Reaction of Thiophenoxides with Nitro- and Halo-Substituted Phthalic Anhydrides

F. J. Williams* and P. E. Donahue

General Electric Research and Development Center, Schenectady, New York 12301

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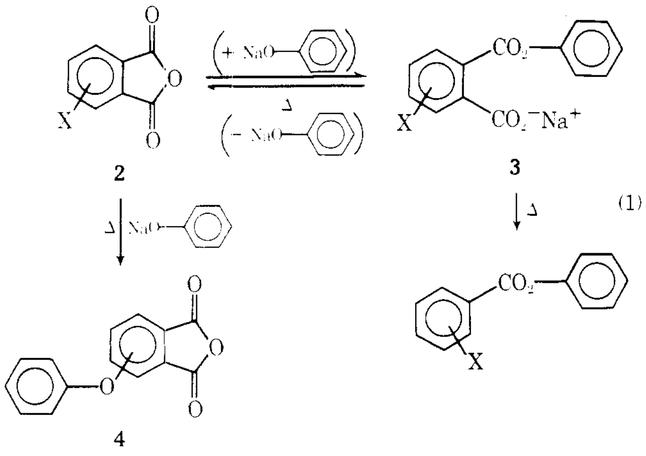
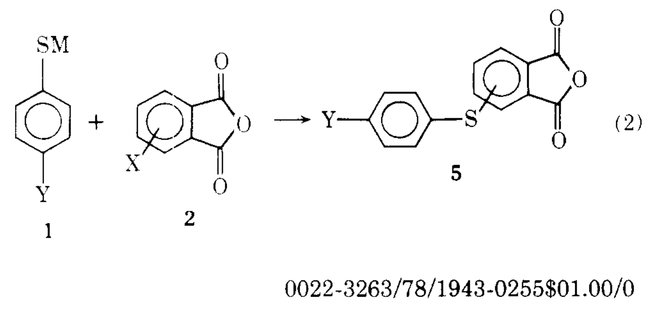
A wide variety of thioether-substituted phthalic anhydride derivatives **5** have been synthesized from the reaction of thiophenoxides with nitro- or halo-substituted phthalic anhydrides **2**. These reactions were carried out at room temperature and gave no indication of attack by the sulfur nucleophile at the carbonyl groups of the anhydride. This is in direct contrast with the room-temperature reactions of **2** with phenoxide nucleophiles, in which the nucleophile attacks only the carbonyl groups. The reaction involving the sulfur nucleophile works well using either preformed salts of the thiophenols or by generating the nucleophile in situ with amine or inorganic salts used as bases. The choice of the base system determines the speed of the reaction, which can vary from <5 min to 3 h at 25 °C. The halo derivatives are preferred over the nitro derivatives to minimize side reactions.

We have recently studied the reaction of thiophenoxide nucleophiles **1** with nitro- and halo-substituted phthalimides.[1] Of particular interest was the comparison between the two different types of nucleophiles, thiophenoxide and phenoxide, and the differences in reactivity that were observed. The reactions of phenoxide derivatives with nitro- and halo-substituted phthalic anhydrides **2** have also been studied,[2] and the course of each reaction was found to be very dependent upon the conditions employed and the identity of the leaving group. In all three systems (X = nitro, chloro, or fluoro), reaction with sodium phenoxide at room temperature resulted in opening of the anhydride ring to produce a mixture of acid ester salts **3**. Upon heating, these salts either decarboxylated (X = NO_2) or ring closed to varying degrees (X = F > Cl ≫ NO_2) to regenerate starting material. This starting material then underwent a displacement reaction with phenoxide to give the desired product **4** with varied success (F > Cl > NO_2) (see eq 1). If the reactions were carried out at 25 °C, *no displacement was observed.*



(1)

Successful reaction of the sulfur nucleophiles **1** with the substituted phthalic anhydrides **2** offers a facile synthesis of a variety of 3- and 4-substituted aromatic thioether derivatives of **5** (eq 2). The synthesis of only one derivative of **5** (3-isomer; Y = H) has been previously reported.[3] This material was prepared by the reaction of maleic anhydride with a 2-furyl thioether (**6**) to give the adduct **7** which was dehydrated to give **5a** in 40% overall yield (eq 3). This route necessitates the synthesis of derivatives of **6** and, in addition, is limited to only the synthesis of 3-isomers of **5**.[4]



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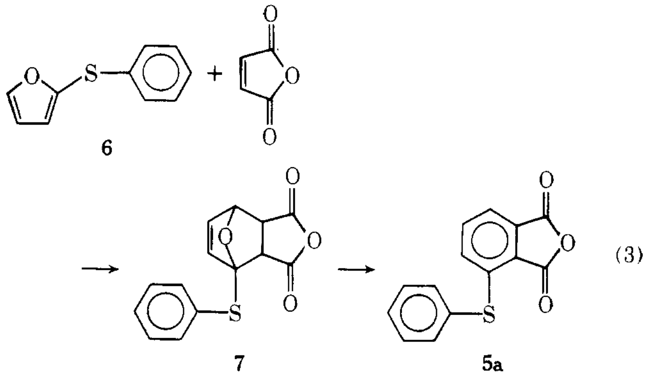

(3)

Results and Discussion[5]

Reaction of sodium 4-methylthiophenoxide (**1**, M = Na; Y = CH_3) with 3-fluorophthalic anhydride (**2e**) in DMF at 25 °C proceeded to completion in less than 5 min and gave a 94% yield of the desired product **5c** (3-isomer; Y = 4-CH_3). The product was isolated by adding the reaction to an ice/water mixture and collecting the product by filtration. The reaction worked equally well for the other halo-substituted derivatives and the results of these reactions are summarized in Table I, section A. All the reactions were extremely clean with less than 2% of the disulfide **8** formed.[6] It is likely that this 2% is present as an impurity in the starting material **1**. No attempts were made to maximize the yields of **5**. In examples where the yield of isolated product is lower, some hydrolysis of the product has taken place during workup. Extraction of the aqueous filtrate permits the recovery of **5** as the corresponding diacid. For example, examination of the reaction of 1 (M = Na; Y = CH_3) with 4-fluorophthalic anhydride (**2d**) by ^{13}C NMR confirmed the exclusive formation of **5d** and showed no trace of hydrolyzed product.

The reaction of 1 (M = Na; Y = CH_3) with 3- or 4-nitrophthalic anhydride was not as straightforward (eq 4). As shown in Table I (section A) not only were the yields of displacement product 5 much lower (42–43%), but a large amount of the disulfide 8 (55–57%) was produced. We feel that the lower yield of 5 is a result of two factors. First, as has been demonstrated previously,[2,7] once the sodium nitrite is produced from the displacement reaction, it can initiate a very fast ring-opening reaction with the starting nitro anhydride to produce **9**. This reaction deactivates the molecule toward further nitro (nitrite) displacement, and if it is competitive

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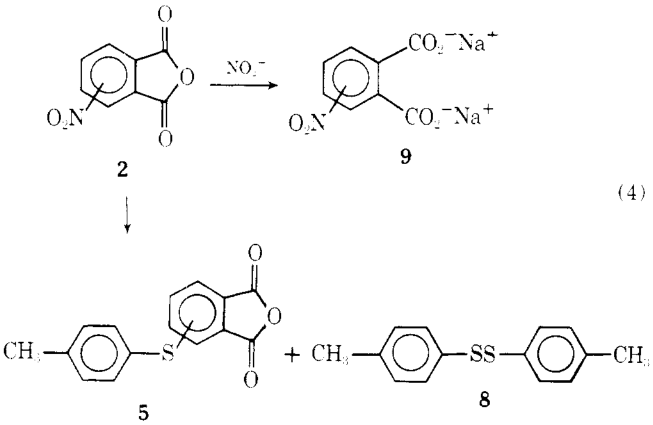
Table I. The Use of Different Base Systems
1 + 2 → 5 + 8

	Group X	Group Y	Isolated % yield of **5**	VPC % yield of **5**	VPC % yield of **8**
		A. Preformed Sodium Salt			
	4-F	CH_3	83	99	~2
	3-F	CH_3	94		
	4-Cl	CH_3	87	99	~2
	3-Cl	CH_3	93		
	4-NO_2	CH_3		42	55
	3-NO_2	CH_3		43	57
	4-Br	CH_3		97	~2
		B. Triethylamine			
	4-F	CH_3	93	93	4
	4-F	Cl	88		
	4-F	H	93		
	3-F	OH	74		
	3-F	H	94		
	3-F	Cl	91		
	4-Cl	CH_3		94	6
	4-Cl	CH_3O	88		
	3-Cl	CH_3	92		
	4-NO_2	CH_3		40	60
	3-NO_2	CH_3		51	46
		C. Other Bases			
K_2CO_3	4-F	CH_3		98	2
$KHCO_3$	4-F	CH_3		91	~4
Na_2CO_3	4-F	CH_3		99	
NaOH	4-F	CH_3		92	5
K_2CO_3	4-NO_2	CH_3		40	60

with the rate of displacement by the sulfur nucleophile a lower yield of the product **5** results. In addition, much coupling of the nucleophile **1** is seen.[8] Control experiments have shown that there is not enough moisture present to form the diacid derivative of **2** and thus the lower yields are not a function of the ring opening of the anhydride by water.



(4)

Experiments designed to improve the yield of nitro (nitrite) displacement were not very successful. Reactions in which the anhydride **2** was added to a homogeneous solution of the nucleophile in DMF or in which cosolvents were used to precipitate the sodium nitrite did not improve the yield. If 2 equiv of **1** was used, the yield of **5d** could be increased to 74%. It is interesting to note that ^{13}C NMR analysis of the reaction mixture indicated that the product **5** was present exclusively in the anhydride form, which demonstrates the preference of nitrite attack for the nitro anhydride **2**.

The relative rates of reaction of a series of nitro- and halo-substituted phthalimides with the nucleophile **1** (M = Na; Y = CH_3) have been obtained.[1] We felt that it would also be of interest to determine the relative rates of reactivity of the halo- and nitro-substituted phthalic anhydride derivatives with **1** under similar conditions. The results of these experiments are presented in Table II. The general order of halo displacement was F > Br > Cl, although there was not a very large difference between any of the halogens. As in the phthalimide system,[1] the 3-isomer was faster than the 4-isomer for fluoro displacement, but the order was reversed for chloro displacement. It appears that nitro (nitrite) displacement is again much faster than halo displacement, but the side reactions due to the sodium nitrite and the disulfide production from **1** made it impossible to obtain accurate values for the competition reactions involving the nitro derivatives. It is interesting to note that the anhydride linkage appears to be a better activating group than the phthalimide linkage for these displacements with the thiophenoxide nucleophile. A competition reaction between 3-chlorophthalic anhydride (**2a**) and 3-chloro-*N*-phenylphthalimide with **1** in DMF showed **2a** to be ca. 20 times more reactive than the imide.

Table II. Relative Rates of Reaction of Sodium 4-Methylthiophenoxide with 2 in DMF at 25 °C

Compound	Relative rate
2a (X = 3-Cl)	1
2b (X = 4-Cl)	1.5
2c (X = 4-Br)	4
2d (X = 4-F)	10
2e (X = 3-F)	20
2f (X = 4-NO_2)	(100)[a]
2g (X = 3-NO_2)	(1400)[a]

[a] May be in error due to side reactions of nitrite.

If a mixture of the desired thiophenol **1** (M = H), phthalic anhydride derivative **2**, and DMF was stirred at 25 °C, then an equivalent amount of triethylamine could be added to effect the displacement reaction. The reaction was slower than if the free anion **1** (M = Na) was used, but proceeded very well for a variety of substituted thiophenols. The results of these experiments are summarized in Table I, section B. Again it can be seen that the use of halo-substituted phthalic anhydrides is favored over the nitro derivatives. As was the case when the free anion **1** (M = Na) was used, the reaction with the nitro anhydrides led to lower yields of the desired products **5** and the formation of the disulfide **8**. In addition to using an amine system as the base, several reactions were carried out in which inorganic bases were used in situ with the thiophenol and phthalic anhydride derivative. The results of these experiments are summarized in Table I, section C. Generally, the rates of reactions using the inorganic bases were about the same as when the amine bases were used. All reactions were complete within 3 h at 25 °C. Control experiments were run to show that the displacement of the group X from **2** would not occur if the anhydride ring were opened to give either the diacid, disalt **9**, or monosalt–monoacid. Thus, if any ring opening does take place when the inorganic bases are used, it must take place after the displacement reaction. A summary of the analytical data for the new compounds synthesized from these displacements is contained in Table III and the chemical shifts from the ^{13}C NMR spectra of these compounds are presented in Table IV (see supplementary material).

Brief attempts were made to carry out the displacement reaction in solvents other than those classified as dipolar aprotic. Reaction of 4-fluorophthalic anhydride (**2d**) with **1** (M = Na; Y = CH_3) in methylene chloride or THF was unsuccessful. However, reaction of **2d** with **1** in acetone gave a 92% yield of **5d** (4-isomer; Y = CH_3). Reactions were also attempted in methylene chloride between **2g** and **1** and between **2d** and 4-methylthiophenol/Et_3N, but they also were not successful.

In summary, a wide variety of thioether-substituted phthalic anhydride derivatives **5** have been synthesized from the facile reaction of thiophenols with nitro- and halo-substituted anhydrides **2**. These reactions, carried out at room temperature, showed no attack by the sulfur nucleophile at the carbonyl groups of the anhydride. These results are in contrast to the reaction of **2** with phenoxide nucleophiles at 25 °C in which attack occurs exclusively at the carbonyl groups.

Experimental Section

Infrared spectra were taken on a Perkin-Elmer 457 grating infrared spectrophotometer in chloroform solution or as a KBr pellet. Mass spectra were determined on a CEC 21-104 analytical mass spectrometer at 70 eV. Vapor-phase chromatography (VPC) was carried out on a Hewlett Packard 5750 research chromatograph using a 6-ft 10% UCW-98 on 80/100 Chromosorb W column with temperature programming from 150 to 300 °C at 15 °C/min. Melting points were determined on a Thomas-Hoover Instrument and are uncorrected. C, H, N analyses were determined on a Perkin-Elmer 240 C, H, N analyzer, and sulfur analyses were determined by conventional analytical techniques either in house or by Galbraith.

Anhydrous DMF was purchased from Burdick and Jackson Laboratories. The THF used was freshly distilled from sodium benzophenone ketyl. The acetone, methylene chloride, and toluene used were reagent grades. The triethylamine was purchased from Eastman. A sample of di-*p*-tolyl disulfide was also purchased from Eastman. The thiophenol derivatives were obtained from commercial sources.

Phthalic Anhydride Derivatives. The starting phthalic anhydride derivatives **2** were obtained as has been described previously.[9] A sample of 4-bromophthalic anhydride (**2c**) was prepared from the bromination of phthalic anhydride followed by separation of the isomer mixture. We thank C. B. Quinn for a sample of this material.

Displacement Reactions. In general, the displacement reactions were run as has been described previously.[1] Conditions which are specific for the anhydride system are described below.

(A) Sodium Methoxide—Preformed (Isolated Yield). The reactions were run for 5 min to 2 h at 25 °C. All crude samples were examined by infrared analysis to ensure that the anhydride ring was intact. Several of the crude samples were also submitted for ^{13}C NMR analysis to verify the anhydride structure.

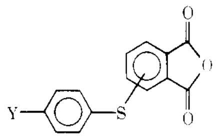
(B) Sodium Methoxide—Preformed (VPC Yield). Mixtures of the starting materials and internal standard (*o*-terphenyl) were stirred at 25 °C under nitrogen. Aliquots were removed at timed intervals and were worked up by shaking them with a 1.2 N HCl/Et_2O mixture. The organic layer was dried and analyzed by VPC. The peak area was determined for the standard and for each of the products, **5** and **8**. VPC yields were then obtained for each compound by using standard procedures, correcting for detector response differences. The results are presented in Table I, section A.

(C) Inorganic Salt. In general, the anhydride and thiophenol derivative were dissolved in DMF, the desired inorganic salt was added, and the reactions were stirred at 25 °C for 1 to 3 h. The salts were standard A.C.S. grade materials and were used as purchased.

(D) Triethylamine. The anhydride and thiophenol were dissolved in the desired solvent and the triethylamine was added by syringe. Reactions were generally run for 3 h at 25 °C or 1 h at 60 °C. All products were again examined by IR to ensure that the anhydride ring was intact. A specific example follows: A mixture of 1.66 g of **2e**, 1.59 g of *p*-chlorothiophenol (Aldrich), and 17 mL of DMF was stirred at 25 °C under nitrogen. To this solution was added 1.52 mL of triethylamine. The reaction mixture was stirred at 60 °C for 1 h to ensure complete reaction and then added to 1.2 N HCl/ice, and the resulting precipitate was collected and dried to give 2.77 g (91%) of **5f**. Analysis by infrared spectroscopy indicated that the anhydride ring was still intact. Analytical data for this compound is contained in Tables III and IV (see supplementary material).

Competition Experiments: Reactivity of Nitro or Halo Derivatives toward Displacement by Sodium 4-Methylthiophenoxide (1, M = Na; Y = CH_3). An arbitrary amount of anhydrous sodium 4-methylthiophenoxide (**1**) was accurately weighed into a flask under nitrogen. An equivalent molar amount of each of the two compounds being studied and an internal standard (*o*-terphenyl) were then dissolved in enough DMF to make a solution containing 10% solids. The solution was then added to the salt and the reaction mixture was stirred for 2 h at 25 °C. After 2 h, an aliquot was removed and worked up with 1.2 N HCl/CH_2Cl_2. The organic layer was dried and analyzed by VPC. The percent yield for each product was determined, and using the equation presented by Huisgen[10] the relative rates of reactivity were calculated. Similar experiments were run to determine the relative rates of reactivity of 3-chloro-*N*-phenylphthalimide and 3-chlorophthalic anhydride.

Table III. Thiophenoxy-Substituted Phthalic Anhydrides[a]



5

Compound	Registry no.	mp,[b] °C	*m/e*
5a (3-isomer; Y = H)	18241-49-1	147.5–149[c]	256
5b (4-isomer; Y = H)	64163-01-5	137–138	256
5c (3-isomer; Y = CH_3)	64163-02-6	136.5–138	270
5d (4-isomer; Y = CH_3)	64163-03-7	129–130	270
5e (4-isomer; Y = OCH_3)	64163-04-8	137.5–138.5	286
5f (3-isomer; Y = Cl)	64163-06-0	159–160	290
5g (4-isomer; Y = Cl)	64163-05-9	132.5–133.5	290
5h (3-isomer; Y = OH)	64163-07-1	166–168	272

[a] Satisfactory analytical data (±0.4% for C, H, S) were reported for all new compounds listed in the table. [b] All samples were recrystallized from toluene. [c] Lit. mp 148.5–149.5 (see ref 4).

Attempts to Run Reactions in Other Solvents. Reactions were run between **1** (M = Na, Y = CH_3) and **2d** exactly as described for "displacement reactions: (B) Sodium Methoxide—Preformed." However, in place of DMF, reactions were run with methylene chloride, THF, acetone, and toluene. In the reactions using methylene chloride or THF, no product was obtained after 68 h. However, in acetone an 85% yield of product was obtained after 45 min at 25 °C.

Attempts to Run Reactions on 4-Fluorophthalic Acid. A mixture of 2.0 g **2d** was stirred with 50 mL of 25% aqueous sodium hydroxide. The basic solution was extracted with ether and the aqueous solution was then acidified with HCl and again extracted with ether. The combined ether extracts were then dried over anhydrous magnesium sulfate and concentrated to give 1.83 g of 4-fluorophthalic acid (**10**). The structure was verified from its ^{13}C NMR spectrum.

A mixture of 0.1752 g of **10**, 0.1390 g of **1** (M = Na; Y = CH_3), 0.0860 g of *o*-terphenyl, and 6 mL of DMF was stirred at 25 °C under nitrogen. After 16 h of stirring, analysis of an aliquot by VPC showed no reaction had taken place. Two equivalents of **1** (0.278 g) was added and the reaction was stirred for 2 h (no further reaction). The reaction mixture was heated at 140 °C for 16 h, but still no displacement reaction was seen.

A mixture of 0.23 g of **10**, 0.172 g of K_2CO_3, 0.150 g of 4-methylthiophenol, and 0.1142 g of *o*-terphenyl was stirred at 25 °C under nitrogen with 6 mL of DMF. An aliquot, removed after 16 h, indicated that no reaction had taken place. Two additional equivalents of K_2CO_3 (0.344 g) was added, but after 6 h at 25 °C no further reaction was seen.

^{13}C NMR of Reaction Mixtures. (A) A mixture of 0.7505 g of sodium 4-methylthiophenoxide, 0.8433 g of 4-fluorophthalic anhydride, and 4 mL of DMF was stirred at 25 °C under a nitrogen atmosphere. After 0.5 h, the light-yellow homogeneous solution was transferred to an NMR tube. Analysis by ^{13}C NMR indicated the absence of 4-fluorophthalic anhydride, a trace of the disulfide **8**, and the formation of the desired product 4-(4-methylthiophenoxy)phthalic anhydride.

(B) A mixture of 0.6960 g of sodium 4-methylthiophenoxide, 0.920 g of 4-nitrophthalic anhydride, and 8 mL of DMF was stirred at 25 °C under nitrogen. After 2 h, the thick yellow solution was filtered and the filtrate analyzed by ^{13}C NMR. The NMR showed that all the displacement product was present in the form of the anhydride and that the disulfide **8** was present. The ratio of **8** to **5d** was 42 to 58 by NMR. The NMR also indicated the presence of 4-nitrophthalic acid or salts of this acid. The difference between these materials could not be distinguished by this spectrum. The solid, which was removed by filtration, was dissolved in 1.2 N HCl and extracted with ether. Analysis by VPC of these extracts indicated the presence of only 4-nitrophthalic anhydride (most likely ring closed upon analysis).

Acknowledgments. We thank H. M. Relles for many helpful discussions concerning this work, and the analytical section of the Materials Characterization Branch for their assistance in obtainind the necessary analytical data.

Registry No.—1 (M = Na; Y = CH_3), 10486-08-5; 1 (M = H; Y = CH_3), 106-45-6; 1 (M = H; Y = Cl), 106-54-7; 1 (M = H, Y = H), 108-98-5; 1 (M = H; Y = OH), 637-89-8; 1 (M = H; Y = OCH_3), 696-63-9; 2 (X = 4-F), 319-03-9; 2 (X = 3-F), 652-39-1; 2 (X = 4-Cl), 118-45-6; 2 (X = 3-Cl), 117-21-5; 2 (X = 4-NO_2), 5466-84-2; 2 (X = 3-NO_2), 641-70-3; 2 (X = 4-Br), 86-90-8; 8, 103-19-5.

Supplementary Material Available. ^{13}C NMR assignments for the thiophenoxyphthalic anhydrides 5 (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) F. J. Williams and P. E. Donahue, *J. Org. Chem.*, **43**, preceding paper in this issue (1978).

(2) F. J. Williams, H. M. Relles, J. S. Manello, and P. E. Donahue, *J. Org. Chem.*, **42**, 3425 (1977).

(3) Ya. L. Danyushevskii, M. A. Marakatkina, and Ya. L. Gol'dfarb, *Zh. Org. Khim.*, **4**, 474 (1968) (english version, page 464).

(4) For an improvement in the synthesis of **6**, see: R. A. Silverman and D. M. Burness, *J. Org. Chem.*, **33**, 1869 (1968).

(5) Some of this work has appeared in F. J. Williams, U.S. Patent 3 850 965, Nov. 26, 1974.

(6) A discussion of possible routes to the formation of **8** is contained in ref 1.

(7) R. L. Markezich, O. S. Zamek, P. E. Donahue, and F. J. Williams, *J. Org. Chem.*, **42**, 3435 (1977).

(8) A ^{13}C NMR spectrum of the displacement reaction mixture shows that the disulfide **8** is present before workup. Thus, the coupling must take place during the reaction and as a result of this side reaction of the nucleophile **1** the yield of **5** is lowered.

(9) F. J. Williams and P. E. Donahue, *J. Org. Chem.*, **42**, 3414 (1977).

(10) U. Burger and R. Huisgen, *Tetrahedron Lett.*, **35**, 3057 (1970).

Effect of Monoalkyl Phosphates upon Micellar-Catalyzed Dephosphorylation and Deacylation[1]

Clifford A. Bunton,* Simon Diaz,[2] G. Michael van Fleteren, and Chang Paik

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

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Disodium *n*-dodecyl phosphate (NaDodP) and to a lesser extent *n*-butyl phosphate are nucleophilic catalysts for the decomposition of *p*-nitrophenyl diphenyl phosphate (I) in cationic micelles, with up to 100-fold rate enhancement over the rate in water. Micelles of NaDodP are poor catalysts, even though they incorporate the substrate, suggesting a role for micellar charge in these reactions. Although *n*-butyl phosphate dianion weakly catalyzes deacylation of 2,4-dinitrophenyl 3-phenylpropionate, it and NaDodP inhibit the reaction in cationic micelles of cetyltrimethylammonium bromide by excluding hydroxide ion.

Micellar catalysis of bimolecular reactions involves concentration of the reagents at the micelle–water interface, in the so-called Stern layer.[3-6] Estimation of the rate constants at the interface depends on the volume element used in measuring concentration, but for a number of such reactions the second-order rate constants are apparently no larger at the interface than in water.[6,7] Functional micelles are often very effective catalysts because concentration of reagents minimizes the unfavorable entropy changes in forming a transition state from two or more reactants.[3-5,8] Many functional micelles are cationic or zwitterionic, and the role of the positive charge is not always obvious. For example, comicelles of acylhistidines and quaternary ammonium ions are excellent deacylating agents, whereas the acylhistidines alone are relatively ineffective,[9] but nonionic micelles of *n*-alkylamines and *n*-alkylimidazoles are often effective.[10]

The reaction of *p*-nitrophenyldiphenyl phosphate (I) with hydroxide ion is catalyzed by micelles of cetyltrimethylammonium bromide (CTABr).[11] At high pH this catalysis is reduced by phosphate and aryl phosphate ions, although at lower pH the nucleophilic attack by these ions becomes important.[12]

In order to obtain evidence on the role of micellar charge, we used micelles of disodium *n*-dodecyl phosphate (NaDodP) and examined its reactions with I giving initially II and its effect on dephosphorylation by fluoride ion.[11]

$$\begin{array}{c} n\text{-}C_{12}H_{25}OPO_2OPO(OPh)_2 + \bar{O}C_6H_4NO_2 \\ \text{II} \\ \uparrow \\ (PhO)_2PO\text{-}OC_6H_4NO_2 + n\text{-}C_{12}H_{25}OPO_3^{2-} \\ \text{I} \\ \downarrow F^- \\ (PhO)_2PO\text{-}F + \bar{O}C_6H_4NO_2 \end{array}$$

Although most work with nucleophilic micelles has been on deacylation, functional cationic micelles having hydroxyl or imidazole head groups are effective catalysts of dephosphorylation.[13] For purposes of comparison, we also examined the effect of NaDodP on the deacylation of 2,4-dinitrophenyl 3-phenylpropionate (III) in CTABr.

Experimental Section

Materials. *n*-Dodecyl- and *n*-butylphosphoric acid were prepared from the alcohols and $POCl_3$ by standard methods.[14] The phosphates were analyzed quantitatively for phosphorus and *n*-dodecylphosphoric acid had mp 58–60 °C (lit.[15] 58 °C). The preparation and purification of the other materials has been described.[11-15]

Kinetics. Reactions were followed spectrophotometrically at 403 and 358 nm for the *p*-nitrophenyl and 2,4-dinitrophenyl compounds, respectively, using a Gilford spectrophotometer with a water-jacketed cell compartment at 25.0 °C.[11-13] The first-order rate constants, k_ψ, are in s^{-1}. The pH of the reaction solution was measured in the presence of the surfactant, and the substrate concentrations were 1–2 $\times 10^{-5}$ M.

Critical Micelle Concentration. The critical micelle concentration (cmc) of disodium *n*-dodecyl phosphate (NaDodP) is 1.6×10^{-2} M at 22 °C in 0.02 M borate buffer, determined by surface-tension measurement. The cmc is considerably higher than that of sodium dodecyl sulfate ($NaDodSO_4$) of ca. 8×10^{-3} M,[16] because of the dianionic phosphate head group.

Products. The products of reaction of I with 2×10^{-3} M NaDodP in 4×10^{-3} M CTABr at pH 9.1 were separated by thin-layer chromatography using Eastman Kodak 6060 Si gel plates. After complete reaction, the pH was brought to 4 and the chromatogram was developed using $MeOH$–$CHCl_3$ (15:85, v/v). The surfactants did not move, and spots were observed at R_f 0.11 (of diphenyl phosphate) and 0.54 (of *p*-nitrophenol) plus a third spot with R_f 0.17 which we assume was that of the diphenyl *n*-dodecyl pyrophosphate (II). When reaction was done in the absence of NaDodP and it was added after complete reaction, this spot with R_f 0.17 was absent. The formation of diphenyl phosphate could have been due to reaction of OH^- with the substrate or to subsequent hydrolysis of the pyrophosphate (cf. ref 12).

We attempted to use the hydroxamic acid test in the detection of an acyl phosphate[17] as an intermediate in the reaction of *n*-dodecyl