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HYDROLYSIS OF HYDRO(PYRROLYL-1)BORATES

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Abstract—The hydrolysis of hydro(pyrrolyl-1)borates ($[BH_n(NC_4H_4)_{4-n}]^-$, $n = 1, 2, 3$) can be treated as a kinetically one-step reaction outside of the mildly acidic region. In strongly acidic medium the hydrolysis takes place in a stepwise manner; the intermediates (boranes and the cationic boron compounds) being hydrolyzed more slowly than the borate anion. In the first step of the hydrolysis of $[BH_3(NC_4H_4)]^-$ the B–H bond, while in case of $[BH_2(NC_4H_4)_2]^-$ and $[BH(NC_4H_4)_3]^-$ the B–N bond is breaking.

In neutral and mildly alkaline medium, the hydrolysis is a general acid catalyzed reaction (A–S_E2 mechanism). It becomes to a special H^+-ion catalyzed reaction (A-1 mechanism) in strongly alkaline region since the protonated intermediate can be reversed to the original borate upon reaction with the OH^- ion. The hydrolysis presumably takes place through an intermediate which is protonated on the pyrrolyl nitrogen. Concomitant to the hydrolysis an isotopic exchange reaction was observed on the C_α and C_β atoms of the pyrrolyl group in heavy water. In the hydrolysis of the $[BH_3(NC_4H_4)]^-$-anion the N-protonated intermediate is assumed to be able to reverse to the original borate even in acidic or neutral region, at least in part.

INTRODUCTION

In a previous paper[1] we established that the hydrolysis of phenyl(pyrrolyl-1)borates ($[B(C_6H_5)_nPyl_{4-n}]^-$, $n = 1, 2, 3$) and of the tetra(pyrrolyl-1)borate is a hydrogen-ion catalyzed reaction and the rate-determining step of the hydrolysis is the reaction between the pyrrolyl-borate and the hydrogen ion:

$$[(B(C_6H_5)_n(NC_4H_4)_{4-n}]^- + H^+ \overset{\text{slow}}{\rightleftharpoons} [H^+B(C_6H_5)_n(NC_4H_4)^-_{4-n}] \longrightarrow B(C_6H_5)_n(NC_4H_4)_{3-n} + HNC_4H_4 \qquad (1)$$

$$B(C_6H_5)_n(NC_4H_4)_{3-n} + (3-n)H_2O \xrightarrow{\text{very fast}} B(C_6H_5)_n(OH)_{3-n} + (3-n)HNC_4H_4 \qquad n = 0, 1, 2, 3. \qquad (2)$$

In the present communication we wish to report on the study of the kinetics and mechanism of the hydrolysis of hydro(pyrrolyl-1)borates ($[BH_n(NC_4H_4)_{4-n}]^-$, $n = 1, 2, 3$). In contrast to the phenyl(pyrrolyl)borates, the hydrolytic stability of the two different bonds (B–H and B–NC_4H_4) is almost identical in the former compounds.[1] Similar to the BH_4^--ion[2] and the phenyl(pyrrolyl)borates[1] the hydro(pyrrolyl-1)borates are quickly hydrolyzed in mildly alkaline buffers[3,5] according to eqn (3):

$$[BH_n(NC_4H_4)_{4-n}]^- + H^+ + 3H_2O = B(OH)_3 + nH_2 + (4-n)HNC_4H_4. \qquad (3)$$

The light absorption at 220–270 nm of the hydro(pyrrolyl-1)-borates is considerably more intensive than that of the hydrolysis products so that the kinetics of hydrolysis can be conveniently followed spectrophotometrically.

EXPERIMENTAL

The preparation of the borates utilized, $Na[BH_3(NC_4H_4)]\cdot C_4H_8O_2$; $K[BH_2(NC_4H_4)_2]$; $Na[BH(NC_4H_4)_3]$ and $Na[BH(NC_4H_4)_3]\cdot 1.5\ C_4H_8O_2$ has been described previously.[4,5] The buffers used have been prepared in the usual manner using analitical grade chemicals from Reanal and Merck. The ionic strengths of the buffers was adjusted to 0.1 with NaCl. pH-values were determined with Radiometer model PHM-4 pH-meter. The concentration of OH^- ions was determined by acid-alcalimetric titrations and the pH was calculated using the relationship $pH = 13.783 + \log[OH^-]$.

The 99.5 atom % heavy water used for the deuteration experiments. ^1H NMR spectra were recorded on a Jeol model MH-100 NMR spectrometer.

Kinetic measurements

The rate of hydrolysis of hydro(pyrrolyl-1)borates was followed by spectrophotometry. The measurements were performed at 235 nm ($Na[BH_3(NC_4H_4)]$), 240 nm ($K[BH_2(NC_4H_4)_2]$) and 246 nm ($Na[BH(NC_4H_4)_3]$) wavelengths at borate concentrations between $2\cdot10^{-4}$ and $4\cdot10^{-4}$ mol/dm^3 at 25°C using samples thermostatted to ±0.1°C.

(a) In the acidic pH range the measurements were performed using a stopped flow apparatus developed at the Physical Chemistry Laboratory of the Lajos Kossuth University. Dead-time of the apparatus was 5 ms. Equivalent amounts of borate and buffer solutions were quickly transferred into the cuvette of a single beam UV-VIS spectrophometer (Hitachi-Perkin-Elmer 139) using a quick mixer. The change in absorption was recorded on a storage oscilloscope (Phillips PM-3220).

(b) In the neutral and alkaline pH range the borates were dissolved in a solution containing 0.01 mol/dm^3 NaOH and 0.09 mol/dm^3 NaCl. The borate solutions were diluted to 1:50 before measurements with rapid stirring and the light absorption of the samples were determined using a Beckman Acta M-IV spectrophotometer. The absorption of the hydrolysis products was measured when eight times the half-life of the reaction has elapsed.

When the half-lifetime exceeded 6 hr (alkaline medium) the measurements were performed with oxygen-free solutions and the samples were kept under nitrogen.

Hydrolysis in the presence of pyridine

1.2 cm^3 pyridine was added to 25 cm^3 of a solution containing

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2.5 mmoles of borate then a HCl solution (1 mol/dm^3) was added dropwise, under vigorous stirring, until it became acidic with respect to methyl orange. After cooling to 0–5°C the crystalline material was filtered out, washed with a small amount of cold water, alcohol and ether and dried in a stream of dry nitrogen gas. The products were identified through their IR spectra.[5] The following products were obtained: $C_5H_5N \cdot BH_2(NC_4H_4)$ (0.123 g, 31%, from $Na[BH_3(NC_4H_4)]$; 0.152 g, 38%, from $Na[BH_2(NC_4H_4)_2]$ and $C_5H_5N{\cdot}BH(NC_4H_4)_2$ (0.045 g, 8%, from $Na[BH(NC_4H_4)_3]$).

Hydrolysis in deuterium oxide

The borates were dissolved in deuterium oxide containing 0.12 mol/dm^3 of $(CH_3)_3COD$ and 0.1 mol/dm^3 of dioxane. The concentration was 0.5 mol/dm^3 with respect to the pyrrolyl group. The relative amounts of hydrogens in the pyrrolyl and tert-butyl groups were measured from the ^1H NMR spectra, then the borate solution was reacted with CH_3COOD (2 mol/dm^3) in deuterium oxide. After hydrolysing the borate the hydrogen ratio in the pyrrolyl- and tert-butyl groups was measured again. The extent of deuteration in α- and β-positions of the pyrrolyl group was calculated from the difference of the hydrogen ratios.

Hydrogen-deuterium exchange studies

The borates were dissolved in deuterium oxide containing 1 mol/dm^3 of NaOD. The solutions were kept at room temperature and the relative amounts of hydrogens in the pyrrolyl group with respect to the HDO was measured from the ^1H NMR spectra at regular intervals. The exchange reaction was followed ultil 15% conversion level in the case of the $[BH(NC_4H_4)_3]^-$ anion and to 50–75% conversion level in the other cases. The exchange rate constants for the α and β hydrogens (k_α^{ex} and k_β^{ex}) were calculated from the following expression:

$$-\ln f_\alpha = \frac{k_\alpha^{ex}}{n} t - \ln f_\alpha^0$$

where f_α (or f_β) is the ratio of the α (or β) hydrogens, respectively, to the total amount of hydrogens in the pyrrolyl group and n is the number of equivalent hydrogens (2, 4, or 6) in the pyrrolylborates.

RESULTS AND DISCUSSION

The hydrolysis of hydropyrrolylborates—according to eqn (3)—in mildly acidic buffers can be described as a kinetically pseudo-first-order reaction:

$$-\frac{d[B^-]}{dt} = k_1^{hydr}[B^-] \qquad (4)$$

B^- denotes the hydro(pyrrolyl-1)borate ($[BH_n(NC_4H_4)_{4-n}]^-$, $n = 1, 2, 3$) and k_1^{hydr} is the pseudo-first-order rate constant. The rate of hydrolysis is proportional to the hydrogen ion concentration (see Table and Fig. 1), but in the pH range between 2 and 4 it increases more slowly than in the weakly acidic region with simultaneous formation of the end-product in—at least—two consecutive first-order reactions with nearly identical rates (Fig. 1). According to the data of Fig. 1 it can be assumed that in the region pH < 3 the hydrolysis of hydropyrrolylborates—like that of the tetrahydroborate[6]—takes place stepwise, and the hydrolysis of the borate anion as well as that of the intermediates formed from the borate may occur with nearly identical rates. One of the intermediates which is relatively stable in acidic solution may be a borane, $BH_n(NC_4H_4)_{3-n}$ ($n = 1, 2$) since, when the hydrolysis is performed in acidic solution in the presence of pyridine, the following reactions take place:

$$[BH_3(NC_4H_4)]^- + H^+ + C_5H_5N = C_5H_5N{\cdot}BH_2(NC_4H_4) + H_2 \qquad (5)$$

$$[BH_2(NC_4H_4)_2]^- + H^+C_5H_5N = C_5H_5N{\cdot}BH_2(NC_4H_4) + HNC_4H_4 \qquad (6)$$

$$[BH(NC_4H_4)_3]^- + H^+ + C_5H_5N = C_5H_5N{\cdot}BH(NC_4H_4)_2 + HNC_4H_4. \qquad (7)$$

The same reactions take place in ethereal solution as well.[5] The products of eqns (5)–(7) were identified. The formation of these products indicates that in the first step of the hydrolysis of $[BH_3(NC_4H_4)]^-$ the B–H bond, while in case of $[BH_2(NC_4H_4)^2]^-$ and $[BH(NC_4H_4)_3]^-$ the B–N bond is breaking. According to our observations the formation of pyridine-borane complexes in aqueous solution is possible only in those pH range where the borate hydrolysis is a stepwise process. When the hydrolysis of hydropyrrolylborates is conducted in 0.02–0.1 mol/dm^3 HCl solution the rate of product formation decreases with increasing HCl concentration (Fig. 1). This trend could be explained by the formation of a hydrolytically very stable boron(1+) cation (e.g. $[BH(NC_4H_4)(H_2O)_2]^+$ cation) or a species containing a protonated pyrrolyl group (e.g. $[(C_4H_5N)B(OH)_2]^+$ cation). The k_1^{hydr} values of the hydropyrrolylborates vary proportionally with the H^+ ion concentration in the weakly acidic pH range. In the more alkaline range, the hydrolysis of the hydropyrrolylborates may also proceed through a reaction which is independent of the H^+ ion concentration (Table 1). Since the rate of hydrolysis in buffers with different boric acid concentrations but identical pH is proportional with the boric acid concentration (Table 2), this H^+ ion-independent hydrolysis may be regarded as a water-catalyzed reaction and the hydroly-

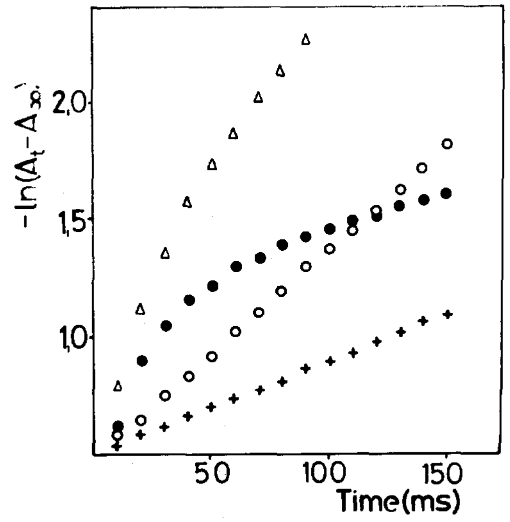


Fig. 1. Function of $\ln(A_t - A_\infty)$ vs time at the hydrolysis of $[BH_3(NC_4H_4)]^-$ in acidic buffers (● ● ● $[H^+] = 0.10$ mole/dm^3; △△△ $[H^+] = 0.02$ mole/dm^3; ○○○ pH = 4.147; + + + pH = 4.419).

Table 1. First-order hydrolysis rate constants (k_1^{hydr}) of hydro(pyrrolyl-1)borates in aqueous buffers at 25°C (a = measured by stopped flow method)

pH	k_1^{hydr} [s^{-1}]		
	$[BH_3(NC_4H_4)]^-$	$[BH_2(NC_4H_4)_2]^-$	$[BH(NC_4H_4)_3]^-$
3.182			7.0 [a]
3.429			3.6 [a]
3.713			1.9 [a]
4.147	8.7 [a]		0.72 [a]
4.419	3.9 [a]		0.37 [a]
4.561	2.9 [a]	7.7 [a]	
6.575			$2.7 \cdot 10^{-3}$
6.809			$1.6 \cdot 10^{-3}$
7.130			$7.3 \cdot 10^{-4}$
7.335			$4.6 \cdot 10^{-4}$
8.127	$8.9 \cdot 10^{-4}$	$2.3 \cdot 10^{-3}$	$8.5 \cdot 10^{-5}$
8.433	$4.5 \cdot 10^{-4}$	$1.2 \cdot 10^{-3}$	
8.636	$3.2 \cdot 10^{-4}$	$7.2 \cdot 10^{-4}$	$1.8 \cdot 10^{-5}$
8.840	$1.9 \cdot 10^{-4}$	$4.5 \cdot 10^{-4}$	
9.050	$1.1 \cdot 10^{-4}$		
9.203	$1.0 \cdot 10^{-4}$	$1.9 \cdot 10^{-4}$	$6.6 \cdot 10^{-6}$
9.583	$3.9 \cdot 10^{-5}$		
9.986	$1.6 \cdot 10^{-5}$	$3.4 \cdot 10^{-5}$	$1.2 \cdot 10^{-6}$
10.056	$1.4 \cdot 10^{-5}$		
10.234	$9.6 \cdot 10^{-6}$		
10.647	$4.9 \cdot 10^{-6}$	$7.2 \cdot 10^{-6}$	$2.5 \cdot 10^{-7}$
10.741	$3.6 \cdot 10^{-6}$		$2.1 \cdot 10^{-7}$
10.921	$2.7 \cdot 10^{-6}$		$1.5 \cdot 10^{-7}$
11.320	$1.1 \cdot 10^{-6}$		$7.5 \cdot 10^{-8}$
11.453			$5.9 \cdot 10^{-8}$
11.855	$3.1 \cdot 10^{-7}$		$3.6 \cdot 10^{-8}$
12.084		$3.2 \cdot 10^{-7}$	
12.362	$9.8 \cdot 10^{-8}$	$1.8 \cdot 10^{-7}$	
12.582		$1.4 \cdot 10^{-7}$	
12.810		$8.4 \cdot 10^{-8}$	
13.144		$4.3 \cdot 10^{-8}$	

Table 2. First-order hydrolysis rate constants (k_1^{hydr}) of hydro(pyrrolyl-1)borates at various concentrations of aqueous borate buffers at 25°C (ionic strength = 0.25)

$C_{H_3BO_3}$	k_1^{hydr} [s^{-1}]		
mole·dm^{-3}	$[BH_3(NC_4H_4)]^-$	$[BH_2(NC_4H_4)_2]^-$	$[BH(NC_4H_4)_3]^-$
0.000	$6.7 \cdot 10^{-5}$ [a]	$1.86 \cdot 10^{-4}$ [a]	$5.7 \cdot 10^{-6}$ [a]
0.029	$7.3 \cdot 10^{-5}$	$1.91 \cdot 10^{-4}$	$6.2 \cdot 10^{-6}$
0.087	$9.7 \cdot 10^{-5}$	$2.13 \cdot 10^{-4}$	$6.8 \cdot 10^{-6}$
0.175	$1.14 \cdot 10^{-4}$	$2.28 \cdot 10^{-4}$	$8.4 \cdot 10^{-6}$

[a] extrapolated value

sis of hydropyrrolylborates may be taken as a general-acid catalyzed reaction:

$$-\frac{d[B^-]}{dt}=[B^-]\sum_{HA}k_{HA}[HA] \tag{8}$$

HA denotes the acid (H^+, H_2O, H_3BO_3, etc.), k_{HA} is the second-order rate constant of the acid-catalyzed reactions. The k_{HA} values for the hydropyrrolylborates are summarized in Table 3. On the basis of the general acid-catalysis mechanism one would expect the k_1^{hydr} values of the hydropyrrolylborates to approach to a constant value in the strongly alkaline range. In contrast to this expectation it was observed that when the measurements were performed in the absence of oxygen and transition metal ions, the k_1^{hydr} values (Table 1) approximated the zero. This was most conspicuous in the case of the $[BH_3(NC_4H_4)]^-$ anion (Fig. 2). This observation can be rationalized by assuming the formation—like the hydrolysis of the BH_4^- anion[9]—in the reaction between the hydropyrrolylborates and acids of an intermediate which can revert to the original borate upon the action of OH^- ions in the alkaline pH range. Thus the hydrolysis of the hydropyrrolylborates can be described by the following equations if only the H^+ ion and the H_2O molecule are being considered as acids:

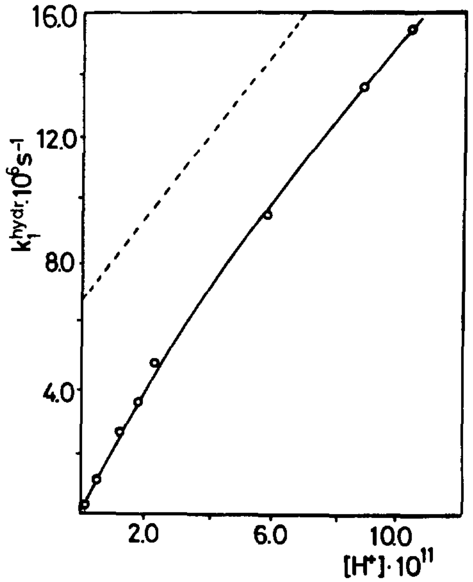


Fig. 2. Pseudo-first-order rate constants (k_1^{hydr}) for the hydrolysis of $[BH_3(NC_4H_4)]^-$ in strong alkaline buffers. (○○○ measured values; --- calculated from eqn (8); —— calculated from eqn 15.)

$$[BH_n(NC_4H_4)_{4-n}]^- + H^+ \underset{k_{-H}}{\overset{k_H}{\rightleftharpoons}} [HBH_n(NC_4H_4)_{4-n}] \tag{9}$$

$$[BH_n(NC_4H_4)_{4-n}]^- + H_2O \underset{K_{-H_2O}}{\overset{k_{H_2O}}{\rightleftharpoons}} [HBH_n(NC_4H_4)_{4-n}] + OH^- \tag{10}$$

$$[HBH_3(NC_4H_4)] \xrightarrow{k_2} BH(NC_4H_4) + H_2 \tag{11}$$

$$[HBH_n(NC_4H_4)_{4-n}] \xrightarrow{k_2} BH_n(NC_4H_4)_{3-n} + HNC_4H_4 \tag{12}$$

$$n = 1, 2$$

$$BH_n(HC_4H_4)_{3-n} + 2H_2O \xrightarrow{\text{very fast}} B(OH)_3 + nH_2 + (3-n)HNC_4H_4 \tag{13}$$

$$n = 1, 2, 3$$

$$B(OH)_3 + OH^- \xrightleftharpoons{\text{very fast}} [B(OH)_4]^-. \tag{14}$$

Since the hydropyrrolylborate is only weakly basic it can be assumed that the concentration of the protonated intermediate ($[HBH_n(NC_4H_4)_{4-n}]$), formed in the reaction between the acid (H^+ and H_2O) and the borate, remains small all the time during the reaction.

Applying the Bodenstein principle

$$\left(\frac{d[HBH_n(NC_4H_4)_{4-n}]}{dt} \approx 0\right)$$

and assuming that $k_2 \gg k_{-H}$ results in the following formula for k_1^{hydr}:

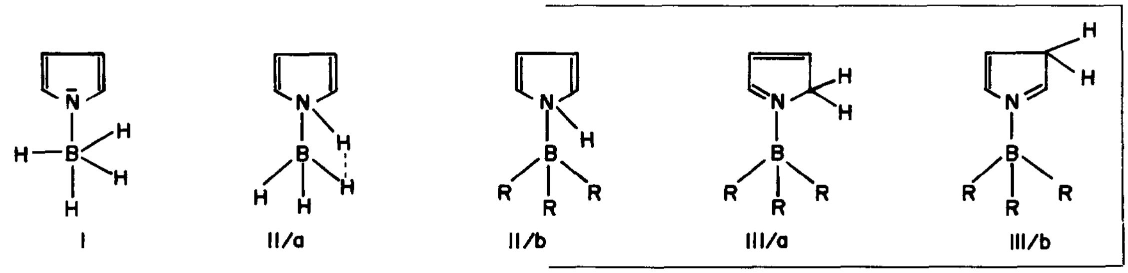
$$k_1^{hydr} = \frac{k_H[H^+]^2 + k_{H_2O}[H^+]}{[H^+] + K_w k_{-H_2O}/k_2}. \tag{15}$$

Equation (15) includes the two limiting cases of the acid-catalysis: the general-acid catalysis ($A\text{–}S_{E^2}$ mechanism) and the specific H^+ ion catalysis (A-1 mechanism). According to eqn (15) in acidic or less basic solutions ($[H^+] \gg K_w k_{-H_2O}/k_2$) the reaction is $A\text{–}S_{E^2}$ type but it is A-1 type in more basic solutions ($k_H[H^+] \ll k_{H_2O}$; $[H^+] \ll K_w k_{-H_2O}/k_2$).

The rate constants in eqn (15) were determined in the following way. From the k_1^{hydr} value measured in the neutral and weakly alkaline region (Table 1) the k_H values were determined then, from the data obtained in the more alkaline range (Table 1) and from the known k_H the k_{H_2O} and $K_w(k_{-H_2O}/k_2)$ values could be obtained. The $[(k_1^{hydr} - k_1^{calcd})/k_1^{hydr}]$ values were minimized in these calculations (k_1^{calcd} means the right side of eqn 15). The calculated values obtained in this manner are summarized in Table 3. (In the case of the $[BH(NC_4H_4)_3]^-$ anion the value of k_{H_2O} is very small and uncertain therefore the $K_w \cdot k_{-H_2O}/k_2$ value was not calculated.)

Due to the general-acid catalysis, the rate-determining step in the hydrolysis of the hydropyrrolylborates is the protonation of the borate anion (eqns 10 and 9). The borate anion may be protonated on the pyrrolyl group or—like the BH_3CN^-[10] and BH_4^-[9]—on the boron as well.

The hydrolysis of hydropyrrolylborates with deuteroacetic acid in D_2O resulted in the formation of 1, 2- and 1,3-dideuteropyrroles (Table 4). This finding indicates that the reaction between borate and acids gives rise to the formation of a product protonated at the pyrrolyl carbon as well as another one protonated at the pyrrolyl N atom since the rate of hydrogen exchange at the nitrogen is 1000-fold greater in D_2O than either at α- or β-carbons of pyrrole.[7,8] Accordingly, the formation of the following intermediates may be taken into consideration in the course of the reaction between the borates and H^+ ion (R denotes pyrrolyl group or H):



The formation of the intermediate I could not be demonstrated experimentally. The reaction of acetone with the residual borate anion after partial hydrolysis of the hydropyrrolyl-borates in D_2O did not result in the formation of $(CH_3)_2CDOD$ in measurable amounts; $(CH_3)_2CHOD$ was obtained instead. On the other hand, considerable hydrogen exchange at the B-atom was observed in the hydrolysis of BH_4^-,[9] BH_3CN^-[10] and amine boranes[11,12] in D_2O.

In the course of the hydrolysis of $[BH_3(NC_4H_4)]^-$ anion H_2 evolution was observed following the protonation reaction (eqns 5 and 11) indicating the appearance of intermediates I or II/a. The lack of B-H exchange makes intermediate II/a more likely but the formation of II/a can also be assumed in the reaction between the borate and H^+ ion followed by conversion to an intermediate type I which, in turn, decomposes into $BH_2(NC_4H_4)$ and H_2-gas.

The hydrolysis of $[BH_2(NC_4H_4)_2]^-$ and $[BH(NC_4H_4)_3]^-$ anions results in the formation of pyrrole in the reaction between the borate and acids (eqns 6, 7 and 12). It is to be expected in the case of the pyrrolylborates that the rate of protonation is faster at the N atom than at the C atom so that the hydrolysis can be assumed to occur through the intermediate type II/b.

We suggest that the hydrolysis of hydropyrrolylborates takes place through an intermediate protonated at the N-atom (II/a and II/b) and the observed exchange reactions of the C-H hydrogens may occur as parallel, nonproductive exchange reactions. However, since the

Table 3. Rate constants of hydrolysis of hydro(pyrrolyl-1)borates at 25°C

Rate constants	$[BH_3(NC_4H_4)]^-$	$[BH_2(NC_4H_4)_2]^-$	$[BH(NC_4H_4)_3]^-$
k_H ($mole^{-1}\cdot dm^3\cdot s^{-1}$)	$(1.25\pm0.09)\cdot10^5$	$(3.10\pm0.06)\cdot10^5$	$(1.00\pm0.02)\cdot10^3$
k_{H_2O} (s^{-1})	$(7.5\pm1.3)\cdot10^{-6}$	$(1.5\pm0.2)\cdot10^{-7}$	$(2.4\pm0.2)\cdot10^{-8}$
$K_w k_{-H_2O}/k_2$ ($mole\cdot dm^{-3}$)	$(3.0\pm0.6)\cdot10^{-11}$	$(2.1\pm0.3)\cdot10^{-13}$	-
$k_{H_3BO_3}$ ($mole^{-1}\cdot dm^3\cdot s^{-1}$)	$(2.8\pm0.4)\cdot10^{-4}$	$(2.4\pm0.7)\cdot10^{-4}$	$(1.5\pm0.2)\cdot10^{-5}$

Table 4. Deuterium contents (f_α, f_β) of pyrrole obtained in acidic hydrolysis ($AcOD/D_2O$). C_α-H and C_β-H exchange rate constants (k_α^{ex}, k_β^{ex}) of the hydro(pyrrolyl-1)borates in alkaline medium (0.1 mole · dm^{-3} NaOD in D_2O)

Borate	f_α [%]	f_β [%]	$k_\alpha^{ex}[s^{-1}]$	$k_\beta^{ex}[s^{-1}]$
$[BH_3(NC_4H_4)]^-$	34.2 ± 4.0	37.6 ± 2.4	$8.6\cdot10^{-7}$	$3.8\cdot10^{-7}$
$[BH_2(NC_4H_4)_2]^-$	5.1 ± 0.5	5.1 ± 0.5	$4.6\cdot10^{-7}$	$1.8\cdot10^{-7}$
$[BH(NC_4H_4)_3]^-$	5.4 ± 0.5	5.6 ± 0.5	$1.3\cdot10^{-7}$	$7.5\cdot10^{-8}$

protonations at the N- and the C_α- and C_β-atoms of the pyrrolyl group are parallel reactions, the study of C–H exchange may yield useful informations concerning the mechanism of hydrolysis reactions. In the case of hydropyrrolylborates (similarly to the observations[7,8] made with pyrrole derivatives) the relative rates of the hydrogen exchange at the α- and β-C atoms depend strongly on the soft or hard character of the acid that catalyses the deuteration reaction. In the weakly acidic and neutral region (where the hydrogen exchange occurs in the reaction catalyzed by D_2O^+ which, itself, can be considered as a hard acid) the rates of H-exchange are almost identical at the C_α- and C_β-atoms. In alkaline media, however (where the hydrogen exchange is a reaction catalyzed by the soft acid D_2O), the exchange is considerably faster at the C_α-atom than at the C_β-atom (Table 4).

The D/H ratio in the pyrrole obtained from the hydrolysis in D_2O of the hydropyrrolylborates in weakly acidic or neutral regions does not depend on the acidity of the medium, i.e. the ratio of the hydrolysis and the C–H exchange rate is constant. In the strongly alklaine range (0.01–0.1 mol/dm^3 NaOD–D_2O) the exchange rates are practically identical but the exchange rate exceeds considerably that of the hydrolysis and the D/H ratio in the hydrolysis products increases regularly with increasing alkalinity of the medium.

These findings can be rationalized by assuming that the intermediate that occurs in the reaction between the borate and D_2O may revert, upon the action of the OD^- anion, into the original borate to a considerable extent so that the conclusions readed upon from the kinetic measurements are supported by the exchange studies as well.

The pyrrole obtained through the acidic hydrolysis of the $[BH_3(NC_4H_4)]^-$ anion in D_2O contains much more deuterium than in the cases of other borates (Table 4). At the same time, the k_H value of the $[BH_3(NC_4H_4)]^-$ anion is much smaller (Table 3) than expected. Both the relatively small k_H value and the increased deuterium content of the hydrolysis product (pyrrole) indicate that the intermediate that occurs in the reaction between the $[BH_3(NC_4H_4)]^-$ anion and the H^+ ion (eqn 9) reverts partially into the original borate even in acidic media.

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