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Diazotation of Butyl Amine by Nitrite Ion in Alkaline Solution Catalyzed by $Fe(CN)_5NH_3{}^{3-}$

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Abstract

Butyl amine reacts with nitrite ion in alkaline media on the catalytic action of $Fe(CN)_5X^{3-}$ ($X = H_2O, NH_3$) to give butyl alcohol and nitrogen gas. The kinetics of the reaction were investigated gas volumetrically. The kinetic rate law has been determined and a reasonable mechanism is suggested. The observed induction period is also interpreted.

Introduction

Nitroprusside, $Fe(CN)_5NO^{2-}$, is known to react with a wide variety of nucleophiles and acts as a nitrosating agent in neutral or weakly basic media, while under the same conditions no nitrosation takes place with nitrous acid.

In the reactions of amines with the complex only one or two products form in high yield [1]; this is another difference to the nitrosation with nitrous acid which reactions result in a number of products. Furthermore, some special products e.g. heterocyclic amino acids are formed from diamino acids in alkaline solutions only [2], so the diazotation by the complex has a great practical importance for organic syntheses as well.

Since the solubility of the complex is limited – and this is a disadvantage in the synthetic use – we developed a catalytic process in which an amine reacts with nitrite ion in basic solution and $Fe(CN)_5X^{3-}$ ($X = H_2O, NH_3$) acts as a catalyst.

To elucidate the mechanism of the catalysis kinetic measurements were carried out with butyl amine as substrate, because its reactions with nitrous acid [3] and $Fe(CN)_5NO^{2-}$ [1e] had already been investigated in detail.

Experimental

All reagents were of analytical grade commercial products. Pentacyanoamminoferrate(II) was prepared by a standard method [4]. The ionic strength was adjusted with $NaClO_4$, and H_3BO_3–NaOH was used as buffer. The reactions were followed gas volumetrically. All solutions were deoxygenated with Ar. The mixture of butyl amine and $NaNO_2$ solution adjusted to the required pH was placed into the reaction vessel and reactions were initiated by injecting the solution of the catalyst.

The gaseous product was analysed by an ATOMKI NZ-850 QGA-2 quadrupole mass spectrometer. The organic products were separated as in ref. 1a and analysed by gas chromatography.

Results and Discussion

The stoichiometry for the reaction of nitroprusside with a primary amine is

$$Fe(CN)_5NO^{2-} + RNH_2 + OH^- \longrightarrow$$

$$\begin{array}{l} Fe(CN)_5H_2O^{3-} + N_2 + ROH \qquad (1) \\ RNH_2 \Big\downarrow\!\Big\uparrow H_2O \\ Fe(CN)_5RNH_2{}^{3-} \end{array}$$

The same products, *i.e.* N_2 and ROH are formed in the butyl amine–$NaNO_2$–$Fe(CN)_5X^{3-}$ system if the pH of the solutions is adjusted to $9 < pH < 11$.

A short induction period can be seen on the $V = f(t)$ curves, the probable explanation of it is given later (Fig. 1). The linear part was used for the determination of the rate equation. The rate of gas evolution is proportional to the concentration of both the nitrite ion and the complex (Fig. 2a and b). The dependence of the rate on the hydrogen ion and butyl amine concentrations is illustrated in Fig. 2c and d. For the interpretation of the rate as a function of the hydrogen ion concentration the protonation equilibrium of amine

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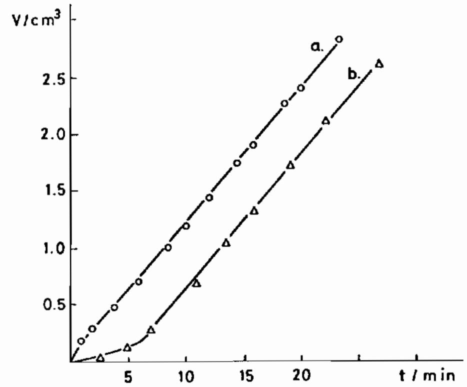


Fig. 1. Time course of gas evolution when the reaction was initiated by (a) butyl amine; (b) complex ($c_{NO_2^-} = 1.2$ M; $c_{amine} = 0.2$ M; $c_{complex} = 1 \times 10^{-2}$ M, pH = 10.20).

$$RNH_2 + H^+ \overset{K_2}{\rightleftharpoons} RNH_3 \tag{2}$$

($K_2 = 5 \times 10^{10}$ [5])

and the hydrolysis of the complex [6]

$$Fe(CN)_5NO_2{}^{4-} + H_2O \overset{K_3}{\rightleftharpoons} Fe(CN)_5NO^{2-} + 2OH^- \tag{3}$$

($K_3 = 2{,}4\ 10^{-8}$ [6f])

have to be considered.

Nitropentacyanoferrate(II) can be formed in the reaction of pentacyanoammineferrate with nitrite ion. The aquation of $Fe(CN)_5NH_3{}^{3-}$ is a very fast and practically quantitative process [7]

$$Fe(CN)_5H_2O^{3-} + NO_2{}^- \overset{K_4}{\rightleftharpoons} Fe(CN)_5NO_2{}^{+} + H_2O \tag{4}$$

($K_4 = 3{,}3\ 10^3$ [6b])

Taking into account reactions (1), (3) and (4), a catalytic cycle can be written

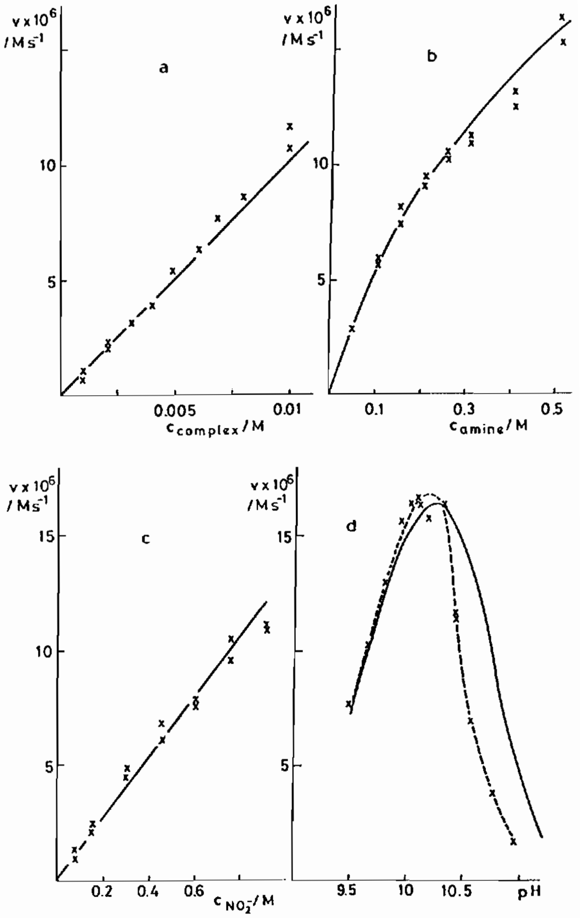


Fig. 2. The dependence of the reaction rate on the concentration of (a) complex ($c_{amine} = 0.25$ M; $c_{NO_2^-} = 1.2$ M; pH = 10.0); (b) butyl amine ($c_{NO_2^-} = 1.5$ M; $c_{complex} = 1 \times 10^{-2}$ M, pH = 10.0); (c) nitrite ion ($c_{amine} = 1$ M; $c_{complex} = 1 \times 10^{-2}$ M; pH = 10.3); (d) hydrogen ion ($c_{NO_2^-} = 1.2$ M; $c_{amine} = 0.5$ M; $c_{complex} = 1 \times 10^{-2}$ M).

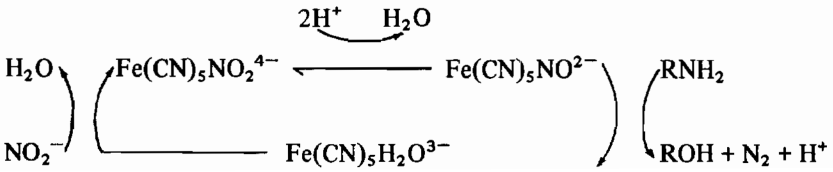
The net chemical change is the same as in the diazotation of amine by nitrous acid

$$H^+ + NO_2{}^- + RNH_2 \longrightarrow ROH + N_2 + H_2O \tag{5}$$

As was shown in our previous investigations the reactions of amines with nitroprusside are catalysed by nucleophiles, and the rate equation is

$$v = k[Fe(CN)_5NO^{2-}][RNH_2][S] \tag{6}$$

where S stands for a nucleophile.



The nitrite ion – as a nucleophile – may also act as a catalyst. The first step is the attack of the amino group on the electrophilic NO^+

$$Fe(CN)_5NO^{2-} + RNH_2 \overset{K_7}{\rightleftharpoons} Fe(CN)_5NORNH_2^{2-} \tag{7}$$

The concentration of the adduct of amine and the complex can be calculated if we take into account the equilibria (2)–(5), the total iron (8) and the total amine (9) concentration

$$[Fe]_t = [Fe(CN)_5H_2O^{3-}] + [Fe(CN)_5NO_2^{4-}] + [Fe(CN)_5NO^{2-}] + [Fe(CN)_5NORNH_2^{2-}] \tag{8}$$

$$[amine] = [RNH_2] + [RNH_3^+] \tag{9}$$

Using rate equation (6), the rate of the catalytic process is

$$v = kK_7[Fe]_t[amine]_t[NO_2^-]\frac{K_3K_4[H^+]^2[NO_2^-]}{1+K_2[H^+]} \cdot \frac{1}{K_W^2 + \dfrac{K_W^2K_4[NO_2^-]}{[H_2O]} + K_3K_4[NO_2^-][H^+]^2 \quad 1 + \dfrac{K_7[amine]}{1+K_2[H^+]}} \tag{10}$$

Applying the data of Fig. 2, the values of the constants (k, K_7) can be determined. In Fig. 2 the points indicate experimentally measured values whereas the continuous lines represent the curves calculated using the constants: $k = 2 \times 10^{-3}$ M^{-1} s^{-1}, $K_7 = 12$ M^{-1}, $K_3 = 1 \times 10^{-9}$, $K_4 = 3 \times 10^3$, $K_2 = 5 \times 10^{10}$. There is a reasonably good agreement between the measured and calculated values, though the literature value of K_3 had to be slightly changed. At pH < 10.1 either the literature value of K_3 or the modified one can be used to get a nice fit to the experimental curve since in these solutions all the iron is in the form $Fe(CN)_5NO^{2-}$.

According to our data the reaction rate decreases above pH ~ 10.1. This can be explained by the transformation of the nitrosyl complex into a nitro-compound not capable of nitrosation.

Using the literature value of K_3 in the calculations a decrease of the reaction rate can be seen only at pH > 11, far from the observed behaviour.

It should be noted that the values of K_3 published in the literature [6] differ somewhat owing to the different ionic strength and NO_2^- concentration (to prevent aquation). The need for the change in K_3 may have its origin in that in our experiments both the ionic strength and the NO_2^- concentration were higher than those used previously.

These assumptions lead to a correct description of the linear part of the $V = f(t)$ curves, however, they cannot explain the observed induction period.

There are two experimental findings suggesting that the induction period is due to the relatively slow formation of the nitrosyl complex at the very beginning of the reactions.

(i) Using the sulphydryl test for nitrosyl complexes, the violet colour immediately occurs when an SH^- compound is added to a solution containing both $Fe(CN)_5NH_3^{3-}$ and nitrite at pH ~ 10. In contrast to this, the characteristic colour develops only after a few minutes when the complex is added to a solution of SH^- and nitrite.

(ii) There is no induction period when the amine is added to an equilibrated solution of $Fe(CN)_5NH_3^{3-}$ and NO_2^-. This behaviour can be easily rationalised by calculating the concentration of the aqua, nitro and nitrosyl species by means of the rate laws corresponding to reactions (6), (11)–(13).

$$Fe(CN)_5H_2O^{3-} + NO_2^- \underset{k_{-11}}{\overset{k_{11}}{\rightleftharpoons}} Fe(CN)_5NO_2^{4-} + H_2O \tag{11}$$

($k_{11} = 0.46$ M^{-1} s^{-1} [6d])

($k_{-11} = 1.4 \times 10^{-4}$ M^{-1} s^{-1} [6d])

$$Fe(CN)_5NO_2^{4-} + H_2O \xrightarrow{\text{fast}} Fe(CN)_5NO_2H^{3-} + OH^- \tag{12}$$

($K_{12} = [Fe(CN)_5NO_2^{4-}]/[Fe(CN)_5NO_2H^{3-}][OH^-] = 3.7 \times 10^7$)

$$Fe(CN)_5NO_2H^{3-} \underset{k_{-13}}{\overset{k_{13}}{\rightleftharpoons}} Fe(CN)_5NO^{2-} + OH^- \tag{13}$$

($k_{13} = 5 \times 10^2$ s^{-1} [6d])

($k_{-13} = 0.2$ M^{-1} s^{-1} [6d])

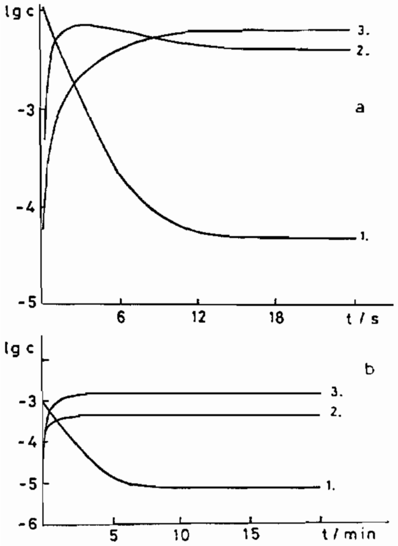


Fig. 3. The concentration of the aqua (1), nitro (2) and nitrosyl (3) complexes with time assuming, that $Fe(CN)_5NH_3^{3-}$ is in a (a) monomeric, (b) dimeric form (pH = 10.0); $c_{amine} = 0.2$ M; $c_{complex} = 1 \times 10^{-2}$ M; $c_{NO_2^-} = 1.2$ M.

The results of such a calculation using the above constants and applying the GEAR algorithm are presented in Fig. 3a. It can be seen that the concentration of the nitrosyl complex reaches a steady state value within ~10 s and there is practically no induction period on the $V_{N_2} = f(t)$ graph calculated by eqn. (6).

In our experiments it was the solution of the catalyst which was added to a mixture of butyl amine and nitrite. It is known that in alkaline solutions $Fe(CN)_5H_2O^{3-}$ can dimerize, and the relative concentrations of the monomer and the dimer depend on the pH and $[Fe]_t$. It is also known that $Fe_2(CN)_{10}^{6-}$ gives $Fe(CN)_5NO_2^{4-}$ in a much slower reaction as does the monomeric aqua species [8]. Since under the conditions of our experiments most of the catalyst was in the form of $Fe_2(CN)_{10}^{6-}$, in the calculations reaction (11) was replaced by reaction (14).

$$Fe_2(CN)_{10}^{6-} + 2NO_2^- \longrightarrow 2Fe(CN)_5NO_2^{4-} \qquad (14)$$

$(k_{14} = 1.63 \times 10^{-2}\ s^{-1})$

The concentration of the nitrosyl complex reaches a steady state value within some minutes (Fig. 3b) and consequently on the gas evolution curves calculated by eqn. (6) an induction period can be seen (similarly to our observation). The assumption of dimerization does not change our conclusion related to the diazotation, because during the reaction the aqua-complex does not accumulate, so the dimerization of it does not occur.

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