Effect of Polyethyleneimine on the Decomposition of *p*-Nitrophenyl Phosphate in Aqueous Solutions at 73 °C

By R. Fernández-Prini* and D. Turyn

(*Departamento de Fisicoquímica, Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires, Buenos Aires, Argentina*)

Summary The hydrolysis of *p*-nitrophenyl phosphate in the presence of polyethyleneimine has a complex pH dependence which may be explained by the electrostatic interaction between substrate and polymeric chains (polyelectrolyte effect); in alkaline solutions this effect is probably coupled with the nucleophilic attack on the substrate by the amino-groups of the polyelectrolyte.

The decomposition of *p*-nitrophenyl phosphate (*p*-NPP) has been studied over a wide pH range in the presence of polyethyleneimine (PEI). According to the pH of the solution the first-order rate constant is observed to decrease or increase with increasing concentration of PEI.

The reaction of aromatic amines with *p*-NPP in alkaline solutions produces *p*-nitrophenol and substituted anilines.[1] Substituted anilines are also formed when the substrate

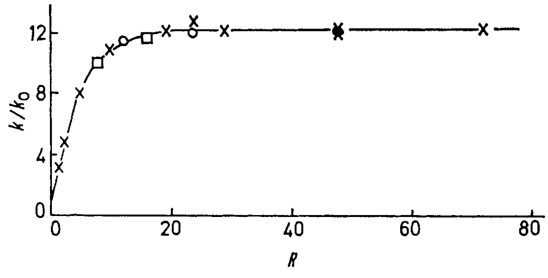

Figure 1. *Relative rate constant for hydrolysis of* p-*NPP against* R = [*PEI*]/[p-*NPP*] at 73 °C *and* pH = 8·3 (k_0 = 0·21 × 10^{-5} s^{-1}). p-*NPP* (mol l^{-1}); ●: 0·5 × 10^{-3}; × : 1 × 10^{-3}; ○ : 2 × 10^{-3}; □ 3 × 10^{-3}.

reacts in the presence of PEI; this is shown by the optical density of the solutions at 400 nm in acid solutions[1] (pH 3). When the reaction is carried out in acid or in very alkaline (pH > 11) solutions, the amount of aniline formed is appreciably reduced. In moderately alkaline solutions the decomposition of *p*-NPP in the presence of PEI at 73 °C proceeds mainly (*ca.* 88%) by formation of *p*-nitrophenol. The overall amount of *p*-NPP hydrolysed at various times was calculated from the optical density of the solution at 400 nm after adjusting the pH to a value $\geqslant 9$[2] and assuming all the product to be *p*-nitrophenol. This approximation is justified by the relatively small amount of aniline formed and the fact that its extinction coefficient may be estimated to differ no more than 20% from that of *p*-nitrophenol.[1] Commercially available *p*-NPP was used without further purification. PEI had an average molecular weight of 40,000 (B.D.H. Polymine P) and an average molecular weight of 60 per ionogenic group (taken as "monomer" molecular weight). The kinetic runs without polyelectrolyte gave results in agreement with previous work at 73 °C.[3] The runs with PEI were carried out without buffer since the weak polyelectrolyte acts as a buffer system.

Figure 1 shows that in alkaline solution the first-order rate constant increases with $R = [\text{PEI}]/[p\text{-NPP}]$ until R is *ca.* 20 when k/k_0 (k_0 = first-order rate constant for hydrolysis in the absence of PEI) reaches a constant value of 12 (at pH 8·3). The fact that k/k_0 depends only on R and not on the concentration of polyelectrolyte, *i.e.* on the overall concentration of amino-groups as is the case for the reaction with monomeric amines,[1] is clear evidence of a polyelectrolyte effect. This dependence is a consequence of the applicability of the domain model to account for the electrostatic interactions in polyelectrolyte solutions,[4] since the distribution of counterions around the chain at constant R is a function of pH only. The electrostatic field attracts the substrate anions near the macro-ion where the free amino-groups are; when the number of free amino-groups exceeds sufficiently that of substrate molecules a maximum value of the rate constant is reached. The importance of electrostatic interactions in presence of PEI is also supported by the observed inhibition of the reaction rate when inert salts were added to the solution, bivalent anions producing a larger inhibition than univalent anions.

Figure 2 illustrates the change in rate constant produced by PEI at different pHs. A notable feature of the curve in Figure 2 is that PEI produces a decrease of the rate of hydrolysis in acid solutions and a sharp enhancement for pH between 7·0 and 9·7. At pH > 11 the first-order rate constant is equal to that without PEI in spite of the increase in the concentration of unchanged amino-groups. At pH 7 the *p*-NPP monoanion would be hydrolysed by proton transfer,[1,5] Figure 2 confirms this if the electrostatic effect of PEI is considered. The monoanion is attracted towards the chain while protons are repelled, hence a decrease of hydrolysis ensues. At very low pH the substrate is unchanged and the addition of PEI has no effect on the rate constant of hydrolysis of *p*-NPP.

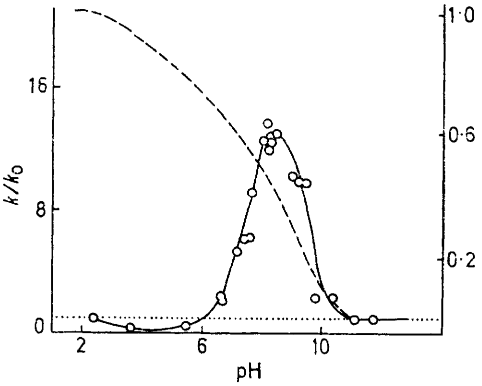

FIGURE 2. *Relative constant for hydrolysis of* p-*NPP* (*left axis and full curve*) *and* i, *degree of neutralization of PEI* (*right ordinate axis and dashed curve*) *against* pH. (*PEI*) $= 4{\cdot}8 \times 10^{-2}$ *monomol* l^{-1}, (p-*NPP*) $= 1 \times 10^{-3}$ mol^{-1}.

In alkaline solutions the *p*-NPP dianion is strongly attracted to the polymeric chain where free amino-groups are located, thus favouring the nucleophilic attack of the substrate by these groups, and producing a net increase in rate constant. (Figure 2 does not exclude the possibility of some attack of the substrate by OH^- which would give an analogous pH dependence). When pH is larger than 10 the ionogenic groups in PEI are uncharged as indicated in Figure 2 by the change of degree of neutralization of PEI (*i*) with pH; hence PEI has no effect on the rate of decomposition of *p*-NPP at high pHs. The sharp maximum of k/k_0 (13·0) at pH 8·5 ($i = 0{\cdot}4$) appears because the amount of free amino-groups in PEI increases with pH and simultaneously the charge density of PEI, which draws the substrate near the chains, decreases. The results of the present work suggest that weak polyelectrolytes may be used to alter substantially the rate of reaction of ionic substrates by conveniently adjusting the pH of the solutions.

(*Received, 2nd May* 1972; *Com.* 746.)

---

[1] A. J. Kirby and W. P. Jencks, *J. Amer. Chem. Soc.*, 1965, **87**, 3209, 3217.

[2] B. H. Gibbons and J. T. Edsall, *J. Biol. Chem.*, 1963, **238**, 3502.

[3] P. W. C. Barnard, C. A. Bunton, D. Kellerman, M. M. Mhala, B. Silver, C. A. Vernon, and V. A. Welch, *J. Chem. Soc.* (*B*), 1966, 227

[4] R. Fernandez-Prini, E. Baumgartner, S. Liberman, and A. E. Lagos, *J. Phys. Chem.*, 1969, **73**, 1420.

[5] A. J. Kirby and A. G. Varvoglis, *J. Amer. Chem. Soc.*, 1967, **89**, 415.