BASE CATALYSIS IN REACTION
OF N-(2,4-DINITROPHENYL)PYRIDINIUM CHLORIDE
WITH ANILINE AND N-METHYLANILINE

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The reaction of N-(2,4-dinitrophenyl)pyridinium chloride with aniline and N-methylaniline in 60% ethanol giving the corresponding dianile of glutaconic dialdehyde is catalyzed by both the lyate ions and nitrogen bases. The values of rate constants of the reactions catalyzed by nitrogen bases are lower than those of alkoxide-catalyzed reaction by about 7 orders of magnitude, in spite of the rate-determining splitting off of the protons being thermodynamically favourable. It is presumed that the proton-transfer to the nitrogen atom of base is mediated by one or several molecules of solvent.

Aniline reacts with N-(2,4-dinitrophenyl)pyridinium chloride (*I*) to give hydrochloride of dianile of glutaconic dialdehyde (*VIa*) or the respective free base[1]. From the kinetics of this reaction in 50% ethanol it was found[2] that the pyridine ring-opening with formation of the compound *V* is the rate-limiting step at low pH values. (Scheme 1; the starting amine is denoted in text as *IIa* and *IIb* for R = H and CH$_3$, respectively).

The reaction rate is directly proportional to the lyate ion concentration. At higher pH values the proton splitting from the intermediate *IIIa* becomes rate-limiting and the reaction is subject to general base catalysis. Besides lyate ions also the solvent molecules, aniline and the pyridine added are catalytically significant, the catalytic effect of the both nitrogen bases (as compared with that of solvent molecules and lyate ions) being much lower than it should be according to their basicity.

It was presumed that the reason of this relatively low catalytic efficiency was in considerable steric requirements of the proton-transfer. To get more experimental data for this presumption, we studied the catalytic influence of other nitrogen bases, and, at the same time, we paid attention to base catalysis in the reaction of the compound *I* with N-methylaniline (*IIb*). The additions of methylaniline to the activated aromatic substrates having substituents in *ortho* position to the addition site are, as a rule, slower than those of aniline (*IIa*), the higher steric requirements in formation of the addition intermediate being given as a reason[3]. Also the reaction of this intermediate with the salt *I* giving N-methyl-N-(5-(N'-methylanilino)penta-2,4-dienylidene)anilinium chloride (*VIb*) is far slower than that with aniline[4] (*IIa*). As the solubility of methylaniline in 50% ethanol is too low for kinetic measurements, all the experiments were carried out in 60% ethanol.

SCHEME 1

$R = H, CH_3$
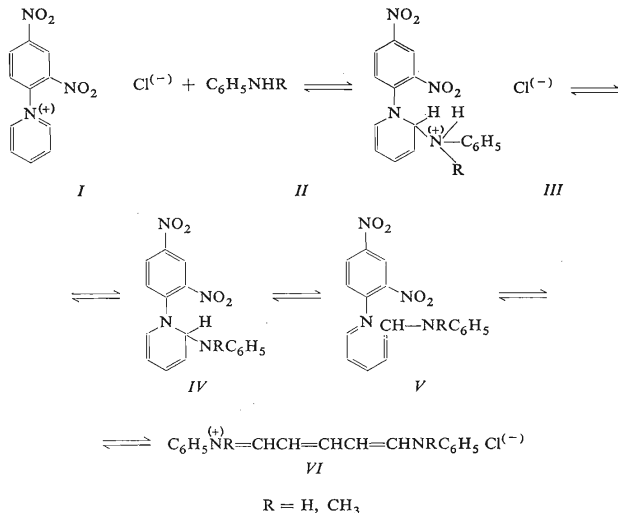
EXPERIMENTAL

N-(2,4-*Dinitrophenyl*)*pyridinium chloride* (I), m.p. 190—198°C, was prepared from pyridine and 2,4-dinitrochlorobenzene by known method[2]. N-Methylaniline (*IIb*) was purified *via* crystallization of its sulphonamide[3]. N-Methyl-N-(5-(N′-methylanilino)penta-2,4-dienylidene)anilinium chloride (*VIb*) was prepared from the compound *I* and amine *IIb* according to known procedure[4]. It was further purified by crystallization from water at 60°C with addition of charcoal. As the compound *VIb* decomposes rapidly in hot water, the raw material was dissolved in preheated water (60—65°C), the solution was quickly filtered and cooled. Yield 68%. The other chemicals used were of analytical purity grade (Lachema, Brno).

Kinetic measurements were carried out at 20°C in 60% (by vol.) aqueous ethanol with ionic strength 0·05 as in the previous work[2] using the spectrophotometer VSU-2P at the wavelengths 490 and 465 nm for *IIa* and *IIb*, respectively. Buffers were prepared by mixing primary and secondary sodium phosphates. In the case of several selected experiments spectra were measured with Unicam SP 800 apparatus in the range 400 to 550 nm at regular time intervals.

RESULTS AND DISCUSSION

The reaction rate was followed by spectrophotometric measurements of reaction products extinction increase (E). The time dependence of $\log E$ was linear in the

whole range studied (2 to 3 half-lives) except for several experiments with methyl-aniline where a slight deviation from linearity was observed at the beginning of the reaction. This observation suggests that concentration of intermediates (inclusive of the compound V) is so small that the steady state is reached already in the initial reaction phase. It agrees with the spectra obtained from the Unicam spectrophoto-meter which do not show any other compounds besides the products (the starting substance does not practically absorb in the range measured). All the experiments were carried out at pH > 7.9 when, according to the analogy with the same reaction in 50% ethanol[2], the splitting off of the proton from the intermediate III is the rate-limiting step. Thus the experimental rate constant k_{exp} is given by Eq. $(1)^*$ where K is the equilibrium constant of formation of the intermediate III and k_0, k_B and k_{RO^-} stand for the rate constants of the splitting off of the proton from the intermediate III by solvent molecules, nitrogen bases and lyate ions, respectively.

$$k_{exp} = K(k_0 + k_B[B] + k_{RO^-}[RO^-]) . \qquad (1)$$

Table I gives the found products of K and the individual rate constants. These values were obtained in the same way as those of our previous work[2]. The product Kk_{RO^-} is about 5× greater in the reaction with aniline (IIa) than that in the reaction with methylaniline (IIb), the corresponding ratio of the products Kk_B being about 20. As the reaction with the lyate ions is thermodynamically advantageous, it can be supposed[5] to be controlled by diffusion, its rate being thus equal for both the amines $IIIa$, $IIIb$. On the basis of this consideration, the ratio of the equilibrium constants K can be estimated to be about 5. This value is comparable with the estimated value of the addition complexes formation in the reactions of aniline and methylaniline with substituted o-nitrochlorobenzenes[3].

If the ratio of equilibrium constants is taken about 5, then the rate of splitting off of the proton by nitrogen bases is about 4× higher for the addition compound $IIIa$ than that for $IIIb$. This difference can be explained by statistical factor (there are two hydrogen atoms which can be split off from the addition compound $IIIa$) and by a relatively worse sterical accessibility of the sole proton of the derivative $IIIb$ by bases.

Small difference was found between the reaction constants of nitrogen bases-cata-lyzed and -non-catalyzed reactions as it was the case in our previous work[2], too. There is, however, a considerable difference (7 orders of magnitude) between the rate constants of the reaction catalyzed by lyate ions and that catalyzed by nitrogen

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*   As a small part of the unprotonated intermediate IV is reversed to the protonated one III, the more complex equation[2] should be used derived on the basis of the Bodenstein approxima-tion. However, the difference between the values of rate constants calculated from the two equa-tions is within experimental error.

bases (Table I). In spite of this fact we suppose that the reactions catalyzed by both lyate ions and nitrogen bases proceed *via* the same mechanism, given in Scheme 1. It is supported by the finding[2] that the catalytic influence of aniline gradually decreases with decreasing pH in accordance with the suggested reaction mechanism and the kinetic equations derived therefrom. The difference between the found values of rate constants is obviously caused by different way of attacks of lyate ions and nitrogen bases. Although the steric requirements of the nitrogen bases used are considerably different, the rate constant did not reflect it. It would indicate that, in the reaction $III \rightarrow IV$, the proton of the intermediate III is not immediately attacked by nitrogen atom of the reacting base. The proton-transfer from the protonated base to the non-protonated one is either direct or mediated by one or several water molecules (or another protic solvent)[6]. This latter mechanism is effective especially in cases where the "direct" reaction is sterically hindered. This is apparently the case of the reaction $III \rightarrow IV$ studied by us. The activated complex of the proton-transfer to the nitrogen base involves several water molecules, which slows down this reaction step (as compared with the reaction involving lyate ions). Even though we cannot give the structure of the activated complex on the basis of the data obtained, we suppose that above consideration represents an acceptable explanation.
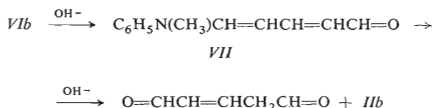
TABLE I

Products of Rate and Equilibrium Constants (k_0K in $1 \, mol^{-1} \, s^{-1}$, $k_{RO}K$ and k_BK in $l^2 \, mol^{-2} \cdot s^{-1}$) for Reactions of Compound I with Amines IIa and IIb in 60% Aqueous Ethanol at 20°C at Ionic Strength 0·05

Amine	$(k_0K) \cdot 10^4$	$(k_{RO}K) \cdot 10^{-3}$	$(k_BK) \cdot 10^3$					
			A	B	C	D	E	F[a]
IIa	15	10	2	—	3·5	2·7	3·0	3·0
IIb	0·75	2·0	—	0·08	0·2	0·17	0·22	0·35

[a] A aniline, B N-methylaniline, C pyridine, D α-picoline, E γ-picoline and F 2,6-lutidine. Experimental error was ±10% and ±15% in the case of amines IIa and IIb, respectively.

Reaction of N-(2,4-dinitrophenyl)pyridinium chloride (I) with aniline (IIa) produces a mixture of hydrochloride VIa and the respective free base[2]. Whereas VIa is relatively stable in the medium used, the base undergoes ring-closure to give N-phenyl-pyridinium chloride[7]. The reaction of I with methylaniline (IIb) produces only VIb which cannot undergo further cyclization. This compound reacts with hydroxide to give 5-(methylphenylamino)penta-2,4-dienal (VII) which is transformed into gluta-conic dialdehyde on further raising of alkalinity:

$$VIb \xrightarrow{\text{OH}^-} C_6H_5N(CH_3)CH{=}CHCH{=}CHCH{=}O \rightarrow$$
$$VII$$

$$\xrightarrow{\text{OH}^-} O{=}CHCH{=}CHCH_2CH{=}O + IIb$$

The both reactions are first order in OH^-. The rate constant of formation of the anil *VII* is 25 l mol^{-1} s^{-1} and the corresponding value of formation of glutaconic dial-dehyde is $3 \cdot 10^{-4}$ l mol^{-1} s^{-1}. Reaction of the compound *VIb* with OH^- ion is slower than the analogous reaction of protonated benzylideneanilines by 5 to 6 orders of magnitude[8,9]. This reaction rate decrease is due, first of all, to the compound *VIb* being a hybrid of two main resonance forms; hence, the positive charge is almost equally distributed between the both nitrogen atoms, the reactivity being thereby considerably lowered. The compound *VII* can be considered to be a vinylogue of N-methylformanilide. We have not found any kinetic data of alkaline hydrolysis of formanilides in literature, so that we can compare our results only with those of acetanilides. Acetanilides are hydrolyzed slower by 3 to 4 orders of magnitude, the reaction order in OH^- being between 1 and 2 (ref.[10,11]).

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Translated by J. Panchartek.