shown in Figure 6. Similar behavior was noted for $Ru(bpy)_2L_2^{3+/2+}$ data.[3] The interesting additional information to be obtained from our studies is an estimate of the extent of fractional charge transfer from the Ru(II) center into the ligand π-acceptor orbitals, i.e.

$$\underset{1.0}{CH_3pz^+} > \underset{0.88}{CO} > \underset{0.73}{dmad} > \underset{0.51}{pz} > \underset{0.31}{CH_3CN} > \underset{0.20}{py}$$

The estimate for the $Ru(NH_3)_5pz^{2+}$ ion is modestly higher than the 0.20 electron (22% ligand character to the ground-state MO),[21,22] which has been estimated from the ground- and excited-state pK_a's. Protonation is sure to alter the solvation in the resultant $Ru(NH_3)_5(pzH)^{3+}$ complex, and this could lead to a small error in the estimate of the extent of back-donation from Ru(II) by the pK_a method.[19] The results here are in good agreement with the estimates of Zwickel and Creutz based on $Ru(NH_3)_4L_2^{2+}$ spectra.[18] The result that CO and the coordinated acetylenic unit occurs with more significant charge transfer than the N-heterocycles is in keeping with prior studies.[10,23,24] This effect has been attributed to the synergistic stabilization of π-accepting/σ-donating with small molecules with triple bonds (e.g. CO, CN^-, R_2C_2, N_2, NO^+).[23] Cook et al. estimated 0.8 ± 0.2 electron transferred from $Pt(PPh_3)_2Pt(C_2H_4)$ and 1.8 ± 0.2 for O_2 as the acceptor.[1] Assuming less good π-donation from a d^6 Ru(II) center compared with a d^{10} Pt(0) center, one might anticipate that C_2H_4 or dmad would receive a somewhat smaller charge from Ru(II). This is observed with ~0.7 electron received with dmad.

Citrin has studied the Creutz-Taube ion in some detail.[2] Values for Δ in these complexes were taken from their published spectra. The (II,II) complex, $[(NH_3)_5Ru]_2pz^{4+}$, shows a Δ value of 4.2 eV compared to the 3.8-eV difference for $[Ru^{II}(NH_3)_5pz](PF_6)_2$ in our work. Similarly Citrin's data[2a] give a Δ value of 1.8 eV for the (III,III) complex compared to 2.4 ± 0.1 eV for Ru(III) complexes in this work. The mixed-oxidation-state (II,III) complex has Δ values of 4.1 eV for the "Ru^{II} site" and 1.8 eV for the "Ru^{III} site".[2a] This is in reasonable agreement with the data presented in Table I for 11 compounds in which Δ values for Ru(II) complexes are larger than those for Ru(III) complexes unless the strongest π-acceptor, CH_3pz^+, is present.

Conclusions

The ESCA spectra of the Ru(II) pentaammines have given a reasonable order to the π-acceptor series of $CH_3pz^+ > CO >$ dmad $>$ pz $> CH_3CN >$ py. The calculated values of fractional electron transfer from the Ru(II) site to the π-acceptor ligands are in concert with estimates in the literature that were derived on the basis of titration data[19] and UV-visible spectra of complexes.[18] The values reported here on the basis of ESCA would seem to be a more reliable quantitative estimate of the extent of back-donation in these complexes because the influence of solvation on the values of the other methods has been minimized by use of a similar series of salts.

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Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Kinetics of Base Hydrolysis of Cyanogen and 1-Cyanoformamide

Yi Lai Wang, Hsiupu D. Lee, Mark W. Beach, and Dale W. Margerum*

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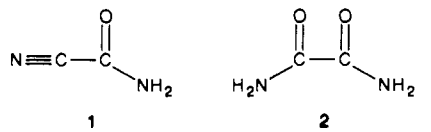
The rate of cyanogen hydrolysis in base is first order in OH^- and first order in $(CN)_2$, but the reaction proceeds by two paths. Only 25% at 5 °C to 33% at 40 °C of the cyanogen reacts directly by C-C bond cleavage to give CN^- and OCN^- ($k_1 = 8.9 \times 10^2$ M^{-1} s^{-1} at 25.0 °C, $E_a = 15.8$ kcal mol^{-1}). The rest of the cyanogen forms 1-cyanoformamide via a second path ($k_2 = 2.17 \times 10^3$ M^{-1} s^{-1} at 25.0 °C, $E_a = 13.8$ kcal mol^{-1}). A common reactive intermediate, $N{\equiv}CC(OH){=}N^-$, is postulated for the k_1 and k_2 paths. The 1-cyanoformamide that forms also decomposes by C-C bond cleavage, but at a much slower rate than cyanogen. The reaction proceeds by deprotonation of 1-cyanoformamide ($pK_a = 10.8$) to give $N{\equiv}CC(=O)NH^-$, which reacts to give CN^- and OCN^- ($k_3 = 0.556$ s^{-1} at 25.0 °C, $E_a = 22.5$ kcal mol^{-1}).

Introduction

Cyanogen is often considered to be a pseudohalogen, and its hydrolysis reaction in base (eq 1) is written to parallel the hydrolytic disproportionation of halogens.[1,2] Evidence for this reaction and preliminary information about its rate were obtained from conductivity studies of Naumann[3] in 1910. No kinetics studies of base hydrolysis of cyanogen have been reported since this early work, with the exception of an unsuccessful attempt to reanalyze Naumann's limited data.[4] In fact, very little information[5] is available about the UV spectrum and molar absorptivity of cyanogen in aqueous solution or about the rate and products of its hydrolysis in acidic, neutral, or basic solutions.

$$(CN)_2 + 2OH^- \rightarrow CN^- + OCN^- + H_2O \qquad (1)$$

It is known that in weakly acidic solution cyanogen hydrolyzes to give 1-cyanoformamide (**1**) and that in very strong acid oxamide (**2**) is formed.[6] Hydrolysis of cyanogen in the presence of



1 **2**

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phosphate in neutral or slightly basic solutions also leads to **1**.[7] Studies of prebiotic condensing agents[7-10] (i.e. chemical condensing agents that helped to link biomonomers into biopolymers on the primitive earth[11]) have considered the roles that cyanogen, cyanoformamide, and cyanate may have played in this process. In their discussion of the hydrolysis of cyanogen, Miller and Orgel[8] suggest that in neutral or weakly basic solution 1-cyanoformamide forms first and hydrolyzes further to give cyanide and cyanate. No data are given. An early study[12] indicates that cyanoformamide reacts in warm aqueous silver nitrate solution to form AgCN, CO_2, and NH_4^+, quantitatively. Welcher[6] reports that "hot 0.5 N caustic" reacts with 1-cyanoformamide in 3 min to give a quantitative yield of CN^-, CO_3^{2-}, and NH_3.

In this work we examine the UV spectrum of cyanogen in aqueous solution and observe a large increase in absorbance at 206 nm as cyanogen hydrolyzes slowly to form 1-cyanoformamide. Our work shows that the base hydrolysis of cyanogen proceeds by two paths. One path (29% at 25 °C) gives direct carbon–carbon bond cleavage and the products in eq 1. However, the dominant path (71% at 25 °C) first gives 1-cyanoformamide, which undergoes a much slower base-catalyzed hydrolysis to give cyanide and cyanate.

Experimental Section

Synthesis of 1-Cyanoformamide. Cyanoformamide was prepared by sublimation of a mixture of oxamide and phosphorus pentoxide.[13] The product was contaminated with a small amount of oxamide and phosphorus pentoxide. It was purified by dissolution in dry ethyl acetate, followed by filtration to remove the undissolved impurities. The filtrate was concentrated to give a thick liquid, which crystallized upon slow addition of *n*-hexane. Even after several recrystallizations, this material was not stable during storage at room temperature. Further purification by sublimation (0.05 mmHg, 80 °C) gave stable, white granular crystals with a melting point of 59–60 °C (Welcher[6] reported 58–60 °C by a different synthetic method). Mass spectrum (70 eV): *m/e* 70 (m^+), 54 ($m^+ - NH_2$), 44 ($m^+ - CN$). Anal. Calcd for $C_2H_2N_2O$: C, 34.29; H, 2.87; N, 40.00. Found: C, 34.24; H, 2.74; N, 39.92. 1-Cyanoformamide gave a 100.0 ± 0.2% yield of cyanide and cyanate in 0.1 M sodium hydroxide.

Reagents. The cyanogen solution (0.01–0.03 M) was freshly prepared before use by bubbling cyanogen gas (>98.5%, Matheson) through a 0.001 M $HClO_4$ solution. Low concentrations of $(CN)_2$ were used to avoid polymerization.[3] The concentration of $(CN)_2$ was determined by measuring the amount of CN^- formed when concentrated base was added to the solution and the reaction was allowed to go to completion. The base was freshly prepared from saturated sodium hydroxide to minimize carbonate contamination. All glassware was treated with 0.1 M EDTA before use to remove traces of metal ions that might affect cyanogen hydrolysis.[5]

Analytical Methods. The concentration of cyanide was determined by potentiometric titration with $AgNO_3$ solution standardized against KCl. A cyanide selective electrode (Orion 94-06A) and a double-junction reference electrode (Orion 90-02) were used to determine the end point of the titration. To determine the concentration of a cyanogen solution, concentrated sodium hydroxide solution was first added to the cyanogen solution to give a 0.1 M OH^- concentration and the cyanide ion formed was titrated with standardized silver nitrate solution within 5 min.[14]

The concentration of the cyanate was determined by an ion chromatographic method. A Wescan Model 266 ion analyzer with a conductivity detector was used. The column was a resin-based anion-exchange column (Wescan Anion/R, 269-029) suitable for a pH range of 2–13. The mobile phase contained 4.0×10^{-3} M 4-hydroxybenzoic acid and 4.5×10^{-3} M NaOH. The pH of the mobile phase was adjusted to 8.2 in order to avoid cyanide ion interference with the cyanate peak. The chromatographic parameters were as follows: flow rate 2.0 mL/min; sensitivity range 10; sample loop 0.1 mL. The cyanate peak was identified by its retention time (about 5.6 min) and peak shape as compared to those of the standard cyanate and the increase of the peak area upon adding potassium cyanate to the sample solution. The area of the cyanate peak, measured by an HP 3390A integrator, was shown to be related linearly to the concentration of the cyanate ion.

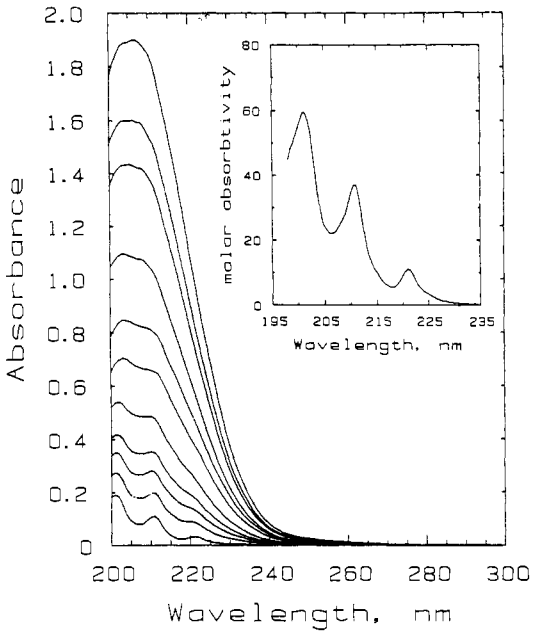

Figure 1. Change of absorption spectra (1-cm cell) of cyanogen (3.0×10^{-3} M) after its generation in 0.01 M $HClO_4$ solution: low to high absorbance taken after 4 min and 4, 8, 12, 18, 32, 44, 72, 116, 140, and 188 h. The insert gives the molar absorptivity of $(CN)_2$.

Kinetics Measurements. The rates of base hydrolysis of cyanogen and of 1-cyanoformamide at 25.0 °C were measured with a Dionex-Durrum Model D-110 stopped-flow spectrophotometer interfaced to a Hewlett-Packard computer (HP 2100). The reactions at 5–45 °C were measured by use of a Hi-Tech Scientific Model SFL-43 multimixing module attached by fiber optics to a Durrum D-110 monochromator and interfaced to a Zenith 151 CPU with a Metrabyte DASH-16 A/D interface. The reactions were run at 230 nm under pseudo-first-order conditions. Iterative nonlinear analysis of the data gave values for the initial and final absorbances and the observed rate constant (k_{obsd}). The reported values are the average of at least four runs. The ionic strength for all reactions was maintained at 0.20 M, adjusted with $NaClO_4$.

Results and Discussion

Cyanogen in Acid. The change of the UV spectrum when a 2.0×10^{-3} M solution of cyanogen in 0.01 M $HClO_4$ hydrolyzes over a period from 4 min to 188 h is shown in Figure 1. Cyanogen shows three peaks above 200 nm in the first spectrum: one peak appears at 221 nm (ϵ 11 ± 1 M^{-1} cm^{-1}), one at 211 nm (ϵ 37 ± 1 M^{-1} cm^{-1}), and one at 201 nm (ϵ 60 ± 1 M^{-1} cm^{-1}). In cyclohexane, $(CN)_2$ was reported[15] to have an absorption band at 222 nm (ϵ 13 M^{-1} cm^{-1}). The gaseous cyanogen molecule was reported[16,17] to have two electronic transition bands at 207 nm ($^1\Delta_u \leftarrow {}^1\Sigma_g^+$) and 220 nm ($^1\Sigma_u \leftarrow {}^1\Sigma_g^+$), which are probably due to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.[18] In 0.01 M acid, the repetitive spectra show an increase in absorbance to give a very intense single peak with the maximum at 206 nm (ϵ 5470 M^{-1} cm^{-1}). This reaction is first order with a rate constant of 5.3×10^{-7} s^{-1} in 0.01 M H^+ at 25 °C.

The UV-absorbing product of the reaction was identifed as 1-cyanoformamide. Its final spectrum is identical with that of synthetically prepared 1-cyanoformamide shown in Figure 2, and the product solution gave cyanide upon addition of sodium hy-

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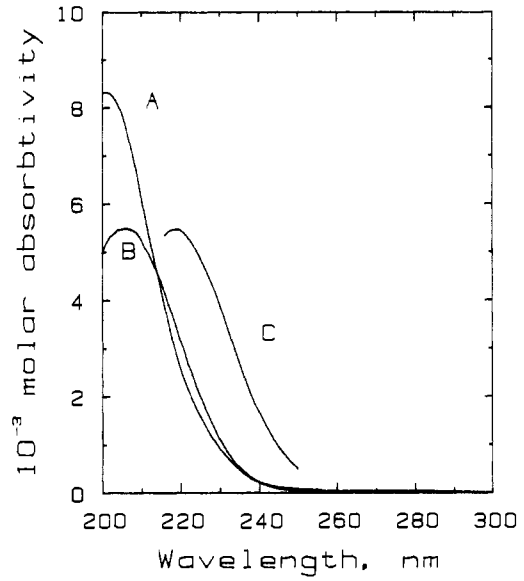

Figure 2. Absorption spectra of oxamide (A) and 1-cyanoformamide (B) in 0.001 M $HClO_4$ and of deprotonated 1-cyanoformamide (C) in 0.05 M NaOH.

Table I. Absorption Spectral Characteristics of Cyanogen and Its Possible Hydrolysis Products in Aqueous Solution

species	λ, nm	ϵ, M^{-1} cm^{-1}	species	λ, nm	ϵ, M^{-1} cm^{-1}
$(CN)_2$	201[a]	60	$NH_2C(O)C(O)NH_2$	202[a]	8290
	211[a]	37		220	2620
	221[a]	11		230	919
$NCC(O)NH_2$	206[a]	5470	$C_2O_4^{2-}$	220	113
	220	3470		230	47
	230	1120	CO_3^{2-}	230	8
$NCC(O)NH^-$	220[a]	5120			
	230	3890			

[a] Absorption peaks.

droxide. There was no evidence that oxamide, which is very insoluble, was formed during the reaction. No precipitate was observed. The spectrum of the product solution would have different features if oxamide had been formed, because the absorption peak for oxamide is more intense (ϵ 8290 M^{-1} cm^{-1}) and is at shorter wavelength (202 nm), as seen in Figure 2. Some of the spectral characeristics of cyanogen, 1-cyanoformamide, oxamide, and related species are given in Table I. At 230 nm, where the kinetics were observed, CN^- and OCN^- have negligible absorbance.

1-Cyanoformamide in Base. Addition of NaOH to 1-cyanoformamide gave an immediate spectral shift as seen in Figure 2. An absorbance jump at 230 nm is observed, followed by an absorbance decay. The magnitude of the absorbance jump depends on the hydroxide concentration as shown in Figure 3. Hydrolysis of 1-cyanoformamide in excess sodium hydroxide (i.e. the decrease of absorbance with time) is a pseudo-first-order reaction. Observed rate constants at different hydroxide concentrations are presented in Figure 4 and Table II. Both absorbance and the observed rate constants show a saturation effect with increase of hydroxide concentration (i.e., the values level off at higher hydroxide ion concentrations). There was no evidence that either carbonate ion or oxamide formed during the reaction. Hydrolysis of oxamide in base is slow, with a second-order rate constant[19] of (6.14 ± 0.06) × 10^{-2} M^{-1} s^{-1}, and this reaction is not detected. Equivalent amounts of cyanide ion and cyanate ion were found in the product solution. The recovery was 100 ± 1% for CN^- and was 100 ± 5% for OCN^- in 0.005 M NaOH.

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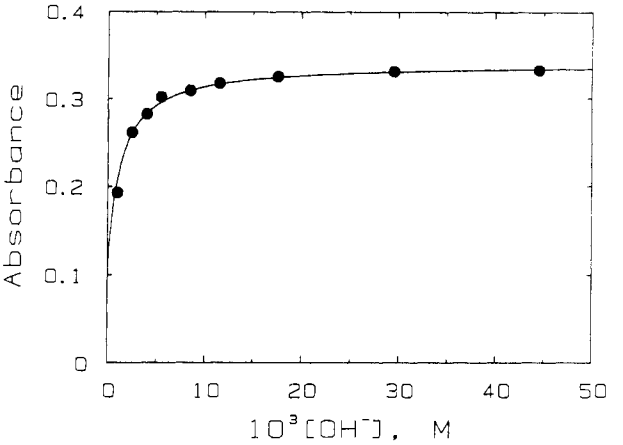

Figure 3. Initial absorbance of 1-cyanoformamide (4.65×10^{-5} M) after addition of base (230 nm, 1.89-cm cell, 25.0 °C, μ = 0.02). The solid line is a fit of eq 7, where K_{OH} = 930 M^{-1}, ϵ_A = 1120 M^{-1} cm^{-1}, and ϵ_B = 3890 M^{-1} cm^{-1}.

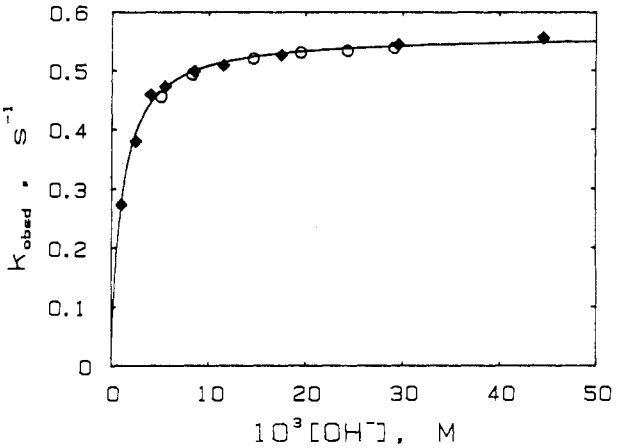

Figure 4. Hydroxide dependence of the pseudo-first-order rate constant for the base hydrolysis of 1-cyanoformamide (◆) and for the second reaction observed in the base hydrolysis of cyanogen (○). The solid line is a fit of eq 6 where K_{OH} = 930 M^{-1} and k_3 = 0.556 s^{-1} at 25 °C, μ = 0.2.

Table II. Effect of Hydroxide Ion on the Observed Rate Constant for the Hydrolysis of 1-Cyanoformamide[a]

10^3[OH⁻], M	k_{obsd}, s^{-1}	10^3[OH⁻], M	k_{obsd}, s^{-1}
1.00	0.273 ± 0.006	11.5	0.509 ± 0.004
2.50	0.380 ± 0.006	17.5	0.527 ± 0.002
4.00	0.459 ± 0.004	29.5	0.545 ± 0.005
5.50	0.473 ± 0.006	44.5	0.556 ± 0.007
8.50	0.499 ± 0.004		

[a] $[1\text{-cyanoformamide}]_{init} = 4.65 \times 10^{-5}$ M; μ = 0.2; 25.0 °C.

The proposed mechanism for the base hydrolysis of 1-cyanoformamide is the rapid deprotonation of the amide nitrogen to form species **3** (eq 2), followed by C–C bond cleavage to form cyanide ion and isocyanic acid (eq 3). This acid rapidly loses a proton to give cyanate ion (eq 4). The rate expression is given

$$N{\equiv}C{-}C(=O){-}NH_2 + OH^- \underset{}{\overset{K_{OH}}{\rightleftharpoons}} N{\equiv}C{-}C(=O){-}NH^- + H_2O \quad \text{fast} \quad (2)$$

3

$$N{\equiv}C{-}C(=O){-}NH^- \xrightarrow{k_3} CN^- + O{=}C{=}NH \quad \text{rds} \quad (3)$$

$$O{=}C{=}NH + OH^- \rightarrow OCN^- + H_2O \quad \text{fast} \quad (4)$$

in eq 5, where $[NCCONH_2]_T = [NCCONH_2] + [NCCONH^-]$.

$$-d[NCCONH_2]_T/dt = k_{obsd}[NCCONH_2]_T \quad (5)$$

$$K_{OH} = [NCCONH^-]/([NCCONH_2][OH^-]) \quad (6)$$

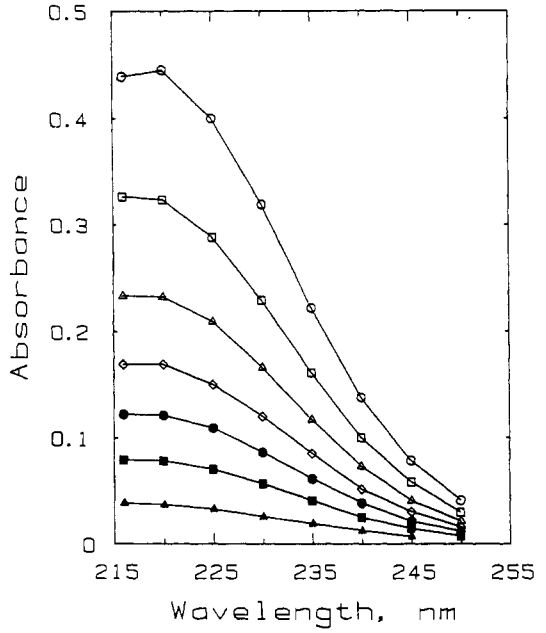

Figure 5. Spectra of deprotonated 1-cyanoformamide as it decays in base (Durrum stopped-flow, 1.89 cm, 0.05 M OH^-, $[NCCONH_2]_i = 4.65 \times 10^{-5}$ M, 25 °C, $\mu = 0.2$). The top curve was extrapolated to zero time; the remaining curves are at 0.6, 1.2, 1.8, 2.4, 3.2, and 4.6 s (bottom).

The equilibrium constant for the deprotonation (K_{OH} in eq 6) can be incorporated into eq 5 to give the observed first-order rate constant in eq 7. A plot of $1/k_{obsd}$ vs. $1/[OH^-]$ gives values of

$$k_{obsd} = K_{OH}k_3[OH^-]/(1 + K_{OH}[OH^-]) \quad (7)$$

$K_{OH} = (9.3 \pm 0.1) \times 10^2$ M^{-1} and $k_3 = 0.556 \pm 0.004$ s^{-1} at 25.0 °C and $\mu = 0.2$. The solid line in Figure 4 shows the excellent fit of these equilibrium and rate constants to the data. A pK_a value of 10.8 (25.0 °C, $\mu = 0.2$) for 1-cyanoformamide is calculated from K_{OH} and a pK_w value of 13.77 for these conditions.

Figure 3 shows the initial absorbance of 1-cyanoformamide at 230 nm after the addition of various concentrations of hydroxide ion. The solid line in Figure 3 gives the fit of eq 8, where K_{OH}

$$A_{230} = \frac{1.89(\epsilon_A + \epsilon_B K_{OH}[OH^-])}{1 + K_{OH}[OH^-]}[NCCONH_2]_T \quad (8)$$

is the value determined from the kinetics data. In eq 8, the effective cell path length for the Durrum stopped-flow spectrophotometer is 1.89 cm at 230 nm, and ϵ_A and ϵ_B are the molar absorptivities of 1-cyanoformamide and its deprotonated form, respectively. A nonlinear fit of eq 8 is obtained from a simplex optimization procedure[20] and gives $\epsilon_B = (3.89 \pm 0.08) \times 10^3$ M^{-1} cm^{-1} at 230 nm for the deprotonated species, which is a substantial increase from the value of $\epsilon_A = 1120$ M^{-1} cm^{-1} at 230 nm for 1-cyanoformamide.

Spectra of the reaction solution at different times after mixing 1-cyanoformamide and 0.05 M NaOH are shown in Figure 5. These are point-by-point values taken from individual rate studies at each wavelength. The "zero time" is an extrapolation of the absorbance to the initial time of mixing. The maximum for the deprotonated 1-cyanoformamide is red-shifted to 220 nm from the initial value of 206 nm for 1-cyanoformamide. This shift is consistent with a greater delocalization of the π-electrons in $N{\equiv}CC(=O)NH^-$. The rate of this deprotonation is too fast to measure by stopped-flow methods, as would be expected for a proton transfer from an amide nitrogen to hydroxide ion.[21]

The products of the base hydrolysis of 1-cyanoformamide are CN^- and OCN^-, rather than CN^-, CO_3^{2-}, and NH_3 as reported in earlier work.[6] It is true that, after cyanate ion forms, it can hydrolyze futher, but this is a very slow process. Even in 0.6 M NaOH at 100 °C, the half-life for the decomposition of OCN^- to give CO_3^{2-} and NH_3 is 3.85 h.[22] The activation energy for this reaction is 23.5 kcal mol^{-1}, so the predicted half-life of OCN^- at 25.0 °C is 469 days in base.[22]

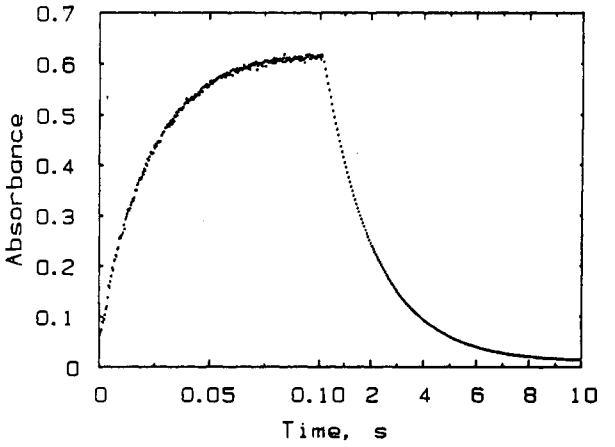

Figure 6. Change of absorbance with time during the base hydrolysis of cyanogen monitored at 230 nm with the Durrum stopped-flow spectrophotometer ($[(CN)_2]_i = 3.0 \times 10^{-4}$ M, $[OH^-] = 0.015$ M, 25.0 °C, $\mu = 0.2$).

Arguments that the hydoxide ion reaction with 1-cyanoformamide occurs by "attack at the amide carbon rather than the nitrile carbon"[6] are inappropriate. Instead, the amide nitrogen is deprotonated, and this leads to an elimination reaction where CN^- is a leaving group. A similar mechanism is found for the alkaline hydrolysis of *p*-nitrophenyl *N*-methylcarbamate[23] and related compounds.[24] The general mechanism (eq 9–11) is a deprotonation followed by an elimination with $^-OR'$ as a leaving group. In some cases saturation kinetics at high hydroxide ion concentrations also is observed.[25] The pK_a values for the deprotonation of the amide nitrogen vary from 11.7 to >14 for different R and R′ groups.[24,25] When OR′ is replaced by CF_3 and CCl_3 groups, the pK_a values drop to 9.51 and 9.98, respectively,[26] but these are not suitable leaving groups and the reaction mechanism changes.[26] The electron-withdrawing ability of CN is much greater than that of $OC_6H_4NO_2$[27] and less than that of CCl_3, so the pK_a value of 10.8 for 1-cyanoformamide is reasonable. Cyanide ion is an excellent leaving group, and the value of $k_3 = 0.556$ s^{-1} is comparable to the rate constant of 1.54 s^{-1} for $^-RNC(O)OR'$ (25.0 °C; R′ = phenyl, *R* = p-nitrophenyl; 4:1 water–dioxane)[26] despite the requirement of C–C bond cleavage with the cyanoformamide reaction.

$$RNHCOR' + OH^- \rightleftharpoons {}^-RN{-}COR' + H_2O \quad (9)$$

$$^-RN{-}COR' \xrightarrow{\text{slow}} RN{=}C{=}O + {}^-OR' \quad (10)$$

$$RN{=}C{=}O + H_2O \longrightarrow RNHCOOH \longrightarrow RNH_2 + CO_2 \quad (11)$$

Cyanogen in Base. Two consecutive reactions are observed in the base hydrolysis of cyanogen. The first reaction shows an increase of absorbance with time at 230 nm, and the second reaction shows a slower decrease of absorbance (Figure 6). The first reaction is pseudo first order in the cyanogen concentration, and the observed rate constants (Table III) increase with hydroxide ion concentration (Figure 7). The second reaction is pseudo first order in the product of the first reaction and exhibits saturation

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Table III. Dependence of the Observed Rate Constants on Hydroxide Ion Concentration[a] and on Temperature[b] in the Hydrolysis of Cyanogen

	k_{obsd}, s^{-1}	
$10^3[OH^-]$, M	1st reacn	2nd reacn
5.10	15.7 ± 0.2	0.455 ± 0.003
8.30	26.0 ± 0.3	0.493 ± 0.003
14.6	44.7 ± 0.5	0.520 ± 0.002
19.5	59.7 ± 0.4	0.531 ± 0.002
24.3	73.8 ± 2.2	0.534 ± 0.001
29.1	89.0 ± 1.7	0.539 ± 0.001
	k_{obsd}, s^{-1}	
temp, °C	1st reacn	2nd reacn
5.0	5.61 ± 0.03	0.0330 ± 0.0001
10.0	8.81 ± 0.03	
15.0	13.6 ± 0.1	0.140 ± 0.001
20.0	20.6 ± 0.3	
25.0	31.3 ± 0.2	0.522 ± 0.001
30.0	46.8 ± 0.4	
35.0	69.0 ± 0.5	1.78 ± 0.01
40.0	104 ± 2	
45.0	162 ± 5	5.58 ± 0.02

[a] $[(CN)_2]_{init} = 2.0 \times 10^{-4}$ M; $\mu = 0.2$; 25.0 °C; 230 nm; on Durrum stopped-flow instrument. [b] $[(CN)_2]_{init} = 3.0 \times 10^{-4}$ M; $[OH^-] = 0.010$ M; $\mu = 0.01$; 230 nm; on Hi-Tech stopped-flow instrument.

Table IV. Yield of 1-Cyanoformamide in the Hydrolysis of Cyanogen with Variation of Hydroxide Concentration[a] and Temperature[b]

$[OH^-]$, M	yield,[c] %	$[OH^-]$, M	yield,[c] %
0.010	72 ± 2	0.030	71 ± 2
0.020	72 ± 2		
temp, °C	yield,[c] %	temp, °C	yield,[c] %
5.0	75 ± 1	25.0	70 ± 2
10.0	74 ± 2	30.0	69 ± 1
15.0	73 ± 2	35.0	68 ± 1
20.0	72 ± 1	40.0	67 ± 1

[a] $[(CN)_2]_{init} = 2.0 \times 10^{-4}$ M; 25.0 °C; 230 nm; on Durrum stopped-flow instrument. [b] $[(CN)_2]_{init} = 3.0 \times 10^{-4}$ M; $[OH^-] = 0.010$ M; 230 nm; on Hi-Tech stopped-flow instrument. [c] Total concentration of 1-cyanoformamide and deprotonated 1-cyanoformamide formed; 1-cyanoformamide, $\epsilon_{230} = 1120$; deprotonated 1-cyanoformamide, $\epsilon_{230} = 3890$; cell path length = 1.89 cm for the Durrum stopped-flow instrument, 0.94 cm for the Hi-Tech stopped-flow instrument.

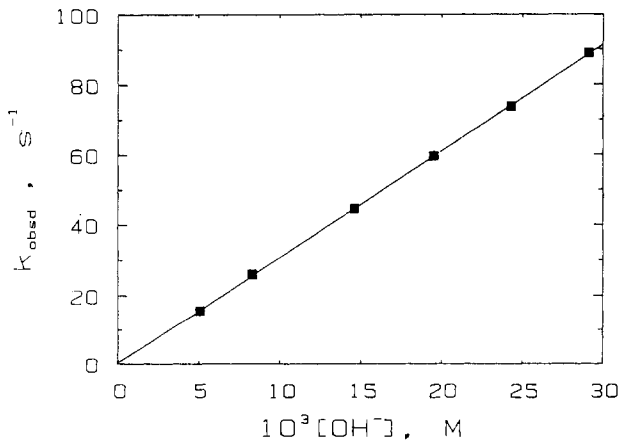
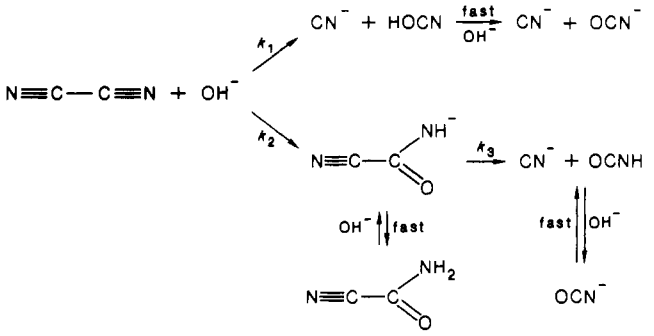


Figure 7. Hydroxide dependence of the observed first-order rate constant for the first reaction in the base hydrolysis of cyanogen (0.20×10^{-3} M, 25.0 °C, $\mu = 0.2$).

kinetics as the hydroxide ion concentration increases (Table III). The absorption spectrum and the kinetics of base hydrolysis of the second reaction (Figure 4) are identical with those of 1-cyanoformamide. Hence, one of the products of the base hydrolysis of cyanogen is 1-cyanoformamide. However, the increase of absorbance for the first reaction is smaller than is calculated

Scheme I



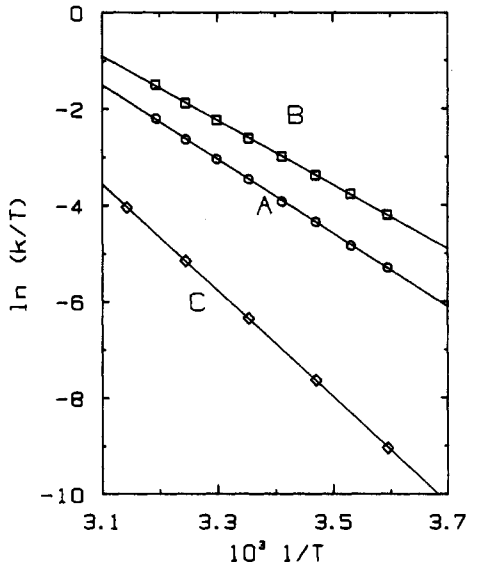


Figure 8. Temperature dependence of the resolved rate constant: (A) k_1; (B) k_2; (C) k_3.

from the molar absorptivities of 1-cyanoformamide and its deprotonated form, on the basis of the initial concentration of cyanogen. The yield of $[NCCONH_2]_T$ does not depend on the OH^- concentration, as seen in Table IV, and is the same even in 1 M NaOH at 25 °C. However the yield is temperature dependent. Tests with the cyanide electrode show that there is a much faster release of CN^- when cyanogen is added to base than would be expected from the reaction in eq 2–3. Hence, cyanogen decomposes by two paths, as shown in Scheme I. In Scheme I, where competing parallel reactions occur simultaneously and give different products, the observed pseudo-first-order rate constant is the sum of rate constants for each path (eq 12) even though only one product is measured.[28] The value of k_2 is determined by the yield of 1-cyanoformamide (eq 13). At 25.0 °C, an average

$$k_{obsd} = (k_1 + k_2)[OH^-] \quad (12)$$

$$k_2[OH^-] = k_{obsd}\frac{([NCCONH_2]_T)_\infty}{[(CN)_2]_i} \quad (13)$$

of 71 (±2)% of the initial cyanogen forms 1-cyanoformamide (and its deprotonated form), so that $k_2 = 2.2 \times 10^3$ M^{-1} s^{-1} and $k_1 = 8.9 \times 10^2$ M^{-1} s^{-1}. Thus, at 25.0 °C the reaction of cyanogen with base gives only 29% immediate C–C bond cleavage with the formation of CN^- and OCN^-. The greater part of the reaction (71%) proceeds by hydroxide addition and proton rearrangement to give $N{\equiv}CC(=O)NH^-$, which also decomposes to OCN^- and CN^-, but at a much slower rate ($k_3 = 0.556$ s^{-1}).

The temperature dependence from 5.0 to 45.0 °C for the first and second reactions in the hydrolysis of cyanogen is given in Table III. The yield of $[NCC(=O)NH_2]_T$ varies from 75% at 5.0 °C

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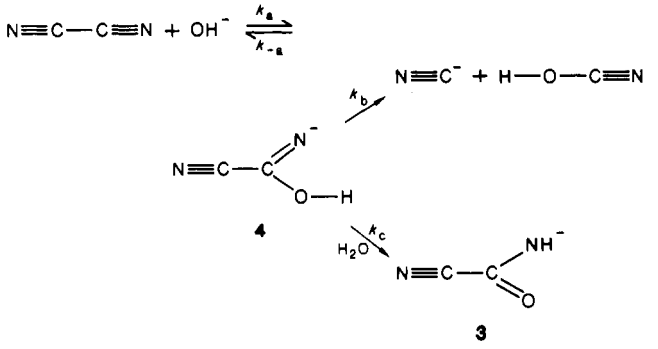
Table V. Resolved Rate Constants and Activation Parameters for the Base Hydrolysis of Cyanogen and 1-Cyanoformamide

	rate const			
param	value at 25.0 °C	E_a, kcal mol^{-1}	ΔH^*, kJ mol^{-1}	ΔS^*, J mol^{-1} K^{-1}
k_1, M^{-1} s^{-1}	8.9×10^2	15.8 (0.1)	63.8 (0.4)	−12.1 (0.1)
k_2, M^{-1} s^{-1}	2.17×10^3	13.8 (0.1)	55.3 (0.3)	−33.8 (0.3)
k_3, s^{-1}	0.556	22.5 (0.1)	91.8 (0.4)	57.7 (0.3)

Scheme II

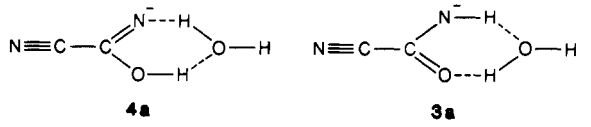


to 67% at 40.0 °C and is independent of base above 0.01 M $[OH^-]$ (Table IV). The corresponding k_1, k_2, and k_3 rate constants are resolved for each temperature, and Figure 8 plots the data used to obtain the activation parameters given in Table V.

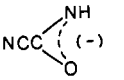
The activation enthalpy for k_3 (the C–C bond cleavage of deprotonated 1-cyanoformamide), $\Delta H_3^* = 91.8$ k J mol^{-1}, is much larger than the activation enthalpies for the more reactive cyanogen molecule. The k_1 path with C–C bond cleavage has a larger activation enthalpy ($\Delta H_1^* = 63.8$ k J mol^{-1}) than the k_2 path ($\Delta H_2^* = 55.3$ k J mol^{-1}) that leads to $N{\equiv}CC(=O)NH^-$.

The activation entropy for k_3 is large and positive ($\Delta S_3^* = 57.7$ J mol^{-1} K^{-1}), as expected for a reaction where one species ($NCC(=O)NH^-$) breaks into two species (CN^- + OCNH). The negative ΔS_2^* value (−33.8 J mol^{-1} K^{-1}) also is expected when two species (OH^- and $(CN)_2$) form one species ($N{\equiv}CC(=O)NH^-$). The activation entropy for the k_1 step (−12.1 J mol^{-1} K^{-1}) would be expected to be closer to zero, because two particles (OH^- and $(CN)_2$) react to form two particles (CN^- + HOCN). Hence, the relative ΔS^* values are in qualitative agreement with the proposed mechanism.

NCC(OH)=N⁻ as a Reactive Intermediate. There are several reasons why the OH^- adduct to cyanogen must form a reactive intermediate, rather than exist only as a transition state. An intermediate is needed because the reaction proceeds by two paths with different activation energies and one of these paths requires a proton rearrangement from oxygen to nitrogen. Thus, the first steps of the reaction can be written in more detail in accord with Scheme II. The relative yield of CN^- + HOCN vs. species **3** depends on the rate of C–C bond cleavage of species **4** (k_b) vs. the rate of proton transfer from oxygen to nitrogen (k_c). Water must play a role in the proton-transfer step through a hydrogen-bonded structure such as species **4a**, which gives species **3a**.

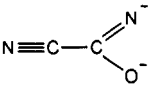


[In all structures the partial double-bond character of the species, i.e.

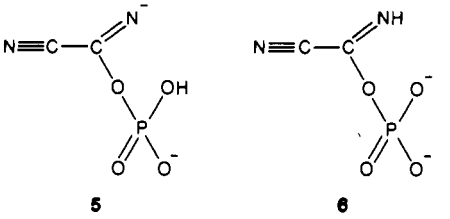


is omitted for simplicity.] The additional water molecule needed for this proton-transfer step helps to explain why the ΔS_2^* value is quite negative despite the expectation that OH^- would be more highly solvated than species **3**.

The need for a proton rearrangement for species **4** to give species **3** led us to test the effect of 1 M OH^- on the reaction. If species **4** lost another proton to give



then this dianion would be expected to dissociate more rapidly to give CN^- and OCN^-. This is not the case because the yield of $NCC(=O)NH^-$ is essentially the same in 1.0 M OH^- as it is in 0.01–0.03 M OH^-. We also tested the effect of 0.4 M $H_2PO_4^-/HPO_4^{2-}$ buffer at pH 7.6 and found that the yield of 1-cyanoformamide decreased to 53% as opposed to 71% in high base. Also the observed pseudo-first-order rate constant (2.06×10^{-2} s^{-1}) was higher than calculated (1.22×10^{-3} s^{-1}) from k_1 and k_2 values at this pH. This is probably due to a change of mechanisms in this reaction. The phosphate ion can attack cyanogen itself to form a cyanogen–phosphate intermediate as postulated from previous studies.[7] Intermediates of the type shown as species **5** and **6** can exist, and P–O bond breakage in **6** is needed



to give 1-cyanoformamide. Hence, the mechanism is substantially different with phosphate and the reactions at pH 7.6 are faster than would be predicted from our k_1 and k_2 values.

The reaction of cyanogen in carbonate buffer (0.20 M HCO_3^-/CO_3^{2-}) at pH 9.8 was also tested. Again, the yield of 1-cyanoformamide was lower (38%) and the reaction was faster (1.54 s^{-1} vs. a calculated value of 0.3 s^{-1} at pH 9.8). This indicates that a carbonato intermediate such as $[N{\equiv}CC(OCO_2){=}N]^{2-}$ may exist and that it undergoes more rapid C–C bond cleavage so that less 1-cyanoformamide is formed.

In conclusion, this study shows that hydroxide ion reacts with cyanogen to form a reactive intermediate, $N{\equiv}CC(OH){=}N^-$, that in part dissociates by C–C bond cleavage, but for the most part undergoes a proton rearrangement to form a much more stable intermediate, $N{\equiv}CC(=O)NH^-$. The latter species undergoes a slower C–C bond cleavage and is in rapid equilibrium with a stable product, 1-cyanoformamide. In base, cyanogen and 1-cyanoformamide are eventually 100% converted to cyanate and cyanide ions.

Acknowledgment. This work was supported by National Science Foundation Grant CHE-8319935.