

## REACTION KINETICS AND MECHANISM OF N-(2,4-DINITROPHENYL)PYRIDINIUM CHLORIDE WITH ANILINE

J. KAVÁLEK and V. ŠTĚRBA

*Department of Organic Chemistry*

*Institute of Chemical Technology, 532 10 Pardubice*

Received February 17th, 1973

Influence of aniline, pyridine and pH on the title reaction has been studied in 50% aqueous ethanol. Transformation of *III* into *IV* is rate-limiting at low pH values, the reaction rate being inversely proportional to the proton concentration. Catalytic effect of both aniline and lyate ions becomes increasingly significant with increasing pH, and deprotonation of the intermediate *II* becomes rate-limiting. The kinetic equations have been derived and the constants of the individual reaction steps calculated.

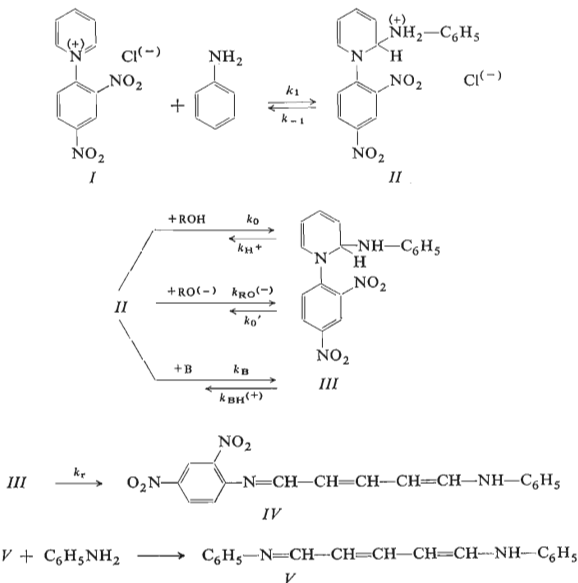
N-(2,4-Dinitrophenyl)pyridinium chloride *I* reacts with aniline to give N-phenyl-5-anilino-2,4-pentadienyldieneimine *V* and its hydrochloride<sup>1</sup>. Mechanism of the reaction was studied in 50% aqueous ethanol<sup>2</sup>. The authors arrived at a conclusion that the reaction is 1. order in aniline, hydroxyl ion and the starting compound *I*. They suggested a reaction mechanism involving the rate-limiting reaction of the protonated adduct *II* (Scheme 1) with hydroxyl ion. A more recent paper<sup>3</sup> states that the reaction is overall 3. order, being 1. order in the substance *I* and 2. order in aniline. The most recent report<sup>4</sup> dealing with the cyclization reaction of the compound *V* into N-phenylpyridinium chloride also presents a preliminary study of reaction of the compound *I* with aniline, and the authors merely state that kinetics of this reaction is complicated. In the context of the studies carried out in our laboratory on the reactions of the arylpyridinium salts with nucleophilic reagents, the present paper forms a part the aim of which was to study the reaction kinetics and mechanism of the compound *I* with aniline in detail.

### EXPERIMENTAL

N-(2,4-Dinitrophenyl)pyridinium chloride *I* was prepared by heating 40.5 g (0.2 mol) 2,4-dinitrochlorobenzene and 16 g (0.2 mol) pyridine in 100 ml toluene on a boiling water bath for 8 h. After cooling the precipitate was filtered off and crystallized from ethanol. Yield 45 g beige needles melting at 190–198°C with decomposition (ref.<sup>5</sup> gives m.p. 185–195°C decomp.).

*Kinetic measurements* were carried out in 50% (by vol.) ethanol at 20°C, the ionic strength being adjusted at 0.05 by addition of KCl. Mixtures of primary and secondary sodium phosphates or anilin-anilinium chloride were used as buffers. Kinetic experiments were carried out in the following way: N-(2,4-dinitrophenyl)pyridinium chloride solution, the amount of which was chosen to make the final concentration  $3 \cdot 10^{-5}$  M, was injected into a mixture of aniline, buffer and KCl. A part of the resulting solution was placed in a 1 cm cell in the thermostated cell compartment of a Zeiss VSU-2P spectrophotometer, and the time dependence of extinction was

determined. The wavelengths 490 nm and 410 nm were used for  $\text{pH} < 8$  and  $\text{pH} > 8$ , respectively, the former being the  $\lambda_{\text{max}}$  of the protonated form of the substance *V* and the latter that of the respective neutral form; in the case of several experiments carried out in the pH range 7.5–8.5 the extinction was measured at both the wavelengths. In selected experiments the spectra were measured by means of a Unicam SP 800 apparatus in the range 350–550 nm at definite time intervals. The experimental rate constants were obtained from the dependence of  $\log(E_{\infty} - E_t)$



SCHEME 1

on time. pH of the reaction mixtures was measured by means of a Radiometer apparatus and a calomel and a glass electrodes at 20°C after finishing each experiment. From the pH value measured 0.2 pH units was subtracted as correction<sup>6</sup> (Correction terms  $E_j - \log_m \gamma_H = \delta$ ). Aqueous solutions of primary and secondary phosphates were used as standards for calibration of pH-meter. In order to find the  $\text{OH}^-$  ion concentrations corresponding to the measured pH values, we measured pH of 0.01, 0.02 and 0.05M-NaOH solutions in 50% ethanol at 20°C and the same ionic strength.

## RESULTS AND DISCUSSION

The overall reaction mechanism can be expressed as it is given in Scheme 1. The time dependence of  $\log(E_\infty - E_t)$  of the reaction products is linear in the whole range investigated. It means that the reaction is 1. order in *N*-(2,4-dinitrophenyl)pyridinium chloride and the concentrations of intermediates *II*–*IV* are very small. This finding was confirmed by the electronic spectra (350–550 nm) measured in the course of the reaction investigated. By this method no other compounds were found besides the products. Bimolecular rate constant  $k_2$ , obtained through dividing the experimental constant by aniline concentration, increases with aniline concentration, and this increase is greater at higher pH values (Fig. 1). The same increase of  $k_2$  (at the same pH value) caused by addition of pyridine instead of aniline (Fig. 1) suggests that aniline resp. pyridine act as basic catalysts in transformation of intermediate *II* into *III*. As only one aniline molecule makes itself felt kinetically as a nucleophilic reagent, the reaction of the intermediate *IV* with a further aniline molecule takes place after the rate-limiting step.

Fig. 2 gives the dependence of  $k_2$  on  $1/[\text{H}^+]$  for various aniline concentrations. The dependence is non-linear up to  $1/[\text{H}^+] \approx 2 \cdot 10^8$ , and its slope gradually decreases. Therefrom it follows that decreasing of the proton concentration results in a change of the rate-limiting step. As the catalytic influence of aniline increases with decreasing proton concentration in the region of non-linear dependence of  $k$  vs  $1/[\text{H}^+]$ , the most probable interpretation of the results is that the transformation of the intermediate *III* into *IV* is rate-limiting at the highest proton concentration, whereas the splitting off of the proton from the intermediate *II* gradually becomes rate-limiting with decreasing proton concentration, water, ethanol,  $\text{OH}^-$ ,  $\text{C}_2\text{H}_5\text{O}^-$ , aniline resp. pyridine acting as bases (Scheme 1). For this presumed mechanism the rate constant  $k_2$  can be defined on the basis of steady state treatment as follows:

$$k_2 = Kk_r(k_0 + k_{\text{OR}^-}[\text{OR}^-] + k_{\text{B}}[\text{B}])/(k_r + k_{\text{H}^+}[\text{H}^+] + k'_0 + k_{\text{BH}^+}[\text{BH}^+]) \quad (1)$$

$K = k_1/k_{-1}$  is the equilibrium constant of the formation of the intermediate *II*,  $k_{\text{OR}^-}[\text{OR}^-]$  is the sum of the terms  $k_{\text{OH}^-}[\text{OH}^-] + k_{\text{OC}_2\text{H}_5}[\text{OC}_2\text{H}_5^-]$  which could not be determined separately. At low pH values the reaction with  $\text{OR}^-$  and the reverse one with  $\text{ROH}$  are insignificant, and Eq. (1) is simplified to (2). At the highest proton concentrations  $k_r$  is negligible as compared to the other term of the denominator and hence Eq. (3) is valid.

$$k_2 = K \frac{k_r(k_0 + k_{\text{B}}[\text{B}])}{k_r + k_{\text{H}^+}[\text{H}^+] + k_{\text{BH}^+}[\text{BH}^+]} = \frac{Kk_r(k_0 + k_{\text{B}}[\text{B}])}{k_r + k_{\text{H}^+}[\text{H}^+](k_0 + k_4[\text{B}])/k_0} \quad (2)$$

$$k_2 = Kk_r k_0 / k_{\text{H}^+}[\text{H}^+] = Kk_r k_{\text{OR}^-}[\text{OR}^-] / k'_0 \quad (3)$$

The reaction rate is proportional to  $1/[H^+]$  and the catalytic influence of aniline is slight. With decreasing proton concentration the expression  $k_r$  ceases to be negligible. The catalytic influence of aniline begins to be increasingly significant (Fig. 1) and slope of the dependence  $k_2$  vs  $1/[H^+]$  decreases (Fig. 2). Also  $OR^-$  becomes increasingly significant as the base, and the relative importance of the reverse protonation of the intermediate *III* by its reaction with  $BH^+$  and the solvated proton decreases. When the values  $1/[H^+]$  are greater than about  $2 \cdot 10^8$ , Eq. (1) is simplified to Eq. (4). The rate constant  $k_2$

$$k_2 = Kk_r(k_{OR}[OR^-] + k_B[B] + k_0)/(k_r + k_0) \quad (4)$$

is directly proportional to  $OH^-$  ion concentration and the magnitude of its change with the aniline concentration change does not depend on pH (Fig. 1). The ratio of the angular coefficients  $dk_2/d[OR^-] = (k_0 + k_r)/k_0$  is about 11 for the regions of the maximum and the minimum proton concentrations and, hence,  $k_r \approx 10k_0$ . From the dependences of  $k_2$  on  $1/[H^+]$  resp. aniline concentration the following complex rate constants were calculated:  $Kk_0k_r/k_{H^+} = (3.5 \pm 1) \cdot 10^{-11} \text{ s}^{-1}$ ,  $Kk_0 = (2.5 \pm 0.4) \cdot 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $Kk_B = (4 \pm 0.2) \cdot 10^{-3} \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$ ,  $Kk_{OR} = (2.5 \pm 0.3) \cdot 10^3 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$ .

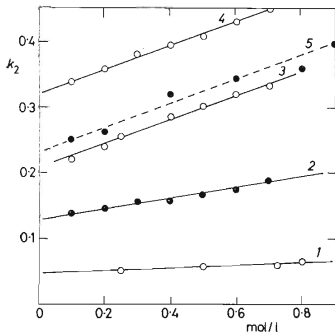


FIG. 1

Dependence of  $k_2$  ( $\text{l mol}^{-1} \text{ min}^{-1}$ ) on Concentrations of Aniline (curves 1–4) and Pyridine (curve 5)

1 pH 7.14, 2 pH 7.75, 3 pH 8.24, 4 pH 8.53, 5 pH 8.19, aniline concentration 0.25M.

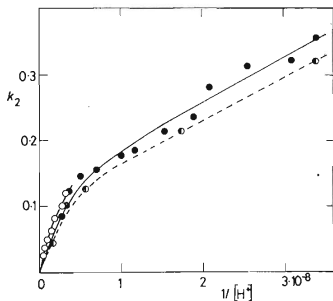


FIG. 2

Dependence of  $k_2$  ( $\text{l mol}^{-1} \text{ min}^{-1}$ ) on  $1/[H^+]$  0.75M Aniline ( $\circ$ ), 0.20M aniline ( $\bullet$ ), the  $k_2$  values obtained by extrapolation to zero aniline concentration ( $\odot$ ).

As the rates of both the reaction of *II* with  $\text{OH}^-$  and the reverse reaction of *III* with  $\text{ROH}_2^{(+)}$  are practically limited by diffusion rate, the constants  $k_{\text{OR}}$  and  $k_{\text{H}^+}$  have the values about  $10^{11}$  and  $5 \cdot 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ , respectively<sup>7</sup>. With the use of these values it can be calculated that  $K$  and  $k_r$  equal about  $2.5 \cdot 10^{-7} \text{ l mol}^{-1}$  and  $10^2 \text{ s}^{-1}$ , respectively. The value used for  $k_{\text{OR}}$  agrees with the intermediate *II* reacting, at  $k_{\text{OR}}/k_0 = 10^6 \text{ l mol}^{-1}$ , equally fast with both  $\text{ROH}$  and  $\text{RO}^{(-)}$  at pH about 8.5.

The great difference between  $k_{\text{B}}$  and  $k_{\text{OR}}$  and, on the contrary, the small one between  $k_{\text{B}}$  and  $k_0$  are rather surprising with respect to the fact that the  $\text{p}K_{\text{a}}$  value of the intermediate *II* cannot be very different from that of the protonated aniline. It would be possible to consider the first two steps to be concerted and general base catalysis of aniline addition to *I* to be operating, the value of the Brönsted coefficient  $\beta$  being about 0.5. However, this mechanism is very unlikely in the case of the reaction with  $\text{ROH}$  which is far weaker base than the intermediate *III* being formed. With respect to sterical requirements of the reaction of aniline with the intermediate *II* it can be presumed that the  $k_{\text{B}}$  value is substantially smaller than that corresponding to the basicity of aniline.

The splitting of N—H bond by  $\text{RO}^{(-)}$  ion, being diffusion-controlled, is rather exceptional as the rate-limiting step. However, as the  $\text{RO}^{(-)}$  concentration used was maximum  $10^{-6} \text{ M}$ , the resulting rate of this reaction was smaller than that of the reverse decomposition of the intermediate *II* into the starting components. A sufficient increase of  $\text{RO}^{(-)}$  concentration should result in such an acceleration of the N—H bond splitting, that the reaction of *I* with aniline would become rate-limiting. This mechanism, however, could not be proved experimentally, because at  $\text{pH} > 9$  the formation of glutamic aldehyde 2,4-dinitroanil becomes the main reaction, its rate being increased with the square of  $\text{OH}^-$  ion concentration<sup>8</sup>.

#### REFERENCES

1. Zincke T.: Ann. 330, 361 (1903).
2. Van den Dungen E., Nasielski J., Van Laer P.: Bull. Soc. Chim. Belges 66, 661 (1957).
3. Oda R., Mita S.: Bull. Chem. Soc. Japan 36, 103 (1963).
4. Marvell E. N., Caple G., Shahidi I.: J. Am. Chem. Soc. 92, 5641 (1970).
5. Suhr H.: Ann. 701, 104 (1967).
6. Bates R. G., Paabo M., Robinson R. A.: J. Phys. Chem. 67, 1833 (1963).
7. Eigen M.: Angew. Chem. (Int. Ed.) 3, 1 (1964).
8. Kaválek J., Polanský J., Štěrba V.: This Journal, in press.

Translated by J. Panchartek.