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Mechanism of the Permanganate–Nitrite Reaction.
II.* The Role of Complex Formation in the Kinetics of the Reaction

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The kinetics of the reaction between permanganate and nitrite in acid medium were studied spectrophotometrically by the stopped flow method. The observed rate equation was

$$v = k_1[HNO_2] + \frac{k_2k_3[HNO_2]^2[Mn(VII)]}{k_3[Mn(VII)] + k_{-2}K[H^+][HNO_2]}$$

In perchloric acid medium at 25 ± 0.1 °C, with an ionic strength of 0.1, the values of the rate constants were $k_1 = 2 \times 10^{-3}$ s^{-1}, $k_2 = 10$ mol^{-1} dm^3 s^{-1}, $k_3 = 5.3 \times 10^7$ mol^{-1} dm^3 s^{-1} *and* $k_2 = 50$ mol^{-1} dm^3 s^{-1}*. According to the suggested mechanism, a complex is formed between Mn(VII) and nitrite, which is inert as regards the redox reaction, its stability constant being* $K = 3.5 \times 10^5$ mol^{-1} dm^3*. During the reaction the accumulation of Mn(IV) as an intermediate was observed.*

The rate is greatly decreased in the presence of the Hg(II) ion owing to the formation of Hg(II)–nitro complexes. Kinetic measurements showed that the stability constant of $HgNO_2^+$ *is* ~10^4 mol^{-1} dm^3*.*

Introduction

The primary aim of the present work was to establish whether it is really necessary to reckon with the formation of $N_3O_3^{3+}$, assumed in the mechanism in our earlier publication [1]. A study was made of the concentration intervals in which the reaction rate is independent of the permanganate concentration, and it was attempted to detect the intermediate formed during the reduction of the permanganate. The effect of the mercury(II) ion on the reaction rate was examined with a view to obtaining information relating to the redox reactivity of the nitrite in the nitro complexes formed.

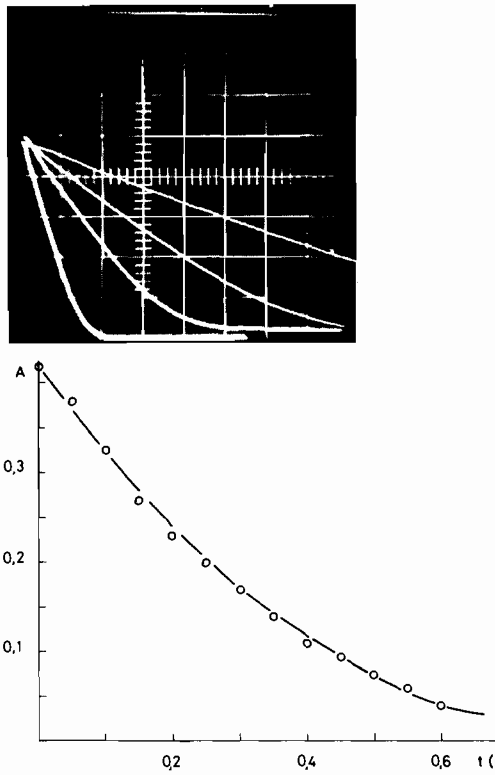

Figure 1. Means of evaluating a reaction: (a) Traces on the oscilloscope screen. Photos of a given reaction, prepared with different velocities of the light point. (b) Absorbance *vs.* time curve calculated by averaging from the traces. $c_N = 9.93 \times 10^{-3}$ mol dm^{-3}; $c_H = 9.85 \times 10^{-2}$ mol dm^{-3}; [KMnO$_4$] = 1.02×10^{-3} mol dm^{-3}; ionic strength = 0.2.

Experimental

The reaction was followed spectrophotometrically at 525 nm by the stopped flow technique. The temperature was 25 ± 0.1 °C. The signal on the oscilloscope coupled to the spectrophotometer was photographed; the picture was transformed to an absorbance *vs.* time curve (Fig. 1).

The rate (v) was calculated from the slopes (dA/-dt) of the tangents drawn at the starting point:

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*Part I.: M. T. Beck and L. Dózsa, *Inorg. Chim. Acta, 4,* 219 (1970).

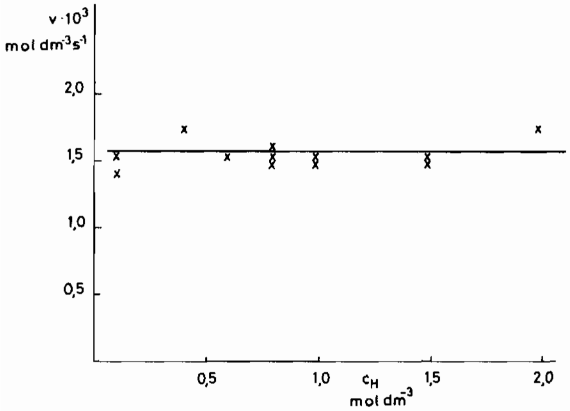


Figure 2. Dependence of the reaction rate on the perchloric acid concentration. $c_N = 0.91 \times 10^{-2}$ mol dm^{-3}; $[KMnO_4] = 0.90 \times 10^{-3}$ mol dm^{-3}; ionic strength = 2.0.

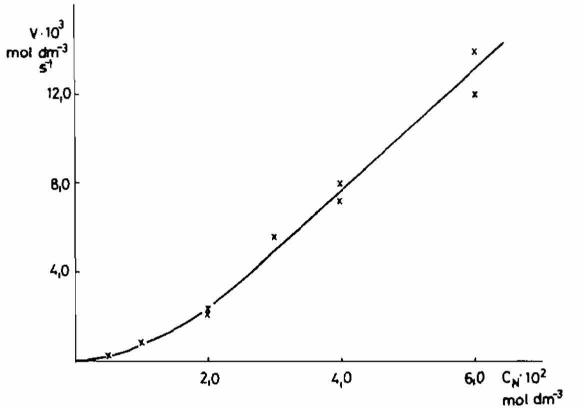


Figure 3. Dependence of the reaction rate on the nitrite concentration. $c_H = c_N = 9.9 \times 10^{-2}$ mol dm^{-3}; $[KMnO_4] = 1.01 \times 10^{-3}$ mol dm^{-3}.

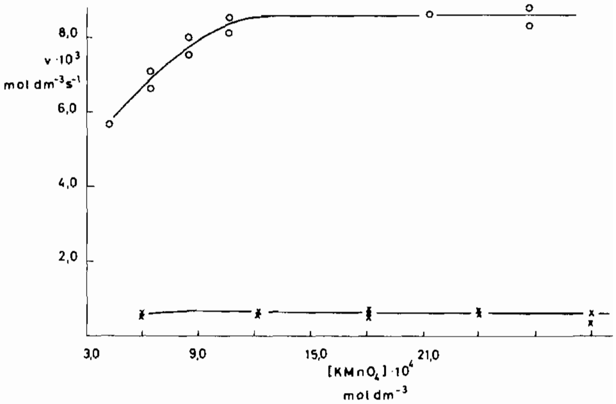


Figure 4. c_N^2/v values as a function of c_N. $c_H = c_N = 9.9 \times 10^{-2}$ mol dm^{-3}; $[KMnO_4] = 1.01 \times 10^{-3}$ mol dm^{-3}.

$$v = \frac{1}{2} \times \frac{1}{\epsilon l} \frac{dA}{dt} \qquad (1)$$

where $\epsilon = 2410$ mmol^{-1} cm^2, and l (cell width) = 0.188 cm.

An Hitachi-Perkin Elmer 39 UV–VIS spectrophotometer fitted with a home-made stopped flow apparatus, a Philips PM 3220 oscilloscope, a Lyubityel camera, and a Radelkis OP–205 precision pH-meter were used.

The materials were commercial products of purest quality, and were used without further purification. The sodium perchlorate employed to adjust the ionic strength was prepared from sodium hydrogen carbonate and perchloric acid.

Results

In the experiments the nitrite concentration was varied in the range 0.50×10^{-2}–6.00×10^{-2}, the permanganate concentration in the range 0.42×10^{-3}–3.01×10^{-3} and the perchloric acid concentration in the range 1.25×10^{-3}–1.58 mol dm^{-3}. The ionic strength was generally adjusted with sodium perchlorate to 0.1. Any differences from this are noted in the text.

At constant nitrite and permanganate concentrations it was found, in agreement with our earlier measurements, that at lower acid concentrations the reaction rate rises sharply with increasing acid concentration and then attains saturation, (Fig. 2). However, the additional ascending section obtained in our earlier measurements is not observed.

At constant permanganate concentration the dependence of the rate on the nitrite concentration was studied; constancy of the hydrogen ion concentration was assured by adding to the reaction mixture 9.9×10^{-2} mol dm^{-3} perchloric acid, plus an additional quantity of acid equivalent to the nitrite present. It follows from the dissociation constant of nitrous acid [2] that at this pH the nitrite is present virtually totally in the form of nitrous acid. The curve of Fig. 3 can be described by the function

$$v = \frac{a c_N^2}{1 + b c_N} \qquad (2)$$

where c_N is the total nitrite concentration, and a and b are constants independent of the nitrite concentration. By rearrangement of eqn. (3):

$$\frac{c_N^2}{v} = \frac{1}{a} + \frac{b}{a} c_N \qquad (3)$$

and if c_N^2/v is plotted as a function of c_N, in fact a straight line is obtained (Fig. 4). From this, $a \sim 9$ mol^{-1} dm^3 s^{-1}, and $b/a \sim 3.3$ s^{-1}.

At constant nitrite and acid concentrations the form of the reaction rate *vs.* permanganate concentra-

TABLE I. Dependence of the Reaction Rate on the Concentration of the Hg(II) ion. c_H = 0.02 mol dm^{-3}; c_N = 2.02 × 10^{-3} mol dm^{-3}; [$KMnO_4$] = 1.02 × 10^{-3} mol dm^{-3}.

[$Hg(NO_3)_2$] mol dm^{-3}	v10^5 mol dm^{-3} s^{-1}
0	2.26
	2.41
0.001	0.51
	0.63
0.002	0.26
	0.28
0.01	0.07
	0.06
0.02	0.03

tion function depends on the value of the nitrite concentration. If this does not exceed 1.23 X 10^{-2} mol dm^{-3}, then the reaction rate is practically independent of the permanganate concentration over the entire permanganate concentration interval measurable. However, at a higher nitrite concentration a dependence is observed in the permanganate concentration range 0.4 X 10^{-3}–1.1 X 10^{-3} mol dm^{-3}. This is shown by Fig. 5.

In the presence of the mercury(II) ion the rate of the reaction is decreased considerably (Table I), but the orders with respect to the partners are practically unchanged.

Discussion

Taking into account our present and earlier results, to a first approximation the following rate equation can be given:

$$v = k_1[HNO_2] + k_2[HNO_2]^2 \qquad (4)$$

where k_1 = 2 X 10^{-3} s^{-1}, and k_2 = 10 mol^{-1} dm^3 s^{-1}. This correlation holds at nitrite concentrations less than 10^{-2} mol dm^{-3}, and at hydrogen ion concentrations higher than 2 X 10^{-2} mol dm^{-3}. From experiments at higher nitrite concentrations, however, it follows that the third rate term assumed previously does not play a role; in such cases rate eqn. (2) is valid (here the first term is negligible). It is interesting that a rate equation of similar type was found in the chromate–nitrous acid reaction [3]. It seems obvious that here too we must reckon with the formation of a relatively stable complex in a rapid reaction, leading to equilibrium between the nitrous acid and the oxyanion, in the present case permanganate:

$$MnO_4^- + HNO_2 + H^+ \overset{k}{\rightleftharpoons} MnO_3ONO + H_2O \qquad (5)$$

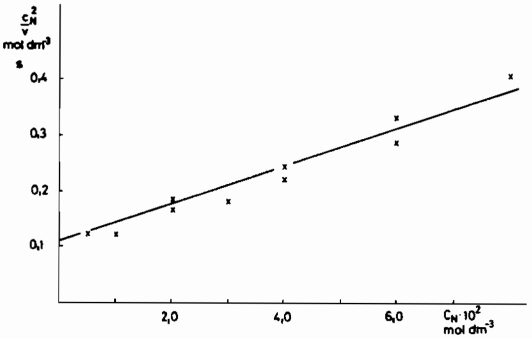


Figure 5. Dependence of the reaction rate on the permanganate concentration. ○ c_N = 4.33 × 10^{-2} mol dm^{-3}, c_H = 9.91 × 10^{-2} mol dm^{-3}; × c_N = 1.23 × 10^{-2} mol dm^{-3}, c_H = 0.102 mol dm^{-3}.

Further, the second-order dependence with respect to nitrite indicates that the nitrous acid reacts *via* the form N_2O_3, as in many other reactions [4]:

$$2\,HNO_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} N_2O_3 + H_2O \qquad (6)$$

As follows from the permanganate dependence, this step is much slower than the redox reaction:

$$N_2O_3 + MnO_4^- \xrightarrow{k_3} Mn^{2+} + NO_3^- + \ldots \qquad (7)$$

(k_3 here relates to the rate-determining elementary step of the overall reaction given). Neglecting the other possible redox reactions, the steady-state treatment leads to

$$v = \frac{k_2k_3[HNO_2]^2[MnO_4^-]}{k_{-2}a_w + k_3[MnO_4^-]} \qquad (8)$$

Taking into account equilibrium (5):

$$[MnO_4^-] = \frac{c_{Mn}}{1 + \frac{K}{a_w}[HNO_2][H^+]}$$

where c_{Mn} is the total Mn(VII) concentration:

$$c_{Mn} = [MnO_4^-] + [MnO_3ONO] \qquad (10)$$

and a_w is the activity of the water. By substitution we obtain

$$v = \frac{k_2k_3[HNO_2]^2c_{Mn}}{k_{-2}a_w + k_3c_{Mn} + k_{-2}K[HNO_2][H^+]} \qquad (11)$$

This agrees with the experimentally found expression (2), since $c_N \approx [HNO_2]$. (Here, $c_N \gg c_{Mn}$). From relation (11) it is understandable why the permanganate order depends on the concentration conditions. At low nitrite concentrations: $k_{-2}a_w + K[HNO_2][H^+] < k_3c_{Mn}$; thus, by neglecting the other term in comparison with k_3c_{Mn} in the denominator, we obtain a zero-order permanganate-dependence. When the nitrite concentration is higher, this approximation is justified at an appropriately higher permanganate concentration, *i.e.* only then does the reaction become independent of the permanganate concentration. At low nitrite concentrations, therefore, this is why the ascending section of the permanganate-dependence curve could not be measured.

From eqn. (11), the value of K may be estimated from the curves of both the nitrite-dependence and the permanganate-dependence. From (2) and (11):

$$K = \frac{k_2}{k_{-2}} \cdot \frac{b}{a} \cdot \frac{c_{Mn}}{[H^+]} \cdot k_3 \qquad (12)$$

Substituting in the values $c_{Mn} = 1.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 0.1$ mol dm^{-3} and $b/a = 3.3$ s^{-1}, and also taking into account that $k_2/k_{-2} = 0.2$ (the formation constant of N_2O_3) [5]

$$K = 6.6 \times 10^{-3}\, k_3 \qquad (13)$$

Further:

$$k_3 = \frac{a k_{-2} a_w}{c_{Mn}(k_2 - a)} \qquad (14)$$

Since graphical determination gives only the lower limit of a, $k_3 > 2.8 \times 10^7$ mol^{-1} dm^3 s^{-1} and $K > 1.9 \times 10^5$ mol^{-1} dm^3.

Rearranging (11) in another way:

$$\frac{1}{v} = \frac{k_{-2}a_w + k_2 K c_N [H^+]}{k_2 k_3 c_N^2} \cdot \frac{1}{c_{Mn}} + \frac{1}{k_3 c_N^2} \qquad (15)$$

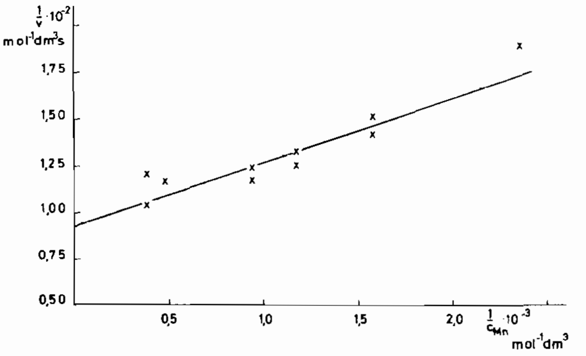


Figure 6. Reciprocal reaction rate as a function of the reciprocal permanganate concentration. $c_N = 4.33 \times 10^{-2}$ mol dm^{-3}; $c_H = 9.91 \times 10^{-2}$ mol dm^{-3}.

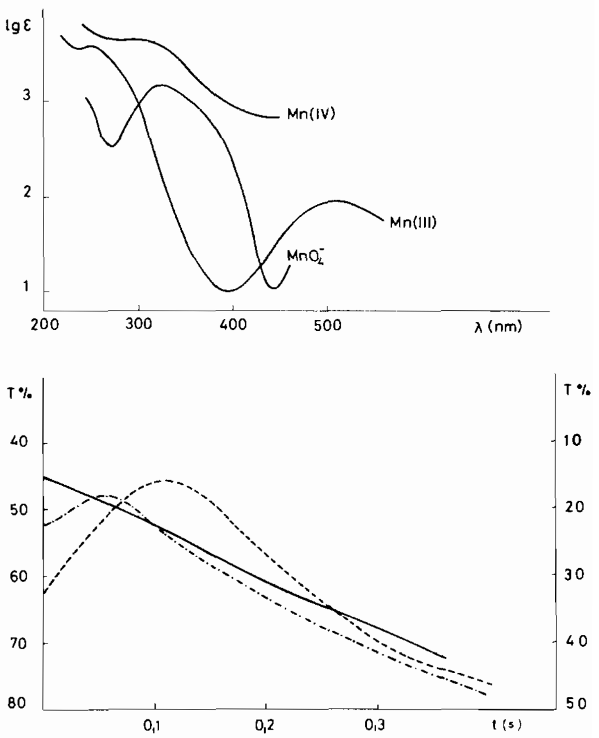
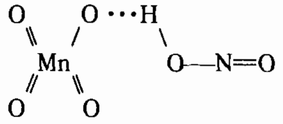


Figure 7. (a) Visible and UV spectra of Mn(III), Mn(IV) and Mn(VII) [7]. (b) Transmittance *vs.* time curves of the reaction at various wavelengths. Left-hand scale: ——— 525 nm, ------- 250 nm; $[KMnO_4] = 1 \times 10^{-3}$ mol dm^{-3}; $c_N = 2 \times 10^{-2}$ mol dm^{-3}; $c_H = 0.1$ mol dm^{-3}. Right-hand scale: – · – · – 300 nm; $[KMnO_4] = 5 \times 10^{-4}$ mol dm^{-3}; $c_N = 2 \times 10^{-2}$ mol dm^{-3}; $c_H = 0.1$ mol dm^{-3}.

If 1/v is plotted as a function of $1/c_{Mn}$ from the permanganate-dependence data (Fig. 6) K may similarly be determined from the slope. In this way, a value of $K = 3.5 \times 10^5$ is obtained, in agreement with the former value. This stability constant appears surprisingly large, but it is nevertheless not an irrealistic value: *e.g.* an equilibrium constant of 6.7×10^5 was found for the corresponding process in the reaction between chromium(VI) and thiosulphate [6]. It must be noted that the mixed anhydride written in equilibrium (6) may also be replaced by a hydrogen-bonded complex:



since the kinetic measurements provide no information regarding the hydrogen ions and water molecules participating in the equilibrium. In this case the stability constant is roughly 300 mol^{-1} dm^3.

The experimental results yield very little information on the mechanism of the redox steps of the reaction. From measurements at various wavelengths (Fig. 7), however, it may be established that Mn(IV) accumulates during the reduction of the Mn(VII).

The rate-decreasing effect of the mercury(II) ion in the reaction may be interpreted in that mercury(II)–nitro complexes are formed in rapid steps leading to equilibrium:

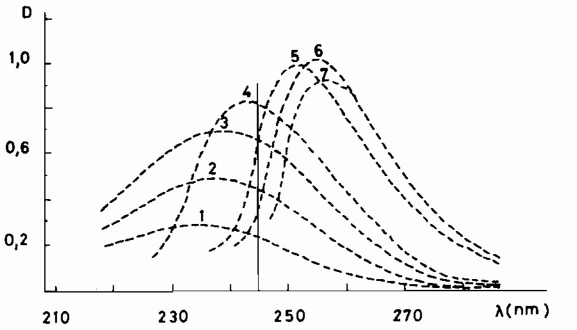


Figure 8. Change of the mercury(II) perchlorate spectrum in the presence of sodium nitrite [8]. $[\mathrm{Hg(II)}] = 1 \times 10^{-4}$ mol dm^{-3}; $[\mathrm{NaNO_2}]$ = (1) 6×10^{-5}, (2) 1.25×10^{-4}, (3) 3×10^{-4}, (4) 2.5×10^{-3}, (5) 3×10^{-3}, (6) 8×10^{-2}, (7) 0.125 mol dm^{-3}.

$$\mathrm{Hg^{2+} + NO_2^- \overset{K_1}{\rightleftharpoons} HgNO_2^+}$$

$$\mathrm{HgNO_2^+ + NO_2^- \overset{K_2}{\rightleftharpoons} Hg(NO_2)_2}$$

These are less reactive than nitrous acid.

From the measured rate value it is possible to calculate the maximum concentration of nitrous acid. The value thus obtained, however, is much lower than the concentration obtained from the stability constants published recently [8] ($K_1 = 255$, $K_2 = 23.7$). We therefore made a critical re-examination of the correctness of these constants. Unfortunately, it is not possible to carry out recalculations on the basis of this paper, but it appears probable that they made an error in calculation. Using the reported spectra (Fig. 8), and plotting the absorbances measured at a selected wavelength (245 nm) as a function of the nitrite concentration (Fig. 9), we can estimate the absorbance corresponding to complete transformation from the resulting curve. It seems reasonable to assume that the maximum in the curve corresponds to formation of the first complex, $\mathrm{HgNO_2^+}$. We may then estimate the total nitrite concentration corresponding to the 50% conversion. This is 0.9×10^{-4} mol dm^{-3}. The free nitrite concentration cannot be calculated exactly, for the pH is not reported, but if $[\mathrm{HNO_2}]$ is neglected (if not, then an even higher stability constant is obtained):

$$[\mathrm{NO_2^-}] = [\mathrm{NaNO_2}]_t - 1/2\,[\mathrm{Hg^{2+}}]_t = 0.4 \times 10^{-4}\ \mathrm{mol\ dm^{-3}}$$

Hence, $K_1 = 2.5 \times 10^4$ mol^{-1} dm^3.

Under the conditions which we used, the free nitrous acid concentration was calculated from the equation $v = 6.03[\mathrm{HNO_2}]^2$, valid to a first approximation. This gave $K_1 = 0.93/\pm0.13/\times 10^4$ mol^{-1} dm^3 (it must be considered, however, that omission of the first-order term means that this value is underestimated). A further datum supports that a value of the correct order of magnitude was obtained. The overall stability product for the complex $[\mathrm{Hg(NO_2)_4}]^{2-}$ was earlier found [9] to be $\beta_4 \times 10^{14}$. Hence, a value of $K_1 > 10^{3.5}$ is obtained by using the correlation valid for the stability constants of successively-formed complexes [10].

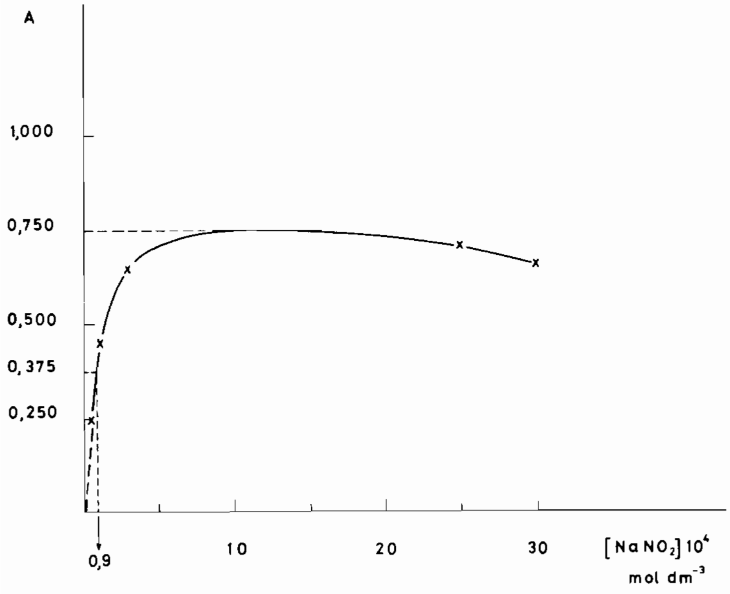


Fig. 9. Absorbances measured at 245 nm as a function of the nitrite concentration.

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