Contribution from the Jaroslav Heyrovský, Institute of Polarograpny, Czechoslovak Academy of Sciences, Vlašská 9, Prague 1, Czechoslovakia

Polarographic Studies of Nitrosyl Compounds. VI.* Contribution to Kinetics and Mechanism of Acid-Base Equilibria of the Nitroprusside Ion

J. Mašek and J. Dempír

Received July 20, 1968

In order to elucidate the mechanism of reactions of the nitroprusside system with certain anions, e.g. *CNS^-, N_3^-, in which the active species is the intermediate, $Fe(CN)_5NO_2H^{3-}$, of the acid base-equilibrium $Fe(CN)_5NO^{2-}$–$Fe(CN)_5NO_2^{4-}$, kinetics and mechanism of this equilibrium were re-examined. It was found that in the equilibrium $Fe(CN)_5NO^{2-} \underset{1}{\overset{OH^-}{\rightleftarrows}} Fe(CN)_5$-$NO_2H^{3-} \underset{2}{\overset{OH^-}{\rightleftarrows}} Fe(CN)_5NO_2^{4-}$ the acid pK_A of the joint-equilibrium 2 is lower than that of 1 so that the equilibrium concentration of the intermediate is very small at all pH values. The equilibrium 2 is established very rapidly so that if the reaction is carried out in the direction $Fe(CN)_5NO_2^{4-} \rightarrow Fe(CN)_5NO^{2-}$ and the pH in the region of pK_{A2} is used then in the course of the reaction a sufficient amount of the intermediate is formed which can react with other reaction partners.*

Introduction

$$Fe(CN)_5NO^{2-} + 2\,OH^- = Fe(CN)_5NO_2^{4-} + H_2O \qquad (1)$$

can be considered as an analogous equilibrium of the nitrosyl group in coordinated state to that of the free nitrosyl group

$$NO^+ + 2\,OH^- = NO_2^- + H_2O \qquad (2)$$

Whilst the equilibrium (2) contains a stable intermediate, *viz.*, the nitrous acid, the intermediate in the equilibrium (1) which can be formulated as $Fe(CN)_5$-NO_2H^{3-} has never been isolated nor detected.

In the study of reactions of various anions with the nitroprusside ion it has been found[1] that some anions, *e.g.* CNS^-, N_3^-, do not react with the nitroprusside ion under equilibrium conditions at any pH, but that the reaction occurs only when acidifying the alkaline nitroprusside solution. It is evident that the explanation of this phenomenon must be looked for in the kinetics of the acid-base equilibrium between $Fe(CN)_5NO^{2-}$ and $Fe(CN)_5NO_2^{4-}$.

The mentioned acid-base equilibrium was studied under different conditions by several authors[2-6] who determined the equilibrium constant $K=[Fe(CN)_5$-$NO^{2-}][OH^-]^2/[Fe(CN)_5NO_2^{4-}]$ of the reaction (1). The kinetics of the reaction (1) was dealt with by Kolthoff and Torren[3] who formulated the reaction as

$$Fe(CN)_5NO^{2-} + OH^- \underset{k_2}{\overset{k_1}{\rightleftarrows}} Fe(CN)_5NO_2^{4-} + H^+ \qquad (3)$$

and determined experimentally the value of the rate constant k_1; the value of k_2 was then calculated by means of the equilibrium constant K. Swinehart and Rock[5,6] reexamined recently the reaction (1) and found that the product $Fe(CN)_5NO_2^{4-}$ undergoes in alkaline medium a further reaction

$$Fe(CN)_5NO_2^{4-} + H_2O = Fe(CN)_5O^{3-} + NO_2^- \qquad (4)$$

for which they determined the equilibrium and rate constants.

However, for the purpose of the study of the reaction of anions with the nitroprusside ion these data are not sufficient since they do not solve the kinetics of the acid-base reaction with respect to the intermediate formed from the nitroprusside ion by the acceptance of the first OH^- group, *viz.*, that of the reaction

$$Fe(CN_5NO^{2-} \xrightarrow[1]{+OH^-} Fe(CN)_5NO_2H^{3-} \xrightarrow[2]{+OH^-}$$
$$Fe(CN)_5NO_2^{4-} + H_2O \qquad (1a)$$

In this connection it is necessary to determine or at least estimate the equilibrium and transient concentrations of the intermediate $Fe(CN)_5NO_2H^{3-}$ at sudden pH changes of the system. Therefore the acid-base equilibrium of the nitroprusside ion and their kinetics were re-examined in more detail.

(*) Part. V: *Coll. Czechoslov. Chem. Communs*, in press. Part of a thesis presented in partial fulfilment of the requirements for . Sc. Degree by J. Dempír, Research Institute of Mineral Raw Materials, Kutná Hora.

(1) J. Dempír and J. Mašek, *Inorg. Chim. Acta*, 2, 402 (1968).

(2) L. Cambi and L. Szegö, *Gazz. Chim. Ital.*, 58, 71 (1928).

(3) I. M. Kolthoff and P. E. Torren, *J. Am. Chem. Soc.*, 75, 1197 (1953).

(4) P. Zuman and M. Kabát, *Coll. Czechoslov. Chem. Communs*, 19, 873 (1954).

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

(6) J. H. Swinehart, *Coordin. Chem. Rev.*, 2, 385 (1967).

Experimental Section

Of both forms $Fe(CN)_5NO^{2-}$ and $Fe(CN)_5NO_2^{4-}$ only the former is polarographically active yielding three polarographic waves.[2-4,7,8] Since the height of the first wave is diffusion controlled and constant in the entire pH range of existence of the form $Fe(CN)_5NO^{2-}$, its limiting current at the potential –0.5 V (SCE) was used as an indication of $Fe(CN)_5NO^{2-}$ concentration.

Polarographs LP 60 and V 301 were used in connection with the Kalousek vessel containing a separated saturated calomel electrode. The mercury dropping electrode had the following characteristics: the outflow velocity of mercury $m = 1.96$ mg/s and the drop-time $t_1 = 3.70$ s in 0.1 N-KCl at the height of the mercury column 64 cm at the potential -1.0 V against SCE.

The reaction was carried out in Britton-Robinson buffers obtained by mixing appropriate amounts of 0.08 *M* acids with 0.4 *M* NaOH. The ionic strength was maintained at $\mu = 0.5$ by additions of $NaNO_2$ which served at the same time for suppressing the reaction (4). When following the reaction in the direction from $Fe(CN)_5NO^{2-}$ to $Fe(CN)_5NO_2^{4-}$ the reaction mixture was prepared simply by addition of a small amount of concentrated aqueous nitroprusside solution to the deaerated buffer of the required pH and by homogenization of the solution with a stream of nitrogen directly in the Kalousek vessel. The time from the moment of the nitroprusside to the start of registration amounted to about 20-30 s. In case of the reverse reaction the solution of a required pH was prepared by mixing equal amounts of two solutions, one containing the nitroprusside in a buffer of the required starting pH and the other one containing the Britton-Robinson acids neutralized to such an extent that the resulting mixture had the required final pH. The mixing was performed by means of a mixing cell put on the Kalousek vessel into which the two solutions were injected by means of syringes. The dead time of this procedure was less than 2 s. The resulting total nitroprusside concentration was 10^{-3} *M*.

Parallel experiments were performed also spectrophotometrically using the spectrophotometer Uvispek (Hilger and Watts). The intensively yellow solutions of $Fe(CN)_5NO_2^{4-}$ have the maximum absorbance at 400 nm whilst the nitroprusside ion does not show at this wave length practically any absorption. Thus in contrast to polarographic measurements, spectrophotometrically the form $Fe(CN)_5NO_2^{4-}$ is followed which is polarographically inactive. The concentration of $Fe(CN)_5NO_2^{4-}$ was related to the medium of 0.13 *M* NaOH in which the conversion of the nitroprusside to this form is practically complete.

Results and Discussion

Equilibrium Constant of the System $Fe(CN)_5NO^{2-}$/ $Fe(CN)_5NO_2^{4-}$. Since the equilibrium constant of the reaction (1) is very sensitive to the nature of the medium and its ionic strength and also because its values reported in the literature[2-6] range over more than one order of magnitude, it was found necessary to determine its value under our conditions in order to be able to rely on it in the examination of the kinetics.

The equilibrium concentrations of $Fe(CN)_5NO^{2-}$ (measured polarographically) and of $Fe(CN)_5NO_2^{4-}$ (measured spectrophotometrically) were determined by adjusting the appropriate pH value in the pH range from 10.5 to 12.5 starting either from the form $Fe(CN)_5NO^{2-}$ ($pH \leqslant 10$) or from $Fe(CN)_5NO_2^{4-}$ ($pH \geqslant 13$). In order to prevent the measurement of the equilibrium concentrations in systems containing unnecessarily long time the form $Fe(CN)_5NO_2^{4-}$ which is substitution labile, at each pH value the time course of the reaction was followed. When the ionic strength was maintained constant by excess of $NaNO_2$ and when following the reaction in the direction $Fe(CN)_5NO^{2-}$–$Fe(CN)_5NO_2^{4-}$ always a purely logarithmic shape of the concentration-time dependence was observed. When following the reaction in the reversed sense deviations were observed at lower pH values at the beginning of the reaction (*vide supra*) but the remainder of the reaction course was logarithmic again. Thus in both cases the equilibrium concentrations could be easily determined by a simple extrapolation to $1/t \rightarrow 0$. On the other hand, when $NaCl_4$ was used for maintaining the ionic strength instead of $NaNO_2$, a slow continuous decrease of concentrations of both forms was observed with longer times indicating the operation of the reaction (4).

If we define the equilibrium constant of the reaction (1) as $K = [{}^*NO_2]_{eq}/[{}^*NO]_{eq}[OH]^2$ (for the sake of simplicity the following abreviations are used: $^*NO$ for $Fe(CN)_5NO^{2-}$, $^*NO_2$ for $Fe(CN)_5NO_2^{4-}$ and $^*NO_2H$ for $Fe(CN)_5NO_2H^{3-}$, then the logarithmic form reads

$$\log[{}^*NO_2]_{eq}/[{}^*NO]_{eq} = \log K + 2\log[OH^-]$$

Figure 1 shows the experimental plot of $\log[{}^*NO_2]_{eq}/$

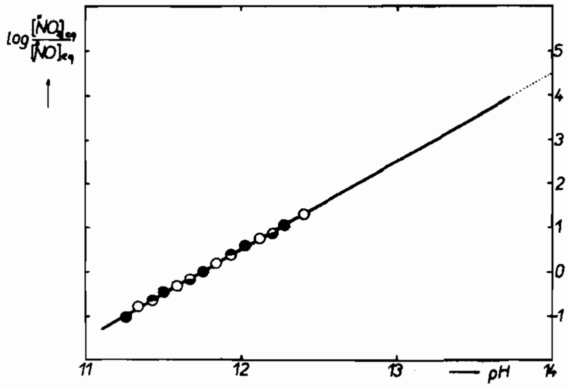

Figure 1. Plot log ($[{}^*NO_2]_{eq}/[{}^*NO]_{eq}$) against pH Used for Determination of the Equilibrium Constant K. Britton-Robinson buffers; $\mu = 0.5$ ($NaNO_2$); total nitroprusside concentration $10^{-3}M$; 25°C. ○, ● determined polarographically (measurement of $[Fe(CN)_5NO]_{eq}^{2-}$) starting from neutral and alkaline solutions, respectively; ◓, ◒ determined spectrophotometrically (measurement of $[Fe(CN)_5NO_2]_{eq}^{4-}$) starting from neutral and alkaline solutions, respectively.

---

[7] J. Mašek and J. Dempír, *Coll. Czechoslov. Chem. Communs*, in press.

[8] J. Mašek and J. Dempír, *Coll. Czechoslov. Chem. Communs*, press.

$[{}^*NO]_{eq}$ against $\log[OH^-]$, the slope of which yields the number of OH^- ions corresponding to one nitroprusside ion and the intersection with the ordinate gives the value of log K. The slope is 2.0 confirming the stoichiometry of the reaction (1), and the equilibrium constant determined in this way has the value $K = 3.17 \times 10^4$ mole^2 l^2. As shown in Figure concordant results are obtained in all four ways of determination of the equilibrium values, *viz.*, polarographically and spectrophotometrically, and with both methods starting either from $Fe(CN)_5NO^{2-}$ or $Fe(CN)_5NO_2^{4-}$. This indicates that the reaction is completely reversible.

The observation reported by Kolthoff *et al.*[3] that after acidifying $Fe(CN)_5NO_2^{4-}$ a lower amount of nitroprusside is always obtained due to the decomposition of $Fe(CN)_5NO_2^{4-}$ could not be confirmed in presence of NO_2^-. In our experiments an irreversible decomposition of $Fe(CN)_5NO_2^{4-}$ was observed only after several days.*

The observation shown in Figure 1 that within experimental errors the same values of the ratio $[Fe(CN)_5NO^{2-}]_{eq}/[Fe(CN)_5NO_2^{4-}]_{eq}$ are obtained for a given pH value both when measuring the $Fe(CN)_5NO^{2-}$ concentration (polarographically) or the $Fe(CN)_5NO_2^{4-}$ concentration (spectrophotometrically) is important for drawing conclusions about the equilibrium concentration of the intermediate species $Fe(CN)_5NO_2H^{3-}$. Under the assumption that the species $Fe(CN)_5NO_2H^{3-}$ is both polarographically and spectrophotometrically inactive the mentioned identity of the results obtained by both methods means that the equilibrium concentration of the intermediate is in the entire pH range negligibly small. Even if there is no experimental evidence of the polarographic or spectrophotometric inactivity of the intermediate the conclusion that its equilibrium concentration is very small under all conditions is consistent also with results of the study of the reaction of the nitroprusside with thiocyanate, azide and other anions.[1] This reaction, in which the active species is $Fe(CN)_5NO_2H^{3-}$, does not proceed namely at any pH at which the nitroprusside system is in equilibrium and occurs only when acidifying the alkaline reaction mixture .

Let us now define the equilibrium constants of the two reaction steps in (la) in the following way: $K_1 = [{}^*NO_2H]/[{}^*NO]\,[OH^-]$ and $K_2 = [{}^*NO_2]/[{}^*NO_2H]\,[OH^-]$; further let us introduce the constants pK_{A_i} denoting the pH values at which two of the three forms of the system are at equal concentration: $pK_{A_1} = pK_1 + 14$ $([{}^*NO] = [{}^*NO_2H])$, $pK_{A_2} = pK_2 + 14$ $([{}^*NO_2H] = [{}^*NO_2])$; $pK_A = (pK + 28)/2$ $([{}^*NO] = [{}^*NO_2])$.

If the equilibrium concentration of the intermediate is negligibly small, as stated above, then the distribution of equilibrium concentrations of the three forms is such that pK_{A_2} is lower than pK_{A_1} which means that $K_1 < K_2$, or in other words that the intermediate $^*NO_2H$ is unstable with regard to $^*NO$ and $^*NO_2$ since the ratio of both equilibrium constants yields $K_1/K_2 = [{}^*NO_2H]^2/[{}^*NO]\,[{}^*NO_2]$. This kind of equilibrium distribution plays an important role in the kinetics of the system if the rates of both steps are extremely different (see further below and Fig. 4).

Kinetics of the System $Fe(CN)_5NO^{2-} \rightleftarrows Fe(CN)_5NO_2^{4-}$. It was found by other authors (3-6) that the reaction $Fe(CN)_5NO^{2-}$—$Fe(CN)_5NO_2^{4-}$ is first order with respect both to nitroprusside and OH^- ions and hence the rate law can be written as

$$\frac{d\,[{}^*NO]}{dt} = -k_f[{}^*NO][OH^- + k_b\,[{}^*NO_2][H^+] \qquad (5)$$

The second therm in equation (5) follows from the fact that the equilibrium constant K of the reaction (1) cointains $[OH^-]^{-2}$ whilst the reaction $Fe(CN)_5NO^{2-} \rightarrow Fe(CN)_5NO_2^{4-}$ is only first order in OH^-; from the equilibrium condition for the rate law (5) $d[{}^*NO]/dt = 0$ a concentration quotient must follow for k_f/k_b which contains, like the equilibrium constant K, a square of the OH^- ion concentration:

$$\frac{k_f}{k_b} = \frac{[{}^*NO_2][H^+]}{[{}^*NO][OH^-]} = \frac{[{}^*NO_2] \times K_w}{[{}^*NO][OH^-]^2} = K \times K_w \qquad (6)$$

In order to determine k_f we have chosen the pH region 12.0-13.2 in which the second term can be neglected and the rate law is

$$\frac{d\,[{}^*NO]}{dt} = -k_f[{}^*NO][OH^-] \qquad (5a)$$

The time change of $^*NO$ concentration was recorded polarographically as the current change at the potential of the limiting current of the nitroprusside first wave. The initial nitroprusside concentrations used were 3.10^{-4}–$3.10^{-3}M$, pH was adjusted by 0.01–0.16N NaOH. In all cases smooth concentration-time curves were obtained of a strictly exponential character. Evaluation of the rate constant $k'_f = k_f\,[OH^-]$ was carried out using the equation $k'_f = 2.303 \log i_0/i$, where i_0 is the height of the nitroprusside first wave in neutral solution, i is the wave height read from the polarograms in 0.5 min. time intervals. By dividing the k'_f values thus obtained by $[OH^-]^1$ a fairly constant value $k_f = 13.5 \pm 0.6$ min^{-1} is obtained confirming at the same time the first order character in OH^- of the reaction.

The rate constant of the reverse reaction k_b computed from equation (6) is then $k_b = 6.8 \times 10^8$ mole^{-1} ls^1.

In order to check the validity of the assumed rate law (5) and of the evaluated rate constants in the entire pH range the reaction $^*NO \rightarrow {}^*NO_2$ was carried out in the medium pH range between 10.5 and 11.8 where the backward reaction cannot be neglected any

(*) The course of the irreversible decomposition which can be followed polarographically is the following. The divalent iron in the complex $Fe^{II}(CN)_5NO_2^{4-}$ is first oxidized in presence of air to the trivalent state yielding the complex $Fe^{III}(CN)_5NO_2^{3-}$. When acidifying the formed complex a polarographic wave corresponding to the reduction of the trivalent iron is observed before the first nitroprusside wave. The oxidation of $Fe^{II}(CN)_5NO_2^{4-}$ to $Fe^{III}(CN)_5NO_2^{3-}$ is catalyzed by light since *e.g.* after passing oxygen for 2 hr through the solution of $Fe^{II}(CN)_5NO_2^{4-}$ in darkness no oxidation occurs. The oxidation product $Fe^{III}(CN)_5NO_2^{4-}$ can be reduced, *e.g.* by ascorbic acid, to $Fe^{II}(CN)_5NO_2^{4-}$ so that this redox reaction is reversible. Only in the next step an irreversible decomposition occurs under deposition of $Fe(OH)^3$ so that the decomposition of $Fe(CN)_5NO_2^{4-}$ can be described formally as follows:

$$Fe^{II}(CN)_5NO_2^{4-} \underset{}{\overset{\text{rev.}}{\rightleftarrows}} Fe^{III}(CN)_5NO_2^{3-} \xrightarrow{\text{irrev.}} Fe(OH)_3,\ NO_2^-,\ CN^-$$

A detailed study of the mechanism of these reactions is still to be carried out.

more. For this purpose the complete equation (5) must be integrated. From (5) we obtain

$$\frac{d[{}^*NO]}{dt} = -(k_f[OH^-] + k_b[H^+])[{}^*NO] +$$

$$k_b[H^+]([{}^*NO]_o + [{}^*NO_2]_o) \qquad (7)$$

Integration of (7) yields

$$\frac{k_f[OH^-][{}^*NO] - k_b[H^+][{}^*NO_2]}{k_f[OH^-][{}^*NO]_o - k_b[H^+][{}^*NO_2]_o}$$

$$= \exp -(k_f[OH^-] + k_b[H^+])t \qquad (8)$$

Substituting now $k_f[OH^-]/k_b[H^+]=[{}^*NO_2]_{eq}/[{}^*NO]_{eq}$ and rearranging we obtain

$$[{}^*NO] = [{}^*NO]_{eq} + ([{}^*NO]_o - [{}^*NO]_{eq}) \exp(-t/\tau/) \qquad (9)$$

where $1/\tau = k_f[OH^-]+k_b[H^+]$. Equation (9) applies both for the reaction $^*NO \rightarrow {}^*NO_2$ and for the reverse reaction $^*NO_2 \rightarrow {}^*NO$. Hence it follows: if acidic $^*NO$ solutions or alkaline $^*NO_2$ solutions are brought through a rapid mixing process to a medium pH (the same in both cases), then the establishment of the new equilibrium concentrations proceeds in both cases according to an exponential time law containing the same time constant τ given by the final pH value.

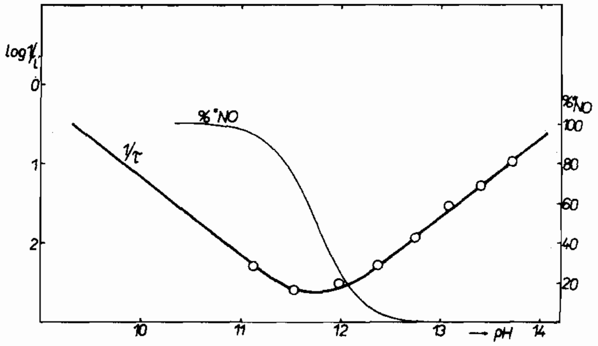

Figure 2. pH Dependence of log $1/\tau$. Full line: theoretical dependence using the constants k_f and k_b; circles: experimental points obtained from concentration-time dependence when following the reaction $Fe(CN)_5NO^{2-} \rightarrow Fe(CN)_5NO_2^{4-}$ For comparison the $Fe(CN)_5NO^{2-}$ distribution is given.

The pH dependence of $1/\tau$ evaluated by means of the rate constants k_f and k_b determined above is shown in Fig. 2 (full line). The circles indicate the experimental points obtained when carrying out the reaction in the direction $^*NO \rightarrow {}^*NO_2$; as seen, the agreement is very good. However when following the reaction in the reverse direction, i.e. $^*NO_2 \rightarrow NO$, a simple exponential shape of the concentration-time curves giving a similarly good agreement with the theoretical time constants is observed only at pH values higher than 11. At lower pH values the concentration-time curves are composed of two portions, *viz.*, an abrupt increase of the current at the beginning of the reaction followed by an exponential course with the time constant corresponding to the theory within 10-15% (Fig. 3). The height of the abrupt portion of the curves for a given pH is not well reproducible but generally increases with decreasing pH.

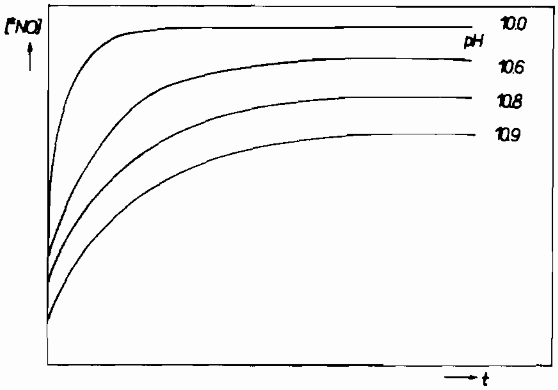

Figure 3. Typical Concentration-Time Curves Obtained Polarographically when Following the Reaction $Fe(CN)_5NO_2^{4-} \rightarrow Fe(CN)_5NO^{2-}$.

This phenomenon can be explained by an incomplete or slow mixing before the beginning of the measurement. The incomplete mixing can cause a local over-acidifying of the solution which shifts the system partially into the pH range of pK_{A2} where the reaction proceeds with regard to our measuring device immeasurably rapidly as will be shown further below.

Mechanism of the Reaction $Fe(CN)_5NO^{2-} \rightleftarrows Fe(CN)_5NO_2^{4-}$. The above demonstrated validity of the rate law (5) is a further reason for anticipating the existence of the intermediate $Fe(CN)_5NO_2H^{3-}$ in the reaction between $Fe(CN)_5NO^{2-}$ and $Fe(CN)_5NO_2^{4-}$ and hence the reaction sequence

$$Fe(CN)_5NO^{2-} + OH^- \underset{k_2}{\overset{k_1}{\rightleftarrows}} Fe(CN)_5NO_2H^{3-} \qquad (10)$$

$$Fe(CN)_5NO_2H^{3-} + OH^- \underset{k_4}{\overset{k_3}{\rightleftarrows}} Fe(CN)_5NO_2NO_2^{4-} + H_2O \qquad (11)$$

The question as to which of the rate constants $k_1 \ldots k_4$ govern the rate of the over-all reaction can be solved by considering the nature of the processes involved. Let us consider first the reaction (11). The forward reaction

$$Fe(CN)_5NO_2H^{3-} + OH^- \xrightarrow{k_3} Fe(CN)_5NO_2^{4-} + H_2O \qquad (11a)$$

is a proton-transfer reaction from a stronger acid ($Fe(CN)_5NO_2H^{3-}$ the pK_{A2} of which can be estimated to be lower than 10) to the conjugated base of a weaker acid ($pK_{(H_2O)} = 16$). Such proton-transfers proceed without additional activation energy and are diffusion controlled.[9] Thus k_3 can be estimated to be at least 10^{10} mole^{-1} l s^{-1}. The rate with which the reaction (11) proceeds can be now estimated in the following way.

From the rate law

$$\frac{d[{}^*NO_2H]}{dt} = -k_3[OH^-][{}^*NO_2H]+k_4[{}^*NO_2] \qquad (12)$$

we obtain by integration

$$\frac{k_3[OH^-][{}^*NO_2H]-k_4[{}^*NO_2]_{eq}}{k_3[OH^-][{}^*NO_2H]_o-k_4[{}^*NO_2]_o} = \exp\{-(k_3[OH^-]+k_4)t\} \qquad (13)$$

Substituting $k_3[OH^-]/k_4=[{}^*NO_2]_{eq}/[{}^*NO_2H]_{eq}$ and rearranging we get

$$\frac{[{}^*NO_2H]_o-[{}^*NO_2H]_{eq}}{[{}^*NO_2H]-[{}^*NO_2H]_{eq}} = \exp\{(k_3[OH^-]+k_4)t\} \qquad (14)$$

When starting from $^*NO_2$ and carrying out the reation $^*NO_2 \longrightarrow {}^*NO_2H$ the initial condition is $[{}^*NO_2H]=O$ and hence for the time t we obtain from (14):

$$t=\frac{2.303 \log [{}^*NO_2H]_{eq}/([{}^*NO_2H]_{eq}-[{}^*NO_2H])}{k_3[OH^-]+k_4} \qquad (15)$$

For a 90% conversion it follows: $[{}^*NO_2H]=0.9 [{}^*NO_2H]_{eq}$ and thus $t_{90\%}=2.3/(k_3[OH^-]+k_4)$. *E.g.* for pH 10 we obtain

$$t_{90\%}=\frac{2.3}{10^{10}\,.\,10^{-4}+k_4}$$

from which it follows that even at pH 10 when the protolytic reaction proceeds relatively slowly it is finished in times of the order of microseconds whatever the value of k_4 might be. Therefore it can be concluded that in the course of the overall reaction (10)+(11) the protolytic reaction (11) is always at equilibrium and thus we can write

$$[{}^*NO_2H]=[{}^*NO_2]\,\frac{H^+}{K_{A2}} \qquad (16)$$

where $K_{A2}=[{}^*NO_2]\,[H^+]/[{}^*HNO_2]$. Equation (16) can be substituted into the rate law of the reaction (10):

$$\frac{d\,[{}^*NO]}{dt} = -k_1[OH^-][{}^*NO]+k_2[{}^*NO_2H] =$$

$$-k_1[OH^-][{}^*NO]+k_2\frac{H^+}{K_{A2}}[{}^*NO_2] \qquad (17)$$

Comparing now the rate law (17) with (5) it is seen that $k_1=k_f$ and $k_b=k_2/K_{A2}$.

The value of K_{A2} could be determined by following the reaction $^*NO_2 \rightarrow {}^*NO$ in the pH range of pK_{A2} and lower where the reaction rate must become successively pH independent with decreasing pH; in this case the pK_{A2} value can be determined by a « kinetic titration ». Under those conditions, however, the reaction proceeds so quickly that it cannot be followed by standard polarographic techniques. For the time being the pK_{A2} can be roughly estimated to be $pK_{A2} \leqslant 10$. For $pK_{A2}=10$ the following values of the equilibrium and rate constants are obtained: $K_1=3.17$ mole^{-1} l; $K_{A1}=3.17\times10^{-14}$ mole l^{-1}; $K_2=10^4$ mole^{-1} l; $k_2=6.8\times10^{-2}$s^{-1}; k_3 (estimated) $=10^{10}$ mole^{-1} l.s^{-1}; $k_4=1\times10^6$ s^{-1}. Independently determined were: $K=3.17\times10^4$ mole^{-2} l^{-2}; $K_A=1.78\times10^{-12}$ mole^2 l^2; $k_f=k_1=2.16\times10^{-1}$ mole^{-1} l.s^{-1}; $k_b=6.8\times10^8$ mole^{-1} l.s^{-1}. The maximum equilibrium concentration of $^*NO_2H$ under these conditions amounts to 4% of the total analytical concentration of the system. The equilibrium distribution of the individual forms is shown in Fig. 4.

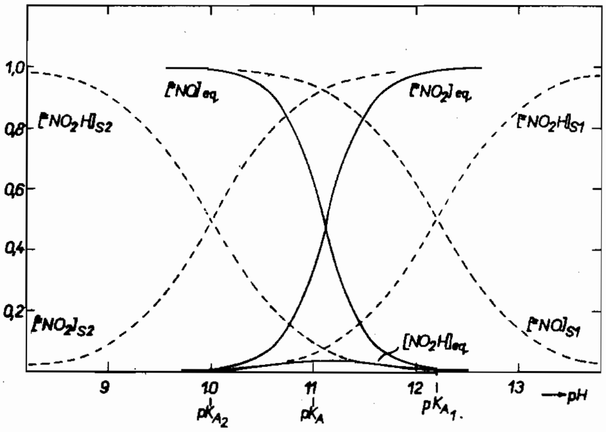

Figure 4. Equilibrium Concentration Distribution in the Nitroprusside System. Full lines: distribution in the combined system $Fe(CN)_5NO^{2-}$—$Fe(CN)_5NO_2H^{3-}$—$Fe(CN)_5NO_2^{4-}$. Dashed lines: distributions in the separated systems $Fe(CN)_5NO^{2-}$—$FE(CN)_5NO_2H^{3-}(K_{A2})$ and $Fe(CN)_5NO_2H^{3-}$—$Fe(CN)_5NO_2^{4-}(K_{A1})$.

The full curves denote the actual concentration distribution under the above defined condition. The dashed curves represent a case in which one of the consecutive equilibria is isolated from the other which could be achieved *e.g.* by a retardation of one of the reactions to such an extent that it does not proceed in the available time. A similar case is encountered in the conditions of the present system where one of the equilibria is established by many orders of magnitude more rapidly than the other one. In our case the isolated equilibrium $^*NO_2H \rightleftarrows {}^*NO_2$ is established much more rapidly than the isolated equilibrium $^*NO \rightleftarrows {}^*NO_2H$. If the reaction is carried out in the direction $^*NO \rightarrow {}^*NO_2$ then practically at all pH values a negligibly small « steady-state » concentration of the intermediate $^*NO_2H$ is obtained. If the reaction is carried out in the reverse sense, *i.e.* $^*NO_2 \rightarrow {}^*NO$, then the time course is strongly dependent on the pH value used since in the moment of mixing the components the equilibrium between $^*NO_2$ and $^*NO_2H$ is established instantaneously more or less according to the diagram for the isolated system $^*NO_2$–$^*NO_2H$. If a low pH is used corresponding according to the diagram for the isolated system to virtually 100% $^*NO_2H$ then

---

(9) M. Eigen, *Angew. Chem.*, *75*, 489 (1963).

in the moment of mixing practically the total amount of the substance being originally in the form $^*NO_2$ is converted to $^*NO_2H$ which then decomposes to $^*NO$. The time course of the three components of the system for this case is schematically shown in Fig. 5.

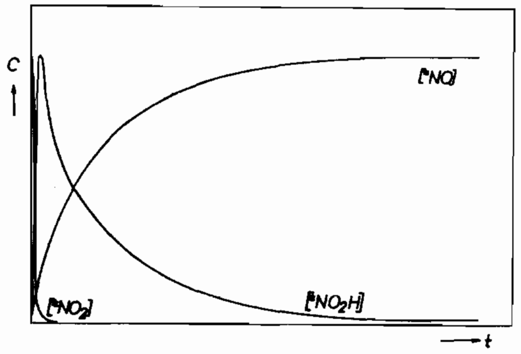

Figure 5. Time Course of the Components of the Nitroprusside System in the Reaction $Fe(CN)_5NO_2^{4-} \rightarrow Fe(CN)_5NO^{2-}$.

Hence follows the explanation of the reaction[1] of the nitroprusside system with CNS^-, N_3^- etc. which proceeds only when the alkaline reaction mixture is acidified; the acidification must be carried out, however, well below the pH at which the combined system contains at equilibrium practically 100% $^*NO$ *i.e.* to the pH range of the isolated $^*NO_2$—$^*NO_2H$ equilibrium since only under these conditions in the course of the reaction a sufficient amount of the intermediate $^*NO_2H$ is formed which can react with the anion.

This mechanism explains also the above mentioned sensitivity of the reaction to local over-acidification during the mixing process causing the abrupt initial current increase when acidifying the $^*NO_2$ form to pH values below 11.

Acknowledgement. The authors are indebted to Dr. H. Wendt, University of Erlangen, West Germany, for valuable discussion of the kinetic formulation of the problem.