should not show any dependence on the concentration of olefin. The absence of any effect of molecular oxygen, which should trap atomic sulfur competitively,[19] on the yield of the reaction also disfavors elemental sulfur as reactive agent in this reaction. These results strongly argue for either **8** or **9** as genuinely novel species, capable of episulfidation of olefins. Based on these results, we envision the following mechanism: Reactive **8** and/or **9** is formed in the rate-determining step from the *N*-oxide **1** and CS_2 via the covalent intermediate **3**;[3] the subsequent bimolecular reaction of **8** and/or **9** with the olefin then competes inefficiently with a rapid monomolecular decomposition of **8**/**9** with a low energy of activation,[15] thus giving only low yields of thiirane. Therefore, this reaction could only be synthetically useful if a large excess of olefin can be employed.

Acknowledgment. M.F.Z. expresses appreciation to the BASF AG of West Germany for a postdoctoral fellowship. This work was supported by a grant from The National Institutes of Health.

---

(17) Strausz, O. P. *Adv. Chem. Ser.* **1972**, *110*, 137.

(18) Davis, D. D.; Klemm, R. B. *Int. J. Chem. Kinet.* **1973**, *5*, 841.

(19) Davis, D. D.; Klemm, R. B.; Pilling, M. *Int. J. Chem. Kinet.* **1972**, *4*, 367.

Hydrolysis of 2,4-Dinitrophenyl Phosphate in Hydrophobic Ammonium Salts

Clifford A. Bunton* and Clifford Quan

Department of Chemistry, University of California,
Santa Barbara, California 93106

Received December 3, 1984

Spontaneous hydrolyses of dinitrophenyl phosphate dianions involve spontaneous breaking of the P–O bond, giving dinitrophenoxide and metaphosphate ion.[1] The metaphosphate ion reacts rapidly with nucleophiles, and this reaction occurs before the partner ions have completely separated.[2]

$$(NO_2)_2C_6H_3OPO_3^{2-} \rightarrow (NO_2)_2C_6H_3O^-PO_3^- \rightarrow P_i$$

Aqueous solutions of micellized cationic surfactants speed decomposition of dinitrophenyl phosphate dianions,[3] although the rate of the corresponding reaction of the monoanion is not affected. This micellar rate enhancement is akin to a submicroscopic solvent effect and in the absence of micelles reaction is speeded by organic solvents.[1] Rates of spontaneous dephosphorylations and decarboxylations[4] increase as the polarity of the solvent is decreased, and micellar polarities, as given by the apparent dielectric constant, or *Z* value, are lower than those of water.[5]

Hydrophobic quaternary ammonium ions containing the tri-*n*-octyl group do not form micelles, but they effectively speed attack by hydrophobic nucleophilic anions.[6,7] These hydrophobic ions can be functionalized with hydroxyl and oxime groups which are effective nucleophiles at high pH,[8] and the overall rate effects are similar to those of cationic micelles, although the magnitude of the rate increases may differ.

Table I. Interaction of 2,4-Dinitrophenoxide Ion with 2a

10^3[**2a**], M	A^a
	0.140
0.5	0.155
0.8	0.164
1.0	0.172
2.0	0.219

[a] Absorbance at 365 nm with 7×10^{-6} M 2,4-dinitrophenol at pH 10 in H_2O/MeCN (95:5 v/v).

Table II. Hydrolysis of 2,4-DNPP in 1[a]

10^3[1], M	10^4k_ψ, s^{-1}	10^3[1], M	10^4k_ψ, s^{-1}
	0.08[b]	3.0	3.2
0.5	4.5	5.0	5.0[c]
0.8	5.2	6.0	5.5[c]
1.0	3.1	7.0	3.8[c]
2.0	4.0	8.0	4.2[c]

[a] At 25.0 °C with 5×10^{-6} M 2,4-DNPP (lutidinium salt) and 10^{-3} M KOH. [b] Reference 1b. [c] Turbid solutions.

Decarboxylation of 5-nitrobenzisoxazole carboxylate ion is speeded by cationic micelles,[9] and (nonmicellizing) tri-*n*-octylmethylammonium chloride also markedly speeds decarboxylation.[10] In the present work we examined rates of spontaneous dephosphorylation of the dianion of 2,4-dinitrophenyl phosphate (2,4-DNPP) in solutions of hydrophobic ammonium ions and compared the reaction rates with those in cationic micelles.[3] The ammonium salts were tri-*n*-octylethylammonium mesylate (**1**) and tri-*n*-octyl(2-hydroxyethyl)ammonium mesylate and bromide (**2a** and **2b**, respectively) which give nucleophilic alkoxide zwitterion **3** at high pH.[8]

$$\underset{\mathbf{2}}{(C_8H_{17})_3N^+CH_2CH_2OH} \rightleftarrows \underset{\mathbf{3}}{(C_8H_{17})_3{}^+NCH_2CH_2O^-} + H^+$$

These salts, which are also phase-transfer catalysts, are only sparingly soluble in water,[6,7] and it is sometimes desirable to increase their solubility by addition of acetonitrile.

Experimental Section

Materials. 2,4-Dinitrophenyl phosphate was prepared as the lutidinium salt, mp 141–142 °C (lit. mp 142 °C) by the method of Rawji and Milburn.[11] It was converted into the acid form by treatment with Dowex 50W-X 8 resin. The hydrophobic ammonium salts were prepared by methods described elsewhere.[7,8] Solvents were purified by standard methods.

Kinetics. Formation of 2,4-dinitrophenoxide ion was followed spectrophotometrically at 358 nm in Gilford or Beckman spectrophotometers at 25.0 °C following standard methods.[1,3] [Substrate] was ca. 7×10^{-6} M. The first-order rate constants, k_ψ, are in reciprocal seconds.

Interactions with Aryloxide Ions. The absorbance of 7×10^{-6} M 2,4-dinitrophenoxide ion in H_2O/MeCN (95:5 v/v) at pH 10 increase with increasing [**2a**] (Table I). There is no effect of **2a** if the water content of the solvent is less than 90%, cf. ref 6.

---

(1) (a) Kirby, A. J.; Varvoglis, A. G. *J. Am. Chem. Soc.* **1967**, *89*, 415. (b) Bunton, C. A.; Fendler, E. J.; Fendler, J. H. *Ibid.* **1967**, *89*, 1221.

(2) Buchwald, S. L.; Knowles, J. R. *J. Am. Chem. Soc.* **1982**, 104, 1438.

(3) (a) Bunton, C. A.; Fendler, E. J.; Sepulveda, L.; Yang, K.-U. *J. Am. Chem. Soc.* **1968**, *90*, 5512. (b) Buist, G. J.; Bunton, C. A.; Robinson, L.; Sepulveda, L.; Stam, M. *Ibid.* **1970**, *92*, 4072. (c) Bunton, C. A.; Diaz, S.; Hellyer, J. M.; Ihara, Y.; Ionescu, L. G. *J. Org. Chem.* **1975**, *40*, 2313.

(4) Kemp, D. S.; Paul, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 7305.

(5) (a) Cordes, E. H.; Gitler, C. *Prog. Bioorg. Chem.* **1973**, *2*, 1. (b) Mukerjee, P. In "Solution Chemistry of Surfactants;" Mittal, K. L., Ed.; Plenum Press, New York, 1979; Vol. 1, p 723.

(6) Kunitake, T.; Okahata, Y.; Sakamoto, T. *J. Am. Chem. Soc.* **1976**, *98*, 7799.

(7) Bunton, C. A.; Hong, Y. S.; Romsted, L. S.; Quan, C. *J. Am. Chem. Soc.* **1981**, *103*, 5784, 5788.

(8) Biresaw, G.; Bunton, C. A.; Quan, C. Yang, Z.-Y. *J. Am. Chem. Soc.* **1984**, *106*, 7178.

(9) Bunton, C. A.; Minch, M. J.; Hidalgo, J.; Sepulveda, L. *J. Am. Chem. Soc.* **1973**, *95*, 3262.

(10) Kunitake, T.; Okahata, Y.; Ando, R.; Shinkai, S.; Hirakawa, S. *J. Am. Chem. Soc.* **1980**, *102*, 7877.

(11) Rawji, G.; Milburn, R. M. *J. Org. Chem.* **1981**, *46*, 1205.

0022-3263/85/1950-3230$01.50/0

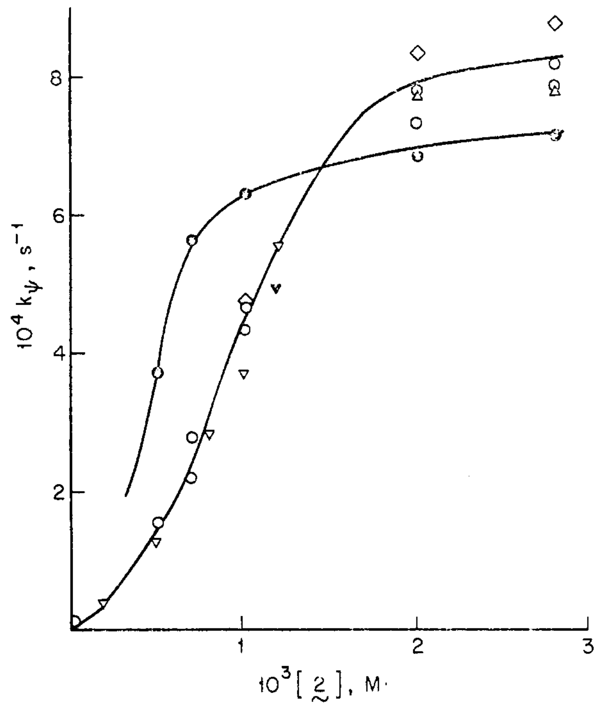

Figure 1. Hydrolysis of 2,4-DNPP (7×10^{-6} M and pH 10) in H_2O/MeCN (95:5 v/v) and **2a** (○); with 7×10^{-6} M 2,6-lutidine, (◇); with 3×10^{-6} 2,4-dinitrophenol (△); substrate added as free acid (●). In the presence of **2b**, with and without 3×10^{-6} M 2,4-dinitrophenol, ▼ and ▽, respectively.

Other aryloxide ions (2×10^{-5} M) interact with the bromide salt **2b**, 2×10^{-3} M in aqueous 10^{-3} M NaOH. The parent phenols were *p*-cyanophenol, *o*- and *p*-nitrophenol, and picric acid, and precipitates formed which could be removed by centrifugation, with *p*-nitrophenol. There appeared to be no precipitation in H_2O/MeCN (80:20 v/v), and all the precipitates dissolved in H_2O/MeCN (50:50 v/v).

Results and Discussion

At pH 10 (NaOH), in the absence of 1 or 2, small amounts of MeCN slightly increase k_ψ. At 25.0 °C the values of $10^6 k_\psi$, s^{-1} are 8.0, 9.6, 12.0, and 12.0 in 100, 95, 90, and 80 vol % H_2O, respectively, in agreement with earlier results.[1] Reaction of 2,4-DNPP dianion is speeded by dilute aqueous 1 (Table II). The rate constants, k_ψ, appear to become constant at higher [1], but the data are scattered and the solutions become turbid as 2,4-dinitrophenoxide ion is formed. The rate is increased by a factor of ca. 50 over that in water, which is larger than that found with micellized cetyltrimethylammonium bromide.[3a] In addition the value of $k_\psi \sim 5 \times 10^{-4}$ s^{-1} (Table II) may be limited by the low solubility of 1, and it may not represent the reactivity of fully bound substrate. This limit can readily be reached with cationic micelles.[3] The rate appears to be increased slightly by an increase in [NaOH] but the increase is by no more than 10% in 0.015 M NaOH, and some of the solutions were turbid. Added NaOH has little effect upon the rate of hydrolysis of 2,4-DNPP in cationic micelles.[3]

Reaction of 2,4-DNPP dianion in solutions of the functionalized ammonium salt (**2a**) gives no 2,4-dinitrophenyl ether, which excludes attack upon the aryl group.[3c] Reactions were followed in aqueous MeCN because solutions in water were turbid. A few experiments were made in H_2O/MeCN (95:5 v/v) where rate enhancements were very similar to those in aqueous solutions of the nonfunctional ion 1 (Figure 1 and Table II), but above 3×10^{-3} M 2, values of k_ψ decreased, probably because of formation of fine precipitates. Most of the experiments were made with the lutidinium salt of 2,4-DNPP in 10^{-4} M NaOH, and variation of k_ψ with [**2a**] was slightly different when 2,4-DNPP was added as acid (7×10^{-6} M) with 10^{-4} M NaOH.

The difference is most pronounced for reaction in H_2O/MeCN (95:5 v/v) with dilute **2a** under conditions in which substrate is only partially bound. It appears that under these conditions very small amounts of 2,6-lutidine change the extent of distribution of substrate between water and the hydrophobic ammonium ions (Figure 1). Addition of further lutidine has little effect, but under conditions in which the substrate is fully bound 2,6-lutidine speeds reaction modestly (Figure 1 and Table III).

Table III. Hydrolysis of 2,4-DNPP in 2a[a]

	H_2O vol %	
10^2[**2a**], M	10	20
0.1	1.71	0.41
0.4	1.94 (2.30)	
0.5	2.00 (2.32)	0.70
0.6	2.00 (2.35)	
0.7	2.16	
0.8	2.29	
0.9	2.29	
1.0	2.34	1.80 (1.17)
1.1	2.37	
3.0		1.70 (1.50)
5.0		1.90
7.0		2.11 (1.91)
9.0		2.34

[a] Values of 10^4 k_ψ, s^{-1}, for 2,4-DNPP added as lutidinium salt with 10^{-4} M NaOH. Values in parentheses are for 7×10^{-6} M 2,4-DNPP added as acid.

Table IV. Effect of NaOH on Reaction in 2a[a]

	H_2O vol %	
10^2[NaOH], M	95[b]	90[c]
0.01	7.8	2.16
0.05	9.3	2.27
0.07	10.7	2.32
0.1		2.74
0.3	9.7	
0.5	10.8	2.87
0.7		3.15
1.0		3.10[d]
1.4		3.50
1.8		4.05
2.0		4.12[e]
2.2		4.16
2.6		4.16
3.0		4.15
3.4		3.94

[a] Values of $10^4 k_\psi$, s^{-1} at 25.0 °C. [b] 2×10^{-3} M **2a**. [c] 7×10^{-3} M **2a**. [d] With 0.005, 0.01, and 0.02 M NaOMs $10^4 k_\psi$ = 3.38, 3.51, and 3.73 s^{-1}, respectively. [e] With 0.005 and 0.01 M NaOMs $10^4 k_\psi$ = 4.16 and 4.86 s^{-1}, respectively.

Addition of 2,4-dinitrophenol or replacement of mesylate counterion by bromide has little effect on k_ψ within the scatter of the data (Figure 1). As for reactions in micellizing surfactant, values of k_ψ in dilute amphiphile are sensitive to factors which change the extent of substrate binding either directly or by changing aggregation of the amphiphile.[1a,7]

We were able to use more concentrated **2a** in solutions containing 10 and 20 vol % MeCN (Table III) but the rate enhancements were decreased by the organic solvent. The rate constants tended toward limiting values, which were similar in the two solvents, although addition of MeCN increased the concentration of **2a** needed to approach these limits (Table III).

Addition of NaOH increases the reaction rate (Table IV). The hydroxy group of **2** is deprotonated at high pH to give nucleophilic alkoxide zwitterion which is reactive toward 2,4-dinitrochlorobenzene, and phosphate di- and triesters.[8] But nucleophilic attack does not seem to be of major importance because there was no ether in the products and addition of sodium mesylate also slightly increases reaction rate (Table IV). It is therefore probable that electrolytes such as NaOH and sodium mesylate speed reaction in solutions of **2a** by increasing the binding of substrate to ammonium ion and perhaps by promoting the growth of clusters of ammonium ions. Both substrate binding and chemical reactivity should increase with increasing cluster size. Deprotonation of **2** generates a zwitterion which should aggregate much more readily than the ammonium ion.

In the absence of ammonium ions addition of MeCN speeds reaction of 2,4-DNPP dianion, and the decrease of k_ψ in solutions of **2a** on addition of MeCN is typical of reactions mediated by micelles[5a,12] or hydrophobic ammonium ions.[8] For nonionic substrates the adverse solvent effect can be ascribed to an increase in solubility of the substrate in the bulk, aqueous phase, as well as to a breaking up of micelles or similar aggregates by disruption of the water structure. Substrate solubility should not be a factor for reactions of 2,4-DNPP, so the main effect of MeCN appears to be the breaking up of the aggregates.

Tri-*n*-octylammonium salts are surface active but they do not micellize; for example, they do not show a critical micelle concentration.[6] Nonetheless they bind nonionic and ionic hydrophobic solutes and, like micelles, they can change rate and equilibrium constants.[6,8] The overall rate enhancements of bimolecular reactions are often larger than those observed with micelles, but this is a consequence of high local concentration of reactants in small aggregates and for reactions in both functional and nonfunctional aggregates of **1** and **2**, for example, second-order rates *in* the aggregate are very similar to those in a micelle.[7,8]

The aryl group of 2,4-DNPP dianion is not attacked by alkoxide ion derived from a hydroxyethyl functionalized micelle, which behaves in that respect like **2a**.[3c] Nucleophilic primary and secondary amines attack the aryl group in water and in aqueous micelles,[3c] but tertiary amines weakly catalyze hydrolysis of 2,4-DNPP dianion in both water and aqueous cationic micelles, by forming a phosphoramidate,[13,15] and the small rate enhancement by 2,6-lutidine (Fig. 1) may have a similar origin.

Addition of aryloxide ion to CTABr decreases the micellar rate enhancement of hydrolyses of dinitrophenyl phosphate dianions by competing for the micelle,[3a] and the small rate decrease on addition of 2,4-dinitrophenoxide ion (Figure 1) may be due to competition. However, this explanation is suspect because mesylate ion does not inhibit reaction.

Micelles have well-defined structures which are not markedly perturbed by addition of small amounts of solutes,[5,14] but structures of small aggregates of **1** or **2** are probably very sensitive to even low concentrations of solutes which may bind to them.

The rate enhancements by the hydrophobic ammonium salts (Figure 1 and Tables II and III) are larger than found with micelles of cetyltrimethylammonium bromide or (2-hydroxyethyl)hexadecyldimethylammonium bromide where rates are increased by factors of ca. 25- and 35-fold, respectively,[3] but the rate enhancement by micellized cetylpyridinium chloride is by a factor of 50[15] and is similar to that by **1**. The highest values of k_ψ for hydrolysis in solutions of the ammonium salts **1** and **2** may not correspond to complete binding of substrate (Figure 1 and Tables II and III) but rate enhancement by **2** in 95% H_2O is more than twice that given by cationic micelles in water.[3]

The transition state for hydrolysis of dianionic 2,4-DNPP has considerable aryloxide character[1-3] and it should be stabilized by interaction with the head groups of cationic micelles or hydrophobic ammonium salts. There is extensive charge neutralization by micellar-bound counterions, and the fractional micellar charge is typically in the range 0.2–0.4,[16] but this neutralization seems to be much less important with nonmicellizing ammonium ions,[7] which should therefore be more able to stabilize an aryloxide-like transition state. The strong interactions between hydrophobic ammonium ions and charge-delocalized organic anions (Table I and ref 6 and 7) are consistent with this explanation of the rate enhancement.

Acknowledgment. Support of this work by the U.S. Army Office of Research is gratefully acknowledged.

Registry No. **1**, 79054-30-1; **2a**, 92642-02-9; **2b**, 92642-00-7; 2,4-dinitrophenyl phosphate dianion, 18962-96-4.

---

(12) Bunton, C. A.; Robinson, L. *J. Am. Chem. Soc.* **1968**, *90*, 5972.

(13) Kirby, A. J.; Varvoglis, A. G. *J. Chem. Soc. B* **1968**, 135.

(14) Fendler, J. H. "Membrane Minetic Chemistry", Wiley-Interscience: New York, 1982.

(15) Dorwin, E., unpublished results.

(16) Romsted, L. S. In "Micellization, Solubilization and Microemulsions"; Mittal, K. L., Ed.; Plenum Press: New York, 1977; Vol. 2, p 509. Anacker, E. W. In "Solution Chemistry of Surfactants"; Mittal, K. L., Ed.; Plenum Press: New York, 1979; Vol. 1, p 247.

Acidity Measurements on Pyridines in Tetrahydrofuran Using Lithiated Silylamines

Robert R. Fraser,* Tarek S. Mansour, and Sylvain Savard

Ottawa-Carleton Chemistry Institute, University of Ottawa, Ottawa, Canada K1N 9B4

Received January 25, 1985

We have recently reported the measurement of acidities of a variety of carbon acids in tetrahydrofuran using lithiated diisopropylamine (LDA) and lithiated 2,2,6,6-tetramethylpiperidine (LTMP) as the strong bases.[1,2] In addition several new lithiated amides have been synthesized which showed enhanced basicity when the nitrogen was more hindered and lesser basicity when silicon replaced the carbon attached to nitrogen.[3] For example, in comparison with diisopropylamine (DA) pK = 35.7, the acidities of isopropyl(trimethylsilyl)amine and bis(trimethylsilyl)amine (BTSA) were reported to be 31.4 and 29.5, respectively. In the present paper we wish to describe acidity measurements on alkylated pyridines using these amines. These studies have revealed an error[4] in the reported pK value for BTSA. The true value is actually much lower at 25.8 pK units. Fortunately, this greater acidity of BTSA now allows the measurement of pK's as low as 24 or less. Two such measurements on fluorene are described. The measurement of the acidity of *N*-isopropyl cyclohexylimine (pK = 31.3) adds to the THF scale 15 imines whose relative pK's were reported earlier.[5]

Method of pK Measurement. As in our earlier studies we have used ^{13}C NMR to measure the relative concentrations of all four species in the equilibrium, (1). By use

$$R_3CH + LiNR'_2 \rightleftharpoons R_3CLi + HNR'_2 \qquad (1)$$

of the value for K in (1), the determination of acidities of α-, β-, and γ-picoline was readily accomplished.[6] However, for the three benzylpyridines (2BP, 3BP, and 4BP) a new problem arose in that no suitable amine was available for the measurement of pK in the range 27–29. (Our initial report of a pK of 29.5 for BTSA, based on an erroneous peak assignment, had led us to conclude that BTSA was partly deprotonated by lithiated isopropyl(trimethylsilyl)amine.[3] The error emerged when we subsequently observed complete deprotonation of BTSA by the less basic lithiated *n*-propyl(trimethylsilyl)amine, pK = 30.9.) To serve as a reference in this region, we first found benzhydryl phenyl sulfide to be suitable, having a pK of 28.7 vs. 3BP. Since the equilibrium measurement used to obtain this pK involved two-carbon acids while all previous pK's have been derived from measurements involving a carbon and a nitrogen acid, the question arises as to the influence of differential solvation or aggregation effects in the two methods. To probe this question we examined this acidity of 3BP vs. xanthene and the acidity of each carbon acid as measured against isopropyl(trimethylsilyl)amine. As the data in Table I show, the value for the pK of 3BP vs. xanthene agrees well with their values as determined against the amine, indicating the absence of a "partner"

---

(1) Fraser, R. R.; Bresse, M.; Mansour, T. S. *J. Chem. Soc., Chem. Commun.* **1983**, 620.

(2) Fraser, R. R.; Bresse, M.; Mansour, T. S. *J. Am. Chem. Soc.* **1983**, *105*, 7790.

(3) Fraser, R. R.; Mansour, T. S. *J. Org. Chem.* **1984**, *49*, 3442.

(4) Fraser, R. R.; Mansour, T. S. *J. Org. Chem.* **1984**, *49*, 5284.

(5) Fraser, R. R.; Bresse, M.; Chuaqui-Offermanns, N.; Houk, K. N.; Rondan, N. G. *Can. J. Chem.* **1983**, *61*, 2729.

(6) For the most recent comprehensive review, see: Streitweiser, A., Jr.; Juaristi, E.; Nebenzahl, L. L. In "Comprehensive Carbanion Chemistry"; Buncel, E., Durst, T., Eds.; Elsevier-North Holland: Amsterdam, 1980; Part A, p 323.

0022-3263/85/1950-3232$01.50/0