Polyhedron Vol. 2, No. 12, pp. 1273–1279, 1983
Printed in Great Britain.

0277-5387/83 $3.00 + .00

HYDROLYSIS OF CYANO(PYRROLYL-1)BORATES

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(*Received* 22 *February* 1983; *accepted* 3 *May* 1983)

Abstract—The kinetics and mechanism of the hydrolysis of several cyano(pyrrolyl-1)borates in aqueous medium has been investigated. The hydrolysis of cyanophenyl(pyrrolyl-1)-borates, cyano(tripyrrolyl-1)borate and cyanohydro(pyrrolyl-1)borates proceeds via two kinds of reactions; (a) a special H^+ ion catalyzed reaction (A-1 mechanism) and (b) a H^+ ion concentration–independent process of S_N1 mechanism. In acidic medium the $[BH_2(NC_4H_4)CN]^-$ anion is reversibly protonated at the α-carbon of the pyrrolyl group and a product with composition $C_4H_5N \cdot BH_2CN$, stable towards hydrolysis is also formed.

In the H^+ ion catalyzed reaction the B–N bond very likely breaks, whereas upon the $[H^+]$ ion concentration–independent reaction a B–CN cleavage occurs. The presence of the cyano substituent significantly increases the hydrolytic stability of the B–N bond, whereas the pyrrolyl-1-substitution remarkably decreases the stability of the B–CN bonding.

In previous papers we have described the kinetics and mechanism of the hydrolysis of phenyl(pyrrolyl-1)borates[1] and hydro(pyrrolyl-1)-borates.[2] In this paper we wish to report on the study of the hydrolysis of several cyano(pyrrolyl-1)borates ($[BH_n(NC_4H_4)_{3-n}CN]^-$ and $[B(C_6H_5)_n(NC_4H_4)_{3-n}CN]^-$, where $n = 0, 1, 2$).

The kinetics and mechanism of the hydrolysis of the borates is significantly changed and modified by the presence of the cyano group. For example, the rate-constant of the hydrolysis of $[BH_3CN]^-$ anion[3] is about 10^8-fold lower than that of the BH_4^- anion.[4] Concomitant to the hydrolysis in D_2O such a rapid B–H isotopic exchange reaction takes place in the case of $[BH_3CN]^-$ that the $[BD_3CN]^-$ salts[3] can be isolated with good yields, whereas H-exchange of low degree has been observed upon hydrolysis of BH_4^- anion.[5] In this paper the effect of the cyano substituent on the kinetics and mechanism of the hydrolysis of (pyrrolyl-1)borates is described.

EXPERIMENTAL

The preparation of the borates utilized, $Na[B(C_6H_5)_2(NC_4H_4)CN]$, $Na[B(C_6H_5)(NC_4H_4)_2CN]$, $Na[B(NC_4H_4)_3CN]\cdot 1,5\ C_4H_8O_2$, $K[BH_2(NC_4H_4)CN]\cdot C_4H_8O_2$ and $Na[BH[NC_4H_4)_2CN]\cdot 3\ C_4H_8O_2$ have been described previously.[6,7]

The buffers used have been prepared in the usual manner using analytical grade chemicals from Reanal and Merck. The ionic strengths of the buffers was adjusted to 0.1 mole/dm^3 or 1.0 mole/dm^3 with NaCl. The pH values of the buffers was determined with a Radiometer model PHM-4 pH-meter. In the case of $K[BH_2(NC_4H_4)CN]$ at $[H^+] > 0.01$ mole/dm^3 the pH value was calculated on the basis of the HCl concentration, while at $[H^+] < 0.01$ mole/dm^3 the pH was measured, and the pH of a solution containing 0.010 mole/dm^3 of HCl was acknowledged 2.00.

Kinetic measurements

The rate of hydrolysis of the cyano(pyrrolyl-1)-borates was followed by spectrophotometric (a) and complexometric (b) methods. The measurements were carried out at 25°C (or at 17.5 and 35°C) using samples thermostated to ±0.1°C.

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(a) The concentration of the cyano(pyrrolyl-1)-borates in the buffer solutions was 2×10^{-4}–4×10^{-4} mole/dm^3. The light absorption of the samples was determined using a Beckman Acta M–IV spectrophotometer at 250 nm ($Na[B(C_6H_5)_2(NC_4H_4)CN]$), 240 nm ($Na[B(C_6H_5)(NC_4H_4)_2CN]$, $Na[BH(NC_4H_4)_2CN]$ and $Na[B(NC_4H_4)_3CN]$) and 247 nm ($K[BH_2(NC_4H_4)CN]$). The solid borate samples were dissolved in the buffer with rapid stirring and the change of absorption was followed for a period of 1–2 half-life time. The absorption of the hydrolysis products was measured when eight times the half-life of the reaction had elapsed.

(b) In neutral and alkaline media the progress of the hydrolysis was followed by measuring the free CN^- ion concentration of the solution. For these experiments 0.02 mole/dm^3 solutions of the borates in the buffers were used. The free CN^- ion concentration was determined by means of 0.1 mole/dm^3 $AgNO_3$ solution. For the determination of the end-point the I^- ion indicator method was applied.

Examination of the influence of acetic acid on the rate of hydrolysis

The rate of the hydrolysis of $Na[B(NC_4H_4)_3CN]$ at 25°C was measured in pH = 4.07 buffers with 0.1 ionic strength at different acetic acid concentrations (0.015, 0.15 and 0.35 mole/dm^3). The following values were obtained for the pseudo-first-order rate constants: 3.26×10^{-4}; 3.08×10^{-4} and $2.97 \times 10^{-4}\,s^{-1}$.

Determination of the activation parameters

The rate of hydrolysis was measured in pH = 5.36; 4.40; 3.90; 3.61 and 3.38 buffers and in the case of $Na[B(NC_4H_4)_3CN]$ in pH = 3.90; 3.38; 2.43; 2.11 and 1.90 buffers at 17.5, 25.0 and 35.0°C. With the knowledge of the measured pseudo-first-order rate constants and the H^+ ion concentration, both the H^+ ion concentration-dependent and H^+ ion concentration-independent rate constants were determined. The actual $[H^+]$ values were calculated from the measured pH values at 17.5, 25.0 and 35.0°C. The activation parameters were calculated in the usual manner from a plot of $\log k$ vs T^{-1} according to the Eyring equation using the determined values of the rate constants.

RESULTS AND DISCUSSION

The cyano(pyrrolyl-1)borates decompose slowly in aqueous acidic media, according to eqns (1) and (2) ($n = 0, 1, 2$):

$$[B(C_6H_5)_n(NC_4H_4)_{3-n}CN]^- + H^+ + (3-n)H_2O = [B(C_6H_5)_n(OH)_{3-n}] + (3-n)C_4H_4NH + HCN \quad (1)$$

$$[BH_n(NC_4H)_{3-n}CN]^- + H^+ + 3H_2O = B(OH)_3 + nH_2 + (3-n)C_4H_4NH + HCN. \quad (2)$$

In contrast with the hydrolysis of the other (pyrrolyl-1)-borates,[1,2] cyano(pyrrolyl-1)borates hydrolyse slowly also in strongly alkaline medium (0.1 mole/dm^3 NaOH) but pyrrole does not form upon the hydrolysis (Fig. 1). In neutral and alkaline medium this process takes place as shown by the following equations ($n = 0, 1, 2$):

$$[B(C_6H_5)_n(NC_4H_4)_{3-n}CN]^- + H_2O = [B(C_6H_5)_n(NC_4H_4)_{3-n}OH]^- + HCN \quad (3)$$

$$[BH_n(NC_4H_4)_{3-n}CN]^- + (n+1)H_2O = [B(NC_4H_4)_{3-n}(OH)_{n+1}]^- + nH_2 + HCN. \quad (4)$$

Since the spectrum of the borate significantly differs from that of the hydrolysis products in the range 220–270 nm, the rate of the hydrolysis of the cyano(pyrrolyl-1)borates can be readily followed by spectrophotometry. The measurement of the cyanide ion concentration is also a good method for determining the rate of hydrolysis in alkaline medium.

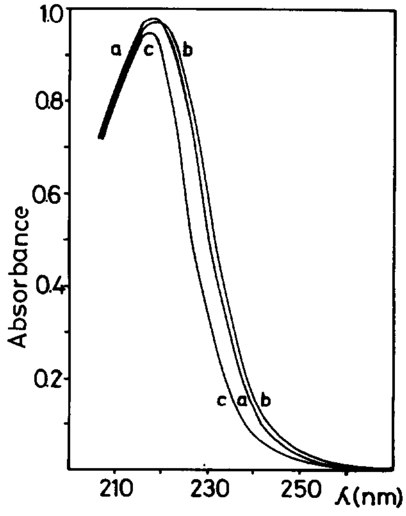

Fig. 1. The change of the spectrum of $K[B(NC_4H_4)_3CN]$ ($c = 1.4 \cdot 10^{-4}$ mole/dm^3) upon hydrolysis in 0.1 mole/dm^3 NaOH solution: (a) before hydrolysis; (b) after hydrolysis; (c) after hydrolysis and adjustment of the pH first to acidic range (3–4) and then to the original value.

According to our studies the hydrolysis of cyano-(pyrrolyl-1)borates in aqueous buffers can be described as a kinetically pseudo-first-order reaction:

$$-\frac{d[B^-]}{dt} = k_1^{hydr}[B^-] \qquad (5)$$

where B^- denotes the cyano(pyrrolyl-1)borate and k_1^{hydr} is the pseudo-first-order rate constant. The measured k_1^{hydr} values of the cyano(pyrrolyl-1)-borates in aqueous buffers are summarized in Tables 1 and 3.

In acidic media the k_1^{hydr} values of the $[B(C_6H_5)_n(NC_4H_4)_{3-n}CN]^-$ anions ($n = 0, 1, 2$) and the $[BH(NC_4H_4)_2CN]^-$ anion varies linearly with the H^+ ion concentration (Table 1) and it can be expressed by the following equation:

$$k_1^{hydr} = k_H[H^+] + k_1 \qquad (6)$$

where k_H is the second-order rate constant of the acid-catalyzed process and k_1 is the first-order rate constant of the H^+ ion concentration-independent reaction. The values of the k_H and k_1 rate constants, determined from the data given in Table 1, and also the ΔH^+ and ΔS^+ values, calculated from the k_H and k_1 constants are summarized in Table 2.

The rate-determining step in the H^+ ion-catalyzed hydrolysis of cyano(pyrrolyl-1)borates may be the cleavage of the B–CN or the B–N bond (in the case of borates containing B–H bond the cleavage of this bond may be also rate-determinant). We believe that in the reaction of the cyano(pyrrolyl-1)borate with H^+ ion the B–N bond is cleaved since the formation of pyrrole and the corresponding amine borane was observed in the reaction between cyano(pyrrolyl-1)borates and pyridine hydrochloride in non-aqueous solvents.[7,8]

On the contrary, the rate-determining step of the H^+ ion concentration-independent reaction can be only the cleavage of the B–CN bonding, as no formation of pyrrole can be observed in alkaline medium (Fig. 1), and also, the value of k_1^{hydr}, measured in alkaline medium, is equivalent with

Table 1. Pseudo-first-order hydrolysis rate constants (k_1^{hydr}) of cyano(pyrrolyl-1)borates in aqueous buffers at 25°C ($\mu = 0.1$) determined by spectrophotometric (pH < 8.8) and complexometric methods (pH > 8.8). (Ph = C_6H_5; Pyl = 1-NC_4H_4)

pH	k_1^{hydr} [s^{-1}]			
	$[BPh_2PylCN]^-$	$[BPhPyl_2CN]^-$	$[BPyl_3CN]^-$	$[BHPyl_2CN]^-$
1.90	-	-	$1.8\cdot10^{-3}$	-
2.11	-	-	$1.2\cdot10^{-3}$	$4.6\cdot10^{-2}$
2.43	-	-	$7.5\cdot10^{-4}$	$2.2\cdot10^{-2}$
3.05	$5.9\cdot10^{-3}$	$4.8\cdot10^{-3}$	$4.2\cdot10^{-4}$	-
3.38	$2.9\cdot10^{-3}$	$2.6\cdot10^{-3}$	$3.6\cdot10^{-4}$	$2.7\cdot10^{-3}$
3.61	$1.8\cdot10^{-3}$	$1.7\cdot10^{-3}$	-	$1.6\cdot10^{-3}$
3.90	$9.8\cdot10^{-4}$	$1.3\cdot10^{-3}$	$3.1\cdot10^{-4}$	$9.1\cdot10^{-4}$
4.19	$6.0\cdot10^{-4}$	$9.1\cdot10^{-4}$	-	$5.2\cdot10^{-4}$
4.40	$4.3\cdot10^{-4}$	$7.9\cdot10^{-4}$	-	$3.8\cdot10^{-4}$
4.64	$3.0\cdot10^{-4}$	-	-	$2.9\cdot10^{-4}$
5.36	$2.2\cdot10^{-4}$	$6.4\cdot10^{-4}$	-	$1.8\cdot10^{-4}$
8.8	-	-	$3.3\cdot10^{-4}$	-
9.3	$1.6\cdot10^{-4}$	$6.1\cdot10^{-4}$	$3.3\cdot10^{-4}$	$1.2\cdot10^{-4}$
9.9	$1.7\cdot10^{-4}$	$5.9\cdot10^{-4}$	-	-
11.2	-	-	$3.2\cdot10^{-4}$	$1.1\cdot10^{-4}$
12.6 [a]	$1.8\cdot10^{-4}$	$6.0\cdot10^{-4}$	$3.2\cdot10^{-4}$	$1.2\cdot10^{-4}$

[a] NaOH-NaCl buffer

Table 2. Rate constants (k_H, k_1) and activation parameters of the hydrolysis of cyano(pyrrolyl-1)-borates at 25°C. ($\mu = 0.1$; Ph = C_6H_5; Pyl = 1-NC_4H_4)

Parameters (units)	Values $[BPh_2Pyl CN]^-$	$[BPhPyl_2CN]^-$	$[BPyl_3CN]^-$	$[BHPyl_2CN]^-$
k_H (mole^{-1}•dm^3•s^{-1})	6.4±0.3	4.7±0.2	0.117±0.003	6.2±0.4
$\Delta H^{\ddagger}$ (KJ•mole^{-1})	80±3	58±3	65±2	-
$\Delta S^{\ddagger}$ (J•mole^{-1}•K^{-1})	31±6	-37±6	44±5	-
k_1 (s^{-1})	(1.7±0.1)•10^{-4}	(6.1±0.2)•10^{-4}	(3.2±0.1)•10^{-4}	(1.2±0.1)•10^{-4}
$\Delta H^{\ddagger}$ (KJ•mole^{-1})	91±3	89±3	87±2	-
$\Delta S^{\ddagger}$ (J•mole^{-1}•K^{-1})	-14±6	-8±6	-21±5	-

that of k_1 determined for the process in acidic medium (Table 1), where the formation of pyrrole can be detected.

Studies with cyano(amino)borates ($[BH_2(NR_2)CN]^-$ anions), having analogous structure with that of the cyano(pyrrolyl-1)-borates, have shown that the rate-determining step of the hydrolysis is also the cleavage of the B–CN bond.[9]

According to the above experimental data, the hydrolysis of cyano(pyrrolyl-1)borates of type $[BR_n(NC_4H_4)_{3-n}CN]^-$ (where R = C_6H_5, $n = 1, 2$; R = H, $n = 0, 1$) can be described by the following equations:

$$[BR_n(NC_4H_4)_{3-n}CN]^- + H^+ \underset{k'_{-H}}{\overset{k'_H}{\rightleftharpoons}} Br_n(HNC_4H_4)(NC_4H_4)_{2-n}CN \quad (7)$$

$$BR_n(HNC_4H_4)(NC_4H_4)_{2-n}CN \xrightarrow{k_2} BR_n(NC_4H_4)_{2-n}CN + C_4H_4NH \quad (8)$$

$$B(C_6H_5)_n(NC_4H_4)_{2-n}CN + (3-n)H_2O \xrightarrow{\text{fast}} B(C_6H_5)_n(OH)_{3-n} + (2-n)C_4H_4NH + HCN \quad (9)$$

$$BH_n(NC_4H_4)_{2-n}CN + 3H_2O \xrightarrow{\text{fast}} B(OH)_3 + nH_2 + (2-n)C_4H_4NH + HCN \quad (10)$$

$$[BR_n(NC_4H_4)_{3-n}CN]^- \xrightarrow{k_1} BR_n(NC_4H_4)_{3-n} + CN^- \quad (11)$$

$$BR_n(NC_4H_4)_{3-n} + H_2O \overset{\text{fast}}{\rightleftharpoons} [BR_n(NC_4H_4)_{3-n}OH]^- + H^+. \quad (12)$$

Since the borate is only weakly basic (i.e. $k'_{-H} \gg k'_H$), the Bodenstein principle can be applied for the reaction, namely, the concentration of $BR_n(HNC_4H_4)(NC_4H_4)_{2-n}CN$ remains small and quasi-constant all the time during the reaction.

At the same time—similarly to the reactions of phenyl(pyrrolyl-1)borates[1]—the reaction between the borate and the H^+ ion is a specific acid-catalyzed process (the rate of the hydrolysis is independent of the acid concentration), thus one can also assume that $k'_{-H} \gg k_2$.

As the hydrolysis takes place according to eqns (8) and (11) thus, the following expression can be given for the k_1^{hydr} value (eqn 5) on the basis of the above considerations:

$$k_1^{\text{hydr}} = k_2 \frac{k'_{\text{H}}}{k'_{-\text{H}}}[\text{H}^+] + k_1. \qquad (13)$$

Equation (6), obtained from the experimental data, is practically identical with eqn (13), namely, the k_{H} value in eqn (6) is identical with the $k_2(k'_{\text{H}}/k'_{-\text{H}})$ value in eqn (13).

The hydrolysis involving the loss of CN^- ion (eqn 11) may be of S_N1 or S_N2-type process. However, the determined great ΔH^+ values and the small ΔS^+ values (Table 2) make the S_N1 mechanism more probable. This mechanism is also supported by the change of the k_1 values measured for $[B(NC_4H_4)_3CN]^-$ in dioxane–water mixtures (Fig. 2), since plotted $\log k_1$ vs $\log [H_2O]$ the slope is 5.7, whereas a value of about 2 would be eexpected if the process were of S_N2-type mechanism.[10]

Our studies have shown that the hydrolysis of $[BH_2(NC_4H_4)CN]^-$ under alkaline and weakly acidic conditions takes place similarly to that of the other cyano(pyrrolyl-1)-borates (Table 3).

Contrary to the results with the other cyano(pyrrolyl-1)-borates (Table 1) the k_1^{hydr} rate constant for $[BH_2(NC_4H_4)CN]^-$ approaches a constant value in more strongly acidic media (Table 3). Also, parallel with the relative decrease of the rate off the hydrolysis such a spectral change of the solution is observable which indicates the formation of a stable amine borane ($C_4H_5N{\cdot}BH_2CN$) containing a pyrrolyl group protonated at the α-position, arising from the reaction between $[BH_2(NC_4H_4)CN)]^-$ and the H^+ ion.[7] The formation of similar compounds, containing α-protonated pyrrolyl group, can be observed in more concentrated sulphuric acid solutions of $L{\cdot}BH(NC_4H_4)CN$-type amine boranes[8] (L = amine) and of the $[BH(NC_4H_4)(CN)_2]^-$ anion.[11]

In the reaction of the $[BH_2(NC_4H_4)CN]^-$ anion with the H^+ ion first either the B–H or the B–N bond is cleaved. According to our results the cleavage of the B–N bond was more probable since neither hydrogen gas evolution was observed upon the reaction of the borate with acid in non-aqueous medium, nor could B–H exchange be detected upon hydrolysis in D_2O.[7] If the hydrolysis proceeds via the cleavage of the B–N bond, protonation at the N atom of the pyrrolyl group gives rise to hydrolysis. At the same time, protonation at the carbon atom results in a stable borane complex with composition $C_4H_5N{\cdot}BH_2CN$, since according to earlier results[12] the rate of the H-exchange at the N atom of the pyrrole derivatives is about 1000-fold greater than at either carbon atom. On the basis of these considerations the hydrolysis of the $[BH_2(NC_4H_4)CN]^-$ anion can be described by the following equations:

$$[BH_2(NC_4H_4)CN]^- + H^+ \overset{K_2}{\rightleftharpoons} C_4H_5N{\cdot}BH_2CN \qquad (14)$$

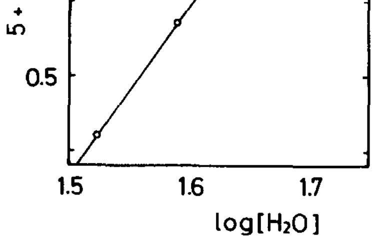

Fig. 2. The change of the rate constant (k_1) of the hydrolysis of $K[B(NC_4H_4)_3CN]$ in water–dioxane mixtures of 0.1 mole/dm³ NaOH concentration at 25°C as a function of the water-concentration.

Table 3. Pseudo-first-order hydrolysis rate constants (k_1^{hydr}) of $KBH_2(NC_4H_4)CN$ in aqueous HCl. (a) H_3PO_4–KH_2PO_4, (b) KH_2PO_4–Na_2HPO_4, (c) buffers at 25°C (ionic strength 1.0) determined by spectrophotometric method

pH	Buffers	k_1^{hydr} [s^{-1}]
0.023	a	$5.5 \cdot 10^{-5}$
0.325	a	$5.6 \cdot 10^{-5}$
0.682	a	$5.6 \cdot 10^{-5}$
0.996	a	$5.2 \cdot 10^{-5}$
1.292	a	$4.9 \cdot 10^{-5}$
1.553	b	$4.1 \cdot 10^{-5}$
1.602	a	$3.9 \cdot 10^{-5}$
1.824	a	$3.2 \cdot 10^{-5}$
1.854	b	$3.4 \cdot 10^{-5}$
1.921	a	$3.1 \cdot 10^{-5}$
2.097	a	$2.6 \cdot 10^{-5}$
2.149	b	$2.2 \cdot 10^{-5}$
2.456	b	$1.4 \cdot 10^{-5}$
2.745	b	$8.9 \cdot 10^{-6}$
5.9	c	$1.5 \cdot 10^{-6}$
6.9	c	$1.6 \cdot 10^{-6}$
7.9	c	$1.5 \cdot 10^{-6}$

$$[BH_2(NC_4H_4)CN]^- + H^+ \underset{k_{-H}}{\overset{k_H}{\rightleftharpoons}} [BH_2(HNC_4H_4)CN] \quad (15)$$

$$[BH_2(HNC_4H_4)CN] \xrightarrow{k_2} BH_2CN + C_4H_4NH \quad (16)$$

$$[BH_2(NC_4H_4)CN]^- \xrightarrow{k_1} BH_2(NC_4H_4) + CN^- \quad (17)$$

$$BH_2CN + 3H_2O \xrightarrow{\text{fast}} B(OH)_3 + 2H_2 + HCN \quad (18)$$

$$BH_2(NC_4H_4) + OH^- \overset{\text{fast}}{\rightleftharpoons} [BH_2(NC_4H_4)OH]^-. \quad (19)$$

Table 4. Rate constants (k_H, k_1) and protonation constant (K_p) of the hydrolysis of $KBH_2(NC_4H_4)CN$ at 25°C (ionic strength 1.0)

Rate constants (units)	Values
$k_2 \dfrac{k_H}{k_{-H}}$ $(mole^{-1} \cdot dm^3 \cdot s^{-1})$	$(4.8 \pm 0.3) \cdot 10^{-3}$
k_1 (s^{-1})	$(1.6 \pm 0.1) \cdot 10^{-6}$
K_p $(mole^{-1} \cdot dm^3)$	80 ± 6

According to eqns (14)–(19), to the preceding results obtained from the hydrolysis studies with the other cyano-(pyrrolyl-1)borates, and also, taking into consideration the following relationship between the total concentration of the non-hydrolysed borate (C_B), the concentration of the borate (B^-) and the concentration of the protonated product (HB):

$$C_B = [B^-] + [HB] = [B^-](1 + K_p[H^+]) \quad (20)$$

the k_1^{hydr} value can be given by eqn (21):

$$k_1^{hydr} = \frac{k_2 k_H / k_{-H}[H^+] + k_1}{1 + K_p[H^+]}. \quad (21)$$

After calculation of the k_1 values, the parameters of eqn (21) were determined by the method described earlier[2] using the data of Table 3. The resulting values are summarized in Table 4. The K_p value (80) obtained from the kinetic measurements is in good agreement with that ($K_p = 69$) determined by the spectrophotometric method.[7]

Comparing the k_H values of the phenyl(pyrrolyl-1)-borates[11] and the hydro(pyrrolyl-1)borates[2] with that of the corresponding cyano derivatives (Tables 3 and 4) it can be established that a H–CN or C_6H_5–CN substituent exchange in the molecule results in a 4–5 orders of magnitude decrease in the value of k_H, but in the case of $[BH_2(NC_4H_4)CN]^-$ a 7 orders of magnitude decrease was observed. Thus the hydrolytic stability of the $[BH_2(NC_4H_4)CN]^-$ anion is much larger than has been expected on the basis of the substituent effect. However, this extra-stability is in good accordance with the results of the H-exchange studies in D_2O: in the case of the $[BH_2(NC_4H_4)CN]^-$ anion the pyrrolyl group can be entirely deuterated[7] whereas only partial deuteration can be observed with the other anions.[2,11] We believe that in the case of the hydrolysis of the cyano(pyrrolyl-1)borates a close connection exists between the alteration of the rate of the hydrolysis from the linear substituent-effect, and the degree of deuteration of the pyrrolyl group of the borate. Similar explanation can be given also for finding that the hydrolytic ability of the $[B(C_6H_5)_2(NC_4H_4)CN]^-$ anion is somewhat larger than that expected according to the linear substituent effect (Table 2).

Contrary to the other (pyrrolyl-1)borates[1,2] the hydrolysis of the cyano(pyrrolyl-1)borates involves a novel reaction—the hydrolytic loss of cyanide anion—which does not take place upon the hydrolysis of the BH_3CN^- ion, but does proceed in the case of amine boranes[9] ($[BH_2(NR_2)CN]^-$ anions). The data summarized in Tables 2 and 4 clearly show that the rate of the S_N1-type hydrolysis (k_1) of the cyano(pyrrolyl-1)-borates increases with the increasing number of the pyrrolyl groups of the molecule. A similar change is characteristic also for the Lewis-acid character of the (pyrrolyl-1)-boranes,[13] namely, the value of the k_1 constants (Tables 2 and 4) is primarily determined by the Lewis-acid character of the borane attached to the CN group.

Acknowledgements—We thank István Csengeri for his cooperation in the kinetic measurements and Zsombor Nagy for his valuable assistance in the preparation of the compounds.

REFERENCES

1. J. Emri, B. Györi and P. Szarvas, *Z. Anorg. Allg. Chem.* 1973, **400**, 321.

2. J. Emri and B. Györi, *Polyhedron* 1982, **1**, 673.
3. M. M. Kreevoy and J. E. C. Hutchins, *J. Am. Chem. Soc.* 1969, **91**, 4329.
4. R. E. Davis, E. B. Bromels and C. L. Kibby, *J. Am. Chem. Soc.* 1962, **84**, 885.
5. M. M. Kreevoy and J. E. C. Hutchins, *J. Am. Chem. Soc.* 1972, **94**, 6371.
6. P. Szarvas, B. Györi, J. Emri and Gy. Kovács, *Magy. Kém. Foly.* 1971, **77**, 495.
7. B. Györi, J. Emri and L. Szilágyi, *J. Organometal Chem.* 1978, **152**, 13.
8. B. Györi and J. Emri, *J. Organometal Chem.* 1982, **238**, 159.
9. C. Weidig, S. S. Uppal and H. C. Kelly, *Inorg. Chem.* 1974, **13**, 1763.
10. E. Tommila, *Acta Chem. Scand.* 1955, **9**, 975.
11. J. Emri and B. Györi, to be published.
12. D. M. Muir and M. C. Whiting, *J. Chem. Soc. Perkin II* 1975, 316; 1976, 388. G. P. Bean and T. J. Wilkinson, *J. Chem. Soc. Perkin II* 1978, 72.
13. P. Szarvas, B. Györi and J. Emri, *Acta Chim. Acad. Sci. Hung.* 1971, **70**, 1.