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Kinetic Studies of the Nitroprusside Acid-Base Equilibria

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With the use of the stopped flow method with spectrophotometric indication the kinetics of the equilibrium $Fe(CN)_5NO^{2-} \rightleftarrows Fe(CN)_5NO_2^{4-}$ *was followed in the pH range 5.7 to 9.4 in order to determine the equilibrium constant* K_{A2} *of the joint equilibrium* $Fe(CN)_5NO_2^{4-} \rightleftarrows Fe(CN)_5NO_2H^{3-}$*. The kinetics in the higher pH range up to pH 13 was re-examined polarographically and spectro-photometrically at 23° and ionic strength* $\mu = 0.35$*. The* pK_{A2} *value was found to be 6.4 which is in accordance with our prediction that* $pK_{A2} < 10$*.*

Introduction

In our previous paper[1] it was shown that the acid-base equilibrium of the nitroprusside ion is established in two steps, *viz.*,

$$Fe(CN_5NO^{2-} + OH^- \underset{k_2}{\overset{k_1}{\rightleftarrows}} Fe(CN_5NO_2H^{3-} \qquad (1)$$

$$Fe(CN)_5NO_2H^{3-} + OH^- \underset{k_4}{\overset{k_3}{\rightleftarrows}} Fe(CN)_5NO_2^{4+} + H_2O \qquad (2)$$

whereas the rate constants k_3 and k_4 are higher than k_1 and k_2 by several orders of magnitude so that the reaction (2) can be considered as a perfectly mobile equilibrium which is established within the time of the order of µsec. Furthermore, from the fact that the intermediate species $Fe(CN)_5NO_2H^{3-}$ occurs under equilibrium conditions in negligibly small concentrations[1,2] it was concluded that the pK_{A1} of the equilibrium (1) has a higher values than the pK_{A2} of the equilibrium (2) (definition of pK_{A1} and pK_{A2} see further below). The pK_{A2} was roughly estimated to lie below 10 but its value could not[2] be established since the reaction $Fe(CN)_5NO_2^{4-} \rightarrow Fe(CN)_5NO^{2-}$ proceeds too fast at pH < 10 to be followed by the polarographic method which was used in the kinetic measurements. Since the only way for determining this equilibrium constant was to evaluate it from kinetic data the stopped flow method was used in the present work which enabled us to follow the kinetics of the system down to the pH 6.

Experimental Section

The stopped flow apparatus was constructed at the University of Erlangen. The two solutions to be mixed entered a four-jet mixing chamber from driving syringes (doubled for each solution) which were forced in together by a screw rotated through a magnetic coupling by means of a synchrone electromotor. The path from the outlet of the mixing chamger to the slit of the observation tube amounted to 1 cm. The dead-time of this arrangement was better than 4 msec. The reaction was followed spectrophotometrically. The beam of the monochromatic light the wave-length of which was adjusted by means of the monochromator was passed through the slit of the observation tube. The light absorption was indicated by means of a photomultiplier RCA type 1P 28 coupled to the Tektronix Model 565 oscilloscope the time base of which was triggered through a retardation device by the arresting piston. The optical density-time curves were recorded from the screen of the cathode-ray tube photographically.

The stopped flow experiments were performed in the pH range 5.7 to 0.4 by acidifying the alkaline form $Fe(CN)_5NO_2^{4-}$ to the required pH. In the pH range 9 to 13 the reaction course was followed both polarographically[1] and spectrophotometrically using the spectrophotometer Zeiss RPQ 20AV. At higher pH values the reaction was carried out also in the reverse sense, *viz.*, starting from the acidic form $Fe(CN)_5NO^{2-}$. The equilibrium constant $K = [Fe(CN)_5NO^{2-}][OH^-]^2/[Fe(CN)_5NO_2^{4-}]$ was determined spectrophotometrically and polarographically in pH region round 12 after allowing the reaction to reach the equilibrium.

In all experiments in which the reaction was followed in the direction $Fe(CN)_5NO_2^{4-} \rightarrow Fe(CN)_5NO^{2-}$ the acidification was carried out by mixing the starting alkaline solution (NaOH) with weak buffer acids carefully chosen according to the required pH (H_3BO_3, $NaHCO_3$, NaH_2PO_4, HAc) in order to prevent the local over-acidification which could occur when using strong acids and to which the system is extremely sensitive.[1] All experiments were performed at 23 ± 2°C and constant ionic strength 0.35 ($NaClO_4$). In order to minimize the substitution reaction $Fe(CN)_5NO_2^{4-} + H_2O = Fe(CN)_5H_2O^{3-} + NO_2^-$ in alkaline media the solutions contained 0.1*M*–$NaNO_2$.

Results and Discussion

The intensely yellow coloured species $Fe(CN)_5NO_2^{4-}$

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(1) J. Mašek, J. Dempír, *Inorg. Chim. Acta*, 2, 443 (1968).
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has under our conditions the absorption maximum at 400 nm, however, it was found that at 390 nm there is a sufficient absorption both of $Fe(CN)_5NO_2^{4-}$ and $Fe(CN)_5NO_2H^{3-}$ which are in mobile equilibrium and therefore their concentration ratio is given only by the pH value and is time independent. This enabled us to follow at 390 nm the dependence of the sum of concentrations of both mentioned species and to evaluate the equilibrium and kinetic parameters of the system in a very simple way since the only measured quantity—the transition time—can be evaluated without knowing the absolute absorbance of the system.

Using for the sake of simplicity the abreviated denotation $Fe(CN)_5NO^{2-} \equiv {}^*NO$, $Fe(CN)_5NO_2H^{3-} \equiv {}^*NO_2H$, $Fe(CN)_5NO_2^{4-} \equiv {}^*NO_2$, the reaction under consideration is

$$^*NO_2 \underset{K_{A_2}}{\overset{H^+}{\rightleftarrows}} {}^*NO_2H \xrightarrow[k_1, OH^-]{k_2} {}^*NO \qquad (1)$$

Since $-d([{}^*NO_2]+[{}^*NO_2H])/dt = d[{}^*NO]/dt$ the time change of the sum $[{}^*NO_2]+[{}^*NO_2H]$ which is followed in the stopped flow experiments can be expressed in terms of $[{}^*NO]$. The corresponding rate law reads (see (1))

$$\frac{d[{}^*NO]}{dt} = -k_1[OH^-][{}^*NO]+k_2[{}^*NO_2H] \qquad (2)$$

Eliminating $[{}^*NO_2H]$ by means of the relations $[{}^*NO] + [{}^*NO_2] + [{}^*NO_2H] = C$ and $K_{A_2} = [{}^*NO_2]\,[H^+] \,/\, [{}^*NO_2H]$ and integrating the resulting equation the following relation is obtained for $[{}^*NO]$:

$$[{}^*NO]_t = \frac{B}{A} + \frac{A[{}^*NO]_o - B}{A} \exp(-A.t) \qquad (3)$$

where

$$A = k_1K_W[H^+]^{-1} + k_2\frac{[H^+]}{K_{A_2}+H^+} \; (K_W=[H^+][OH^-]=10^{-14}) \qquad (4)$$

and

$$B = k_2\frac{[H^+]}{K_{A_2}+[H^+]}C \qquad (5)$$

From eq. (3) it follows that $A = 1/\tau$, where τ is the transition time of the reaction.

Equation (3) can be rewritten to

$$[{}^*NO]_t = [{}^*NO]_\infty + ([{}^*NO]_o - [{}^*NO]_\infty) \,.\, e^{-t/\tau} \qquad (3a)$$

where

$$1/\tau = k_1K_W[H^+]^{-1} + k_2\frac{[H^+]}{K_{A_2}+[H^+]} \qquad (6)$$

and $[{}^*NO]_t$, $[{}^*NO]_o$ and $[{}^*NO]_\infty$ are the concentrations of the species $^*NO$ at the time t, at the beginning of the experiment and after the equilibrium is established, respectively.

Figure 1 shows the plot log $1/\tau$–pH in which the empty circles denote the experimental points determined by the stopped flow method or polarographically and the curve represents the experimental dependence logically extrapolated at extreme pH values where the experiments were not carried out. This dependence can be divided into several sections from which the kinetic and equilibrium parameters of the reaction (1) can be evaluated. The bend of the curve in the pH range 6-7 indicates the region of pK_{A_2}. On the basis of this estimate the other quantities can be evaluated from eq. (4).

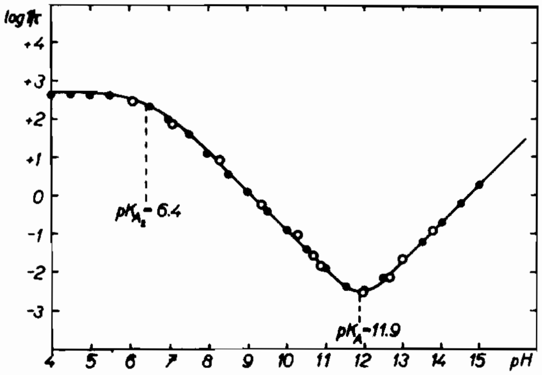

Figure 1. *Dependence of log $1/\tau$ on pH.* Empty circles are experimental points on which the curve is based, full circles are theoretical points calculated from eq. 4 using the experimental values of k_1, k_2 and K_{A_2}.

From equation (6) the following limiting behaviour of $1/\tau$ can be expected.

(a) For $[H^+] \gg K_{A_2}$ it follows that $1/\tau \cong k_2$, *i.e.* $1/\tau$ becomes pH independent for pH lower than K_{A_2}. Since log $1/\tau$ in this pH region equals 2.7 ± 0.1 it follows that $k_2 = (5 \pm 1) \,.\, 10^2$ sec^{-1}.

(b) When $[H^+] = K_{A_2}$ it follows that $k_1 \,.\, K_W\, [H^+]^{-1} \ll k_2\frac{H^+}{K_{A_2}}$ and eq. (6) reduces to $1/\tau = \frac{k_2}{K_{A_2}}[H^+]$ or $\log 1/\tau = -pH + \log\frac{k_2}{K_{A_2}}$. Thus between pH 7 and 11 we obtain a linear log $1/\tau$–pH plot with the slope −1. For $1/\tau = 1$ it follows $[H^+] = K_{A_2}/k_2 = 10^{-9.1\pm0.05}\,M$ sec^{-1} and hence $k_{A_2} = 10^{-6.4\pm0.1}\,M$.

(c) At higher pH values the first term in (6) becomes greater than the second one and finally for high pH's it follows that $1/\tau = k_1 \,.\, K_W[H^+]^{-1}$ or $\log 1/\tau = pH + \log k_1 \,.\, K_W$. Thus for pH > 13 we obtain a linear dependence log $1/\tau$ vs. pH with the slope +1 and for $\log 1/\tau = 0$ it follows $k_1K_W = [H^+] = 10^{-14.7\pm0.05}\,M$ sec^{-1} and hence $k_1 = 0.02 \pm 0.02\,M^{-1}$ sec^{-1}.

The « theoretical » points denoted in the graph by full circles and obtained by introducing the mentioned values of k_1, K_2 and K_{A_2} into the eq. (6), show a very good agreement with the experimental dependence.

Between the pH regions of (b) and (c) $1/\tau$ will have a minimum at pH at which $[^+NO]_\infty = [^*NO_2]_\infty$, so that $[H^+]_{min} = K_A$ where $K_A = ([^*NO_2][H^+]^2/[^*NO])^{1/2}$. This follows from the fact that the pH of intersection of the two strainght lines by which the dependence log $1/\tau$–pH is approximated sub (b) and (c) is given by the relation $[H^+] = (K_1 \,.\, K_W \,.\, K_{A_2}/k_2)^{1/2}$ where the right-hand term equals K_A. Since the slopes of both straight lines differ only in sign the pH of their intersection corresponds to the pH of the minimum of the curve. The minimum of the dependence in Figure 1 is attained at pH 11.9 so that $K_A = 10^{-11.9\pm0.1}\,M$.

The same value is obtained from the rate constants k_1 and k_2, *viz.*, $K_A = (K_1 \,.\, K_W \,.\, K_{A_2}/k_2)^{1/2} = 10^{-11.91}\,M$. This value is also in a very good agreement with the spectrophotometrically found value $K_A = 10^{-11.94}\,M$. By means of the ionic product of water the value for $K = [^*NO_2]/[^*NO][OH^-]^2 = 10^{4.1}\,M^{-2}$ is obtained from K_A. The value of this constant was determined by several authors[3-5] with a considerable scatter and most recently by Swinehart and Rock[6] who found $K = 10^{6.18}\,M^{-2}$. The difference by two orders of magnitude can be explained by different ionic strength ($\mu = 1$ in case of Swinehart *et al.* and 0.35 in our case). The higher ionic strength favours[7] considerably the higher charged particles such as $Fe(CN)_5NO_2^{4-}$ in comparison with the lower charged species $Fe(CN)_5NO^{2-}$.

In the following are summarized all the equilibrium and kinetic parameters of the reaction (1) obtained from the measurements in the present paper ($t = 23°C$, $\mu = 0.35$) and in paranthesis are given values obtained in our previous paper[1] under slightly different conditions ($t = 25°C$, $\mu = 0.5$). Values from the paper[1] based on the estimated value $K_{A_2} = 10^{-10}$ are not given.

$$K_1 = \frac{[^*NO_2H]}{[^*NO][OH^-]} = \frac{k_1}{k_2} = \frac{K_{A_1}}{K_W} = 10^{-3.4\pm0.1}\,M^{-1}$$

$$K_{A_1} = \frac{[^*NO_2H][H^+]}{[^*NO]} = 10^{-17.4\pm0.1}\,M$$

$$K_2 = \frac{[^*NO_2]}{[^*NO_2][OH^-]} = \frac{K_{A_2}}{K_W} = \frac{k_3}{k_4} = 10^{+7.6\pm0.1}\,M^{-1}$$

$$K_{A_2} = \frac{[^*NO_2][H^+]}{[^*NO_2H]} = 10^{-6.4\pm0.1}\,M$$

$$K = \frac{[^*NO_2]}{[^*NO][OH^-]^2} = 10^{4.1\pm0.2}\,M^{-2} \quad (10^{4.5}\,M^{-2})$$

$$K_A = (K_{A_1} \,.\, K_{A_2})^{1/2} = 10^{-11.9\pm0.2}\,M \quad (10^{-11.75}\,M)$$

$$k_1 = (2.0\pm0.02)\times10^{-1}\,M^{-1}\,sec^{-1} \quad (2.16\times10^{-1}\,M^{-1}\,sec^{-1})$$

$$k_2 = 5.0\pm1\times10^2\,sec^{-1}$$

As mentioned above the rate constants k_3 and k_4 belong to the rapid protolytic equilibrium, their values exceed by several orders of magnitude the possibilities of the stopped flow method and therefore only their ratio can be evaluated by means of $K_2 = k_3/k_4$.

According to the data of the present paper the maximum equilibrium concentration of $^*NO_2H$ at pH = pK_A amounts to 1.5×10^{-4}% of the total analytical concentration of the nitroprusside ion.

As regards the structural and mechanistic interpretation of the results obtained in this and the two preceding papers[1,2] the following can be said.

The existence of the acid-base equilibria $Fe(CN)_5NO^2 \rightleftarrows Fe(CN)_5NO_2H^{3-} \rightleftarrows Fe(CN)_5NO_2^{4-}$ which are analogous to those of the free ligand system $NO^+ \rightleftarrows HNO_2 \rightleftarrows NO^{2-}$ shows that the coordinated nitrosyl group in the nitroprusside ion in its acid-base behaviour is more close to the nitrosium ion NO^+ than to the nitric oxide NO. Using this as a criterion for the valence state of the central atom it is more appropriate to formulate the nitroprusside ion as $[Fe^{II}(CN)_5NO^+]^{2-}$ than as pentacyanonitrosylferrate (III). This is further substantiated by the fact that the species $Fe(CN)_5NO_2^{4-}$ undergoes in cyanide media readily a substitution reaction yielding $Fe(CN)_6^{4-}$. Thus if the reaction sequence $Fe(CN)_5NO^{2-} \rightarrow Fe(CN)_5NO_2H^{3-} \rightarrow Fe(CN)_5NO_2^{4-} \rightarrow Fe(CN)_4^{6}$ which is not subject to any external redox process yields as a final product a species which behaves unambigously as containing the divalent iron ($Fe(CN)_6^{4-}$) then also the first member must be considered as behaving chemically as a Fe^{II} species. The same conclusion is arrived at from comparison of the polarographic reduction pattern of the free NO^+ group[8] and that of the nitroprusside ion[9,10] which also are qualitatively very similar. Hence it follows that the acid-base equilibria of the nitroprusside ion can be considered in a good approximation as those of the NO^+ group coordinated in the particular complex.

It is a well established fact that the nitrosium group NO^+ is one of the strongest π-accepting ligands known while the groups NO_2H and NO_2^- show a negligible π-acidity. From this it follows that in the acid-base equilibria of the nitroprusside ion a considerable electron shift occurs which accounts qualitatively for the observed values of the corresponding rate and equilibrium constants. It is of interest in this connection to compare the values of the equilibrium constants of the nitroprusside system with equally defined quantities for the free NO^+–HNO_2–NO_2^- system. The pK_A for the free ligand system[11] amounts to 3.4 which is only by 3 pK units lower than for the nitroprusside system. This difference can be for a considerable part thought of as being due to the different charge type of the species in both systems from which it follows that in this case where both ligands have practically no π-acidity the coordination has little influence on the acid-base pro-

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perties of the ligands. On the other hand, while the pK_{A_1} value for the nitroprusside system is 17.4 that of the free ligand system[12] is –7.86.

This immense difference in the pK_{A_1} values reflects the fact that the equilibrium involves ligands (NO^+ and HNO_2) differing strongly in their π-acidity because the coordination of the NO^+ group combined with the back donation leads to a strong decrease of the electrophillic affinity of this group towards the OH^- group. In addition, by the attachment of the hydroxyl ion to the coordinated NO^- group the NO_2H group is formed which has a negligible π-acidity so that this step must be combined with withdrawal of negative charge from the ligand to the iron atom. The activation energy of this charge distribution is reflected in the low values of the rate constants k_1 and k_2 as compared with k_3 and k_4 the latter ones being by several orders of magnitude higher than the former ones although formally in both steps the same kind of process occurs.

The large shift of the pK_{A_1} value in the nitroprusside system leads to the seversal of the mutual position of K_{A_2} and pK_{A_2} in this system as compared with the free ligand system. From this follows the difference in the occurence of the intermediate species HNO_2. In the free ligand system the pK_{A_1} has a considerably lower value than pK_{A_2} and therefore for the nitric acid there exists a rather broad pH region in which it occurs as practically the only species in the system. However, in the nitroprusside system in which pK_{A_1} is higher than pK_{A_2} the species $Fe(CN)_5NO_2H^{3-}$ exists only in presence of the other two species, its maximum concentration is very small (1.5×10^{-4}% of the total analytical concentration) and could be detected only by the presence of colour reactions[2] in the course of transition of $Fe(CN)_5NO_2^{4-}$ to $Fe(CN)_5NO^{2-}$.

It is now of interest to consider the quantitative extent of back donation in the nitroprusside ion which accounts for the above mentioned effects. According to the results by Manoharan and Gray[13] the MO structure of the nitroprusside ion and some other related pentacyanonitrosyl complexes is, as regards the highest filled levels, $(6e)^4(2b_2)^2$. The extent of the back donation to the NO^+ group is then expressed by the π *NO character of the fully occupied 6e level which in case of the nitroprusside ion is 24.79% and increases in the isoelectronic series of complexes to 42.22% for $Mn(CN)_5NO^{3-}$ and to 73.68% for $V(CN)_5NO^{5-}$. If, in the first approximation, the effect of back donation observed in the nitroprusside ion is linearly extrapolated to the $Mn(CN)_5NO^{3-}$ case, then for the pK_{A_1} of the manganese complex the unrealistic value 43 is obtained which shows that no acid-base equilibria similar to those observed in the free ligand and nitroprusside system can be expected in the attainable pH range. This has been confirmed also experimentally. This is also the explanation why the nitroprusside ion has a unique position among other pentacyanonitrosyl complexes showing qualitatively similar acid-base behaviour as the free NO^+ ion.

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