Notes

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The Kinetics of the Aqueous Hydrogen Sulfide–Nitroprusside System

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The reaction in aqueous solution between salts containing sulfide and the pentacyanonitrosylferrate(II) ion (nitroprusside), $(NC)_5FeNO^{2-}$, has been known for many years. In 1850 Playfair observed a transient reddish violet coloration when nitroprusside and sulfide were mixed.[1] From methanolic solutions of nitroprusside and sodium or potassium sulfide the corresponding salts of $(NC)_5FeNOS^{4-}$ can be isolated. On long standing, aqueous solutions of these salts have been reported to yield ferrocyanide and ferrous oxide on decomposition.[1]

A comprehensive investigation of the reaction between hydrogen sulfide ion and nitroprusside has not been carried out. This note reports such an investigation.

Experimental Section

Reagents.—Solutions were prepared from J. T. Baker reagent grade chemicals which were used without further purification: NaCl (assay: 99.5%), $NaNO_2$ (98.9%), $Na_2Fe(CN)_5NO \cdot 2H_2O$ (99.6%), $Na_2S \cdot 9H_2O$ (99%). Stock solutions were stored in the dark and all reactions were carried out in subdued light to prevent photochemical reactions. Oxygen has no effect on the kinetics observed.

Instruments.—All absorbancy measurements were made with an Applied Physics Corp. Cary 14 recording spectrophotometer. Temperature control was ±0.5° using a variable-temperature cell block. The stop-flow kinetic experiments were performed on a Durrum–Gibson stop-flow spectrophotometer manufactured by Durrum Instruments Corp., Palo Alto, Calif. Temperature control was also ±0.5°. The lower limit on the observation of half-lives was 5 msec. A picture was taken from a Tektronix 561A oscilloscope of the per cent transmission *vs.* time curve, which was converted to the kinetic form required for evaluation of the rate constant. All pH measurements were made on a Beckman expandomatic pH meter using a low sodium error E-2 glass electrode.

Results

Upon mixing excess hydrogen sulfide ion with nitroprusside, the solution immediately becomes red and then gradually fades. The spectrum of the faded solution is moderately stable, but after some time the solution further decolorizes and a precipitate forms. The spectra of the species formed immediately upon mixing, A, and the species present after the initial fading of the solution, B, are contained in Figure 1. The spectrum of A was obtained by extrapolation of the kinetic curves at various wavelengths to zero time. It is necessary to use excess hydrogen sulfide ion over nitroprusside (greater than 10^{-2} M HS^- at 1.25×10^{-4} M nitroprusside) in order to convert the nitroprusside to species A quantitatively. The spectra of A and B are independent of temperature over the range in which the kinetics were carried out (277–312°K). Added nitrite had no effect upon the spectral properties of the system above 400 mμ. If any $(NC)_5FeH_2O^{3-}$ was produced in the reaction, as in the aqueous hydroxide–nitroprusside reaction, the final spectrum would depend on the presence of nitrite.[2]

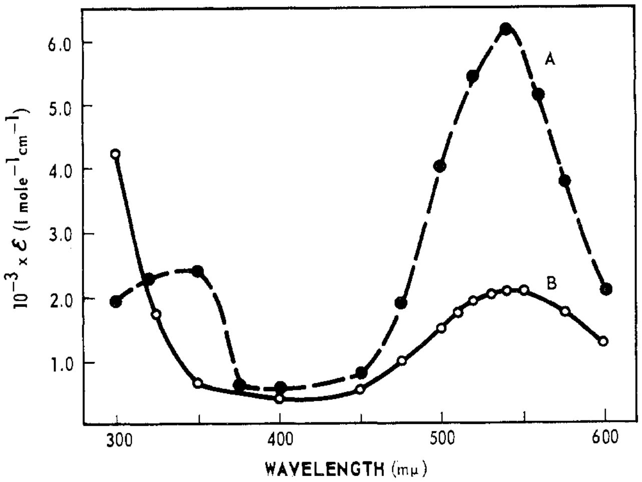

Figure 1.—Spectra of species formed immediately upon mixing excess hydrogen sulfide ion with nitroprusside, A, and species present after initial fading of solution, B. Spectra are independent of temperature; μ = 1.00 (NaCl).

Table I

Kinetic Data for the Formation of Species A

μ = 1.00 (NaCl)

Run	T,[a] °K	$10^4[(NC)_5FeNO^{2-}]_{initial}$, M	$10^2[HS^-]$, M	pH[b]	$t_{1/2}$, sec	k_{12},[c] M^{-1} sec^{-1}
1	298	1.2_5	6.7	12.6	0.060	172
2	298	1.2_5	3.3	12.3	0.124	167
3	298	2.5_0	0.12	10.6	3.5	170
4	298	2.5_0	0.12	10.2	3.5	170
5	285	1.2_5	6.7	...	0.109	95
6	285	1.2_5	3.3	...	0.204	101
7	277	1.2_5	6.7	...	0.180	59
8	277	1.2_5	3.3	...	0.340	61

[a] Temperature to ±0.50°. [b] A biphosphate–hydroxide buffer was used in run 3. All other runs were at the pH dictated by the sulfide hydrolysis. Sodium chloride was used to bring the ionic strength to 1.00. [c] Each rate constant is an average of three runs. The precision is ±3 M^{-1} sec^{-1}.

Table I contains a summary of kinetic data obtained from stop-flow experiments for the formation of species A when excess hydrogen sulfide ion is mixed with nitroprusside. The pseudo-first-order plots of the data were linear over at least two half-lives.

The rate of formation of species A was found to be

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[1] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford University Press, London, 1950, p 1345.

[2] J. H. Swinehart and P. A. Rock, *Inorg. Chem.*, **5**, 573 (1966).

first order in nitroprusside and hydrogen sulfide ion, $d[A]/dt = k[(NC)_5FeNO^{2-}][HS^-]$, under the experimental conditions used. This rate law indicates that the activated complex for the rate-determining step contains one hydrogen sulfide ion and one nitroprusside ion. The reaction of either hydrogen sulfide or sulfide ion with nitroprusside to form species A is inconsistent with the observed rate law. This is not to say that in more basic solutions sulfide cannot react directly with nitroprusside.

The activation parameters calculated from the data in Table I are $\Delta H_{12}^* = 7.2 \pm 0.3$ kcal/mole and $\Delta S_{12}^* = -24 \pm 1$ eu.

The kinetic curves at constant temperature for the conversion of species A to B ("fading reaction") are independent of the hydrogen sulfide ion, nitrite ion, and hydrogen ion concentrations. Assuming A and B to be the only iron-containing species present, first-order rate constants can be calculated for the conversion of A to B. Typical kinetic data are presented in Table II.

The activation parameters calculated from the data in Table II are $\Delta H_{23}^* = 19.4 \pm 0.5$ kcal/mole and $\Delta S_{23}^* = -3.0 \pm 1.5$ eu.

TABLE II

KINETIC DATA FOR CONVERSION OF A TO B

$\mu = 1.00$ (NaCl), $[(NC)_5FeNO^{2-}]_{initial} = 1.25 \times 10^{-4}$ M

T,[a] °K	$t_{1/2}$, sec	10^2k_{23},[b] sec^{-1}
293.0	81 ± 1	0.85 ± 0.01
303.0	26 ± 1	2.67 ± 0.05
311.0	11 ± 1	6.30 ± 0.50

[a] Temperature to ±0.5°. [b] Average of three runs at several hydrogen sulfide ion concentrations ($[HS^-]_{initial}$ from 3×10^{-2} to 10^{-1} M and pH from 11.5 to 12.8).

Discussion

Species B is identified as the ion $(NC)_5FeNOS^{4-}$ by a comparison of the spectrum of B with the spectrum of an aqueous solution of $Na_4[(NC)_5FeNOS]$ prepared by the reaction of nitroprusside and sulfide in methanol.[1] Analysis of our preparation of this salt shows that the $(NC)_5FeNO_2^{4-}$ ion can be a contaminant of about 10%. However, after the $(NC)_5FeNO_2^{4-}$ has been allowed to aquate, the spectra of the salt in aqueous solution and of B are identical. From the experimental data it is clear that in the rate-determining step for the formation of A a hydrogen sulfide ion reacts with a nitroprusside. This reaction is similar to that occurring in the hydroxide–nitroprusside system. The rate law for the formation of $(NC)_5FeNO_2^{4-}$ is $d[(NC)_5FeNO_2^{4-}]/dt = k_{12,OH^-}[OH^-][(NC)_5FeNO_2]$. At 298°K, k_{12,OH^-} is 0.55 ± 0.01 M^{-1} sec^{-1}, while in the hydrogen sulfide system k_{12,HS^-} is 170 ± 3 M^{-1} sec^{-1}. The larger value for k_{12,HS^-} can be rationalized on the basis of the lower value of ΔH_{12}^* in the hydrogen sulfide system ($\Delta H_{12}^*{}_{OH^-} = 12.6$ kcal/mole and $\Delta H_{12}^*{}_{HS^-} = 7.2$ kcal/mole). Owing to the larger size of hydrogen sulfide ion compared to hydroxide, hydrogen sulfide ion does not have to approach so closely as hydroxide to react with nitroprusside, accounting for the lower value of ΔH_{12}^*. The values of ΔS^* for k_{12,OH^-} and k_{12,HS^-} are -17.5 ± 0.7 and -24 ± 1 eu, which are of the magnitude expected for a reaction between a 1− and a 2− ion.[3]

The question arises as to the nature of species A and its conversion to $(NC)_5FeNOS^{4-}$ (species B). There are a number of possibilities. The hydrogen sulfide ion certainly attacks the nitrosyl group (NO^+) bound to the iron(II) in the diamagnetic nitroprusside ion to form an addition product.[1] The succeeding steps leading to the conversion of species A to the $(NC)_5FeNOS^{4-}$ ion may involve the rearrangement of the –NOSH group followed by the loss of a proton or the rapid addition of a second hydrogen sulfide ion followed by a rate-determining elimination of H_2S. However, our kinetic data give no information concerning the solution of this problem.

The $(NC)_5FeNOS^{4-}$ ion is unstable in solution and after some time the solution further decolorizes. The addition of acid increases the rate of decolorization. If $[H^+] = 10^{-3}$ M, the decolorization of the solution containing $(NC)_5FeNOS^{4-}$ at a concentration of 1.25×10^{-4} M is complete in less than 1 sec. It appears that at least two species are formed as products. One is $(NC)_5FeH_2O^{3-}$, which is identified from the spectral change in the solution (gradually increasing absorption in the ultraviolet) and the disappearance of this spectral characteristic when excess cyanide is added (formation of ferrocyanide). The second is probably $(H_2O)(NC)_4FeNOS^{3-}$, since the absorbance around 5500 A in the partially decolorized solution can be enhanced by addition of cyanide. Solutions of $(NC)_5FeNOS^{4-}$ allowed to decolorize in the presence of excess cyanide yield clear solutions containing $Fe(CN)_6^{4-}$, whereas in the absence of excess cyanide the "decolorized" solution are yellow. Apparently $(NC)_5FeNOS^{4-}$ can eliminate either CN^- or NOS^- as opposed to the nitroprusside–hydroxide system in which only NO_2^- is eliminated from $(NC)_5FeNO_2^{4-}$. The reaction $(NC)_5FeNOS^{4-} + H_2O \rightarrow (NC)_5FeOH_2^{3-} + NOS^-$ analogous to the reaction $(NC)_5FeNO_2^- + H_2O \rightleftharpoons (NC)_5FeOH_2^{3-} + NO_2^-$ does not attain equilibrium but is apparently irreversible, possibly owing to the instability of the postulated NOS^- species.

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(3) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1962, p 145.

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A Kinetic Study of the Formation of the Ferrous–Nitric Oxide Complex

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The rapid substitution of ligands into the inner hydration sphere of metal ions has recently been the