0.01	314.10	368.91	0.42 ± 0.1	1.05 ± 0.1

Micellar association constant of paraoxon in CTAB and TTAB ($K_m^{paraoxon}$) = 200 M^{-1}

Table 3 Kinetic parameters obtained by applying pseudophase model for the reaction of parathion in the presence of cationic micelles

[Nu$^-$]	$10^5k_2^w$ (M^{-1} s^{-1})	K_m^{Nu} (M^{-1})		$10^3k_2^m$ (M^{-1} s^{-1})	
		CTAB	TTAB	CTAB	TTAB
SOx	3.50 ± 0.13	394.64	461.96	3.10 ± 0.1	2.10 ± 0.1
2-PyOx	3.25 ± 0.12	482.38	414.70	1.70 ± 0.1	2.10 ± 0.1
4-PyOx	2.96 ± 0.12	328.95	431.69	1.40 ± 0.1	2.40 ± 0.1
2-PyHA	0.17 ± 0.13	345.61	365.34	1.70 ± 0.1	0.50 ± 0.1
3-PyHA	0.11 ± 0.10	345.76	299.25	1.20 ± 0.1	0.50 ± 0.1
4-PyHA	0.08 ± 0.12	325.62	298.45	1.10 ± 0.1	0.50 ± 0.1

Micellar association constant of parathion in CTAB and TTAB ($K_m^{parathion}$) = 366 M^{-1}

Table 4 Kinetic parameters obtained by applying pseudophase model for the reaction of fenitrothion in the presence of cationic micelles

[Nu$^-$]	$10^5k_2^w$ (M^{-1} s^{-1})	K_m^{Nu} (M^{-1})		$10^3k_2^m$ (M^{-1} s^{-1})	
		CTAB	TTAB	CTAB	TTAB
SOx	0.060 ± 0.11	374.02	103.70	0.20 ± 0.1	0.20 ± 0.1
2-PyOx	0.043 ± 0.10	307.65	96.61	0.08 ± 0.1	0.20 ± 0.1
4-PyOx	0.031 ± 0.10	235.36	92.20	0.08 ± 0.1	0.10 ± 0.1
2-PyHA	0.032 ± 0.11	349.07	148.64	0.04 ± 0.1	0.06 ± 0.1
3-PyHA	0.023 ± 0.11	255.24	90.07	0.05 ± 0.1	0.08 ± 0.1
4-PyHA	0.020 ± 0.11	339.43	88.83	0.03 ± 0.1	0.07 ± 0.1

Micellar association constant of fenitrothion in CTAB and TTAB ($K_m^{Fenitrothion}$) = 327 M^{-1}

employed. The same trend followed for the cleavage of parathion and fenitrothion with oximate and hydroxamate ions in the presence of cationic micelles. The micellar catalysis of surfactant with parathion by SOx^- and 2-PyHA are 88- and 1000-fold was observed. In micellar system the order of rate enhancement of nucleophiles is CTAB > TTAB. All nucleophile shows higher rate constant with paraoxon than parathion and fenitrothion. This may be due to the incorporation of paraoxon and parathion into the micelle core and would be inert to hydroxide ion and nucleophile catalyzed hydrolysis. It can be seen that the alliance of oxime group of pyridinealdoxime with surfactants are more facile than hydroxamic group of pyridinehydroxamic acid, therefore the surfactants carrying reactants in close proximity by binding the substrates via hydrophobically binding and coulombically attracting the negatively charged nucleophile of oxime and hydroxamic acid.

4 Conclusions

Kinetic studies relevant to pesticide detoxification are reported for the hydrolysis of model phosphate esters in aqueous buffer and alkyltrimethylammonium bromide with Ox^- and HA^-. Comparison of the reactivity of Ox^- ions with those of corresponding HA^- ions for the reaction of triester provides a reliable evidence for the large α-effect of Ox^- ions. The pK_a value of PyHA and PyOx decreased in the cationic micelle due to an enhanced local pH at the cationic surface of the aggregate, and this is not expected to modify the nucleophilicity of the micellar HA^-s. The micellar-mediated hydrolysis of paraoxon, parathion and fenitrothion with SOx^-/CTAB in oximate and 2-$PyHA^-$/CTAB in hydroxamate are most effective system for the cleavage of OP pesticides. The ratio k_2^m/k_2^w for the hydrolysis of paraoxon is much larger relative to parathion and fenitrothion.

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Supporting Information Determination of acid dissociation constant (pK_a) of oxime and hydroxamic acid, Repeat scan spectra of production of 3-methyl-4-nitrophenoxide ion (λ_{max} = 398 nm) for the reaction of fenitrothion and nucleophilic effect data are available in supporting information.

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