Kinetics and Mechanism of the Phenolysis of Asymmetric Diaryl Carbonates

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The reactions 4-methylphenyl 4-nitrophenyl carbonate (MPNPC), 4-chlorophenyl 4-nitrophenyl carbonate (ClPNPC), 4-methylphenyl 2,4-dinitrophenyl carbonate (MPDNPC), and 4-chlorophenyl 2,4-dinitrophenyl carbonate (ClPDNPC) with a homogeneous series of phenoxide anions are subjected to a kinetic investigation in aqueous solution (25.0 °C, ionic strength 0.2 M (KCl)). Under an excess of phenoxide with respect to the substrate, all of these reactions obey pseudo-first-order kinetics and are first order in phenoxide. The Brönsted-type plots for the nucleophilic rate constants (k_N) are linear, with slopes $\beta = 0.48$ (MPNPC), 0.67 (ClPNPC), 0.41 (MPDNPC), and 0.32 (ClPDNPC). The magnitude of these slopes and the absence of a curvature in the Brönsted plot at $pK_a = 7.1$ for the ClPNPC reactions are consistent with concerted mechanisms (one step). The carbonates MPDNPC and ClPDNPC are more reactive than MPNPC and ClPNPC, respectively, toward phenoxide nucleophiles. This can be explained by the presence of a second nitro group in the nucleofuge of the dinitro derivatives, which (i) leaves their carbonyl carbon more positively charged, making them better electrophiles, and (ii) makes 2,4-dinitrophenoxide a better leaving group than 4-nitrophenoxide. The 4-chloro derivatives are more reactive than the corresponding 4-methyl derivatives. This should be due to the greater electron withdrawal of 4-chloro than 4-methyl, which makes the former carbonyl more electrophilic. Comparison of the concerted phenolysis of MPNPC with the stepwise reactions of secondary alicyclic amines with the same substrate indicates that substitution of a secondary alicyclic amine group in a zwitterionic tetrahedral intermediate by a phenoxy group greatly destabilizes the intermediate. An equation is deduced for log k_N in terms of the basicity of the nucleophile, the nonleaving moiety, and the leaving group. This equation shows that for these reactions, the sensitivity of log k_N to the basicity of the nonleaving moiety ($\beta_{nlg} = -0.27$) is very similar to that of the nucleofuge ($\beta_{lg} = -0.25$).

Introduction

Although the kinetics and mechanisms of the phenolysis of esters and thioesters have been the subject of many reports,[1−4] the mechanisms of the phenolysis of carbonates and thiocarbonates have received little attention.[5,6]

We have studied kinetically the phenolysis of *S*-(4-nitrophenyl), *S*-(2,4-dinitrophenyl), and *S*-(2,4,6-trinitrophenyl) ethyl thiocarbonates.[5] In this work, linear Brönsted-type plots were obtained and interpreted through a concerted reaction path.[5]

Lately, we have also performed mechanistic studies of the phenolyses of 4-nitrophenyl, 2,4-dinitrophenyl, and 2,4,6-trinitrophenyl methyl carbonates (**1**, **2**, and **3**, respectively)[6a] and also of phenyl 4-nitrophenyl and 2,4-dinitrophenyl phenyl carbonates (**4** and **5**, respectively).[6b] In all these investigations, concerted mechanisms were proposed on the basis of the Brönsted-type plots obtained.[6]

Recently, we have investigated the phenolysis of bis-(4-nitrophenyl) carbonate (**6**), bis(4-nitrophenyl) thionocarbonate, and methyl 4-nitrophenyl thionocarbonate.[6c] A linear Brönsted plot of slope $\beta = 0.66$ found for the former reactions is consistent with a concerted mechanism. The biphasic Brönsted plots with a sharp curvature (with slopes from $\beta = 0.3-0.4$ to $\beta = 1.3-1.6$) obtained for the two latter reactions indicate that these reactions are stepwise, through an anionic tetrahedral intermediate.[6c]

On the other hand, we have also examined kinetically the reactions of secondary alicyclic amines with 4-nitrophenyl and 2,4-dinitrophenyl 4-methylphenyl carbonates (MPNPC and MPDNPC, respectively).[7] On the basis of the sharp curvature of the Brönsted-type plot obtained

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Table 1. Values of pK_a of Phenols and k_N for Reactions of Phenoxides with Diaryl Carbonates[a]

phenoxide substituent	pK_a of phenol	k_N/s^{-1}M^{-1}			
		MPNPC	ClPNPC	MPDNPC	ClPDNPC
4-methoxy	10.3	12.7 ± 0.3	26.0 ± 0.8		
none	9.9	5.3 ± 0.1	12.6 ± 0.5	17.5 ± 0.6	23.7 ± 0.6
3-chloro	9.0	2.8 ± 0.03	6.25 ± 016		
3-cyano	8.6			6.4 ± 0.4	15.7 ± 0.9
4-cyano	7.8	0.64 ± 0.02	1.59 ± 0.04	2.85 ± 0.1	5.95 ± 0.2
2,6-difluoro	7.1		0.202 ± 0.006	12.4 ± 0.06	4.49 ± 0.15
pentafluoro	5.3				0.40 ± 0.02

[a] Both the pK_a and k_N values were determined in aqueous solutions, at 25.0 °C and an ionic strength of 0.2 M (KCl).

for MPNPC, we concluded that these reactions are stepwise, through the formation of a zwitterionic tetrahedral intermediate ($T^{\pm}$). On the other hand, the slight curvature found for MPDNPC indicates that the reactions of these amines with MPDNPC are concerted.[7]

To extend our mechanistic investigations on diaryl carbonates, in the present work, we studied kinetically the phenolysis of 4-methylphenyl 4-nitrophenyl carbonate (MPNPC), 4-chlorophenyl 4-nitrophenyl carbonate (CIPNPC), 4-methylphenyl 2,4-dinitrophenyl carbonate (MPDNPC), and 4-chlorophenyl 2,4-dinitrophenyl carbonate (CIPDNPC).

The object of this work is threefold: (i) to verify the destabilizing effect of a phenoxy substituent in a tetrahedral intermediate relative to a secondary alicyclic amino group, (ii) to examine the influence of the leaving and nonleaving groups of the substrate on the kinetics and mechanisms by comparing the reactions of the present investigation among them and with the phenolyses of **4**−**6**, and (iii) to assess the above effects through a multiparametric equation involving the basicity of the nucleophile, the nucleofuge, and the nonleaving group.

Experimental Section

Materials. The phenols were purified by distillation or recrystallization. The carbonates MPNPC and MPDNPC were synthesized as published elsewere.[7] The substrates CIPNPC and CIPDNPC were synthesized by a modification of a standard procedure,[8] as reported.[6b]

The crystallized (diethyl ether) CIPNPC melted at 113.4−114.4 °C and was identified as follows: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.34 (d, 2H, J = 9.0 Hz), 7.45 (m, 4H), 8.32 (d, 2H, J = 9.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 121.70 (C-2′/6′), 122.13 (C-2/6), 125.45 (C-3/5), 129.82 (C-3′/5′), 132.24 (C-4′), 145.72 (C-4), 149.13 (C-1′), 150.80 (C-1), 155.13 (C=O). Anal. Calcd for $C_{13}H_8NO_5Cl$: C, 53.17; H, 2.75; N, 4.77. Found: C, 53.38; H, 2.52; N, 4.67.

The crystallized (diethyl ether) CIPDNPC melted at 103−104 °C and was identified as follows: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.25 (sd, 2H, J = 9.1 Hz), 7.42 (sd, 2H, J = 9.1 Hz), 7.67 (d, 1H, J = 8.9 Hz), 8.60 (dd, 1H, J = 8.9, 2.7 Hz), 9.07 (d, 1 H, J = 2.7 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 121.21 (C-6′), 122.13 (C-2/6), 126.24 (C-3′), 129.67 (C-5′), 129.91 (C-3/5), 132.55 (C-4), 141.10 (C-2′), 145.59 (C-4′), 148.07 (C-1), 149.10 (C-1′), 149.96 (C=O). Anal. Calcd for $C_{13}H_7N_2O_7Cl$: C, 46.15; H, 2.07; N, 8.28. Found: C, 46.03; H, 1.86; N, 8.23.

Kinetic Measurements. These were performed spectrophotometrically by following the production of 4-nitrophenoxide or 2,4-dinitrophenoxide ions at 400 or 360 nm, respectively, using a diode array instrument. The reactions were studied in aqueous solutions, at 25.0 ± 0.1 °C and an ionic strength of 0.2 M (maintained with KCl). At least a 10-fold excess of total phenol with respect to the substrate was employed. The initial concentration of the substrates was 3×10^{-5} M in all the reactions. The preparation of the kinetic samples and the pH adjustments were carried out as reported.[6b] Pseudo-first-order rate coefficients (k_{obsd}) were found in all cases. The experimental conditions of the reactions and the k_{obsd} values obtained are shown in Tables S1−S4 (pages S2−S5 in Supporting Information).

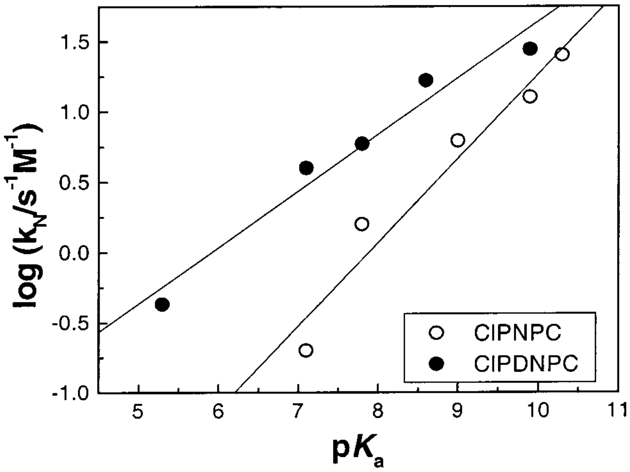

Figure 1. Brönsted-type plots for the phenolysis of 4-methylphenyl 4-nitrophenyl carbonate (MPNPC) and 4-methylphenyl 2,4-dinitrophenyl carbonate (MPDNPC), in aqueous solution (25.0 °C, ionic strength 0.2 M). Slopes are $\beta = 0.48$ and 0.41, respectively.

Product Studies. 4-Nitrophenoxide or 2,4-dinitrophenoxide anions were identified as one of the products of the corresponding title reactions by comparison of the UV−vis spectra after completion of some of these reactions with those of authentic samples of 4-nitrophenol or 2,4-dinitrophenol under the same experimental conditions.

Results and Discussion

The kinetic law found for all the reactions studied is given by eq 1, where k_{obsd} is the pseudo-first-order rate constant, k_0 and k_N are the rate coefficients for hydrolysis and phenolysis of the substrates, respectively, and ArO^- represents the substituted phenoxide nucleophile.

$$k_{obsd} = k_0 + k_N[ArO^-] \qquad (1)$$

The values of k_0 at ca. pH 10 are $10^2 k_0/s^{-1}$ = 0.2, 1.0, 0.3, and 1.5 for the hydrolysis of MPNPC, ClPNPC, MPDNPC, and ClPDNPC, respectively.

Plots of k_{obsd} vs [ArO^-] at a constant pH were linear for the reactions of both substrates, with slopes (k_N) independent of the pH. The values of k_N are shown in Table 1. With these values and the pK_a of the phenols, the Brönsted-type plots (shown in Figures 1 and 2) were obtained.

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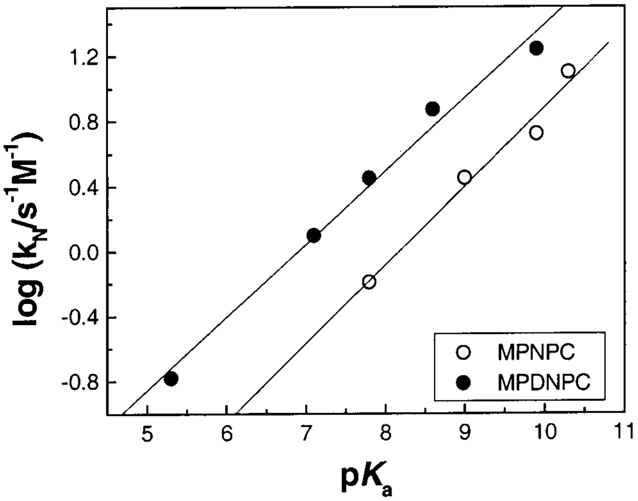

Figure 2. Brönsted-type plots for the phenolysis of 4-chlorophenyl 4-nitrophenyl carbonate (ClPNPC) and 4-chlorophenyl 2,4-dinitrophenyl carbonate (ClPDNPC), in aqueous solution (25.0 °C, ionic strength 0.2 M). Slopes are $\beta = 0.67$ and 0.32, respectively.

The Brönsted plots are linear with the following slope (β) values: $\beta = 0.48$, 0.41, 0.67, and 0.32 for the reactions of MPNPC, MPDNPC, ClPNPC, and ClPDNPC, respectively. The magnitudes of these β values suggest that these reactions are concerted. Similar β values have been found in the concerted phenolyses of aryl methyl carbonates **1**, **2**, and **3** ($\beta = 0.67$, 0.48, and 0.52, respectively),[6a] of aryl phenyl carbonates **4** and **5** ($\beta = 0.61$ and 0.49, respectively),[6b] and for the symmetrical diaryl carbonate **6** ($\beta = 0.66$).[6c]

The concerted aminolyses of related substrates show β values similar to those above. Linear Brönsted plots with slopes $\beta = 0.56$ and 0.48 are exhibited in the reactions of secondary alicyclic amines with *S*-(2,4-dinitrophenyl) and *S*-(2,4,6-trinitrophenyl) ethyl thiolcarbonates.[9] In the reactions of the same amines with carbonates **3**[10] and MPDNPC,[7] the β values are found to be 0.36 and 0.55, respectively. Also, methoxycarbonyl transfer between isoquinoline and pyridines shows a linear Brönsted plot of slope $\beta = 0.58$.[11]

The anionic tetrahedral intermediates formed in the phenolysis of diaryl carbonates must be very unstable due to the three *O*-aryl groups attached to the central carbon of the intermediate. Williams has argued that two *O*-aryl groups are sufficient to destabilize anionic tetrahedral intermediates (T^-), for instance, those formed in the phenolysis of aryl acetates.[2a] Therefore, it is reasonable that the "intermediates" formed in the reactions of the present work would be so unstable as to prevent their existence, enforcing a concerted mechanism.[12]

On the other hand, we have found that the aminolysis (secondary alicyclic amines) of MPNPC is stepwise, i.e., the zwitterionic tetrahedral intermediate ($T^\pm$) formed in these reactions exists.[7] The fact that the anionic "intermediate" T^- formed in the phenolysis of aryl acetates is either nonexistent or highly unstable[2a] means that substitution of an amino moiety in $T^\pm$ by a methyl group greatly destabilizes this intermediate.

The magnitude of the slope of the Brönsted plot alone does not prove that the reactions are concerted. One must be sure that there is no Brönsted break at the pK_a expected for a change in the rate-determining step for a hypothetical stepwise reaction.[12] If the phenolyses of MPNPC and ClPNPC were stepwise, the Brönsted plot break for both reactions would be at pK_a = 7.1, the pK_a of 4-nitrophenol. The lack of break in the Brönsted plot for the phenolysis of ClPNPC (Figure 2) indicates that this reaction is concerted. For the phenolysis of MPNPC, the values of k_N found are very similar to those obtained in the phenolysis of **4**.[6b] Since the latter reaction is concerted, it is very likely that the phenolysis of MPNPC is also driven by a concerted mechanism, in view of the similar pK_a values of phenol and 4-methylphenol.[13]

The hypothetical Brönsted break for the phenolysis of MPDNPC and ClPDNPC for a stepwise reaction would be at pK_a = 4.1 (the pK_a of 2,4-dinitrophenol). This breakpoint lies beyond the pK_a range of the phenols used in this work. However, if the phenolyses of MPNPC and ClPNPC are concerted, it is reasonable that the phenolyses of MPDNPC and ClPDNPC would also be concerted. This is because of the better nucleofuge involved in the latter intermediate, which would destabilize it even more compared to the intermediate in the mononitro derivatives.

The phenolysis of MPNPC is concerted (this work), whereas the aminolysis (secondary alicyclic amines) of this compound is stepwise.[7] This means that substitution of a secondary alicyclic amino moiety in a zwitterionic tetrahedral intermediate by a phenoxy group destabilizes the intermediate. This result is in agreement with the fact that the phenolyses of ethyl *S*-(4-nitrophenyl) thiolcarbonate[5] and carbonate **1**[6a] are concerted, in contrast to their aminolyses, which are stepwise.[14,15]

The greater reactivity toward phenoxides of MPDNPC and ClPDNPC than that of the corresponding mononitro substrates, MPNPC and ClPNPC (Figures 1 and 2), should be due to the presence of the second nitro group in the dinitro substrates, which leaves their carbonyl carbon more positive and makes them better electrophiles. Moreover, since the second nitro group is in the nucleofuge, this should be expelled faster from MPDNPC and ClPDNPC than 4-nitrophenoxide anion from MPNPC and ClPNPC, respectively.

On the other hand, the greater reactivity of ClPDNPC than MPDNPC and of ClPNPC than MPNPC toward phenoxides (Table 1) could be explained by the greater electron-withdrawing effect of 4-chloro than 4-methyl.

To evaluate the influence of the nonleaving moiety on the kinetics of these reactions, the Brönsted plots for the phenolyses of MPNPC, ClPNPC, **6**,[6c] and **4**[6b] are compared in Figure 3. In this figure, pK_a (nlg) is the pK_a of the conjugate acid of the "nonleaving" group and each line corresponds to a different phenoxide nucleophile. As seen in Figure 3, the plots are linear; the slopes vary from −0.24 to −0.33. The negative slopes are due to the fact

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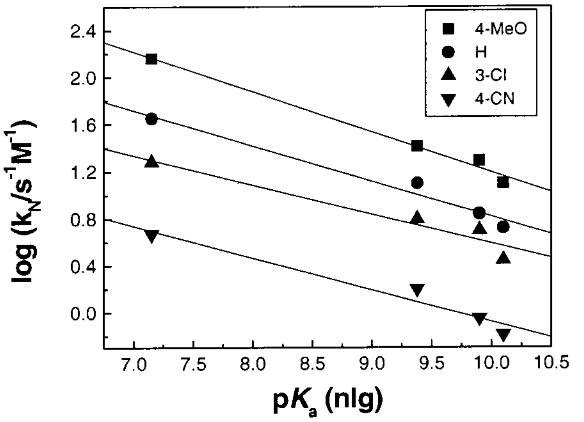

Figure 3. Brönsted-type plots (for the nonleaving group) for the phenolysis of aryl 4-nitrophenyl carbonates, in aqueous solution (25.0 °C, ionic strength 0.2 M). Substituents in the phenoxide nucleophiles are 4-MeO, H, 3-Cl, and 4-CN.

that nucleophilic attack is hindered by electron donation from the nonleaving group.

The Brönsted plots for the nonleaving group (not shown) obtained for the phenolysis of MPDNPC, ClPDNPC, and **5**[6b] are also linear with slopes similar to those found for the phenolysis of the mononitro derivatives (Figure 3). Unfortunately, the Brönsted plots for the dinitro compounds contain only three points for each nucleophile and the pK_a span is smaller than that for the mononitro derivatives.

With the k_N values found in the present reactions and those for the phenolysis of **4**−**6**, together with the pK_a values of the nucleophiles (Table 1), the leaving groups (7.1 and 4.1 for 4-nitro- and 2,4-dinitrophenols, respectively),[13] and the nonleaving groups (10.1, 9.9, 9.4, and 7.1 for 4-methyl, H, 4-chloro-, and 4-nitrophenols, respectively),[5,13] eq 2 can be deduced by regression analysis ($n = 37$, $R^2 = 0.952$). In this expression, N, nlg, and lg refer to the nucleophile and the nonleaving and leaving groups, respectively; the pK_a coefficients (β) are subjected to an error of ±0.1.

$$\log k_N = -0.038 + 0.54\mathrm{p}K_a(\mathrm{N}) - 0.25\mathrm{p}K_a(\mathrm{lg}) - 0.27\mathrm{p}K_a(\mathrm{nlg}) \quad (2)$$

A logarithmic plot of the experimental k_N vs the calculated one through eq 2 is shown in Figure 4; the slope is unity.

The sensitivity of log k_N to the nucleophile pK_a ($\beta_N = 0.54$) is in agreement with those exhibited in the concerted phenolysis of aryl methyl carbonates[6a] and in the concerted aminolysis of carbonyl compounds, as mentioned above.[7,9−11]

On the other hand, the sensitivity of log k_N to the leaving group basicity ($\beta_{lg} = -0.25$) is similar to that found in the phenolysis of aryl methyl carbonates;[6a] but its absolute value is greater than that exhibited by the concerted aminolysis ethyl *S*-aryl thiolcarbonates ($\beta_{lg} = -0.19$)[9] and lower than the corresponding ones for the concerted phenolysis of aryl acetates (from −0.5 to −0.6) and aryl formates (from −0.3 to −0.9).[4]

However, the β_{lg} value in eq 2 is also similar to those found in stepwise aminolyses of acetate esters,[16] diaryl carbonates,[8] and *O*-ethyl dithiocarbonates.[17] In all of these works, the low β_{lg} value (between 0 and −0.3) has been associated with a stepwise mechanism where the formation of the zwitterionic tetrahedral intermediate is the rate-determining step. For the aminolysis of the less reactive aryl thiolcarbonates, where the breakdown to products of the tetrahedral intermediate is the rate-determining step, the values of $-\beta_{lg}$ are in the 0.7−0.8 range.[18]

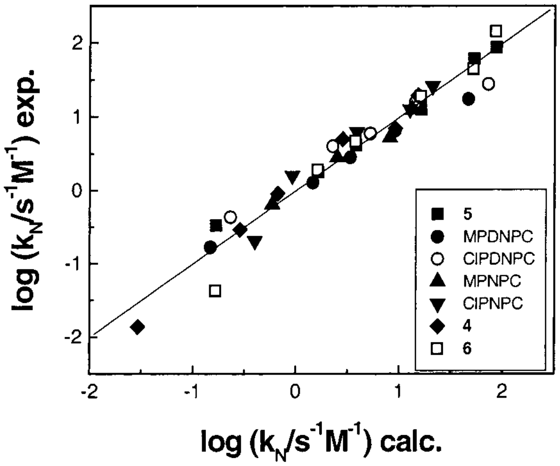

Figure 4. Logarithmic plot of experimental vs calculated (through eq 2) k_N for the reactions of a series of phenoxide ions with a series of diaryl carbonates, in aqueous solution (25.0 °C, ionic strength 0.2 (KCl)). Carbonates are phenyl, 4-methylphenyl, and 4-chlorophenyl 2,4-dinitrophenyl carbonates for **5**, MPDNPC, and ClPDNPC, respectively, and phenyl, 4-methylphenyl, 4-chlorophenyl, and 4-nitrophenyl 4-nitrophenyl carbonates for **4**, MPNPC, ClPNPC, and **6**, respectively.

The similar sensitivity of log k_N to the basicity of both the nonleaving and leaving groups is probably due to the fact that both are phenoxy groups. On the other hand, it is noteworthy that the sum of sensitivities to the nucleophile (β_N) and leaving (β_{lg}) and nonleaving (β_{nlg}) groups is approximately zero (see eq 2). This means that for the phenolysis of bis(aryl) carbonates with the same aryl group in the nucleophile and the leaving group, the rate constants must be the same, independent of the aryl group. Namely, the rate constant for the reaction of phenoxide anion with bis(phenyl) carbonate should be approximately equal to that of 4-nitrophenoxide anion with bis(4-nitrophenyl) carbonate. Unfortunately, this is not possible to prove experimentally since these reactions are indistinguishable. Nevertheless, it seems reasonable that a strong nucleophile will have a great difficulty in displacing a strongly basic leaving group because a good nucleophile is a bad nucleofuge.

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Supporting Information Available: Tables S1−S4 containing the values of k_{obsd} and experimental conditions for the reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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