JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 10, 27–32 (1997)

PHOSPHATE CLEAVAGE BY ORGANOIODINANE OXYANION ANALOGUES OF *o*-IODOSOBENZOATE: EXPERIMENTAL AND COMPUTATIONAL STUDIES

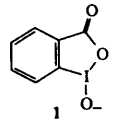
ROBERT A. MOSS,* SUSMITA BOSE AND KARSTEN KROGH-JESPERSEN*

Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, U.S.A.

1,3-Dihydro-1-oxido-3-methyl-1,2,3-benziodoxaphosphole 3-oxide (4) and 1-*H*-1-oxido-5-methyl-1,2,3-benziodoxathiole 3,3-dioxide (5) were used to cleave *p*-nitrophenyl diphenyl phosphate (PNPDPP) (2) in aqueous micellar cetyltrimethylammonium chloride (CTACl) in phosphate buffer at pH 8. The maximum pseudo-first-order cleavage rate constants (with $1{\cdot}0\times10^{-4}$ M 4 or 5 and $1{\cdot}0\times10^{-5}$ M 2) were $0{\cdot}0016\ s^{-1}$ for 4 ([CTAC1] = 0·01 M) and $0{\cdot}0013\ s^{-1}$ for 5 ([CTAC1] = 0·001 M). Reagents 4 and 5 were, respectively, 44 and 57 times less reactive toward PNPDPP than iodosobenzoate (1) under comparable conditions. *Ab initio* electronic structure calculations were carried out on 1, 4 and 5 and their protonated forms. Calculated structural parameters were compared with crystallographic data where possible. The computed atomic net charge on the oxido oxygens of 1, 4 and 5 was found to track the reactivity toward PNPDPP.

1. INTRODUCTION

In its closed 1-oxido-1,2-benziodoxolin-3-one valence tautomeric form (**1**), *o*-iodosobenzoate in basic aqueous micellar solutions of cetyltrimethylammonium chloride (CTACl) is a remarkably efficient catalyst for the cleavage of reactive esters, phosphonates and phosphotriesters, e.g. *p*-nitrophenyl diphenyl phosphate (PNPDPP) (**2**).[1,2]



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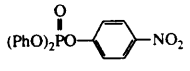

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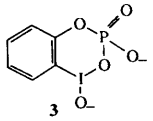

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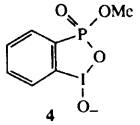
Given the continuing need for decontaminants to be deployed against toxic phosphonates and phosphates,[3] it is important to note that micellar **1** is also active against the fluorophosphonate nerve agents sarin and soman and the *p*-nitrophenyl diethyl phosphate insecticide paraoxon.[4]

Not surprisingly, the broad phosphorolytic reactivity of **1** stimulated a wide survey of the like properties of related oxidoiodinanes, including *o*-iodosonaphthoates[5] and 9,10-iodosophenanthroate,[6] as well as *o*-iodosophenylphosphate (**3**).[7] Simultaneously with the experimental work, computational studies indicated that the phosphorolytic reactivities of various 1-oxidoiodinanes were correlated with the calculated negative charge at the exocyclic I—O$^-$ site.[5,8,9]

Here we describe the phosphorolytic kinetics and computed properties of two additional analogues of **1**, 1,3-dihydro-1-oxido-3-methyl-1,2,3-benziodoxaphosphole 3-oxide (**4**)[10] and 1-*H*-1-oxido-5-methyl-1,2,3-benziodoxathiole 3,3-dioxide (**5**).[11] The results support the above-mentioned correlation of reactivity and negative charge at I—O$^-$ and underline the importance of combined kinetic/theoretical studies to our understanding of oxidoiodinane phosphorolytic reactivity.



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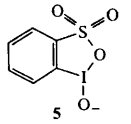

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RESULTS AND DISCUSSION

Materials

Reagents **4** and **5** were synthesized in accord with the published procedures.[10,11] They had appropriate NMR spectra, were homogeneous to TLC and exhibited I=O titers of 98% (**4**) and 103% (**5**) in standard iodimetric titrations[12] (we take the deviations in our observed

* Auhor to whom correspondence should be addressed

CCC 0894–3230/97/010027–06

Received 18 June 1996
Revised 31 July 1996

iodoso titers to be within experimental error of 100%). Substrate **2** was also prepared by literature methods.[13]

pK_a Determinations

The reactive forms of catalysts **4** and **5** are the I—O$^-$ anions, the concentrations of which are pH dependent. We therefore determined their pK_a values under the micellar reaction conditions utilized in our kinetic studies (see below). A pH–rate constant profile[1b,6,7] was determined at 25 °C for the cleavage of 1×10^{-5} M PNPDPP by 1×10^{-4} M **4** in 0·01 M CTACl (this is the CTACl concentration at which we observed the maximum rate constant for PNPDPP cleavage by this catalyst; see below) in 0·02 M aqueous phosphate buffers (0·01 M in KCl) adjusted to the appropriate pH values. The solutions also contained 1·0 vol.% of DMF and 0·33 vol.% of CH_3CN due to reagent and substrate additions.

For catalyst **4**, pseudo-first-order rate constants (k_ψ) were determined spectrophotometrically for the release of *p*-nitrophenolate ion at 400 nm at seven pHs between 6·33 and 8·33. A plot of log k_ψ vs pH (Figure 1) gave a sharp discontinuity at pH 6·8 which was taken as the systemic pK_a of **4** under the micellar reaction conditions. This pK_a implied that **4** was *ca* 94% in the anionic form at pH 8, where our phosphorolytic kinetic studies were conducted.

A pH–rate constant profile (Figure 2) was determined between pH 5·88 and 8·25 for catalyst **5** under analogous conditions, except that here [CTACl] was maintained at 1×10^{-3} M (this is the CTACl concentration at which we observed the maximum rate constant for PNPDPP cleavage by this catalyst; see below). Again, a sharp, clear

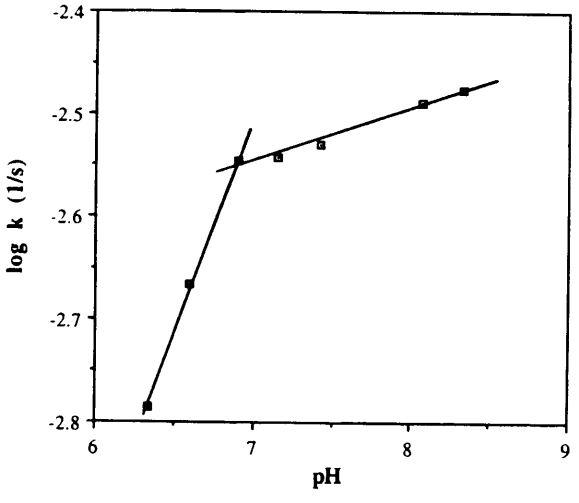

Figure 1. pH–rate profile for the cleavage of 1×10^{-5} M PNPDPP by 1×10^{-4} M **4** in 0·01 M CTACl: log k_ψ (s^{-1}) vs pH. The discontinuity at pH 6·8 is taken as the systemic pK_a of **4**

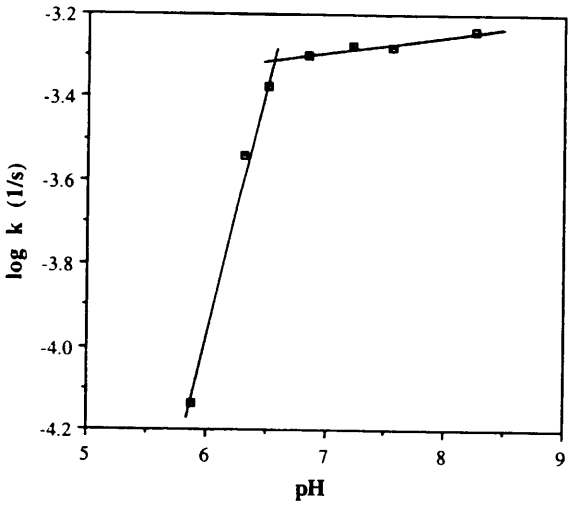

Figure 2. pH–rate profile for the cleavage of 1×10^{-5} M PNPDPP by 1×10^{-4} M **5** in 1×10^{-3} M CTACl: log k_ψ (s^{-1}) vs pH. The discontinuity is observed at pH 6·5. See text for a discussion of the pK_a of **5**

discontinuity was observed in the profile, this time at pH 6·5, which we took as the pK_a of **5** under our reaction conditions. This pK_a corresponds to *ca* 97% conversion of catalyst **5** in to its active anionic form at pH 8.

A conventional pH titration (pH vs volume of added base) of phosphole **4** in 0·01 M CTACl (this is the CTACl concentration at which we observed the maximum rate constant for PNPDPP cleavage by this catalyst; see below) with 0·00965 M NaOH in 0·01 M CTACl afforded a pK_a value of 7·05, as read at the half-equivalence point. This is in good agreement with $pK_a = 6{\cdot}85$ determined from the pH-rate constant profile (Figure 1). However, an analogous conventional titration of thiole dioxide **5**, with [CTACl] = 0·.001 M (this is the CTACl concentration at which we observed the maximum rate constant for PNPDPP cleavage by this catalyst; see below), led to $pK_a = 3{\cdot}4$, much lower than the value of 6.5 obtained from the pH–rate constant profile (Figure 2). We are unable to account for the discrepancy. Previous comparisons (as with **4**) have shown agreement between pK_as measured either by pH titration or from pH–rate constant profiles. For example, these methods afford pK_as of 7·75 and 7·78, respectively, for the parent oxidoiodoxolinone (see structure **7**-OH).[8]

Catalysis of phosphate cleavage is a property only of the closed form of these 'iodoso' reagents,[1] so that the kinetic enhancement that **5** brings to the phosphorolytic hydrolysis of PNPDPP (see below) must in any event be attributed to the benziodoxathiole form. The present uncertainty in the pK_a of **5**-OH has little effect on our kinetic experiments which are carried out at pH 8. For present purposes, we shall use the pH–rate constant profile pK_a for **5** (6·5)

because the conditions of this determination most closely mimic those of our kinetic studies.

Kinetic studies

The catalytic properties of **4** and **5** were assessed from full rate constant–[surfactant] profiles for the cleavage of 1×10^{-5} M PNPDPP by 1×10^{-4} M catalyst at 25 °C under the buffer and ionic conditions described above. The concentration of CTACl was incrementally varied between 1×10^{-4} and 5×10^{-2} M and pseudo-first-order rate constants were determined by monitoring the release of *p*-nitrophenolate ion at 400 nm. The reproducibility of k_ψ was better than ± 3%.

The data for both catalysts appear in Figure 3, where k_ψ^{max} for **4** is $1{\cdot}64 \times 10^{-3}$ s^{-1} observed at [CTACl] = 0·01 M and k_ψ^{max} for **3** is $1{\cdot}30 \times 10^{-3}$ s^{-1} observed at [CTACl] = 1×10^{-3} M. The shapes of the two profiles are typical of micellar catalysis, where the apparent rate constants increase with increasing surfactant concentration, reach a maximum when the reactant concentrations are maximized in the micelles and then decrease with the addition of further surfactant (i.e. dilution of the micellar phase).[14] The sharper rise and tenfold lower CTACl concentration at k_ψ^{max} of catalyst **5** suggests that it has a greater binding constant to the micelles than does **4**.

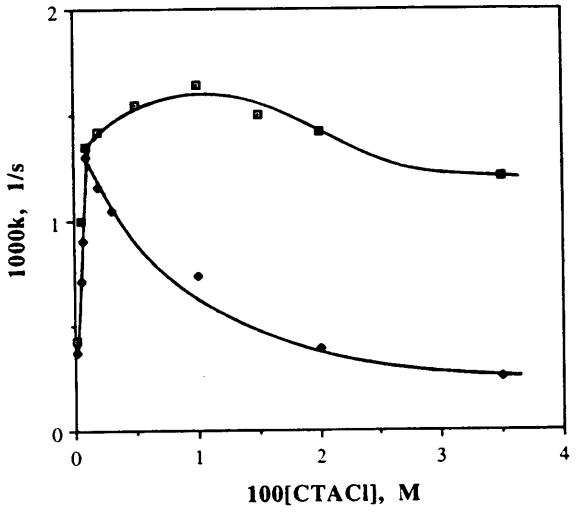

Figure 3. Pseudo-first-order rate constants (k_ψ, s^{-1}) for the cleavages of 1×10^{-5} M PNPDPP by 1×10^{-4} M **4** (□) or **5** (◆) as a function of [CTACl] (M) at pH 8. See text and Table 1 for k_ψ^{max} values

In Table 1, we summarize kinetic data for PNPDPP phosphorolysis by reagents **4** and **5**, iodosobenzoate itself and micellar CTACl in the absence of an additional catalyst. The newly studied reagents accelerate PNPDPP cleavage by factors of 7–9 over hydroxide ions in 1×10^{-3} M aqueous micellar CTACl at pH 8. However, the kinetic potencies of **4** and **5** are markedly inferior to that of iodosobenzoate (**1**), which is 44–57 times more reactive (k_{cat}) toward PNPDPP under optimum conditions. This reactivity trend can be best rationalized in structural terms.

The reactivity of (e.g.) iodosobenzoate depends on the maintenance of the closed iodoxolone valence tautomeric form (i.e. **1**), where the negative charge resides on I—O$^-$, as opposed to the open iodoso form (**6**),[1a] where the negative charge is relocated to the carboxylate group. X-ray crystallographic data reveals that, in its protonated (**1**-OH) form, the endocyclic O—I bond of **1**-OH is longer than the O—I single bond distance predicted from the sum of O and I covalent radii (*ca* 2·07 Å)[15] (the structure and bonding of iodinanes and iodoxolones has been reviewed[6,8,9,16,17]). This key bond is measured at 2·30 Å in **1**-OH[18] and 2·.35 Å in the 5-methyl derivative of **1**-OH,[19] so that the iodoxolone ring even in the protonated species appears to be partially 'open'.

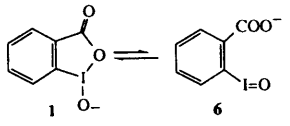

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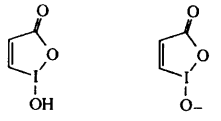
Table 1. Kinetics of I—O$^-$ cleavages of PNPDPP (**2**)[a]

Catalyst	pK_a[b]	$10^2 k_\psi^{max}$ (s^{-1})[c]	10^2 [CTACl] (M)[d]	k_{cat} (l mol^{-1} s^{-1})[e]	Ref.
None		0·018	0·1		7
1	7·25	6·45	0·1	759	1b
4	6·8	0·164	1·0	17·4	This work
5	6·5	0·130	0·1	13·4	This work

[a] Conditions: 0·02 M phosphate buffer, μ = 0·08 (NaCl), 25 ± 0·5 °C, [PNPDPP] = $1{\cdot}0 \times 10^{-5}$ M, [catalyst] = $1{\cdot}0 \times 10^{-4}$ M, 1·0 vol.% DMF, 0·33 vol.% CH_3CN.
[b] Determined from pH–rate constant profiles; see above.
[c] Maximum pseudo-first-order rate constant for PNPDPP cleavage taken from rate constant–[CTACl] profile.
[d] Concentration of CTACl at which k_ψ^{max} was observed.
[e] $k_{cat} = k_\psi^{max}$/[catalyst], corrected for 100% ionization to I—O$^-$.
[f] This work; μ = 0·01 (kCl).

Deprotonation results in further lengthening of the endocyclic O—I bond as the increased negative charge is distributed over the iodoxolone ring.[8,9] For example, in the parent hydroxyiodoxolone, **7**-OH, ionization to **7** is calculated (*ab initio* Hartree–Fock calculation with split valence quality basis sets) to result in lengthening of the endocyclic O—I bond from 2·1 to 2·6 Å;[8] similar results were obtained on **1**-OH and **1**.[9] Nevertheless, considering the large computed negative charge on the exocyclic I—O^- bond of **7** or **1**, and the 'long' calculated I—O^- bond lengths (*ca* 1·9 vs *ca* 1·6 Å expected for I=O), **7** and **1** are best regarded as iodoxolones.[8,9] Similar considerations apply to the 4-nitro derivative of **1**,[19] although in all cases, some relaxation toward the open geometry must be admitted.



7-OH 7

How are the foregoing considerations reflected in the structures of **4** and **5**? X-ray crystallographic data indicate that, in their protonated forms, they are about as closed as **1**-OH. Hence the endocyclic O—I bonds of **4**-OH and **5**-OH are 2·29 Å[10] and 2·37 Å,[11] respectively, similar to the 2·30 Å[18] and 2·35 Å[19] bond lengths reported for **1**-OH and 5-Me-**1**-OH, respectively. In the absence of x-ray crystallographic data for the I—O^- anions, **4** and **5**, their structures and charge distributions are best dealt with by computational methods.

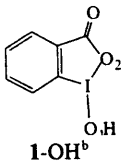
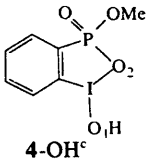
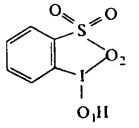
Computational details

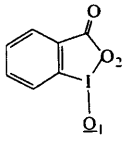
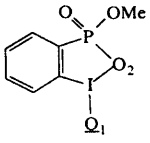
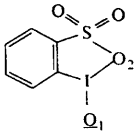
Ab initio electronic structure calculations were carried out on **1**, **4** and **5** and their protonated forms using the Gaussian 94 package of programs.[20] As in our past work on analogous organoiodinane species,[8,9] we have represented the 'chemically unimportant' core electrons on all atoms by effective core potentials. For I, S and P we used the potentials of Wadt and Hay,[21] whereas for C and O we used the potentials created by Stevens *et al.*[22] The valence basis sets provided with these potentials were split to double-zeta quality[21,22] and the 3–21G basis set was used for the H atoms.[23] The I and O basis sets were each augmented by a set of diffuse sp-type functions and a set of d-type polarization functions.[24] (*I*: sp exponent = 0·038; d exponent = 0·25). Geometries of all species were optimized using analytical gradients with electron correlation incorporated through second-order Møller–Plesset perturbation theory (MP2).[25] Charge distributions were analysed by applying the NBO procedures[26] to the MP2 wavefunction.

Computed and crystallographic structural parameters relating to the T-shaped geometry observed around the formally hypervalent iodine atom are shown in Table 2. Even though the present calculations are of considerably higher quality (larger basis sets, geometry optimizations with correlated wavefunctions) than those presented earlier,[8,9] comparisons of computed and experimental structures for the protonated forms still indicate systematic differences. Overall, the computed structures are too 'closed' compared with the experimental structures and, in particular, the measured disparity in exo- and endocyclic I—O bond lengths appears considerably underestimated by the calculations. For example, in **1**-OH the exocyclic I—O bond (I—O_1) length is computed *ca* 0·15 Å too long and the endocyclic I—O bond (I—O_2) length is *ca* 0·2 Å too short. Such discrepancies between computed and measured bond lengths also occur with **4**-OH and **5**-OH. Note, however, that the potential energy surface is very flat with respect to both bond length and angular distortions around the I atom. Thus, the computed structural parameters describing the environment around the I atom are very sensitive to the computational level employed. (Geometries optimized at the independent-particle Hartree–Fock level actually compare more favorably with the available x-ray structures than do the optimized, electron correlated MP2 structures; however, Hartree–Fock level calculations fail for the anions and predict far too 'open' structures. Density functional theory with the hybrid B3LYP functionals performs poorly for the geometries of both the neutrals and the anions.) Experimentally, intermolecular contacts involving the I atom on one molecule and O_1 on another molecule are common in the iodosyl crystals (and identified in crystalline 5-Me-**1**-OH),[19] which may distort the observed coordination geometry away from that pertaining to an isolated monomer. Furthermore, the crystallographically determined I—O bond lengths may reflect a high sensitivity to substitution. I—O_1 and I—O_2 bond lengths of 1·93 and 2·35 Å, respectively, were determined recently[19] for 5-Me-**1**-OH, whereas an earlier[18] x-ray determination on **1**-OH led to less dissimilar I—O_1 and I—O_2 bond lengths (2·01 and 2·30 Å, respectively).

Turning now to the deprotonated species, the present calculations produce a geometry for **1** which is in good agreement with the crystallographically determined structure for a 4-nitro sodium tetrahydrate derivative of **1**,[19] a surprise considering the problems encountered above with the neutrals and that the calculations on **1** refer to an anion in a hypothetical gas-phase situation. Thus, the exocyclic I—O_1 bond length computed for **1** is notably short at 1·88 Å (x-ray: 1·89 Å), and the endocyclic I—O_2 distance is long at 2·49 Å (x-ray: 2·45 Å), displaying substantial 'opening' of the iodoxolone ring. The geometry around the I atom in **4** is very similar to that of **1**, whereas in **5** the endocyclic I—O_2 bond length is larger (*ca* 0·05 Å) and the exocyclic I—O_1 bond length correspondingly slightly smaller (*ca* 0·01 Å).

Table 2. Computed[a] and crystallographic (in parentheses) structural parameters, with distances in Å and angles in degrees

	 1-OH[b]	 4-OH[c]	 5-OH[d]
C—I	2·120 (2·085)	2·154 (2·128)	2·146 (2·125)
I—O_1	2·078 (1·939)	2·069 (1·952)	2·056 (1·933)
I—O_2	2·149 (2·347)	2·128 (2·286)	2·157 (2·372)
O_2—C	1·372 (1·282)		
C—I—O_1	84·6 (94·8)	89·8 (91·8)	88·8 (92·3)
C—I—O_2	80·7 (74·8)	83·3 (79·9)	82·1 (76·9)

	 1[e]	 4	 5
C—I	2·141 (2·077)	2·167	2·157
I—O_1	1·884 (1·890)	1·886	1·875
I—O_2	2·492 (2·447)	2·487	2·541
C—I—O_1	97·5 (94·5)	96·2	96·9
C—I—O_2	73·1 (72·9)	77·9	76·2

[a] Geometries optimized at the MP2 level using effective core potentials and valence basis sets of better than double-zeta quality; see text.
[b] X-ray data on 5-Me-1-OH.[19]
[c] X-ray data from Ref. 10; averaged values for two unique molecules in the unit cell.
[d] X-ray data from Ref. 11.
[e] X-ray data on a 4-nitro sodium tetrahydrate derivative of **1**.[19]

CONCLUSIONS

From the kinetic data in Table 1, it is clear that **4** and **5** are inferior to **1** as reagents for the phosphorolytic cleavage of PNPDPP. Indeed, in terms of k_{cat}, they are also less reactive than **3** ($k_{cat} = 91$)[7] or **7** ($k_{cat} = 160$).[8] Why are **4** and **5** so kinetically impotent?

We found previously that the amount of charge residing on the I—O^- unit was the single best indicator for phosphorolytic reactivity toward PNPDPP.[5,8,9] Whereas the computed atomic net charge on O_1 in **1** is $-1{\cdot}18_1$, it is $-1{\cdot}17_4$ in **4** and $-1{\cdot}15_1$ in **5**. Thus, the observed correlation persists with **4** and **5**. The kinetic activity of oxidoiodinanes toward PNPDPP appears to be a very sensitive function of the negative charge at I—O^-. This charge, in turn, depends intimately on the precise structure of the heterocyclic ring of the reacting species, particularly the extent of closure or openness at the endocyclic I—O bond. Although far from perfect, *ab initio* electronic structure calculations appear to provide a means to model these reagents' structures and charges, and hence to predict their phosphorolytic reactivity.

EXPERIMENTAL

Materials. Substrate **2** was prepared by a literature method.[13] 1,3-Dihydro-1-hydroxy-3-methyl-1,2,3-benziodoxaphosphole 3-oxide (**4**)[10] and 1-*H*-1-oxido-5-methyl-1,2,3-benziodoxathiole 3,3-dioxide (**5**)[11] were prepared using the published procedures. CTACl (Eastman) was recrystallized several times from methanol–water and dried under vacuum.

Kinetic studies. Reactions were followed on a Gilford Model 250 spectrophotometer at 25 °C in 0·02 M aqueous phosphate buffer (0·01 M in KCl) adjusted to the appropriate pH. Buffers were prepared from 'steam-distilled water' (distilled, USP, Electrified

Water, East Orange, NJ, U.S.A.). For concentrations of CTACl, and incidental additives (DMF, MeCN), see above. Rate constants were obtained from computer-generated correlations of $\log(A_\infty - A_t)$ with time for the appearance of *p*-nitrophenoxide ion at 400 nm. Results appear in Figures 1–3 and Table 1; conditions for the kinetic runs are described above.

ACKNOWLEDGMENT

We are grateful to the US Army Research Office for financial support.

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