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# Kinetics and Mechanism of Hydrolysis of Some Amine–Cyanoboranes in Acid Perchlorate Media

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In acid media ($[H^+]$ = 0.02–0.2 mol $dm^{-3}$), isopropylamine– and diisopropylamine–cyanoborane are hydrolysed completely to boric acid, hydrogen, hydrogen cyanide and the salt of the corresponding amine. The reaction occurs in steps, *viz.* (1) rapid loss of $CN^-$ as HCN and one $H^-$ as $H_2$, (2) rate-determining B–H bond breaking and loss of the second $H^-$ as $H_2$ and (3) very slow B–N bond breaking. The B–H bond breaking is rate determining also in the acid hydrolysis of $BH_3(CN)^-$ ion. Step (2) is first order both in [substrate] and $[H^+]$. Rate constant and activation parameters for step (2) have been determined. Cyanoborane adducts of tertiary amines, $Me_3N$ and $Pr^i_3N$, do not hydrolyse and it appears that the steric bulk of the non-leaving amine group has the dominant effect on the rate of hydrolysis of the adducts.

The kinetics of solvolysis of amine–boranes,[1–3] amine–halogenoboranes,[4,5] amine–cyanoboranes,[6] lithium cyanoborohydride[7,8] and cyano (pyrrol-1-yl)borates[9] has been the subject of previous investigations. In all cases, $H_2$, boric acid and the amine were obtained as the reaction products along with HX (X = halide or $CN^-$) whenever possible. The reactions are complex because they must involve several bond-breaking and -making steps. It is at best difficult to establish the stoichiometric mechanism and ascertain the rate-determining step for such processes.

The kinetics of all the above reactions was monitored by measuring $[H^-]$ volumetrically at different times and rate of the reaction was equated to $-d[H^-]/dt$. This is permissible if the loss of hydride is either rate determining or very rapid and succeeds a rate-determining step which may be cleavage of the B–N or B–X bonds. It has not always been established which of these two conditions prevails. Consequently, the interpretation of the kinetic results seems ambiguous.

In this perspective we report the results of investigation on the kinetics of acid hydrolysis of isopropylamine– and diisopropylamine–cyanoborane. The rate was measured by monitoring the decrease in $[H^-]$, the increase in volume of dihydrogen gas evolved and also spectral changes. It has thus been possible to establish the correct reaction sequence. We attempted similar studies on triisopropylamine– and trimethylamine–cyanoborane but found that neither undergoes acid hydrolysis.

## Experimental

*Materials.*—Sodium cyanotrihydroborate (Aldrich, USA), sodium perchlorate (E. Merck, FRG), perchloric acid (Merck, India) and trimethylamine hydrochloride (Fluka, FRG) were used as received. Commercial grade isopropylamine, diisopropylamine and triisopropylamine were dried and purified by distillation over KOH pellets. Tetrahydrofuran was kept over $FeSO_4$ for 48 h and then dried by refluxing over lithium aluminium hydride and distilled prior to use. Potassium iodide, potassium bromide, potassium bromate, sodium thiosulphate and starch were all analytical grade reagents. All aqueous solutions were prepared in triply distilled water[10] prior to use.

The amine-cyanoboranes were prepared by published methods.[11] Their purity was ascertained by elemental analyses (C, H, N, B) and estimation of total soluble hydride. Boron was estimated volumetrically,[12] while a Perkin-Elmer 240C elemental analyser was used for C, H and N. The results indicate that the purity of the substrate is better than 99%.

*Product Analyses.*—Cyanide in solution was detected and quantified by the formation of coloured picrates.[13] The hydrogen evolved was collected by the downward displacement of NaOH solution in a 50 $cm^3$ burette connected to the reaction vessel by pressure tubing. A pressure equalizer was used for the addition of acid and to initiate the reaction for volumetric measurements. Boric acid in the reaction product was determined by conversion into borate ester with MeOH followed by azeotropic distillation.[12]

*Stoichiometry.*—An aqueous solution (100 $cm^3$) of 2.0 mmol $dm^{-3}$ of an amine–cyanoborane in 0.2 mol $dm^{-3}$ $HClO_4$ was allowed to react at 50 °C for 1 h to ensure complete reaction. The total volume of dihydrogen gas evolved and $[H_3BO_3]$ in the product solution were measured as stated above. The measured volume of $H_2$ was converted into weight as usual. In this reaction $CN^-$ evolves as HCN. This was absorbed in NaOH and estimated as stated above.

*Kinetic Studies.*—Reactions were monitored by measuring, at suitable time intervals, the total soluble hydride iodometrically.[4,6] In some cases the rate was measured spectrophotometrically and also by measuring the volume of hydrogen evolved. Spectrophotometric measurement was made at 214 nm ($\lambda_{max}$) with a Philips Analytical SP8-400 or a Hitachi U2000 spectrophotometer.

Reactions were carried out in the presence of a large excess of $HClO_4$ (0.02–0.2 mol $dm^{-3}$) over the substrate boranes in aqueous media at $I$ = 1.0 mol $dm^{-3}$ ($NaClO_4$) in the temperature range 20–50 °C. A sample quenching technique was adopted in the titrimetric measurements and 10–12 titration data were collected in each set. Pseudo-first-order rate constants $k_0$ were evaluated from the slopes of plots of $\ln[H^-]_t$ against time. In a few kinetic runs $k_0$ was also obtained from plots of $\ln(A_\infty - A_t)$ and $\ln(V_\infty - V_t)$ against time, where $A$ is the absorbance at 214 nm and $V$ the volume of $H_2$.

The HCN liberated in the reaction was absorbed in aqueous NaOH with a special water aspirator (Eyela A-3S, Japan) by passing the liberated gas through an improvized hood equipped with a large inverted funnel.

## Results

Product analysis and stoichiometric measurements show that each mol of substrate amine–cyanoborane on complete hydrolysis produces 0.98 ± 0.04 mol of $CN^-$, 1.00 ± 0.02 mol boric

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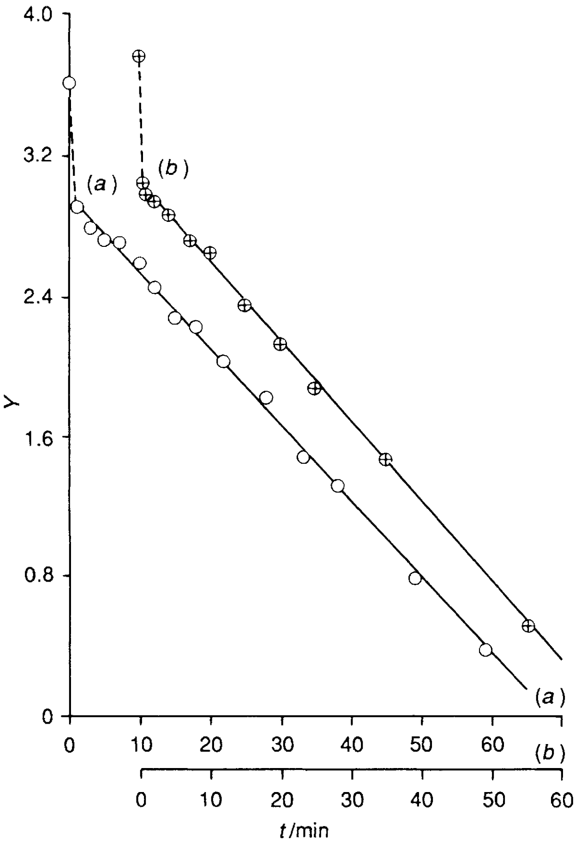

**Fig. 1** Evaluation of rate constant $k_0$ for the acid-catalysed hydrolysis of diisopropylamine–cyanoborane at 30 °C, $[H^+] = 0.08$ mol dm$^{-3}$, $I = 1.0$ mol dm$^{-3}$. (*a*) Hydride decomposition data, $Y = 7 + \ln[H^-]_t$. (*b*) Hydrogen evolution data, $Y = \ln(V_\infty - V_t)$, $V$ = volume of hydrogen evolved at different times. In both curves (*a*) and (*b*) the zero-time reading is the theoretical value. The next reading refers to the first experimental point which corresponds to approximately 50% loss of $[H^-]$ within the time of mixing; $k_0 = 7.2$ s$^{-1}$ from (*a*), $= 7.6$ s$^{-1}$ from (*b*)

acid and 1.9 ± 0.2 mol $H_2$. The stoichiometric equation is thus as in (1) where $R^1 = Pr^i$, $R^2 = H$; or $R^1 = R^2 = Pr^i$.

$$R^1R^2NH{\cdot}BH_2(CN) + 3H_2O + H^+ \longrightarrow R^1R^2\overset{+}{N}H_2 + HCN + B(OH)_3 + 2H_2 \quad (1)$$

The overall reaction must occur in steps. On the basis of the evidence discussed below, the sequence (2)–(5) seems most plausible under the present experiment conditions (r.d.s. = rate-determining step). In compliance with this scheme it has been found that all cyanide and 50 ± 1% of the total soluble hydride is lost immediately after acidification and 50 ± 1% of the total dihydrogen [expected to evolve on the basis of equation (1)] accumulated in the burette. Loss of the remaining hydride and the parallel evolution of the remaining 50% of $H_2$ is a

$$R^1R^2NH{\cdot}BH_2(CN) + H_2O \xrightarrow[\text{fast}]{H^+} R^1R^2NH{\cdot}BH_2(OH) + HCN \quad (2)$$

$$R^1R^2NH{\cdot}BH_2(OH) + H_2O \xrightarrow[\text{fast}]{H^+} R^1R^2NH{\cdot}BH(OH)_2 + H_2 \quad (3)$$

$$R^1R^2NH{\cdot}BH(OH)_2 + H_2O \xrightarrow[\text{slow (r.d.s.)}]{H^+} R^1R^2NH{\cdot}B(OH)_3 + H_2 \quad (4)$$

$$R^1R^2NH{\cdot}B(OH)_3 + H^+ \xrightarrow{\text{very slow}} R^1R^2\overset{+}{N}H_2 + B(OH)_3 \quad (5)$$

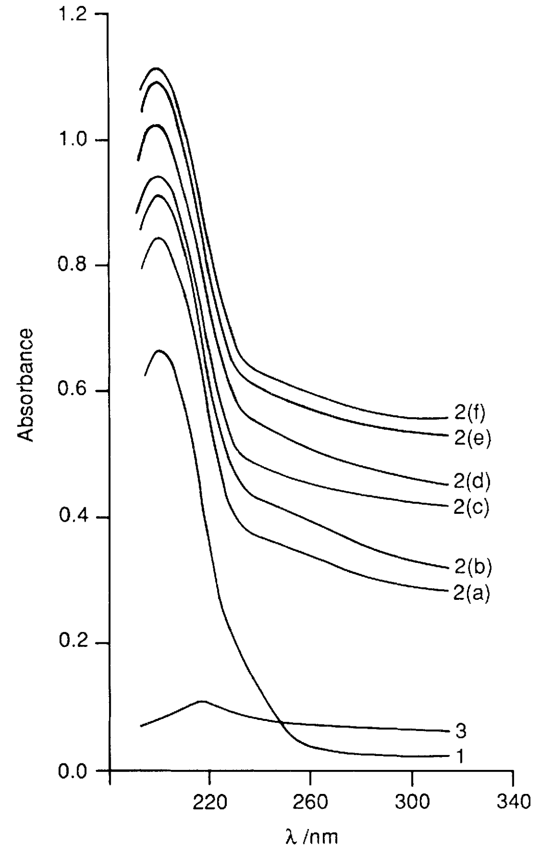

**Fig. 2** Spectra of diisopropylamine–cyanoborane: 1, aqueous solution ($1.14 \times 10^{-2}$ mol dm$^{-3}$); 2(a) to 2(e), acid solution of 1 at different time intervals increasing from (a) to (e); 3, after 48 h. In all the cases $I = 1.0$ mol dm$^{-3}$

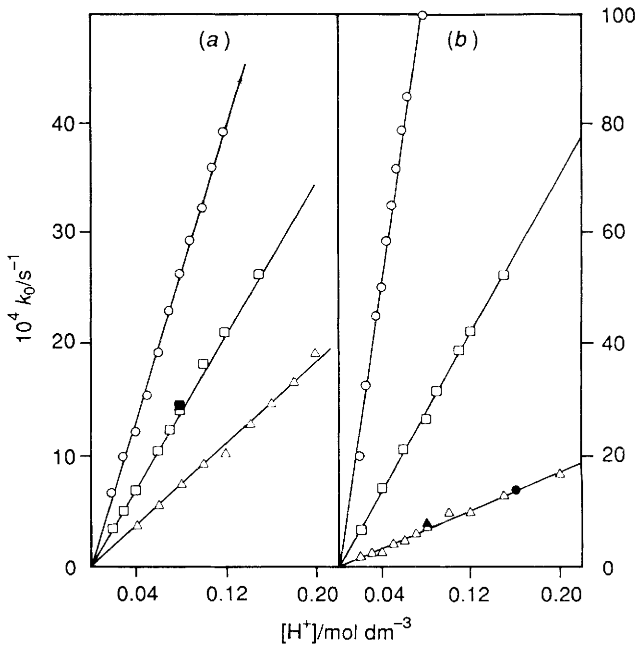

**Fig. 3** Plots of $k_0$ against $[H^+]$. [Substrate] $= 1.86 \times 10^{-3}$ mol dm$^{-3}$, $I = 1.0$ mol dm$^{-3}$. (*a*) Isopropylamine cyanoborane at 20.0 (△), 30.0 (□) and 40.0 °C (○); (*b*) diisopropylamine–cyanoborane at 30.0 (△), 40.0 (□) and 50.0 °C (○). The values of $k_0$ were mostly collected by measurement of $[H^-]$. However, ▲ refers to hydrogen evolution kinetics, ■ and ● to spectrophotometric kinetics

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**Table 1** Kinetic parameters for acid hydrolysis of amine–cyanoboranes. [Substrate] = $1.86 \times 10^{-3}$ mol dm$^{-3}$, $I = 1.0$ mol dm$^{-3}$ ($NaClO_4$)

| $T$/°C | $10^2[H^+]$/ mol dm$^{-3}$ | $10^4k_0$/ s$^{-1}$ | $10^2k_2$[a]/ dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| Substrate: $Pr^iNH_2{\cdot}BH_2(CN)$ | | | |
| 20 | 4 | 3.6 | 0.90 |
| | 4 | 3.9[b] | 0.97[c] |
| | 6 | 5.4 | 0.90 |
| | 8 | 7.3 | 0.91 |
| | 10 | 9.1 | 0.91 |
| | 12 | 10.0 | 0.83 |
| | 15 | 13.0 | 0.87 |
| | 16 | 14.4 | 0.90 |
| | 18 | 16.3 | 0.90 |
| | 20 | 18.8 | 0.94 |
| | | | Av. 0.90 ± 0.03[d] |
| 30 | 2 | 3.4 | 1.7 |
| | 3 | 5.0 | 1.67 |
| | 4 | 6.8 | 1.7 |
| | 5 | 6.65 | 1.33[c] |
| | 6 | 10.3 | 1.72 |
| | 7 | 12.1 | 1.73 |
| | 8 | 13.9 | 1.73 |
| | 8 | 14.5[e] | 1.81 |
| | 10 | 17.9 | 1.79 |
| | 12 | 20.8 | 1.67 |
| | 15 | 25.9 | 1.73 |
| | | | Av. 1.72 ± 0.04[d] |
| 40 | | | |
| | 2 | 6.8 | 3.4 |
| | 3 | 9.8 | 3.27 |
| | 4 | 11.9 | 2.98 |
| | 5 | 15.2 | 3.04 |
| | 6 | 19.0 | 3.17 |
| | 7 | 22.7 | 3.24 |
| | 8 | 26.0 | 3.25 |
| | 9 | 29.2 | 3.24 |
| | 10 | 32.0 | 3.20 |
| | 11 | 35.8 | 3.25 |
| | 12 | 39.1 | 3.26 |
| | | | Av. 3.21 ± 0.1[d] |

| $T$/°C | $10^2[H^+]$/ mol dm$^{-3}$ | $10^4k_0$/ s$^{-1}$ | $10^2k_2$[a]/ dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| Substrate: $Pr^i{}_2NH{\cdot}BH_2(CN)$ | | | |
| 30 | 2 | 1.7 | 0.850 |
| | 3 | 2.56 | 0.853 |
| | 4 | 2.6 | 0.650[c] |
| | 5 | 4.25 | 0.850 |
| | 6 | 4.7 | 0.783 |
| | 7 | 6.0 | 0.857 |
| | 8 | 7.6[b] | 0.950 |
| | 8 | 7.2 | 0.900 |
| | 10 | 9.9 | 0.850 |
| | 12 | 10.2 | 0.850 |
| | 15 | 12.6 | 0.840 |
| | 16 | 13.6[e] | 0.850 |
| | 20 | 16.8 | 0.840 |
| | | | Av. 0.86 ± 0.04[d] |
| 40 | 2 | 6.8 | 3.40 |
| | 4 | 14.3 | 3.58 |
| | 6 | 21.2 | 3.53 |
| | 8 | 26.9 | 3.36 |
| | 9 | 31.7 | 3.52 |
| | 10 | 40.3 | 4.03[c] |
| | 11 | 38.8 | 3.53 |
| | 12 | 42.2 | 3.52 |
| | 15 | 52.2 | 3.48 |
| | | | Av. 3.49 ± 0.07[d] |
| 50 | 2 | 20.1 | |
| | 2.5 | 32.7 | 10.04[c] |
| | 3 | 33.4 | 13.1 |
| | 3.5 | 45.1 | 11.1[c] |
| | 4 | 50.5 | 12.9 |
| | 4.5 | 58.8 | 12.6 |
| | 5 | 65.5 | 13.1 |
| | 5.5 | 72.2 | 13.1 |
| | 6 | 79.2 | 13.1 |
| | 6.5 | 85.2 | 13.2 |
| | 8 | 100.0 | 13.1 |
| | | | 12.5 |
| | | | Av. 13.0 ± 0.2[d] |

[a] $k_2 = k_0/[H^+]$. [b] Data obtained from dihydrogen evolution kinetics. [c] Excluded from average $k_2$. [d] Indicated error is standard deviation. Activation parameters associated with $k_2$: $\Delta H^\ddagger = 45 \pm 4$ kJ mol$^{-1}$, $\Delta S^\ddagger = -132 \pm 12$ J K$^{-1}$ mol$^{-1}$ for $Pr^iNH_2{\cdot}BH_2(CN)$, and $\Delta H^\ddagger = 110 \pm 8$ kJ mol$^{-1}$ and $\Delta S^\ddagger = 77 \pm 23$ J K$^{-1}$ mol$^{-1}$ for $Pr^i{}_2NH{\cdot}BH_2(CN)$. [e] Data obtained from the rate of spectral changes.

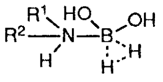
relatively slow process and continues for a period of *ca.* 60 min (see Fig. 1). The spectrum of an aqueous solution of diisopropylamine–cyanoborane is shown in Fig. 2 (curve 1). A sharp spectral change from 1 to 2(a) occurs on acidification. The change is very fast and is plausibly associated with the fast steps (2) and (3). Spectrum 2(a) then gradually changes to 2(f) (Fig. 2) in parallel with the evolution of $H_2$ and decay of $[H^-]$. All the three processes proceed at equal rate and all obey first-order kinetics in presence of excess of acid and yield the same value (within 8%) for the first-order rate constant $k_0$ under same reaction conditions (see Table 1). The rate exhibited a first-order dependence also on the acid concentration under all conditions used (see Fig. 3) in conformity with the rate equation (6). Here $[H^-]$ represents the total soluble hydride. Addition of

$$\text{Rate} = -\frac{d[H^-]}{dt} = \frac{d[H_2]}{dt} = \frac{d[A]}{dt} = k_2[H^-][H^+] \qquad (6)$$

amine salts does not affect the rate. Intercepts of plots of $k_0$ against $[H^+]$ (see Fig. 3) did not vary statistically from zero in conformity with equation (6), and the fact that none of the amine–cyanoboranes in this work undergoes appreciable loss of $[H^-]$ in neutral or alkaline media. The average value of $k_2$, its standard deviation, and associated activation parameters are also shown in Table 1. The solution obtained after step (4) undergoes a very slow decrease in absorbance from spectrum 2(f) to 3 over *ca.* 48 h at room temperature (*ca.* 28 °C). Spectrum 3 is same as that of a 1 : 1 mixture of boric acid and the amine. This very slow spectral change is assigned to step (5), which has been found to be accelerated by acid and alkali.

According to the foregoing discussion, the kinetic parameters in Table 1 refer to step (4) not the step (2), (3) or (5). With the $BH_3(CN)^-$ ion also we have observed that evolution of dihydrogen gas bubbles is perceptible for about 15 min in aqueous medium (pH 5.3) but HCN is completely lost immediately after dissolution. This strongly suggests rate-determining cleavage of a B–H not B–CN bond in $BH_3(CN)^-$ ion. Earlier literature[8] is confused at this point.

The rate-determining loss of hydride as $H_2$ (step 4) plausibly involves an intermediate **A** comprising a five-co-ordinated boron species as proposed before[3] for the acid catalysed hydrolysis of amine–borane. For $Pr^iNH_2{\cdot}BH_2(CN)$ $\Delta H^\ddagger$ is low and



**A**

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$\Delta S^\ddagger$ is strongly negative. In this case, therefore, it appears that the B–H bond breaking in **A** is solvent assisted and synchronous or nearly synchronous with the formation of a B–$OH_2$ bond by the solvent water molecule carried along with the $H^+$ attacking the boron centre. Subsequent deprotonation should lead to a B–OH bond. In the case of the secondary amine–cyanoborane $Pr^i_2NH{\cdot}BH_2(CN)$, the non-leaving group $Pr^i_2NH$ is much more bulky. It might be anticipated that, with this substrate, bond breaking should be more important and solvent assistance poorer than with $Pr^iNH_2{\cdot}BH_2(CN)$. As observed this should require a higher $\Delta H^\ddagger$ and more positive $\Delta S^\ddagger$ for $Pr^i_2NH{\cdot}BH_2(CN)$ than for $Pr^iNH_2{\cdot}BH_2(CN)$. In the case of tertiary amine–cyanoboranes, steric congestion may prevent attack of a solvated $H^+$ on the boron centre and hydrolysis is not observed.

## Acknowledgements

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