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THE EFFECT OF SUBSTITUENTS ON THE REACTIVITY OF ANILINE WITH PHOSPHATE RADICAL

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Abstract - The reaction between aromatic amines and phosphate radical has been investigated. The reaction is accelerated by electron-releasing substituents and retarded by electron-withdrawing substituents pointing to an electrophilic attack by the $PO_4^{2\cdot-}$ radical. σ^+_{para} values correlate the effect of substituents well. The rho value for $PO_4^{2\cdot-}$ is more positive than that for $CO_3^{\cdot-}$ indicating higher reactivity of phosphate radical towards aromatic amines than the carbonate radical.

INTRODUCTION

In recent years studies relating to flash photolytic generation of inorganic radicals and the kinetics of their reactions have received much attention[1,2]. Besides providing a direct method of production of the radicals, kinetic flash spectrophotometric technique enables one to determine the rate constants of their reactions with a variety of substrates. Thus substituent effects and other related correlations for radical induced reactions can be investigated in a straightforward manner. We have investigated the reactivities of several radicals with organic substrates[3-5]. In this paper we report our results relating to the phosphate radical.

Phosphate radical is a good oxidising agent and can react with organic substrates either by direct electron transfer or by hydrogen atom abstraction[6,7]. The reaction of the phosphate radical with a series of para-substituted anilines has been studied by the flash photolysis technique with a view to obtain insight into the mechanism.

RESULTS AND DISCUSSION

The phosphate radical, $PO_4^{2\cdot-}$, is produced by the flash photolysis of a deaerated aqueous solution containing 0.1mM peroxydiphosphate at pH 11.0[8,9].

$$P_2O_8^{4-} \xrightarrow{h\nu} 2PO_4^{2\cdot-} \qquad (1)$$

The absorption of the phosphate radical at 530 nm (ϵ = 2150 $M^{-1}cm^{-1}$)[7] was observed immediately after the light pulse. The decay of the radical is second order in the absence of any scavenger (decay rate constant = 2.0×10^8 $M^{-1}s^{-1}$) and becomes pseudo-first order in the presence of added scavenger[5]. The pseudo-first order rate constants (k') were determined for atleast three different initial concentrations of the scavenger and at each concentration atleast three kinetic curves were processed. The second order rate constants (k_s) were determined from the slope of the plots of k' vs [scavenger] (Fig.1). These values obtained for aniline and some para-substituted anilines at pH 11.0 are given in Table 1. These data are subject to the errors inherent in flash photolysis studies (±10%).

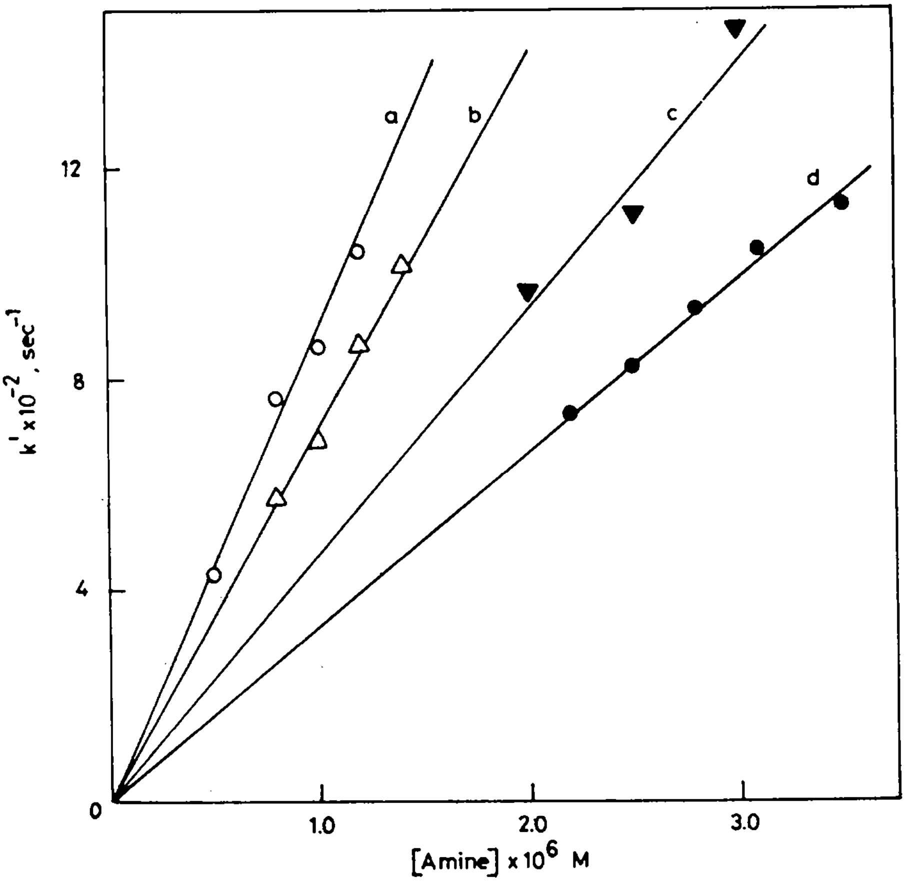


Fig. 1 Dependence of k' on amine concentration at pH 11.0 a) p-Fluoroaniline b) Aniline c) p-Bromoaniline and d) p-Aminoethylbenzoate.

Effect of pH

The rate constants for the reaction of phosphate radical with aniline are markedly influenced by pH in the range 5-11 (Table 1). Since the pK_a of aniline is 4.63, it remains virtually in the basic form throughout the pH range studied. Hence the observed wide variations in the rate constants with pH are primarily due to the different acid-base forms of phosphate radical[7] (eqn. 2).

$$\underset{pK_a}{H_2PO_4^{\cdot}} \quad \underset{5.7}{\rightleftharpoons} \quad HPO_4^{\cdot -} \quad \underset{8.9}{\rightleftharpoons} \quad PO_4^{2\cdot -} \qquad (2)$$

Phosphate radical exists as $H_2PO_4^{\cdot}$ below pH 5.7, $HPO_4^{\cdot -}$ between pH 5.7-8.9 and $PO_4^{2\cdot -}$ above pH 8.9. The rate constants have been calculated for the reaction at

Table 1. Rate constants and Hammett constants for para-substituted anilines (pH 11.0).

Amine	k_s / $M^{-1}s^{-1}$	σ_{meta}	σ_{para}	σ^+_{para}
Aniline	7.10×10^8 1.47×10^9 (pH 7.0)[a] 10^{10} (pH 5.0)[b]	0.00	0.00	0.00
p-Chloroaniline	6.00×10^8	0.37	0.23	0.11
p-Bromoaniline	5.75×10^8	0.39	0.23	0.15
p-Aminoethyl-benzoate	3.31×10^8	0.37	0.45	0.48
p-Aminobenzoic-acid	3.12×10^8	0.37	0.45	0.42
p-Nitroaniline	1.62×10^8	0.71	0.78	0.79
p-Fluoroaniline	8.71×10^8	0.34	0.06	-0.07
p-Toluidine	1.34×10^8	-0.07	-0.17	-0.31

[a] involves $HPO_4^{\cdot -}$; [b] involves $H_2PO_4^{\cdot}$

these pHs. It may be concluded that the rate constants for the reaction of aniline with $H_2PO_4^{\cdot}$, $HPO_4^{\cdot -}$ and $PO_4^{2\cdot -}$ are 7.10×10^8, 1.47×10^9 and $\sim 10^{10}$ $M^{-1}s^{-1}$ respectively (Table 1). This is in agreement with the stronger oxidising character of $H_2PO_4^{\cdot}$ radical[6]. Since aniline is in the uncharged basic form throughout this pH range, the variation in the rate constants cannot be attributed to the effect of ionic strength. The reaction of $PO_4^{2\cdot -}$ with aniline is likely to involve a direct electron transfer from aniline to $PO_4^{2\cdot -}$. Studies with other types of inorganic radical ions have indicated that the protonated forms of inorganic radicals have more or less same rate constants for substrates undergoing reaction via hydrogen abstraction or addition mechanism[3], and the rate constants differ only when electron transfer takes place.

Effect of substitutents

As a study of the influence of substituents on the rate of reaction often leads to a better understanding of the mechanism, the rates have been measured with para-substituted anilines. The results showed that the rate of the reaction is enhanced when electron releasing substituents are present while it is retarded when electron withdrawing sustituents are present. This reflects the electrophilic nature of the phosphate radical.

The Hammett plot has been widely used to correlate the influence of meta- and para-substituents on the reactivity of aromatic substrates[10]. The values of the Hammett substitution constants[11], σ_{meta}, σ_{para} and σ^+_{para}, are given in Table 1. Among the plots of log k_s vs the Hammett substitution constants (σ_p^+, σ_p and σ_m) only the plot of log k_s vs σ_p^+ (Fig.2) gives a good correlation coefficient of 0.997. The ρ value (-0.83) obtained is less negative compared to that obtained for the reaction of carbonate radical with substituted anilines ($\rho = -1.0$)[3] indicating higher reactivity of phosphate radical towards aromatic amines. For the correlation of rate constants for the reaction of phosphate radical ($H_2PO_4^{\cdot}$) with substituted benzoic acid, a ρ value of -1.8 has been reported[6]. This demonstrates the ease with which the electron deficient phosphate radical removes an electron from substituted anilines compared to substituted benzoic acid.

Substituent effect on the electrooxidation of para-substituted anilines has

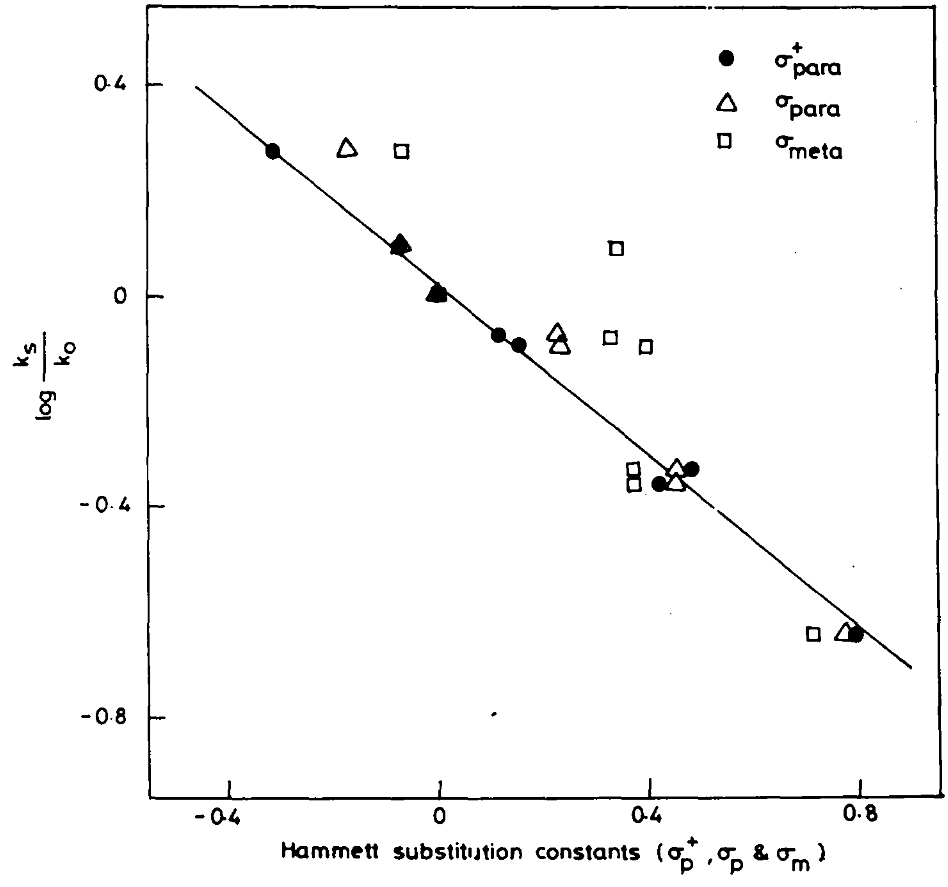


Fig. 2 Hammett plot for the reaction of $PO_4^{2\cdot-}$ radicals with substituted anilines at pH 11.0

been studied by Kazua et al[12]. The standard oxidation potentials determined by the potential drop method were found to correlate well with the Brown-Okamoto[13] σ^+ substituent constants. Crable and Kearns[14] also found that the ionization potentials of para-substituted anilines correlate well with σ^+_{para} values. The good correlation obtained in the phosphate radical reaction (Fig.2) suggests that the rate constants are influenced by the ionization potential or oxidation potential of para-substituted anilines and that there is a possible electron transfer from the aniline to phosphate radical.

Hence attempts have been made to identify the possible anilino-radical intermediate. For the protonated ($C_6H_5\overset{\cdot+}{N}H_2$) and basic ($C_6H_5\dot{N}H$) forms of the anilino radical, absorption maxima of 423 and 300 nm respectively, have been reported by Land and Porter[15]. With aniline a transient absorption around 424 nm (Fig. 3a) has been observed at pH 6.0 and is identical with that reported for $C_6H_5\overset{\cdot+}{N}H_2$ [15]. (The absorption around 300 nm could not be followed due to limitations of the monitoring source). Similarly with p-nitroaniline at pH 5.0, a transient absorption having maxima at 440 and 490 nm (Fig. 3b) was observed which is due to the formation of the p-nitroanilino cation radical, p-$NO_2C_6H_4\overset{\cdot+}{N}H_2$ [16]. At pH 11.0 the anilino cation radical that is formed probably gets deprotonated to give the anilino radical, $C_6H_5\dot{N}H$ (pK_a = 7.0)[15], which can further dimerise to give hydrazobenzene, ben-

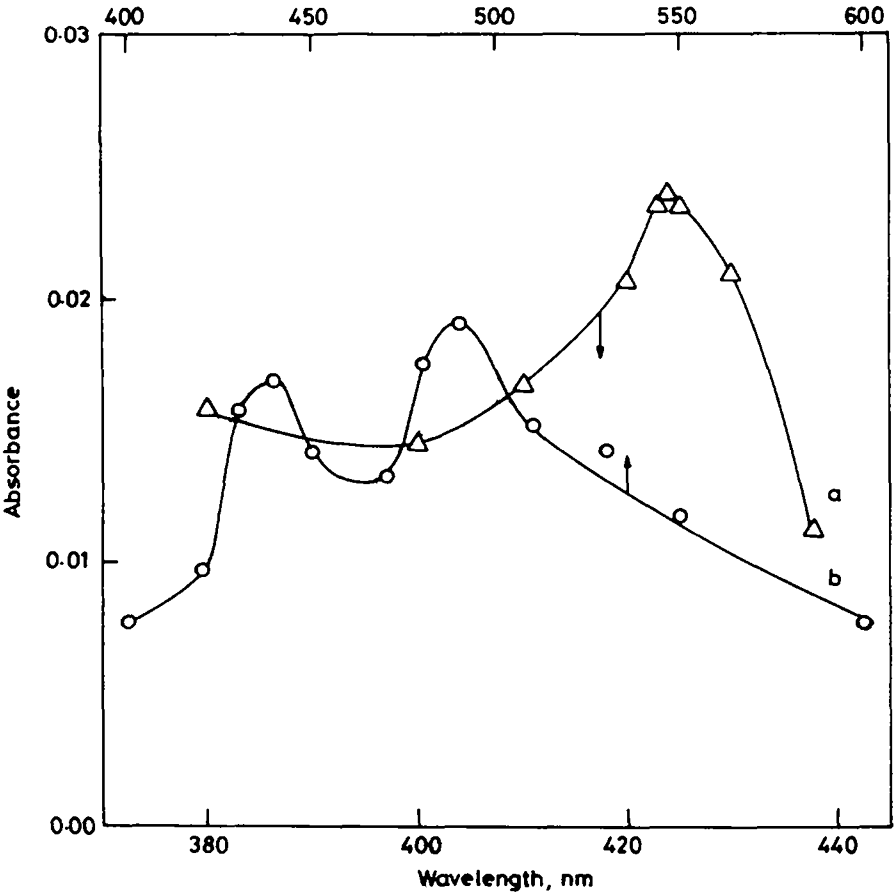


Fig. 3 Transient absorption spectra produced following the flash photolysis of 0·1 mM peroxydiphosphate and a) 0·1 mM aniline (pH 6.0) b) 0·1 mM p-nitroaniline (pH 5.0). Absorbance measured 1 ms after start of flash.

zidine, 2- and 4-aminodiphenylamine and other products as shown in Scheme I[5].

All these observations clearly demonstrate an electron transfer from the aromatic amine to the phosphate radical. The reaction of phosphate radical with aliphatic amines has also been studied and the rate constants are found to be one or two orders of magnitude lower than those for aromatic amines. Detailed studies of these systems are in progress.

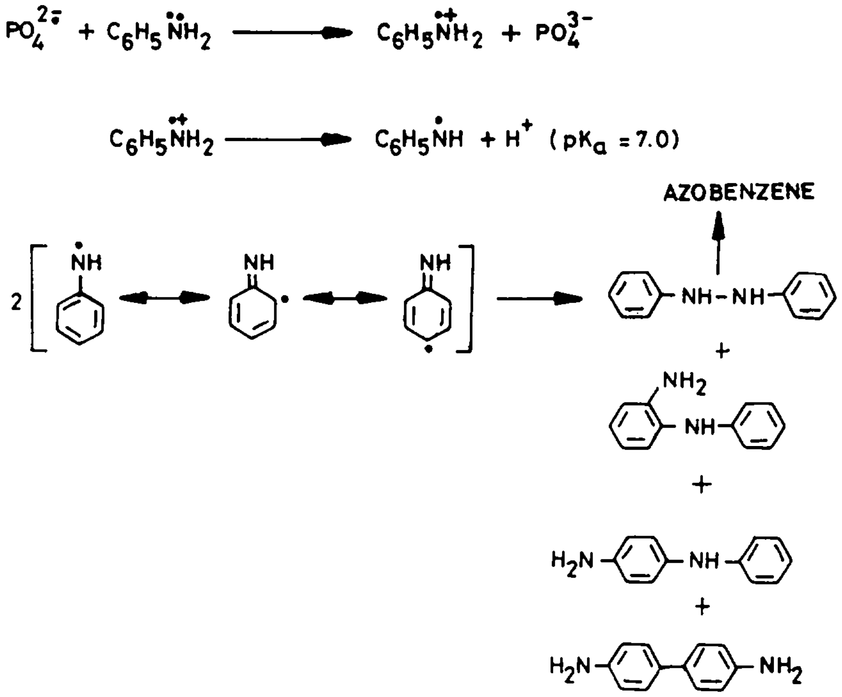
EXPERIMENTAL

All chemicals used in this investigation were of analytical grade. Lithium peroxydiphosphate was prepared and purified as reported in the literature[17]. Freshly distilled samples of amines were used for preparing the solutions. In the case of solid amines, recrystallised samples were used and their purity checked from their melting points.

Flash photolysis experiments were carried out in a Nortech Flash Photolysis unit type FPX-1 using a 10 cm quartz cell and the transient was recorded using a Kikusui Digital Storage Oscilloscope (DSS-5040) combined with a chart recorder (Omnigraphic 2000 recorder). The flash lamps dissipated upto 200J of energy with a flash duration of about 30 microseconds. The decay of the phosphate radical was monitored by following the absorbance at 530 nm and measurements were made at 23.0±1.0°C.

All solutions were prepared with triply distilled water and deaerated with purified nitrogen before flashing.

Scheme 1



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