Kinetic Study of the Reactions of *p*-Nitrophenyl Acetate and *p*-Nitrophenyl Benzoate with Oximate Nucleophiles

SHUCHI TIWARI,[1] SANCHEETA KOLAY,[1] KALLOL K. GHOSH,[1] KAMIL KUCA,[2] JAN MAREK[2]

[1]*School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur, C.G., 492010, India*
[2]*Center of Advanced Studies and Department of Toxicology, Faculty of Military Health Sciences, Trebesska 1575, 500 01 Hradec Kralove, Czech Republic*

Received 27 February 2008; revised 26 April 2008, 13 June 2008; accepted 14 June 2008

DOI 10.1002/kin.20363
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The reactions of *p*-nitrophenyl acetate (PNPA) and *p*-nitrophenyl benzoate (PNPB) with α-nucleophile oximates, that is, butane 2,3-dione monoximate, pralidoximate, and other oximates have been studied in the presence of different cationic surfactants. The first-order rate constant increases with increasing surfactant concentration. The extent of acceleration is dependent on the head group structure of surfactants. The PNPA is more reactive than PNPB toward all the nucleophiles at higher concentration of surfactants. © 2008 Wiley Periodicals, Inc. Int J Chem Kinet 41: 57–64, 2009

INTRODUCTION

Oximates are used as potential reactivators of organophosphate-inhibited acetylcholinesterase (AChE) due to their α-effect nucleophilic reactivity. They have proved to be very efficient in promoting acyl, phosphoryl, and sulfuryl transfer processes [1–8]. AChE is a crucial enzyme in the human body [9–17]. It catalyzes the hydrolysis of the neurotransmitter acetylcholine and terminates the impulse transmission at cholinergic synapses. AChE is the key enzyme that is targeted by organophosphate chemical warfare agents (nerve agents), because acute toxin's organophosphate esters irreversibly inhibit AChE to form relatively stable phosphorylated OP–AChE adducts, leading to fatal toxic effects on the active site of the enzyme by forming a covalent bond to the serine hydroxy group oxygen. By inhibiting AChE, organophosphate esters disrupt the nervous system of a living organism, which causes the victim serious clinical complications including respiratory disorders, which leads ultimately to death [15]. Considerable attention has been directed toward detection and methods of the hydrolysis or decomposition of organophosphates and carboxylates due to their potential toxicity [5,9,12–14]. The complex of AChE and OP can be reversed by introducing AChE reactivators (called "oxime") into the system. Dissociated oximes were

Correspondence to: Kallol K. Ghosh; e-mail: kallolkghosh@yahoo.com.

shown to be able to restore organophosphate-inhibited AChE. Therefore, these compounds are known as reactivators of phosphorylated AChE. Reactivation of organophosphate-inhibited AChE by oximes is the primary reason for their effectiveness in the treatment of organophosphate, especially nerve agents poisoning. Recently, Buncel and coworkers [18] studied the reactivities of fenitrothion with a series of oximate α-nucleophiles with pK_a values ranging from 7.7 to 11.8. Quite recently, Kuca et al. [19] studied the structure–biological activity relationship for reactivators of tabun-inhibited AChE.

It is well known that micelles and similar colloidal assemblies generally increase the nucleophilic reactivity [20–25]. The structure and properties of surfactants play an important role in determining chemical reactivity. The objective of the present investigation is to evaluate the potency of monoximes (butane 2,3-dione monoxime, pralidoxime, acetaldoxime, α-benzoin oxime) and other oximes to cleave *p*-nitrophenyl acetate (PNPA) and *p*-nitrophenyl benzoate (PNPB).

EXPERIMENTAL SECTION

Materials

Butane 2,3-dione monoxime (BDMO), acetaldoxime, and α-benzoin oxime were procured from Sigma–Aldrich (St. Louis, MO). Pralidoxime and alkylchinolinium bromide surfactant were prepared in the laboratory of Dr. Kamil Kuca, Department of Toxicology, Faculty of Military Health Sciences, Trebesska, Czech Republic. PNPA and PNPB were purchased from s.d. fine-chem (Mumbai, India) and Lancaster (Newgate, Lancashire, UK), respectively. Cetyltriphenylphosphonium bromide ($C_{16}PPh_3Br$), cetyltributylphosphonium bromide (CTBuPBr), and cetyldimethylethanolammonium bromide (CDMEA) were obtained from the laboratory of Prof. R. M. Palepu, St. Francis Xavier University, Antigonish, NS, Canada. Surfactants such as cetyltrimethylammonium bromide (CTAB), cetylpyridinium bromide (CPB), and cetyldimethylethylammonium bromide (CDMEABr) used in the study were procured from Sigma. All solutions were prepared in triply distilled water.

Kinetics

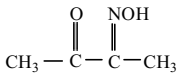
The reactions were studied spectrophotometrically with Varian Cary-50 spectrophotometer and Systronics (type-104) spectrophotometer by monitoring the appearance of the leaving *p*-nitrophenoxide at 400 nm at 27 $\pm$ 0.2°C. All of the kinetic experiments were performed at an ionic strength of 0.1 M (with KCl). Phosphate buffer was employed to control the pH of the media. All pH measurements were obtained using a Systronics pH meter. All reactions were conducted under pseudo-first-order conditions with the nucleophile in excess. For all of the kinetic runs, the absorbance/time result fits very well to the first-order rate equation.

$$\ln(A_\infty - A_t) = \ln(A_\infty - A_o) - kt \qquad (1)$$

The pseudo-first-order rate constants are determined by the method of least squares. Each experiment was repeated at least twice, and the observed rate constant was found to be reproducible within a precision of about 3% or better.

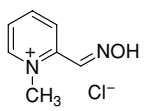
RESULTS AND DISCUSSION

First-order rate constants for the nucleophilic substitution reaction of PNPA and PNPB with a series of α-nucleophile oximates, that is, BDMO and pralidoximate (Scheme 1) and other oximates, have been



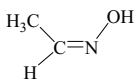
Butane 2,3 –dione monoxime (pK_a = 9.42)

(I)



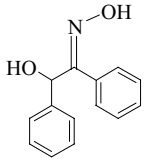
Pralidoxime (pK_a = 8.23)

(II)



Acetaldoxime (pK_a = 11.82)

(III)



α-Benzoin oxime (pK_a = 12.0)

(IV)

Scheme 1

Table I Kinetic Rate Data for the Reaction of PNPA and PNPB with and without Nucleophile in the Presence of CTBuPBr

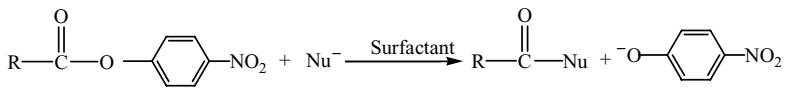
	$k_{obs}\cdot10^3$ (s^{-1})			
	PNPA		PNPB	
[CTBuBr](mM)	Without Nu^-	With Nu^-	Without Nu^-	With Nu^-
0	0.054	2.87	0.018	1.05
0.50	0.12	3.50	0.13	4.20
1.00	0.21	6.80	0.20	8.50
2.00	0.54	13.1	0.23	11.4
3.00	0.71	20.0	0.40	12.2
5.00	1.08	24.0	0.70	16.1
7.00	1.54	25.3	1.02	12.5
8.00	1.80	24.5	1.14	12.6
11.0	2.42	20.3	1.45	12.4
13.1	2.86	19.6	1.75	12.4
15.0	3.38	19.4	2.13	12.4
20.0	4.40	–	2.67	–
25.0	5.06	–	2.88	–

k^0_{obs} (PNPA) $= 0.054 \times 10^3$ (s^{-1}), k^0_{obs} (PNPB) $= 0.032 \times 10^3$ (s^{-1}).
Conditions: Temperature = 27°C, pH 8.0, [substrate] $= 0.5 \times 10^{-4}$M, [BDMO] $= 1.0 \times 10^{-3}$ M, $\mu = 0.1$ M KCl.

determined in pseudo-first-order condition, that is, nucleophiles in the large excess over the substrate in the presence and absence of CTBuPBr surfactant. The rate data have also been determined using CTBuPBr in the absence of nucleophile. The rate data for PNPA and PNPB using CTBuPBr in the absence and presence of nucleophile are presented in Table I. Observed rate constants for PNPA and PNPB increase monotonically with increasing surfactant concentration in the absence of Nu^-. As [surfactant] increases and micelles form, they dissolve premicellar assemblies and the rate surfactant profiles are then characteristic of micellar-assisted reactions. According to the data shown in Table I, under comparable conditions the k_{obs} values for hydrolysis of PNPA were found to be greater than those for hydrolysis of PNPB. Head group bulk in micelles or a high degree of organization in an assembly should reduce the availability of water from the surface of a colloid, and reaction rates should correspondingly increase. The effect of other oximates (pralidoxime, acetaldoxime, and α-benzoin oxime) on the hydrolysis of PNPA and PNPB is not very significant.

Effect of Surfactant Concentration in the Presence of Nucleophile

Table I summarizes the kinetic rate data for the reaction of PNPA and PNPB in the presence of CTBuPBr at different concentrations. It is shown that observed first-order rate constants increase sharply with increasing the concentration of surfactants in the reaction medium and then decreases smoothly upon further addition of surfactant in the presence of nucleophile. This dependence can be explained by considering that an increase in the surfactant concentration results in further incorporation of substrate into the micelles, where the oximate ions concentration is higher than that in the bulk phase since cationic micelles bind anionic nucleophiles. When the PNPA and PNPB molecules fully bound to the micelles, the process occurs wholly in the micellar pseudophase, and the observed rate constant reaches its maximum value. In the absence of α-nucleophile, the rate constant increases with surfactant concentration. The cationic surfactant favored the presence of OH^- at the micellar pseudophase.



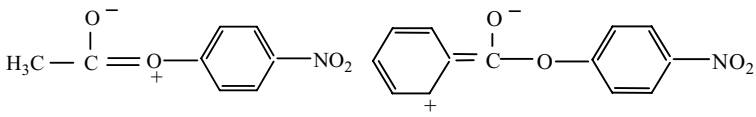
R = CH_3 *p*-nitrophenyl acetate (PNPA)

R = C_6H_5 *p*-nitrophenyl benzoate (PNPB)

The k_{obs} values of the nucleophilic substitution reactions obtained are characteristic of micellar-catalyzed reactions. The hydrophobic interaction of the substrate and the electrostatic attraction of the anionic nucleophile into the micelle is the factor that governed the rate enhancement. The hydrolytic reactivity of the PNPA and PNPB is expected to occur at the micellar interfacial region. The rate increases in the micellar medium due to the favorable electrostatic attraction of the positively charged surfaces of the cationic micelles with the negatively charged anions of oximes. This interaction not only allows tight binding of oximates on to the aggregate surfaces but also brings the catalyst closer to the substrate, which should be around the micellar interface due to the hydrophobic effect. Examination of Table I reveals that the effect of micelle on rate constants is more significant for the reactions of PNPB than the PNPA, although the PNPB is less reactive than the PNPA. The result is expected since PNPB would be more hydrophobic than PNPA.

The micellar catalysis involves incorporation of nucleophile into the micellar interface. The concentration of reactant in the micellar pseudophase can be calculated in terms of total volume of the Stern layer.

The nucleophilic attack occurs at the electrophilic centers (C=O). The center is modified by the attached group, R (CH_3 or C_6H_5). According to Um et al. [26], the contribution of resonance structures of acetate (V) and benzoate (VI) is more important for reactivity.



(V) (VI)

The resonance structure (VI), which is not possible for PNPA, is likely to be responsible for the decrease in reactivity of PNPB in nucleophilic substitution reaction with α-nucleophile [27,28].Thus, the replacement of the methyl group in PNPA by a phenyl group (PNPB) would cause a rate retardation owing to stabilization of the ground state in PNPB by the resonance (VI) and enhanced steric hindrance.

Effects of Head and Tail Groups on k_{obs} Values

There is little information on the effect of micellar structure of variation of head group. Table II summarizes the k_{obs} values for the nucleophilic reaction of PNPA and PNPB with BDMO in the presence of different surfactants having the same hydrophobic tail length but different head groups such as CTPPBr, CTBuPBr, cetyldimethylethanol ammonium bromide (CDMEA), CTAB, cetylpyridinium bromide (CPB), cetyldimethylethylammonium bromide (CDMEABr), and cetylchinolinium bromide (CCB) (Scheme 2). The argument that the variation of k_{obs} values of the reactions depends on the micellar structure can be further supported from the rate-surfactant profiles with varying hydrophobic tail length. The differences in catalytic efficiency depend on the head group structure and the extent to which the cationic head groups become less accessible to water rather than the overall micellar structure. Cationic micelles speed up the reaction in part, providing a reaction environment that is less polar than water. Rates of these reactions increase sharply with decreasing solvent polarity. Micellar rate enhancements increase as the cationic head group is made less polar. It appears from Table II that the bulky triphenyl groups, for example CTPPBr, tend to exclude water from the micellar surface and so assist the reaction significantly.

The hydrolysis of PNPA has also been studied under same conditions (temperature 27°C, pH 8.0, [PNPA] 1.0×10^{-4} M, [BDMO] 1.0×10^{-3}M, KCl 0.1 M), but in the presence of different cationic surfactants having same surfactant head group structure (Quinoline), but varying hydrophobic chain length (dodecyl chinolinium bromide C_{12}, tetradecyl chinolinium bromide C_{14}, and hexadecyl chinolinium bromide C_{16}). Table III summarizes the k_{obs} values for the nucleophilic reaction of PNPA with an oximate ion in micellar solutions of the same surfactant head group, but varying hydrophobic chain length surfactant (C_{12}–C_{16}). There is a decrease in the observed rate with a decrease in hydrophobic chain length for the same head group. This may be due to decreased space for accommodation of the substrate at the micellar surface, since decreased hydrophobic chain lengths correspond to a smaller micellar radius.

Reaction with Different Oxime-Based Nucleophiles

When pralidoxime, α-benzoin oxime, and acetaldoxime have been used as nucleophile for the hydrolysis of PNPA under pseudo-first-order conditions,

Table II Kinetic Rate Data for the Reaction of PNPA and PNPB with Butane 2,3-Dione Monoxime in the Presence of Different Surfactants

[Surfactant] (mM)	$k_{obs} \cdot 10^3$ (s^{-1})											
	CTPPBr (0.16 mM)		CTBuPBr (0.9 mM)		CDMEA (0.95 mM)		CTAB (0.96 mM)		CPB (0.95 mM)		CCB		CDMEABr (0.96 mM)	
	PNPA	PNPB	PNPA	PNPB	PNPA	PNPB	PNPA	PNPB	PNPA	PNPB	PNPA	PNPB	PNPA	PNPB
3	69.7	44.7	20.0	12.2	16.9	12.3	18.8	16.5	17.5	16.3	6.1	5.43	23.8	16.1
8	83.0	58.0	24.5	12.6	28.3	12.6	34.7	14.3	34.2	15.6	7.2	2.92	42.2	16.6
13	–	69.0	19.6	12.4	24.1	10.5	45.2	16.0	41.7	13.3	–	–	39.1	17.7

Conditions: Temperature = 27°C, pH 8.0, [substrate] = 0.5×10^{-4}M, [BDMO] = 1.0×10^{-3}M, μ = 0.1 M KCl, the cmc values are given in parenthesis. PNPB is in 1.6% MeCN–H_2O medium (v/v).

Table III Kinetic Rate Data for the Reaction of PNPA with Butane 2,3-Dione Monoxime in the Presence of Different Surfactants with Varying Chain Length

Surfactant	$k_{obs} \cdot 10^3$ (s^{-1})
Dodecyl chinolinium bromide	3.36
Tetradecyl chinolinium bromide	4.42
Hexadecyl chinolinium bromide	6.02

Temperature = 27°C, pH 8.0, [substrate] = 0.5×10^{-4} M, [BDMO] = 1.0×10^{-3} M, μ = 0.1 M KCl, [surfactant] = 5×10^{-3} M.

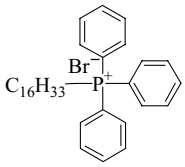
results show that α-benzoin oxime and acetaldoxime are not very effective, but pralidoxime shows more reactivity for the PNPA. Table IV summarizes the kinetic rate data for the reaction of PNPA and different oximes in the presence of CTBuPBr. Rate enhancement on addition of surfactant would be expected to be less significant for the oximate II compared with oximate I. This is because oximate I is anionic, whereas oximate II is zwitterionic. The electrostatic interaction between the cationic micelle and the anionic oximate I will be much larger than that between the cationic micelle and zwitterionic oximate II.

Application of the Pseudophase Model

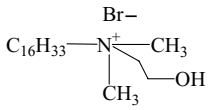
The quantitative treatment of micellar effects on the chemical reactivity was generally based on the generalization that aqueous micelles could be regarded as submicroscopic reaction media [29–33]. Reactants are distributed rapidly between water and micelles, which are regarded as distinct reaction regions [34–36], and the overall reaction rate is the sum of the rates in the water and micelles. Depending on the interaction of substrate into the micelle, the rate of reaction is accelerated or inhibited. The rate effects of aqueous micelles can be analyzed by the pseudophase model, where substrate, S, reacts in the aqueous or micellar pseudophase designated by the subscripts w and m, respectively. The first-order rate constants for the reaction will follow Eq. (2).

$$k_{obs} = \frac{k'_w + k'_m K_s[D]}{1 + K_s[D]} \quad (2)$$

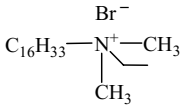
where k'_w and k'_m are the first-order rate constants and K_S is the binding constant of S to micellized surfactant, D, whose concentration is taken as the total concentration less the critical micelle concentration (cmc) under kinetic conditions. Simulated rate-surfactant profiles for the reaction of PNPA and PNPB in the presence of CTBuPBr micellar solutions are shown in Fig. 1.



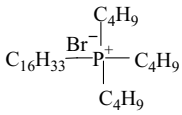
Cetyltriphenylphosphonium bromide (CTPPBr)



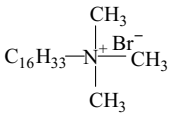
Cetyldimethylethanol ammonium bromide (CDMEA)



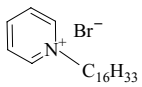
Cetyldimethylethyl ammonium bromide (CDMEABr)



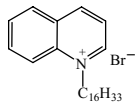
Cetyltributylphosphonium bromide (CTBuPBr)



Cetyltrimethylammonium bromide (CTAB)



Cetylpyridinium bromide (CPB)



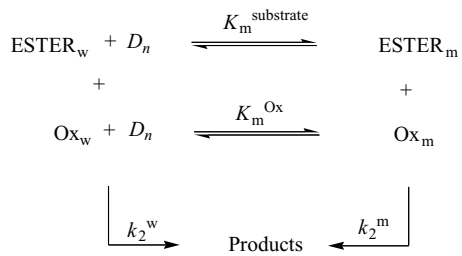
Cetylchinolinium bromide (CCB)

Scheme 2

The influence of cetyltributylphosphonium bromide micelles on the k_{obs} values for the nucleophilic bimolecular reactions of PNPA and PNPB with oximate ions can be described as illustrated in Scheme 3.

In Scheme 3, subscripts w and m indicate aqueous and micellar pseudophases, respectively, and D_n represents the micellized surfactant, that is, $[D_n] = [D]_T -$ cmc, where $[D]_T$ is the stoichiometric surfactant concentration and cmc is the critical micellar concentration, obtained under the experimental conditions as the minimum surfactant concentration required to observe any kinetic effect.

Scheme 3 considers the distribution of PNPA and PNPB between the aqueous and micellar pseudophases, K_m^{PNPA} and K_m^{PNPB}. The association constants of PNPA and PNPB have been obtained from fitting the reaction data with the values of $K_m^{PNPA} = 17.1 \pm 1.0\ M^{-1}$ and $K_m^{PNPB} = 13.2 \pm 1.7\ M^{-1}$ in micelles.



Scheme 3

$$k_{obs} = \frac{k_2^w + \frac{k_2^m}{\bar{V}} K_m^{ESTER} K_m^{Ox} [D_n]}{\left(1 + K_m^{ESTER}[D_n]\right)\left(1 + K_m^{Ox}[D_n]\right)} [Ox]_T \quad (3)$$

The first-order rate constants for the reaction will follow Eq. (3), where k_2^w is the second-order rate constant in the aqueous phase and k_2^m is the second-order rate constant in the micellar phase. The experimental data were fitted to the model to estimate the best value of K_m^{ESTER} and K_m^{Nu}. Table V shows the calculated parameters that explain the experimental results. Although the rate surfactant profiles in the presence of nucleophiles would be fitted to the model, the derived kinetic parameters were not very satisfactory. The effect of surfactant concentration on the k_{obs} value is shown in Fig. 2.

The distribution of the oximate ion, Ox^-, between both pseudophases is considered through the distribution constant K_m^{Ox}. 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 the absence of the surfactant. We assume $\bar{V}$ is equal to the partial molar volume of the interfacial reaction region in the micellar pseudophase, determined by Bunton et al. [37] as $0.14\ dm^3\ mol^{-1}$. Micellar binding of both substrates, PNPA and PNPB and oximate ions, Ox^-, is governed

Table IV Kinetic Rate Data for the Reaction of PNPA and Different Oximes in Presence of CTBuPBr

	$k_{obs} \cdot 10^3$ (s^{-1})		
[CTBuPBr] (mM)	Pralidoxime	α-Benzoinoxime	Acetaldoxime
0	4.33	0.11	0.08
3	7.90	3.88	0.23
5	9.20	4.95	0.24
8	12.3	2.46	0.23
11	12.2	–	–
13	12.0	–	–
15	10.5	–	–

Temperature = 27°C, pH 8.0, [substrate] = 0.5×10^{-4} M, [Nu^-] = 1.0×10^{-3} M, μ = 0.1 M KCl.

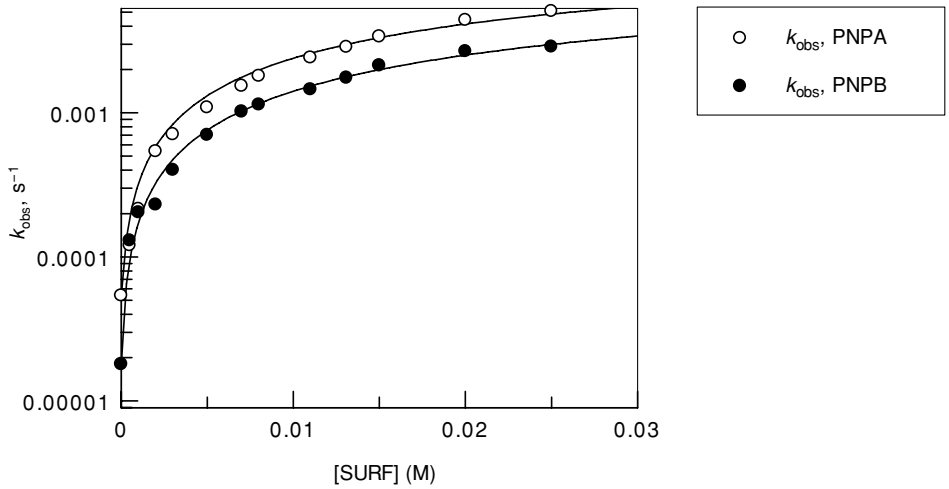


Figure 1 Simulated rate-surfactant profiles for the reaction of PNPA and PNPB in CTBuPBr micellar solutions (solid lines are predicted values with the model).

by hydrophobic interactions, and the equilibrium constants K_m^{PNPA},K_m^{PNPB}, and K_m^{Ox} are expressed by referring these concentrations to the total volume of the micelle.

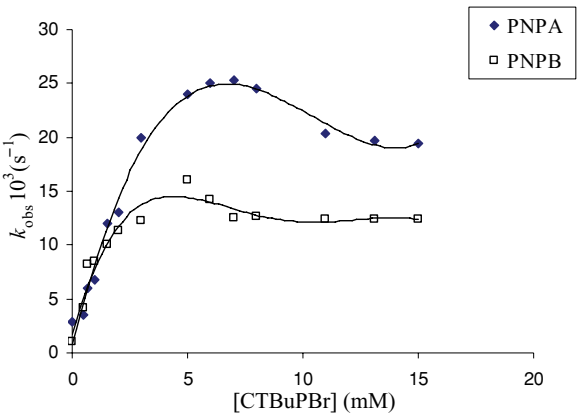


Figure 2 Rate-surfactant concentration profile for the reaction of PNPA and PNPB with butane 2,3-dione monoxime in CTBuPBr (the curves are predicted).

Table V Kinetic Parameters Obtained by Applying Pseudophase Model for the Nucleophilic Reaction of PNPA and PNPB with Oximate Ions in the Presence of CTBuPBr Micelles

	PNPA	PNPB
k_2^w ($M^{-1}s^{-1}$)	48.60	17.79
K_m^{PNPA} (M^{-1})	17.1	13.2
K_m^{Nu} (M^{-1})	325	325
k_2^m ($M^{-1}s^{-1}$)	4.72	3.79

CONCLUSION

An important objective of this study was to determine the kinetic efficiencies of oxime-based α-nucleophiles for the cleavage of carboxylic ester. BDMO and pralidoxime both have been very effective deacylating agents, and these can be used as a reactivator of AChE. In comparison to pralidoxime and other oximes,

BDMO appears to be the most potential nucleophilic agents for the cleavage of PNPA.

The authors are grateful to Prof. Rama Pande, Head, School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur (C.G.), India, for providing laboratory facilities. The synthesis of the detergents was supported by the project OPUOFVZ 200603.

BIBLIOGRAPHY

1. Wang, J.; Gu, J.; Leszynski, J.; Feliks, M.; Andrzej, W. J Phys Chem 2007, 111, 2404–2408.
2. Antonijevic, B.; Stojilkovic, M. P. Clin Med Res, 2007, 5, 71–82.
3. Ghosh, K. K.; Kolay, S.; Satnami, M. L.; Moore, S.; Palepu, R. M. J. Dispersion Sci Technol 2007, 28, 213–218.
4. Radic, B.; Vrdoljak, A. L.; Zelezic, D.; Fuchs, N.; Berend, S., Kopjar, N. Acta Biochim Pol 2007, 54, 583–593.
5. Kassa, J.; Kuca, K.; Cabal, J., Paur, M. J Toxicol Environ Health 2006, 69, 1875–1882.
6. Picha, J.; Cibulka, R.; Hamal, F.; Liska, F.; Parik, P.; Pytela, O. Collect Chem Commun 2004, 69, 397–413.
7. Eddleston, M.; Szinicz, L.; Eyer, P.; Buckley, N. Q J Med 2002, 95, 275–283.
8. Buncel, E.; Cannes, C.; Chatrousse, A. P.; Terrier, F. J Am Chem Soc 2002, 124, 8766,8767.
9. Jun, D.; Kuca, K.; Cabal, J.; Bartoova, L.; Kunesova, G., Kassa, J. Chem-Biol Interact 2005, 157, 385–387.
10. Worek, F.; Thiermann, H.; Szinicz, L. Arch Toxicol 2004, 78, 212–217.
11. Su, C. T.; Wang, H.; FeLiu, R.; Shin, J. H.; Ma, C.; Lin, C. H.; Liu, C. Y.; Wu, M. T. Toxicol Sci 1986, 6, 506–515.
12. Kuca, K.; Jun, D.; Cabal, J.; Hrabinova, M.; Bartosova, L.; Opletalova, V. Basic Clin Pharmacol Toxicol 2006, 98, 389–394.
13. Kuca, K.; Musilek, K.; Paar, M.; Jun, D.; Stodulka, P.; Harbinova, M.; Marek, J. Molecules 2007, 12, 1964–1972.
14. Patocka, J.; Cabal, J.; Kuca, K. Jun, D. J Appl Biomed 2005, 3, 91–99.
15. Bajgar, J. Adv Clin Chem 2004, 38, 151–216.
16. Bajgar, J. J Med Chem Def 2004, 1, 1–16.
17. Kuca, K.; Bielavsky, J.; Cabal, J.; Bielavska, M. Tetrahedron Lett 2003, 44, 3123–3125.
18. Han, X.; Balakrishnan, V. K.; vanLoon, G. W.; Buncel, E. Langmuir 2006, 22, 9009.
19. Kuca, K.; Jun, D.; Musilek, K.; Bajgar, J. Front Drug Des Discovery: Struct-Based Drug Des 21st Century 2007, 3, 381–394.
20. Han, X.; Balakrishnan, V. K.; vanLoon, G. W., Buncel, E. Langmuir 2007, 23, 6519.
21. Simanenko, Y. S.; Prokop'eva, T. M.; Bunton, C. A.; Savelova, V. A.; Turovskaya, M. K.; Karpichev, E. A.; Mikhailov, V. A., Popov, A. F. Theor Exp Chem 2002, 37, 288.
22. Ghosh, K. K.; Vaidya, J.; Satnami, M. L. Int J Chem Kinet 2005, 38, 26–31.
23. Coudrec, S.; Toullec, J. Langmuir 2001, 17, 3819–3828.
24. Fendler, J. H. Pure Appl Chem 1982, 54, 1809.
25. Dwars, T; Paetzold, E.; Oehme, G. Angew Chem, Int Ed 2005, 44, 7174.
26. Um, I. H.; Lee, J. Y.; Bac, S. Y.; Buncel, E. Can J Chem 2005, 83, 1365.
27. Um, I. H.; Kim, K. H.; Park, H. R.; Fujio, M.; Tsuno, J. J Org Chem 2004, 69, 3937.
28. Um, I. H.; Han, H. J.; Ahn, J. A.; Kang, S.; Buncel, E. J Org Chem 2002, 67, 8475.
29. Romsted, L. S.; Cordes, E. H. J Am Chem Soc 1968, 90, 4404.
30. Romsted, L. S.; Bunton, C. A., Yao, J. Curr Opin Colloid Surf Sci 1997, 2, 622.
31. Bunton, C. A. Arch Biol Med Exp 1988, 21, 9.
32. Bunton, C. A.; Nome, F.; Quina, F. H.; Romsted, L. S. Acc Chem Res 1991, 24, 357.
33. Funaski, N. J.; Murata, A. Chem. Pharm. Bull 1980, 28, 805.
34. Bunton, C. A.; Moffatt, J. R. J Phys. Chem 1986, 90, 538.
35. Bunton, C. A.; Moffatt, J. R. J Phys Chem 1988, 92, 2896.
36. Quina, F. H., Chaimovich, H. J Phys Chem 1979, 83, 1844.
37. Bunton, C. A.; Carrasco, N.; Huang, S. K.; Paik, C. H.; Romsted, L. S. J Am Chem Soc 1978, 100, 5420–5425.