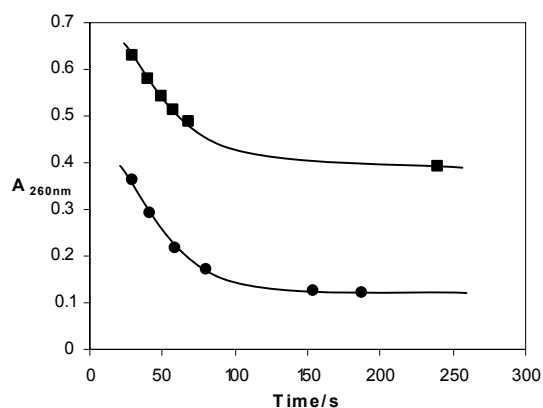
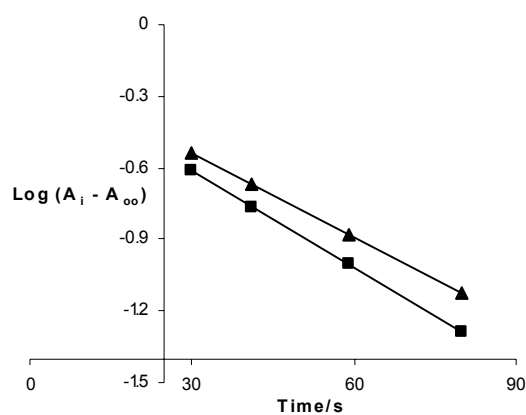


## Supplementary Data A

The product formed in 0.3 M NH<sub>3</sub> and 0.3 M NH<sub>4</sub>Cl containing 1×10<sup>-4</sup> M OPA was after 45 min acidified by addition of acetic acid to pH 4.7. The characteristic absorption band of OPA was rapidly formed, but decreased with time (Fig. A1). The rate of that decreases with a rate constant  $k_{\text{obs}} = 1.2 \times 10^{-2} \text{ s}^{-1}$  were practically identical with the  $k_{\text{obs}} = 1.3 \times 10^{-2} \text{ s}^{-1}$  obtained for the rate of hydration (Fig. A2). The later was determined, when a solution of OPA was added to an acetate buffer of pH 4.7. This indicates that the conversion of product **9** results in a generation of the unhydrated form of OPA, **1**. The conversion of **9** to OPA thus involves initial formation of the unhydrated form **1** as the rate determining step.

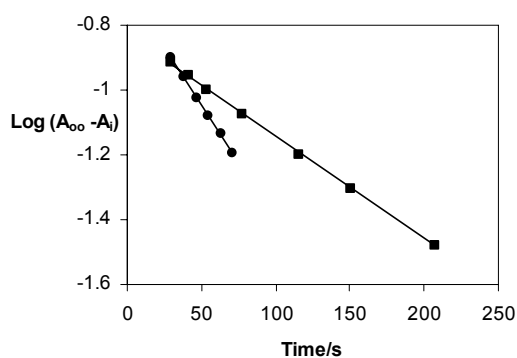


**Fig. A1** Time dependence of absorbance at 260 nm (●) in a solution obtained after acidification of 1×10<sup>-4</sup> M OPA in 0.3 M NH<sub>3</sub> 0.3 M NH<sub>4</sub>Cl (pH 9.3) left to reach equilibrium. After 45 min the pH was adjusted by acetic acid to pH 4.7. The dependence of absorbances compared with the dependence of absorbance at 260 nm in a solution of 1×10<sup>-4</sup> M OPA OPA added directly to an acetate buffer pH 4.7 (■).



**Fig. A2** Plot of logarithm of the absorbance of 260 nm as a function of time, recorded after acidification of the solution of the product of the reaction of  $1 \times 10^{-4}$  M OPA in 0.3 M  $\text{NH}_3$  0.3 M  $\text{NH}_4\text{Cl}$  (▲). For comparison a similar plot obtained after addition of a stock solution of OPA in acetonitrile to an aqueous solution of an acetate buffer pH 4.7 (■).

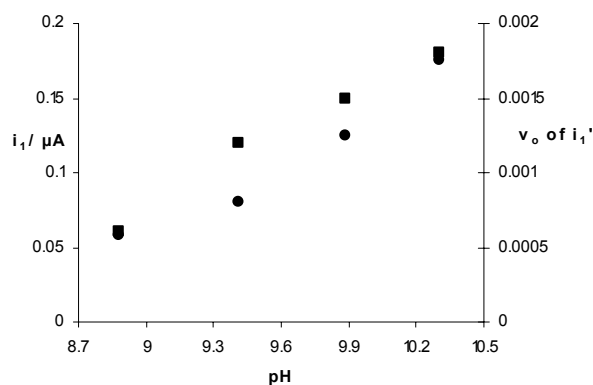
### Supplementary Data B



**Fig. B1** First order kinetics of the fast reaction of OPA with ammonia followed using changes of absorbance at 250 nm in solutions containing  $1 \times 10^{-4}$  M OPA and 0.001M

$\text{NH}_3$  in a solution containing  $0.001\text{M NH}_4^+\text{Cl}$  at pH 9.3 (●) and  $0.01\text{M NH}_4^+\text{Cl}$  at pH 8.3 (■).

### Supplementary Data C

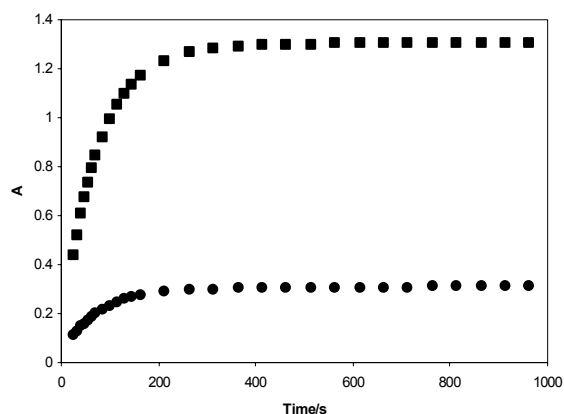


**Fig. C1** Comparison of the dependence of the current  $i_1$  in a solution of  $1 \times 10^{-4}$  M OPA in ammonia-ammonium chloride buffers at constant  $[\text{NH}_3]$  on pH (left axis, ●) with the pH-dependence of the initial rate ( $v_0$ ) of the fast reaction of OPA with  $\text{NH}_3$  (right axis, ■).

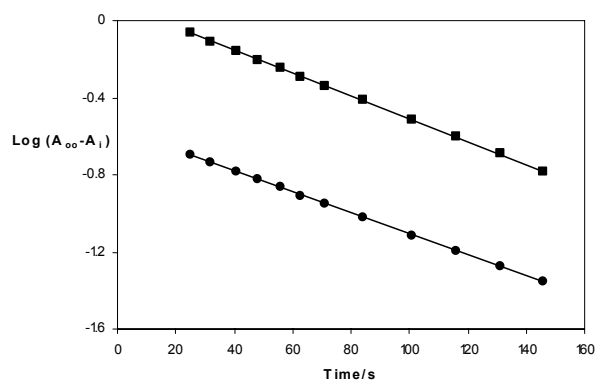
The rate of formation of the imine in the fast reaction is controlled by the rate of dehydration of OPA.

### Supplementary Data D

Fast reaction of OPA with 2-aminoethanol



**Fig. D1** Time dependence of absorbance in a solution containing  $1 \times 10^{-4}$  M OPA in the presence of 0.005 M 2-aminoethanol and 0.005 M protonated form of the amine. ■ absorbance at 235 nm, ● absorbance at 285 nm.



**Fig. D2** Dependence of logarithm of absorbance on time in a solution of  $1 \times 10^{-4}$  M OPA in a buffer containing 0.005M 2-aminoethanol and 0.005 M of its protonated form at pH 9.5. ■ absorbance at 235 nm; ● absorbance at 285 nm.