Contribution from the Institute of Physical Chemistry,
Kossuth Lajos University, Debrecen, Hungary.

The Mechanism of the Permanganate-Nitrite Reaction

L. Dózsa and M. T. Beck

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A simple method is elaborated for the kinetic study of moderately fast (0.5 $t_{1/2}$ 20 sec) reactions. The permanganate-nitrite reaction was studied by this method. The rate of the reaction is independent of the permanganate concentration in the range 5×10^{-5}–5×10^{-3} M, and between pH 1.8 and 2.6. There is no induction period. The rate as a function of nitrite and hydrogen ion concentrations can be described by the following equation:

$$Rate = k_1[HNO_2]+k_2[HNO_2]^2+k_3[HNO_2]^3[H^+]^3$$

This dependence can be explained by the following mechanism: the rate-determining steps are the formation of different reactive N^{III}-containing species, NO^+, N_2O_3, and $N_3O_3^{3+}$. For the rate constants the following values were obtained in a glycine-perchloric acid buffer at 25°C at ionic strength 0.1: $k_1 = 1.2\pm0.2\times10^{-2}$ sec^{-1}; $k_2 = 66\pm5$ M^{-1} sec^{-1}; $k_3 = 3.2\pm0.2\times10^9$ M^{-5} sec^{-1}. Activation energy values were also determined. It was found that glycine and phthalic acid also influence the rate due to an interaction between these compounds and nitrite. The dissociation constant of nitrous acid also was determined from the kinetic measurements; the value obtained agrees well with published values obtained under similar conditions using conventional methods.

Introduction

A few years ago we began a study of the effect of coordination on the reactivity of the nitrite ion.[1] When the results are evaluated, naturally a knowledge of the behaviour of the free nitrite ion and of nitrous acid too is needed. When the literature was examined, however, it turned out that neither in the case of the reduction with iodide nor the oxidation with permanganate had a kinetic investigation been carried out.[2] Hence our experiments were extended to the elucidation of these reaction mechanisms. In this communication we report our results relating to the permanganate-nitrite reaction. After this experimental work was completed, a short paper by Yatsimirskii and Budarina was published relating to this reaction.[3] Their results and conclusions, however, differ significantly from ours; we shall return to their paper in some detail in the final section.

We studied the reaction in acidic medium when the following overall reaction unambiguously occurs:

$$2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O \qquad (1)$$

Experiments were carried out to determine the dependence of the reaction-rate on the concentrations of the reactant permanganate, nitrite and hydrogen ions, and on the ionic strength and temperature; the possible catalytic effect of Mn^{II} and Ag^I ions, frequently used as catalysts in permanganate oxidations, was also investigated.

Experimental Section

Method. The reaction was followed by measuring the absorbance of the permanganate at 530 nm. Since the reaction is too fast for the employment of classical measuring techniques, and a stopped-flow apparatus was not available at the time of this investigation, experiments were performed as follows: the acidic permanganate solution was put into the cell, then the nitrite injected into it by means of a spinrg-powered syringe.[4] Under suitably chosen conditions the complete mixing takes place in less than 50 msec. The varying absorbance readings of the direct-reading spectrophotometer were filmed; a stop-watch was placed just above the dial of the instrument. With the aid of a microfilm-reader the individual extinction values at various points of time were read off from the film-frames, and extinction *vs.* time graph constructed. The frame-number gives the time-coordinate in the case or a given film speed. By this means, for those reactions where a change of extinction occurs on mixing the reactants, and for those where no change of extinction takes place due to mixing, it is possible to follow reactions with half-times of 2 sec and 0.5 sec. respectively quite reliably. The values of the initial rate were determined graphically from the tangents to the curves extrapolated to zero time. The half-lives of the reactions studied were between 2 and 500 sec.

Apparatus. Beckman B spectrophotometer; Kiev 16 cine-camera; Thompson-Gordon spring syringe; Radelkisz precision pH-meter.

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(1) Beck M. T. and Dózsa L., *Inorg. Chim. Acta.*, *1*, 134 (1967).
(2) Ladburry J. W. and Cullis C. F., *Chem. Rev.*, *58*, 403 (1958).
(3) Yatsimirskii K. B. and Budarina A. N., *Kinetika i Kataliz*, *9*, 422, (1968).
(4) Thompson R. and Gordon G., *J. Scientific Instruments*, *41*, 480 (1964).

Materials. Chemicals of p.a. quality were used without further purification. The $KMnO_4$ stock solution was standardised with sodium oxalate, the nitrite with the permanganate. The strengths of the solutions were checked every few days. $NaClO_4$ was used as an indifferent salt, perchloric acid for acidification. The experiments were performed at 25± 0.1°C unless otherwise indicated.

Experimental results

Figure 1 shows the values of the initial rate of the reaction as a function of the permanganate concentration. it may be seen that over a wide range of permanganate concentrations, in series of experiments performed under substantially differing conditions, the reaction rate is independent of the permanganate concentration.

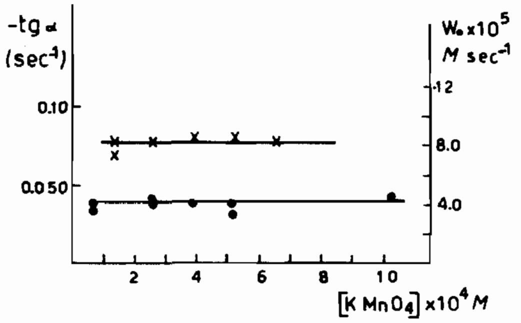

Figure 1. The dependence of the reaction rate on the permanganate concentration. × × × $c_{HClO_4} = 1.5\times10^{-2}\,M$, $c_{NaNO_2} = 1.25\times10^{-3}\,M$; ●●●● $c_{NaNO_2} = 0.834\times10^{-3}\,M$ in a pH 2.63 glycine $HClO_4$ buffer, $c_{glycine} = 0{,}064\,M$; $c_{HClO_4} = 0.031\,M$.

The dependence of the initial rate on the nitrite concentration is given in Figure 2. For various pH values and at different temperatures (16.0, 25.0 and 30.0°C), a reaction order of between 1 and 2 was obtained for the nitrite, depending on the pH and temperature (Figure 3).

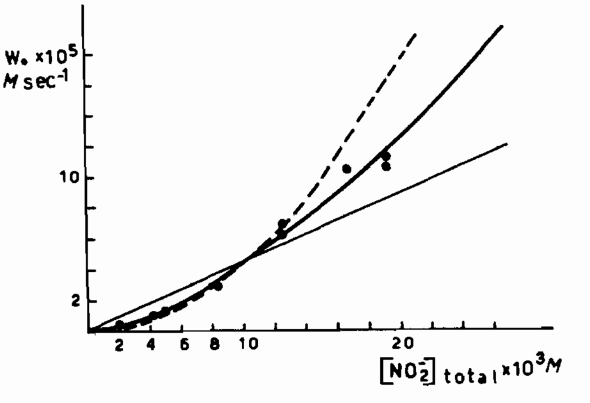

Figure 2. The dependence of the reaction rate on the nitrite concentration at pH 2.63 (thickly drawn line); ——— the first order function; — — — — the second order function; $c_{KMnO_4} = 5.56\times10^{-4}\,M$.

A plot of reaction-rate as a function of hydrogen ion concentration leads to an interesting graph (Figure 4). In the hydrogen ion concentration range $0.2–4\times10^{-3}\,M$ the reaction-rate depends on the hydrogen ion concentration in approximately a first-order manner; from $4–10\times10^{-3}\,M$ there is a zero-order dependence; finally at still higher hydrogen ion concentrations it tends to an order higher than zero. However, the shape of the curve depends on the nitrite concentration and also in which buffer medium experiments are performed.

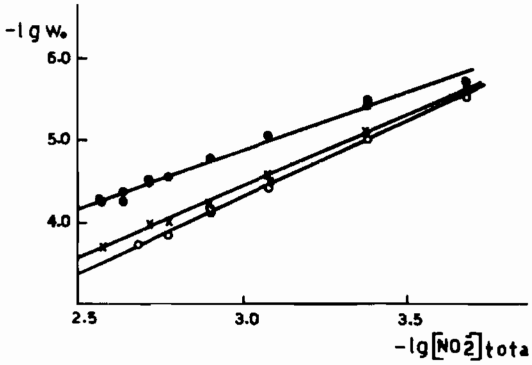

Figure 3. The dependence of the nitrite order on pH. The order calculated from the gradient of the log w—log $c_{NO_2^-}$ functions: ●●● at pH 3.28 (1.4); × × × at pH 2.63 (1.7); ○○○○ at pH 2.08 (1.9) (at pH 3.28 $c_{glycine} = 0.087\,M$; $c_{HClO_4} = 0.011\,M$; at pH 2.08 $c_{glycine} = 0.046\,M$; $c_{HClO_4} = 0.047\,M$).

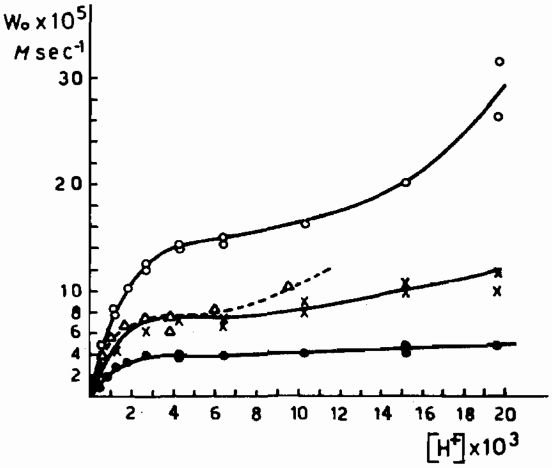

Figure 4. The dependence of the reaction rate on the hydrogen ion concentration ●●● $0.834\times10^{-3}\,M$, × × × $1.25\times10^{-3}\,M$, ○○○○ $1.67\times10^{-3}\,M$ nitrite concentration, all in a glycine perchloric acid buffer; ◁◁◁◁ $1.23\times10^{-3}\,M$ nitrite in a hydrochloric acid potassium hidrogen phthalate buffer.

According to our investigations, for values of the ionic strength between 0.05 and 0.5 the reaction-rate is independent of ionic strength. At greater ionic strengths the reaction-rate increases a little (Figure 5).

Further experiments showed that neither Mn^{II} nor Ag^{I} ions show a catalytic effect, not even in equivalent concentrations to the reactants. No induction period was observed in the reaction.

From the experimental results it appears that in the reaction-rate equation the permanganate concentration occurs to the power zero. It is possible to explain the observed nitrite order most easily in that the reaction proceeds in parallel routes in which the nitrite concentration is involved to the first and second powers. From the pH dependence it may be inferred that the nitrite reacts in the form of nitrous acid the concentration of which changes as a function of pH according to a saturation curve. However, because of the upwards slope of the function at higher hydrogen ion concentrations it is necessary to add to the rate equation an extra term varying as the third power of hydrogen ion concentration. The experiments carried out at various nitrite concentrations show that this term also varies as the third power of the nitrite concentration.

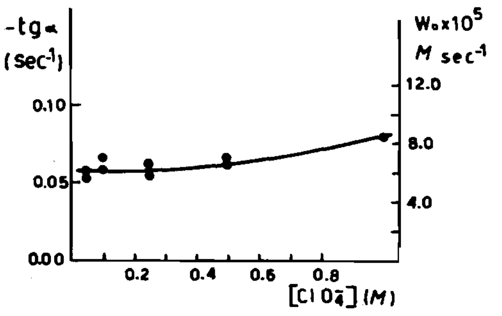

Figure 5. The dependence of the reaction rate on the ionic strength $c_{NaNO_2} = 1.25\times10^{-3}\,M$, $c_{KMnO_4} = 5.56\times10^{-4}\,M$, $c_{HClO_4} = 1.5\times10^{-2}\,M$.

When all these factors are taken into account it is possible to write the following rate-equation:

$$w = k_1[HNO_2]+k_2[HNO_2]^2+k_3[HNO_2]^3[H^+]^3 \qquad (2)$$

Expressing the nitrous acid concentration in terms of the total nitrite concentration, c, and the nitrous acid stability constant, K_s, the rate-equation becomes:

$$w = k_1\left(\frac{K_s[H^+]}{1+K_s[H^+]}\right)c+k_2\left(\frac{K_s[H^+]}{1+K_s[H^+]}\right)^2c^2 + k_3\left(\frac{K_s[H^+]}{1+K_s[H^+]}\right)^3[H^+]^3c^3 \qquad (3)$$

The constants involved in the rate-equation having been suitably selected ($K_s = 1.056\times10^3$, $k_1 = 1.17\times10^{-2}$ sec^{-1}, $k_2 = 66.3\,M^{-1}$ sec^{-1}, $k_3 = 3.2\times10^9\,M^{-5}$ sec^{-1}), the function calculated on the basis of the equation closely fits the experimentally found initial rate versus hydrogen ion concentration (Figure 6) and initial rate versus nitrite concentration (Figure 7) curves. We shall return later to the reasons for the deviations exceeding experimental error.

With the use of the rate-equation the reaction conversion curve was calculated. Figure 8 shows the calculated and experimentally found conversion curves for the case of a given reaction mixture composition. It may be seen that the calculated curve fits well with the experimentally found one until 70% of the permanganate is reacted. It is evident that for a very small permanganate concentration the above rate equation can not be valid, but with an infinitely small permanganate concentration a finite reaction rate occurs.

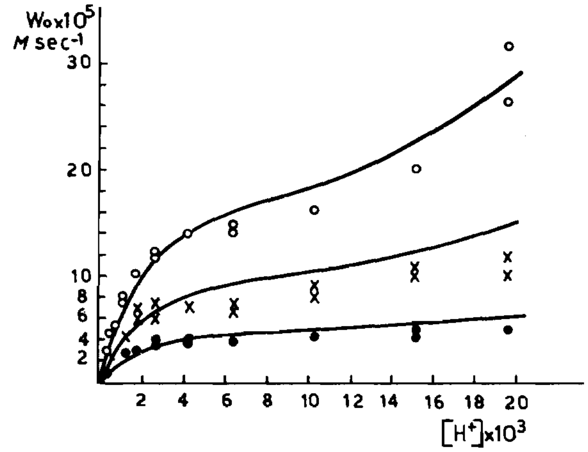

Figure 6. The hydrogen ion concentration reaction rate functions calculated on the basis of the rate equation: ●●● $0.837\times10^{-3}\,M$, × × × $1.25\times10^{-3}\,M$, OOOO $1.67\times10^{-3}\,M$ nitrite (continuously drawn line). The indicated points are the experimentally found values.

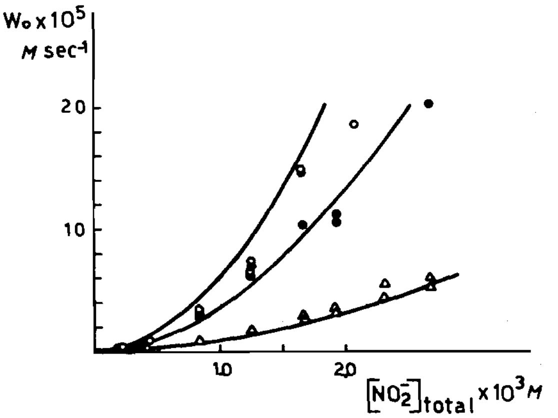

Figure 7. The nitrite concentration reaction rate relations calculated from the rate equation (drawn line). ◁◁◁◁ pH 3.28, ●●● pH 2.63, OOOO pH 2.08.

From the measurements at various temperatures with regard to the nitrite the first order (k_1) and second order (k_2) rate constants were determined grapically. From equation (3) it may be seen that at such hydrogen ion concentrations where the third term may be neglected, the various values of k_1 and k_2 may be calculated with the use of the values of K_s[5] from the gradients of the tangents to and the intercepts of the $\frac{w}{c}$ —c curves. From the temperature

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(5) Lumme P. and Tummavuori *J.*, *Acta Chem. Schand.*, *19*, 2175 (1965).

Table I. The activation enthalpy and entropy of the permanganate-nitrite reaction at 25°C

	pH	glycine	k	ΔH* (Kcal./mole^{-1})	ΔS* (e.u.)
First-order process	3.28	0.087	1.3×10^{-2} sec^{-1}	20.2	0.0
	2.08	0.046	1.2×10^{-2} sec^{-1}	13.8	−21.6
Second-order process	3.28	0.087	83 M^{-1} sec^{-1}	12.7	−6.4
	2.08	0.046	69 M^{-1} sec^{-1}	15.6	1.8

dependence (Figure 9) it is possible to determine the values of the activation enthalpy (ΔH*) and activation entropy (ΔS*) of the first and second order processes (Table I).

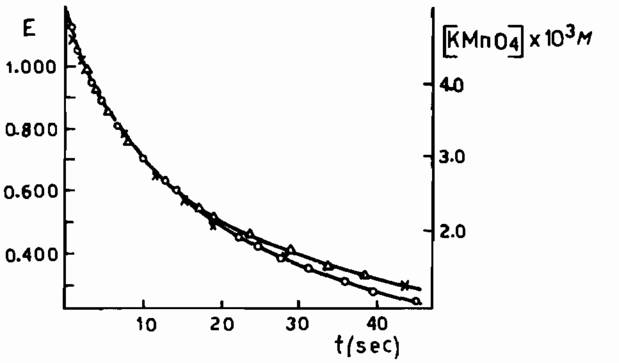

Figure 8. The calculated and experimentally found reaction conversion curves. $c_{NaNO_2} = 1.25\times10^{-3} M$, $c_{KMnO_4} = 5.14\times10^{-4} M$, pH = 2.26, glycine—HClO$_4$ buffer; OOOO the calculated curve; × × × and ◁◁◁◁ two parallel measured series of points.

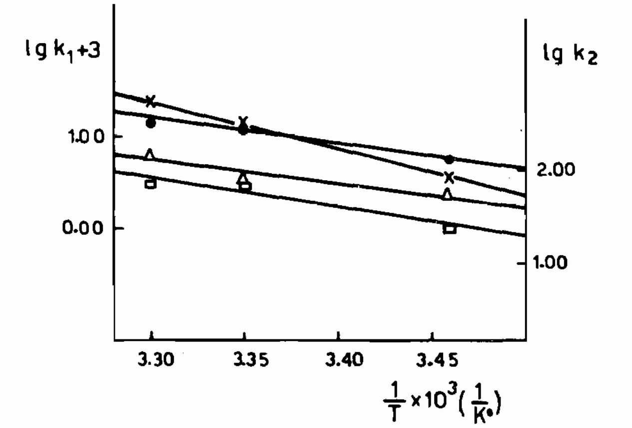

Figure 9. The dependence of the logarithms of the first and second order rate constants on the reciprocal of the absolute temperature. Left hand side, log k$_1$ values at × × × pH 3.28 and ●●●● pH 2.08. Right hand side, log k$_2$ values ◁◁◁◁ at pH 3.28 and □□□□ pH 2.08.

It is evident from Table I that the characteristic parameters of the reaction depend on the concentration of the glycine buffer (several experiments were carried out in the absence of the buffer. It was found that the same rate law is valid in this case, but the numerical values of the rate constants were different).

Evaluation of the results

Perhaps the most characteristic feature of the reaction is that the reaction-rate is independent of the permanganate concentration. At first sight this seems rather surprising but it may be relatively simply understood if one considers other reactions of the two reactants. Among permanganate reactions there are some well-known cases where the permanganate concentration appears to the zero order;[2,6] in addition, there are quite a few nitrite reactions in which the rate is independent of the concentration of the nitrite's co-reactant.

In Table II are summarised the presently-known data relating to kinetically examined nitrite reactions. It may be seen that the most different reactions (oxidation to nitrate, and reductions leading to the most diverse products) show similar features. The reactions in general take place via the formation from the nitrite of reactive species, NO$^+$, N_2O_3, *etc.*[11] In those reactions in which the reaction-rate is independent of the concentration of the co-reactant the formation of the reactive species is the rate-determining step. The order obtained for the nitrite, however, refers to the N^{III} content of the reactive species. In general, the rate-equations of the reactions are drivd as for the following reaction-scheme.

In the first step the active species, $H_zN_xO_y$, is formed:

$$(4x-2y+z)H^+ + xNO_2^- \xrightarrow{k_1} H_zN_xO_y^{3x-2y+z} + (2x-y)H_2O \qquad (4)$$

which either reverts to the inactive species:

$$H_zN_xO_y^{3x-2y+z} + (2x-y)H_2O \xrightarrow{k_{-1}} (4x-2y+z)H^+ + xNO_2^- \qquad (5)$$

or reacts with the co-reactant present:

$$H_zN_xO_y^{3x-2y+z} + R \xrightarrow{K'} T_1 + T_2 + \qquad (6)$$

forming products T$_1$, T$_2$, *etc.* The reaction-rate is thus

$$w = k'[H_zN_xO_y][R] \qquad (7)$$

Using the stationary state condition for the nitrite

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(6) Wiberg B. and Geer R. D., *J. Amer. Chem. Soc.*, *87*, 5202 (1965).
(7) Li J. C. M. and Ritter D. M., *J. Amer. Chem. Soc.*, *75*, 3024, 5823 (1953).
(8) Seel F. and Schaebel R., *Z. anorg. u. allgem. Chem.*, *274*, 169 (1953).
(9) Frank J. A. and Spence J. T., *J. Phys. Chem.*, *68*, 2131 (1964).

Table II. The redox reactions of nitrite

Co-reactant	Rate dependence	ΔH^* Kcal./mole	Reactive species	Ref.
$(SO_3)NO^{2-}$	$k[HNO_2]^2$	20.1	N_2O_3	7
N_3^-	$k[HNO_2][H^+]$	12.8	NO^+	8
Mo^V	$k[HNO_2]$	13.1	NO^+	9
SO_3^{2-}	$k_1[HNO_2][H^+]+k_2[SO_3^{2-}][HNO_2][H^+]$	10	NO^+	10, 11
$S_2O_3^{2-}$	$k[S_2O_3^2]^{0.2}[H^+][HNO_2]$		NO^+	12
H_2O_2**	$k[HNO_2][H^+]$		NO^+	13
$C_6H_5NH_2$	$k[HNO_2][H^+][NO_2^-]$		N_2O_3	14
HCO_2^-	$k[HCO_2^-][HNO_2][H^+]$		NO^+	15
$SO_3NH_2^-$	$k[SO_3NH_2^-][HNO_2][H^+]$		NO^+	16
I^-	$k[I^-][HNO_2][H^+]$		NO^+	17, 11
$C_2O_4^{2-}$	$k[C_2O_4^{2-}][HNO_2][H^+]$		NO^+	18
ClO_3^-	$k[ClO_3^-][HNO_2][H^+]$		NO^+	19, 11
BrO_3^-	$k[BrO_3^-][HNO_2][H^+]$		NO^+	19, 11
H_2O_2	$k_1[H_2O_2][HNO_2]^2+k_2[H_2O_2][HNO_2][H^+]$		N_2O_3, NO^+	20
Fe^{2+}	$k_1[Fe^{2+}][HNO_2]+k_2[Fe^{2+}][HNO_2][H^+]+\dfrac{k_3[Fe^{2+}][HNO_2]^2}{P_{NO}}$		N_2O_3, NO^+ HNO_2	21
MnO_4^-	$k_1[MnO_4^-][NO_2^-]+k_2[MnO_4^-][H^+][NO_2^-]$	11.5	HNO_2, NO_2^-	3
MnO_4^-	$k_1[HNO_2]+k_2[HNO_2]^2+k_3[HNO_2]^3[H^+]^3$	14.20 14	NO^+, N_2O_3, $(NO)_3^{3+}$	This work

** Rate dependence valid only at high H_2O_2 concentrations

concentration:

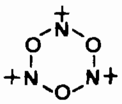
$$\frac{d[H_zN_xO_y]}{dt} = 0 = k_1[NO_2^-]^x[H^+]^{4x-2y+z} - k_{-1}[H_zN_xO_y] - k'[H_zN_xO_y][R] \tag{8}$$

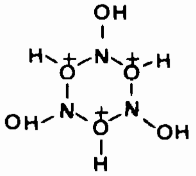
and substituting for the $H_zN_xO_y$ stationary concentration in (7) the following rate-equation is obtained:

$$w = \frac{k_1k'[NO_2^-]^x[H^+]^{4x-2y+z}[R]}{k_{-1}+k'[R]} \tag{9}$$

It may be seen that if $k'[R] \gg k_{-1}$ the rate of reaction is independent of the concentration of the co-reactant R. It is clear in the case when $k' \sim k_{-1}$ the reaction may be dependent on the concentration of the co-reactant, being zero and first order also with regard to this reactant. An example of this is the hydrogen peroxide nitrite reaction. After the appropriate substitutions have been made, the outlined scheme can be used for a specific reaction.

In the case of the permanganate-nitrite reaction it must be presumed as a result of the three rate terms that three types of reactive species take part in the reaction. As regards the nitrite in the first and second order processes the species taking part are probably NO^+ and N_2O_3, whilst in the third order process we presume the formation of an hitherto not proved (nor even suspected) species, $(NO)_3^{3+}$ or $(H_2NO_2)_3^{3+}$:





It must be noted that in high nitrite and acid concentrations these species may take an important role. Of the reactions examined so far merely the dissociation of nitrous acid has been studied in strongly acidic solution. Abel and Schmid[22] found that there is a fourth order nitrite term too in the rate-equation. It is possible to explain this rate-equation too as a result of our proposed species.

Taking the above into consideration we include the following steps in the permanganate-nitrite reaction.

The first step is the equilibrium protonation of the nitrite ion:

$$\text{I.}\quad NO_2^- + H^+ \overset{K_s}{\rightleftarrows} HNO_2 \tag{10}$$

then the active species are formed from the nitrous acid:

$$\text{IIa.}\quad HNO_2 \xrightarrow{k_1} NO^+ + OH^- \tag{11}$$

$$\text{IIb.}\quad 2HNO_2 \xrightarrow{k_2} N_2O_3 + H_2O \tag{12}$$

$$\text{IIc.}\quad 3HNO_2 \xrightarrow{k_3} N_3O_3^{3+} + 3H_2O \tag{13}$$

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(10) Seel F. and Degener E., *Z. anorg. u. allgem. Chem., 284*, 101 (1956).

(11) Turney T. A. and Wright G. A., *Chem. Rev., 59*, 497 (1959).

(12) Edwards J. D., *Science 113*, 392 (1951).

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(14) Hughes E. D., Ingold C. K. and Ridd J. H., *J. Chem. Soc., 58*, (1958-58).

(15) Longstaff J. V. L. and Singer K., *J. Chem. Soc.*, 2604 (1954).

(16) Li J. C. M. and Ritter D. M., *J. Amer. Chem. Soc., 75*, 5828 (1953).

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(19) Lowe W. G. and Browne D. J., *Z. anorg. u. allgem. Chem., 221*, 173 (1934).

(20) Silov E. A. and Stepanova Z. S., *Zhur. Fiz. Kim., 24*, 800 (1950).

(21) Abel E., Schmid H. and Pollak F., *Monatsh. Chem., 69*, 125 (1930).

(22) Abel E. and Schmid H., *Z. physik. Chem., 136*, 430 (1928).

These steps comprise the slow rate-determining steps. (Naturally processes IIb and IIc can take place in more steps).

After this the reactive species react with the permanganate. The experimental data at our disposal do not give any evidence as regards the rate and mechanism of the electron transfer reaction. We can suppose for example the following oxygen transfer steps:

$$\text{IIIa.}\quad NO^+ + MnO_4^- \xrightarrow{\text{fast}} NO_2^+ + MnO_3^- \qquad (14)$$

$$\text{IIIb.}\quad N_2O_3 + MnO_4^- \xrightarrow{\text{fast}} NO_3^- + MnO_3^- + NO^+ \qquad (15)$$

$$\text{IIIc.}\quad N_3O_3^{3+} + MnO_4^- \xrightarrow{\text{fast}} NO_2^+ + MnO_3^- + N_2O_2^{2+} \qquad (16)$$

The unstable species thus formed take part in further fast reactions leading finally to nitrate and Mn^{II}. Clearly, however, one can conceive of many other possible reaction-routes.

In the above mechanism, uncharged nitrous acid molecules take part in the rate-determining reactions in agreement with the experimental finding that the reaction-rate is independent of the ionic strength (in the experiments concerning the effect of ionic strength the third rate term may be neglected. Theoretically that is the ionic strength may influence this process).

The mechanism also reveals why there is no observable catalytic effect of either Mn^{II} or Ag^{I} ions. These ions show catalytic activity in Mn^{VII} reactions by producing even more reactive species.[2] In our case however, the Mn^{VII} does not take part in the rate-determining steps; thus these ions would accelerate an otherwise fast reaction, producing practically no effect on the overall rate of reaction. It may be similarly explained that the reaction is not of an autocatalytic nature and that we do not find an induction period.

As referred to already, the reaction-rate versus hydrogen ion concentration function calculated curves does not completely fit with that found experimentally. That is, if the functions are calculated using the constants indicated, good agreement is found with the experimental curve only in the hydrogen ion concentration range $1-4\times10^{-3}$ *M*. At smaller hydrogen ion concentrations the experimentally found rate is greater, at higher concentrations smaller than that calculated. Similarly the values of the activation enthalpy and entropy obtained with the various pH buffer mixtures also differ. When certain buffer mixtures differ merely in glycinc concentration, disregarding the hydrogen ion concentration which is already included in the rate equation, the effects must be attributed to the glycine. In weakly acidic buffer mixturs where the glycine concentration is high the reaction-rate is greater than that calculated. It follows from this that the « constant » appearing in the rate equation depend on the glycine concentration We were not able to express this dependence in a quantitative form from the experimental result obtained. It is difficult to establish in what way the glycine affects the various constants.

The glycine presumably affects the rate of reaction in that its carbonyl or amine group interacts with the nitrous acid. The interaction affects the reaction-rate in two ways. First, it is evident that the equilibrium concentration of nitrous acid will be different. This would make it appear as if the values of the equilibrium constant is altered. Such interactions are probably also responsible for the differences in the values of the stability constants which may be found in the literature (for this reason we calculated stability constants from our kinetic measurements) secondly, these interactions can give rise to new active species. For example:

$$HNO_2 + NH_2CH_2CO_2H \rightleftarrows NH_2CH_2CO_2NO + H_2O \qquad (17)$$

$$NH_2CH_2CO_2NO + HNO_2 \longrightarrow N_2O_3 + NH_2CH_2CO_2H \qquad (18)$$

It should be noted that Hughes, Ingold and Ridd observed the catalytic effect of phthalate and acetate on the analine-nitrite reaction and explained it in a similar manner.[14,11]

The difference of the results obtained using glycine or phthalate buffers can also be explained on the above grounds. In both cases the same rate equation is valid, but in the case of the phthalate buffer a larger stability constant must be used (1.8×10^3 instead of 1.06×10^3). The dependence of the formation constant on ionic strength results in the fact that the rate decreases over the ionic strength range 0.5–1.

In the following we must make some comments on Yatsimirskii and Budarina's investigations. They also studied the permanganate-nitrite reaction kinetics, but made their measurements with a stopped-flow apparatus and so examined reactions faster by several orders of magnitude with half-times of 10^{-4}–0.1 sec. Their experimental conditions and conclusions are compared with our own in Table III.

They observed an induction period for the reaction and stated that HSO_4^- ions have an inhibiting effect.

They gave the following rate equation:

$$w = K[MnO_4^-][NO_2^-](1+b[H^+]) \qquad (19)$$

which may be written in the following form:

$$w = k_1[MnO_4^-][NO_2^-] + k_2[MnO_4^-][HNO_2] \qquad (20)$$

It is a result of this rate equation that both nitrite and nitrous acid take part in the reaction.

The mechanism for the nitrous acid was given by the following steps:

$$MnO_4^- + HNO_2 \rightleftarrows [MnO_4 . HNO_2]^- \rightarrow Mn^{III} + NO_3^- + H_2O \qquad (21)$$

It was presumed that the formation of the $[MnO_4 . HNO_2]$ causes the induction period.

Table III. Comparison of our experimental results with those of vatsimirskii and Budarina

	Concentration M		Effect on rate	
Ion	Y and B	This work	Y and B	This work
NO_2^-	0.0047-0.047	0.0002-0.002	1st order	1st-2nd order
H^+	0.3-1.8	0.0002-0.02	1st order	1th-1st order
MnO_4^-	0.0024	0.001-0.05	1st order	0th order
Mn^{2+}	0.001	0.001	no effect	no effect

It may be seen that our results differ substantially from those found by Yatsimirskii and Budarina and naturally the two reaction mechanisms postulated also differ. The variations in reaction conditions can only partially account for the differences, and if their results are considered thoroughly their conclusions seem unjustified.

1. The reaction-rate versus hydrogen ion concentration function was extrapolated to zero hydrogen ion concentration, and then, since the value of the rate was not zero, it was concluded that the free nitrite ion also reacts with permanganate. In this particular case, however, the extrapolation to zero is completely unjustified because their measurements were made only at hydrogen ion concentrations greater than 0.3 M.

2. The dependency on the permanganate concentration was determined from a single decreasing reaction conversion curve at high nitrite concentration. From their conversion curve it may be seen that according to their measured points up to at least 50% conversion the rate may be independent of the permanganate concentration. That is, during the significant conversion a well-fitting straight line may be drawn to the reaction curve; this means that during the initial part of the reaction the rate hardly changes.

3. Similarly, neither does the induction period seem unambiguous from the reported conversion curve. It could possibly be that the induction period is caused by the delayed response of the apparatus itself.

4. Their measured points with regard to the nitrite definitely indicate an order of between 1 and 2.

Having considered all these facts, we hold that their conclusions as to the mechanism, based on very few determinations compared with our own results, are not acceptable.

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