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Reaction Rate Method for Determining Trace Concentrations of Cyanamide

T. A. Nieman,[1] F. J. Holler, and C. G. Enke*

Department of Chemistry, Michigan State University, East Lansing, Mich. 48824

The complexation of sodium pentacyanoammineferrate(II) (SPF) was studied to develop an initial rate method for trace amounts of cyanamide. The initial rate is measured as the rate of increase in absorbance at 530 nm due to the purple SPF–cyanamide complex. Stopped flow mixing and both multichannel (vidicon) and single channel (photomultiplier) detection were used. The reaction was shown to be first order in SPF and first order in the concentration of the cyanamide monoanion. A calibration curve for cyanamide is linear from 3×10^{-7} M to 1×10^{-7} M with a limit of detection of 13 ppb. A precision of 3.5% at the 95% confidence level was calculated for cyanamide determinations using this curve.

Although cyanamide (H_2NCN) has widespread use as a chemical intermediate, and in fertilizer (*1*), textile fireproofing (*2*), weed control (*3*), defoliants (*4*), and wood pulp processing (*5*), only limited attention has been directed toward development of fast and sensitive methods for its analysis. Such methods are environmentally important, because cyanamide has been shown to be moderately toxic either by ingestion or inhalation (*6, 7*).

Traditionally, cyanamide has been determined by precipitation with ammoniacal silver nitrate followed by titration of the silver in the precipitate (*7*). Offsetting the advantage of being an absolute method, this approach is time consuming, applicable only to macro amounts of cyanamide and quite costly due to present silver prices. Buyske and Downing (*1*) developed a spectrophotometric method for cyanamide based on the formation of a purple complex with sodium pentacyanoammineferrate(II) ($Na_3[Fe(CN)_5NH_3]$, from this point on called SPF) in a carbonate buffer at pH 10.5. The absorption of this complex was measured at 530 nm after a reaction time of almost an hour. Their method had a limit of sensitivity of 1 μg of cyanamide in 1.3 ml of sample, or 0.77 ppm, and exhibited linear response from 1 to 52.5 μg. The cyanamide content of soil, blood, and urine was determined in this manner, but heavily colored samples interfered with measurement. Other workers (*8*) have analyzed for cyanamide using a similar reaction with sodium nitroprusside ($Na_3[Fe(CN)_5NO]\cdot 2H_2O$).

Equilibrium studies have been performed on the SPF–cyanamide reaction (*9*). Slope-ratio and mole-ratio experiments indicated that the stoichiometry is 1 mol of cyanamide and 2 mol of SPF; the molar absorptivity of the complex was determined to be 2860 at 530 nm. The complex was not isolated for structural determination.

This paper describes work performed to study the SPF–cyanamide reaction to determine if an initial rate method for cyanamide would be feasible and offer significant advantage over existing methods. The majority of the work was conducted using a computer-controlled silicon vidicon spectrometer which had been developed in our laboratory (*10, 11*). This enabled the reactants and products to be observed simultaneously during the course of the reaction.

EXPERIMENTAL

Reagents. SPF (Fisher) for the study was analyzed for carbon, hydrogen, and nitrogen by Chemalytics (Tempe, Ariz.). It was found to contain 16.71% carbon, 2.34% hydrogen, and 23.02% nitrogen which is consistent with the formula $Na_3[Fe(CN)_5NH_3]\cdot 5H_2O$ giving a formula weight of 362. Aqueous solutions of SPF were prepared at twice the desired concentration. Only enough solution to be used in 1 day was prepared and this was stored in the dark, since over several days the solution begins to decompose, especially upon exposure to light. Cyanamide (Eastman) was used without further purification. Stock solutions (aqueous) were standardized by precipitating silver cyanamide with ammoniacal $AgNO_3$, then dissolving the yellow precipitate in dilute nitric acid and finally, determining silver by the Volhard titration (*7, 12*). Buffers were prepared at 0.2 M and equal volumes of buffer and SPF solutions were mixed a few minutes prior to reaction with the cyanamide solution in the stopped flow apparatus. The final buffer concentration was 0.05 M.

Instrumentation. The vidicon spectrometer employed in this study has been described in detail elsewhere (*10, 11*). The spectrometer can monitor a 230-nm window in the range of 380–900 nm with about 4-nm resolution and wavelength linearity better than 0.3%. Scan times as fast as 2 msec were used. Detector operation was controlled by a PDP 8/I minicomputer with 16K memory and DEC tape. The light source used was a tungsten lamp from a GCA/McPherson EU-701-50 light source module. The dispersion system was a modified GCA/McPherson EU-700 Czerny-Turner monochromator. The original grating with 1180 grooves/mm was replaced by a Bausch and Lomb certified precision grating with 133.6 grooves/mm and blazed at 546 nm. This resulted in a reciprocal linear dispersion of 18 nm/mm in the focal plane, where the vidicon detector was placed.

For studies using the vidicon detector, solutions were mixed using a stopped flow device built by the Hacker Machine Co. Pneumatically driven syringes injected a total of about 1.2 ml each time they were triggered. The observation cell was 2-cm long with quartz windows at each end. The dispersion system was placed between the stopped flow module and the vidicon detector. All reactions were run at room temperature.

For the studies using single wavelength detection at pH 9, the stopped flow mixing system described by Beckwith and Crouch (*13*) was used. The response of the photomultiplier tube was converted to a logarithmic output by connection through a Keithley Model 427 current amplifier and finally a Teledyne Philbrick Model 4351 Logarithmic Amplifier module. The resulting output was displayed on a Tektronix type 564 Storage Oscilloscope equipped with a Type 2A63 Differential Amplifier and a Type 2B67 Time Base. The initial rate of the reaction for each concentration of cyanamide was determined by photographing five consecutive traces on the scope face and manually computing and averaging the slopes of the linear portions of the curves.

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra recorded by the vidicon spectrometer for several solutions (buffered at pH 10.5) having different ratios of SPF and cyanamide, with the initial SPF concentration held constant. In each case the solutions have been allowed to sit after mixing to reach equilibrium. The only absorption bands observed are the one at 394 nm due to the yellow SPF and the one at 530 nm due to the purple SPF–cyanamide complex. Only a single

[1] Present address, School of Chemical Sciences, University of Illinois, Urbana, Ill. 61801

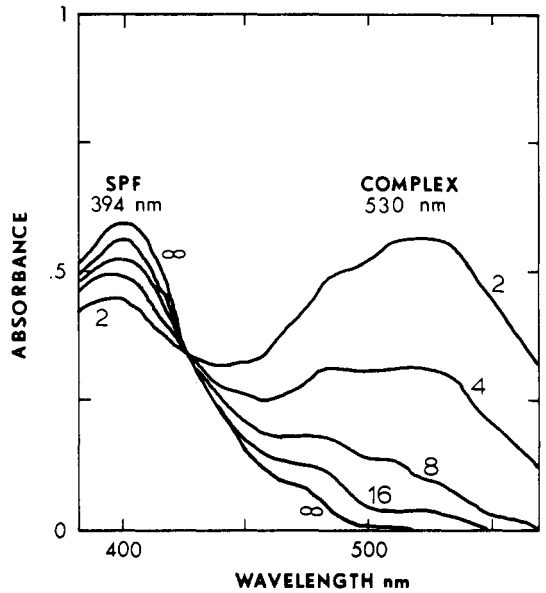

Figure 1. Absorption spectra for equilibrium solutions of SPF and cyanamide. Different values of $[SPF]_0/[cyanamide]_0$; pH 10.5

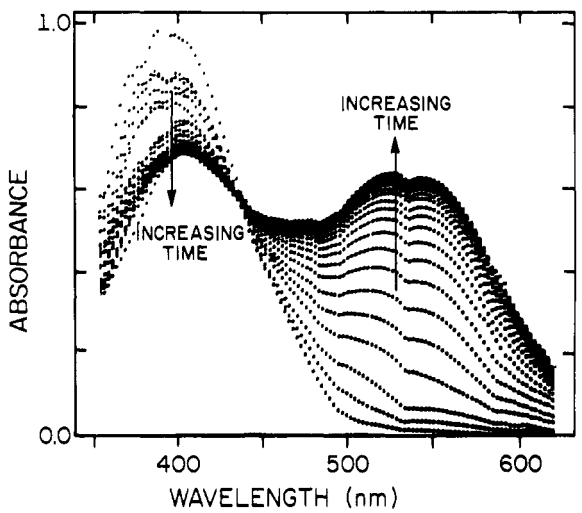

Figure 2. Absorption spectra during the reaction of 7.5×10^{-4} M SPF and 1.38×10^{-3} M cyanamide. Time between spectra is 500 ms; pH 10.5

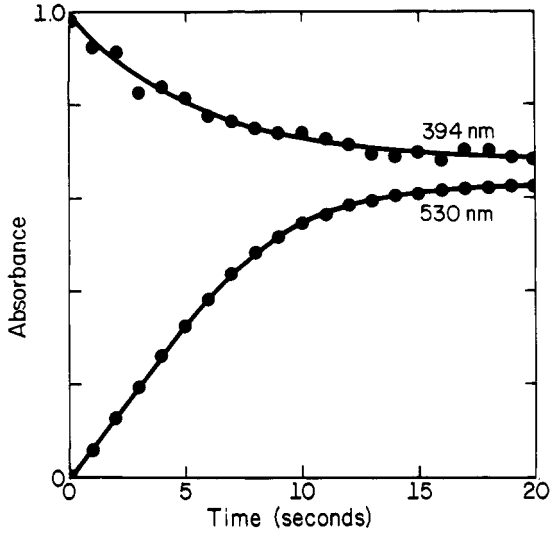

Figure 3. Absorbance vs. time for SPF and for the SPF–cyanamide complex; pH 10.5

Table I. Reaction Order Data at pH 10.5

Initial concn (after mixing)		Initial rate absorbance/s
Cyanamide	SPF	(530 nm)
2.754×10^{-3}	2.530×10^{-3}	0.4469
2.203×10^{-3}	2.530×10^{-3}	0.3489
1.652×10^{-3}	2.530×10^{-3}	0.2505
1.102×10^{-3}	2.530×10^{-3}	0.1582
5.508×10^{-4}	2.530×10^{-3}	0.0996
2.754×10^{-4}	2.530×10^{-3}	0.0443
2.203×10^{-4}	2.530×10^{-3}	0.0322
1.652×10^{-4}	2.530×10^{-3}	0.0223
1.102×10^{-4}	2.530×10^{-3}	0.0142
5.508×10^{-5}	2.530×10^{-3}	0.0070
2.754×10^{-5}	2.530×10^{-3}	0.0028
1.652×10^{-5}	2.530×10^{-3}	0.0017
1.102×10^{-5}	2.530×10^{-3}	0.0013
1.377×10^{-3}	2.533×10^{-3}	0.2388
1.377×10^{-3}	1.013×10^{-3}	0.1193
1.377×10^{-3}	5.065×10^{-4}	0.0504
1.377×10^{-3}	2.532×10^{-4}	0.0181
1.377×10^{-3}	1.520×10^{-4}	0.0118

isosbestic point is seen. The spectrum for the solution containing stoichiometric (2:1) amounts of SPF and cyanamide shows that a significant fraction of the SPF still remains free. Thus, the SPF–cyanamide complex does not have a large apparent formation constant at this pH.

The change in the absorption spectrum during the course of the reaction can be seen in Figure 2. Each spectrum is defined by 128 points with 0.5 s between spectra. The discontinuities in the spectra (e.g., at 535 nm) are the result of blemishes which appeared in the vidicon tube during another application. They, however, did not detract from the usefulness of the vidicon system for the investigation of the reaction process, the determination of the reaction rate, and the selection of the best wavelength for single-channel rate measurements. The reactant band at 394 nm decreases with time, and the product band at 530 nm increases with time. As in the spectra of the equilibrium solutions, the reaction appears to be simple with no sign of intermediates. Figure 3 illustrates a plot of absorbance vs. time at 394 and 530 nm. Since the uv response of the detector was poor, data for the 394-nm band were quite noisy and used mainly for qualitative and not quantitative observations. The remainder of the work reported concentrated on the 530-nm band. Data were taken on a time scale to be in the initial linear region of the reaction.

Initial Rate Studies. In a pH 10.5 carbonate buffer, with an initial SPF concentration of 2.530×10^{-3} M, the initial rate was measured (absorbance at 530 nm vs. time) as the cyanamide concentration was varied from 2.754×10^{-3} to 1.102×10^{-5} M (Table I). At lower concentrations the total absorbance change was too small for the rate to be measured due to the noise level of the vidicon detector. A plot of log (initial rate) vs. log ($[cyanamide]_0$) was linear over this range with a slope of 1.08 indicating that the reaction is first order in cyanamide. The intercept of the log–log plot is 2.43.

Next the order in SPF was determined. In a pH 10.5 carbonate buffer, the initial cyanamide concentration was held at 2.754×10^{-3} M while the SPF concentration was varied from 2.533×10^{-3} to 1.520×10^{-4} M (Table I). A plot of log (initial rate) vs. log ($[SPF]_0$) was linear over this range with a slope of 1.12 indicating that the reaction is first order in SPF. The intercept of the log–log plot is 2.35. Combining

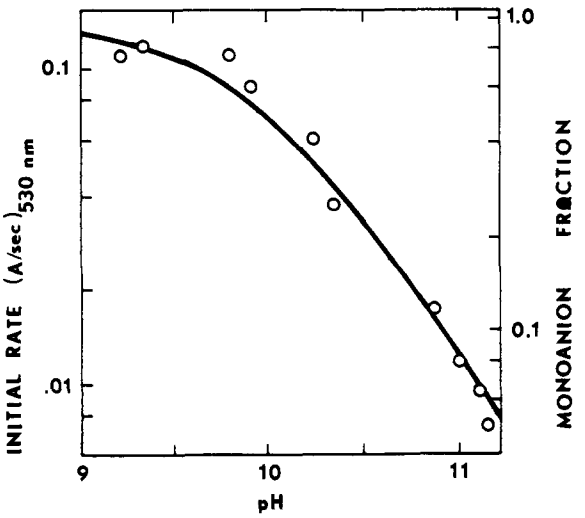

Figure 4. Effect of pH on initial rate, compared to the monoanion fraction; circles are rate data; solid line is monoanion fraction calculated from $pK_2 = 9.96$

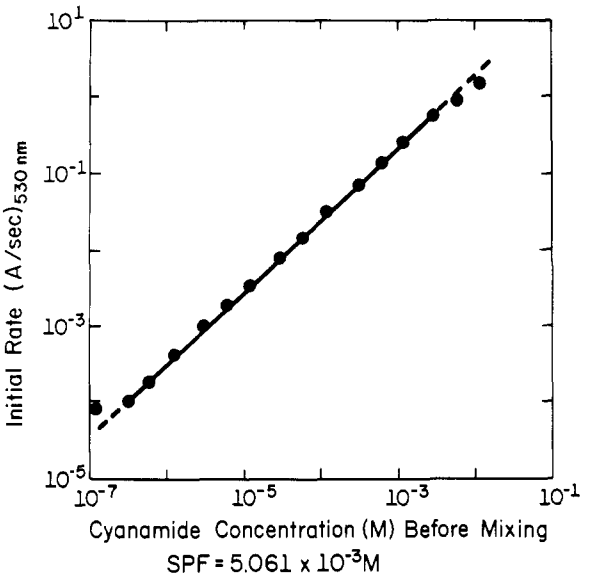

Figure 5. Calibration curve for cyanamide determinations. $[SPF]_0 = 2.530 \times 10^{-3}$ M; pH 9.0

the results for SPF and cyanamide and using the value of 2860 for the molar absorptivity at 530 nm (*9*), we can say that the initial rate of appearance of the complex is given by

$$(d[\text{complex}]/dt)_0 = k[\text{SPF}]_0[H_2NCN]_0 \quad (1)$$

where $k = 16.4$ l. mol^{-1} s^{-1} at pH 10.5.

pH Effect. The effect of solution pH on the rate was determined by preparing a series of ten carbonate buffers spanning the range from pH 9.2 to 11.1. The initial rate for the reaction of 3.000×10^{-3} M SPF and 1.372×10^{-3} M cyanamide was measured in each buffer. On a plot of log (initial rate) vs. pH (Figure 4) the data do not exhibit a good linear region but show the rate to decrease as pH increases. The relationship between pH and rate can be understood by considering the forms of cyanamide present in solution.

$$H_2NCN \underset{K_1}{\overset{OH^-}{\rightleftharpoons}} HNCN^- \underset{K_2}{\overset{OH^-}{\rightleftharpoons}} NCN^{-2} \quad (2)$$

Cyanamide has a pK_1 of 1.1 and a pK_2 of 10.27 (*14*). In the pH region studied (9 to 11), all of the cyanamide will be divided between the monoanion and dianion. If a plot of the log of the monoanion concentration vs. pH is constructed from the equilibrium relationship, it is seen to have a shape similar to that of the reaction rate vs. pH (data circles in Figure 4). If 9.96 is chosen as the apparent pK_2 of cyanamide, the monoanion concentration (solid line in Figure 4) is seen to follow the rate data very closely. The value of 9.96 for the apparent pK_2 of cyanamide provides the best fit to the points in Figure 4 and is not an unreasonable value in a solution of 0.1 M ionic strength. On the basis of these results it was determined that use of the initial rate method for cyanamide measurements would be more sensitive at a pH of about 9 rather than 10.5 (as Buyske and Downing used in their original method). At pH 10.5 only 23% of the cyanamide exists as the monoanion while at pH 9.0, 90% is in the monoanion form. Correcting the rate constant expression for the monoanion fraction yields

$$(d[\text{complex}]/dt)_0 = k[\text{SPF}]_0[HNCN^-]_0 \quad (3)$$

where $k = 71.3$ l. mol^{-1} s^{-1}.

Ammonia Effect. To run the reaction at pH 9, it was originally planned to replace the carbonate buffer with ammonia. Ammonia has a pK_a of 9.25 while carbonate has a pK_{a_2} of 10.25. In addition, it was felt that the ammonia buffer would suppress displacement of the ammonia ligand in SPF by water, and thereby make the reagent more stable. (Fearon (*15*) had observed that the NH_3 ligand on SPF was easily replaced.) However, in an ammonia buffer the reaction does not proceed at all; no purple complex is formed. Thinking that perhaps the reaction was specific for carbonate buffer, a borate buffer was used and the reaction proceeded as in the carbonate buffer. At this point the reaction was attempted in a carbonate buffer to which solid NH_4Cl had been added; the purple complex did not form. Also, if the purple complex was allowed to form in carbonate buffer and then solid NH_4Cl was added, within a few minutes the purple color disappeared leaving a yellow solution which displayed a single absorption band at about 394 nm. As a result of these observations, all further reactions were run in a carbonate buffer.

Method at pH 9. To set up an analytical method for cyanamide, a calibration curve was constructed. In a pH 9.0 carbonate buffer, with an initial SPF concentration of 2.530×10^{-3} M, the initial rate was measured as the cyanamide concentration was varied from 1.262×10^{-2} to 1.262×10^{-7} M. Since the multichannel studies with the vidicon detector indicated that the reaction was simple and that single wavelength observation was satisfactory, the application of this reaction to routine measurements was studied using a simple photomultiplier detector at 530 nm. The inherently wide dynamic range and high sensitivity of the photomultiplier tube were found to extend the useful range of the method to two orders of magnitude lower concentration than those obtainable with the vidicon spectrometer. A plot of log (initial rate) vs. log ($[H_2NCN]_0$) (Figure 5) is linear from about 3×10^{-7} to 1×10^{-3} M. The relative standard deviation for five measurements of the initial rate was less than 2% at above 10^{-5} M, increasing to about 20% at 10^{-7} M. The lower limit corresponds to 13 ppb. At this point we were limited by noise in the current and logarithmic amplifiers. Observation time at the upper end of the cyanamide concentration range was 0.1 s, while at the lower end the time was 10 s. The linear portion of the log–log calibration plot was fitted to the equation $\log(y) = a + b \log(x)$. Least-squares estimates obtained were $\hat{a} = 2.88$, $\hat{b} = 0.937$, $s_a = 0.032$, $s_b = 0.0063$, and $s_e = 0.0063$ where s_e^2 is the estimate of the variance of the y measurements at a single x value. From the intercept, a second-order rate constant of 52.6 l. mol^{-1} s^{-1} is obtained at pH 9.

Correction for the cyanamide monoanion fraction yields a value of 58.4 l. mol^{-1} s^{-1} which agrees to within 20% of the value determined at pH 10.5.

Using inverse prediction methods (*16*), the least-squares parameters indicate a relative precision of about ±3.5% at the 95% confidence level using this calibration curve to determine cyanamide concentrations from measurements of the initial rate. In order to determine whether the manual data collection procedure used in this study contributed any imprecision to the measurements, an automated data collection system employing a PDP 8/e minicomputer and A/D converter input was also used for one series of measurements. Over the entire useful range of cyanamide concentrations, a comparison of the precisions of the two collection procedures showed no significant difference. Thus computerized data collection can be used for convenience, but is not necessary for good accuracy.

CONCLUSION

The preceding evaluation has shown that sensitive and fast determinations of cyanamide can be made by measuring the initial rate of the complexation reaction between cyanamide and SPF in basic solution. At pH 9.0 the limit of detection is 13 ppb H_2NCN. The total time for each determination is less than 1 min. Since the method requires a calibration curve, it is necessary to use the traditional silver precipitation to standardize a stock solution of cyanamide, but this needs to be done only infrequently (once a month). Due to the equilibrium between SPF and ammonia, this method would require extensive modification to be applicable to samples containing ammonia (like urine).

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Radiochemical Extraction of Copper with Metal–Diethyldithiocarbamates

Sixto Bajo and Armin Wyttenbach*

Swiss Federal Institute for Reactor Research, 5303 Würenlingen, Switzerland

Cu can be extracted with $Bi(DDC)_3$ or $Zn(DDC)_2$ in chloroform from aqueous solutions up to 5 N in HF, HF_4B, H_2SO_4, H_3PO_4, $HClO_4$, up to 3 N in HCl, and up to 1 N in HNO_3. In most cases, extraction times of 1 min are sufficient for quantitative extraction. Washing of the organic phase without loss of Cu is possible with NaOH or with water. Cu can be back-extracted into an aqueous phase by HNO_3, $KMnO_4$ or Tl^{3+}. Extractions from 0.1 N H_2SO_4 or from a citrate buffer with $Bi(DDC)_3$ are selective except for Au^{3+}, Tl^{3+}, Hg^{2+}, and Ag^+; these elements can be eliminated by first extracting the sample with $Ni(DDC)_2$. Application of the $Bi(DDC)_3$ reagent to solutions of neutron activated geological or plant material yielded samples containing ^{64}Cu in excellent radiochemical purity with one single extraction. Detailed procedures and results of the analysis of standard materials are given.

Although the reaction $^{63}Cu(n,\gamma)^{64}Cu$ offers an excellent sensitivity for the determination of copper by activation analysis, counting of samples by nondestructive γ-ray spectrometry is very often not possible. This is especially true for samples of biological or geological interest and is due to the interferences caused by ^{24}Na: the γ-line at 1345 keV (^{64}Cu) is emitted with a very low probability of 0.5% and is hard to measure in the presence of a large activity at 1369 keV (^{24}Na). The annihilation radiation of ^{64}Cu is abundantly emitted, but is not specific enough; in particular, this line will also be generated by ^{24}Na. In view of the relative sensitivities and contents of Cu and Na (Table I), the necessity for chemical separation of Cu is evident.

Another situation where the separation of Cu is mandatory is when examining metallic samples (e.g., coins and other samples of archeological interest), where a great activity of ^{64}Cu will preclude the determination of minor activities with half-lives smaller or similar to the 12.7-h half-life of ^{64}Cu.

Many different procedures have been used to isolate Cu from an activated sample, among which we will note electrolysis (*1*); amalgamation with mercury (*2, 3*); exchange with solid CuCNS (*4, 5*); and extraction with various chelating agents, with an excess (*6, 7*) or with a substoichiometric amount of the reagent (*8–13*).

Although all these procedures can yield radiochemically pure ^{64}Cu, they usually involve many steps (which makes