

**Redox reactions of complexes of cations
in higher oxidation states. VII.*
Kinetics of the redox reaction of the Mn(III)
ions with hydrazoic acid**

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The kinetics and mechanism of the redox reaction of the Mn(III) ions with hydrazoic acid in the medium of 54% acetic acid was studied. The curve representing the dependence of the rate constant on the concentration of azides rises linearly at first, reaches a maximum and afterwards sinks non-linearly. The values of the enthalpy and entropy of activation depend on temperature considerably. From the temperature dependence of these values the activation heat capacity was calculated $\Delta C_p^* = 1569 \text{ J mol}^{-1} \text{ K}^{-1}$. The probable reaction mechanism according to which the redox reaction goes through the intermediary complex $\text{MnHN}_3(\text{Ac})_2^+$ is discussed. However, in the region of higher concentrations of azides the less reactive $\text{Mn}(\text{HN}_3)_2(\text{Ac})_2^+$ complex ion competes with that intermediary complex.

Была изучена кинетика и механизм окислительно-восстановительной реакции ионов Mn(III) с азотистоводородной кислотой в среде 54%-ной уксусной кислоты. Кривая зависимости измеренной константы скорости от концентрации азидов сначала линейно возрастает, достигает максимума и потом нелинейно падает. Значения энтальпии и энтропии активации в значительной мере зависят от температуры. На основании их температурной зависимости были получены значения теплоемкости активации $\Delta C_p^* = 1569 \text{ Дж моль}^{-1} \text{ K}^{-1}$. Обсуждается вероятный механизм реакции, согласно которому она протекает через образование промежуточного комплекса $\text{MnHN}_3(\text{Ac})_2^+$, которому при более высокой концентрации азотистоводородной кислоты конкурирует комплексный ион $\text{Mn}(\text{HN}_3)_2(\text{Ac})_2^+$ с меньшей реакционной способностью.

The redox reactions of the Mn(III) ions with organic or inorganic ligands are remarkable from the view-point of a more comprehensively conceived research into the kinetics of redox reactions. The Mn(III) ions are a strong oxidation agent. The redox potential of the system Mn(II)/Mn(III) has the value +1.5 V in non-complexing media [1—3]. Though these ions are relatively unstable, the

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number of the papers on their redox reactions increased recently [4—22]. The relatively stable solutions of the Mn(III) ions in a medium of 2—5 M perchloric or sulfuric acid are usually used for kinetic measurements. The presence of pyrophosphate ions or ethylenediaminetetraacetic acid stabilizes the Mn(III) ions even at lower concentrations of H_3O^+ ions. For instance, the pyrophosphate complex of the Mn(III) ions used in the oxidations of aliphatic aldehydes and ketones, oxalic acid, malonic acid, phenols [23], α -hydroxy acids [24], and mandelic acid [25]. The kinetics of the oxidation of organic compounds with the Mn(III) ions was also investigated in the medium of ethylenediaminetetraacetic acid [26—28] or acetate [15, 29—32]. The redox reactions of the Mn(III) ions with substrates usually follow a mechanism involving the formation of intermediary complexes owing to changes inside the sphere. We proved a successive formation of intermediary complexes with increasing number of coordinately bonded ligands for the redox reaction of the Mn(III) ions with SCN^- ions [13] and for the redox reaction of the Mn(III) ions with oxalic acid in the medium of acetic acid [15]. In this medium we also investigated the temperature dependence of the activation parameters and found the value $\Delta C_p^\ddagger = 699 \text{ J mol}^{-1} \text{ K}^{-1}$.

The redox reaction of the Mn(III) ions with hydrazoic acid was studied in a solution of perchloric acid [33, 34]. Since it was observed that the reaction was of second order with respect to hydrazoic acid and of first order with respect to the Mn(III) ions, the authors [33] assumed that the rate-determining step was the reaction of the $\text{Mn}(\text{H}_2\text{O})_5\text{HN}_3^{3+}$ ion with a molecule of HN_3 giving a H_2N_6^+ radical which subsequently reacted rapidly with another Mn(III) ion. According to [34], the intermediary complex of this reaction is $\text{Mn}(\text{N}_3)_2^{2+}$ the intramolecular redox step of which is rate-determining. In the medium of acetic acid the redox reaction of Mn(III) with hydrazoic acid shows a different kinetic character and for this reason we have chosen the study of this reaction as topic of the present paper.

Experimental

The kinetic measurements of the redox reaction of the Mn(III) ions with hydrazoic acid were carried out polarographically and spectrophotometrically. For polarographic measurements a polarograph OH 102, Radelkis was used. The limiting diffusion current of the Mn(III) ions was recorded as a function of time at the constant potential of -0.3 V against the potential of a $\text{Hg}_2(\text{C}_2\text{H}_3\text{O}_2)_2$ electrode in a solution of 0.1 M sodium acetate in 70% acetic acid. A Kalousek vessel with nitrogen supply was used. This vessel was equipped with a thermostating jacket which was connected with a universal Wobser thermostat U 3. Before entering the Kalousek vessel, nitrogen passed through a washing bottle with 54% solution of acetic acid. A dropping mercury electrode with the dropping time of 5 s and flow rate of 1.24 mg s^{-1} at the above-mentioned potential and at the height of mercury column of 75 cm was used as an indication electrode. The spectrophotometric kinetic measurements

were performed with a spectrophotometer Specord UV VIS (Zeiss, Jena), which was equipped with a thermostating block connected with a thermostat of the above type.

Before every kinetic measurement the solution of the Mn(III) ions was prepared by electrooxidation of a solution of 2.6×10^{-3} M-MnSO₄ and 0.1 M sodium acetate in 70% acetic acid on a platinum electrode. This electrooxidation always took 30 min. In the course of day between measurements the solution was kept in a refrigerator in order to prevent disproportionation of the Mn(III) ions. All chemicals were anal. grade reagents and the solutions were prepared from redistilled water.

Results

By using the differential and integral method it was found that the reaction order with respect to the Mn(III) ions was equal to one in the temperature interval from 5 to 35°C (Fig. 1). In order to formulate the equation for the rate of the reaction studied, it was necessary to find out the dependence of the rate constant on the concentration of sodium azide. This relationship is not simple. Initially, the value of the rate constant increases linearly with the concentration of sodium azide (interval from 0.1 to 0.225 M) to reach a maximum and afterwards it decreases non-linearly (Fig. 2). The redox reaction studied is an acid-catalyzed reaction. The rate constant measured increases with the concentration of perchloric acid almost linearly in the concentration range from 0.04 to 0.2 M. In the region of higher concentrations of perchloric acid (0.2–0.3 M) it increases non-linearly (Fig. 3). In

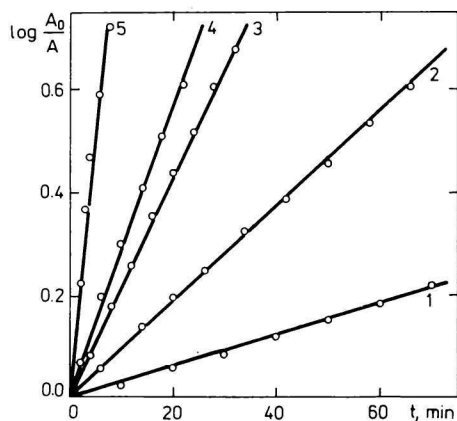


Fig. 1. Verification of the order of reaction at different temperatures.

2×10^{-3} M-Mn(III), 2×10^{-1} M-NaN₃, 54% CH₃COOH, 0.08 M-CH₃COONa.

A₀ is absorbance of the Mn(III) solution at the beginning of reaction, A is absorbance at any time of reaction.

1. 5°C; 2. 10°C; 3. 15°C; 4. 20°C; 5. 30°C.

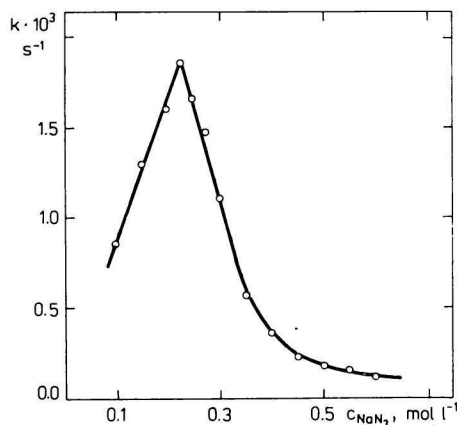


Fig. 2. Experimental rate constant as a function of the concentration of azides.

2×10^{-3} M-Mn(III), 54% CH₃COOH, 0.08 M-CH₃COONa, $T = 303.16$ K.

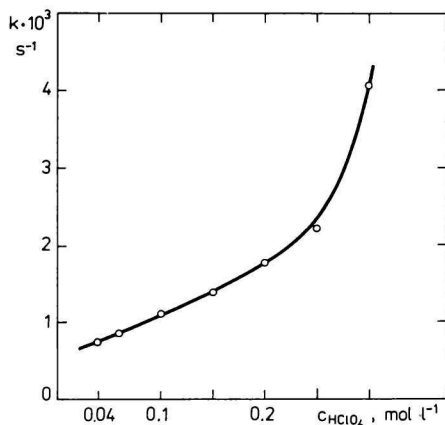


Fig. 3. Rate constant as a function of the concentration of perchloric acid.
 2×10^{-3} M-Mn(III), 2×10^{-1} M-NaN₃, 54%
 CH₃COOH, 0.08 M-CH₃COONa,
 $T = 303.16$ K.

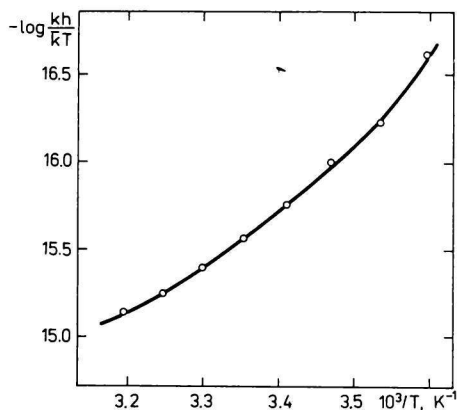


Fig. 4. Variation of the rate constant with temperature.
 Experimental conditions see in Fig. 1.

the first concentration interval the relationship may be expressed approximately by the equation

$$k = k_0 + k_{\text{H}^+} [\text{H}_3\text{O}^+]$$

where $k_0 = 5 \times 10^{-4} \text{ s}^{-1}$ and $k_{\text{H}^+} = 6.2 \times 10^{-3} \text{ s}^{-1} \text{ l mol}^{-1}$.

The rate of reaction does not practically change with the ionic strength of electrolyte. In order to verify a radical mechanism, the effect of acrylonitrile on the rate of this reaction was examined. The presence of this substance in solution raises the rate of the redox reaction to such a degree that it cannot be measured by the method used in these investigations. In the absence of sodium azide acrylonitrile does not affect the change in the concentration of the Mn(III) ions.

The relationship between the logarithm of the rate constant measured and the reciprocal value of absolute temperature in the interval from 5 to 35°C shows a non-linear character (Fig. 4). By using the Eyring equation the activation parameters — the values of the enthalpy and entropy of activation — could be calculated from two neighbouring points $(T_i + T_j)/2$ in particular temperature intervals. As obvious from Fig. 5, the value of the activation enthalpy decreases with increasing temperature practically linearly from 288 to 310 K on the basis of which the value of the activation heat capacity could be determined $\Delta C_p^\ddagger = (-\partial \Delta H^\ddagger / \partial T)_p = 1569 \text{ J mol}^{-1} \text{ K}^{-1}$. Similarly the values of the entropy of activation were calculated by means of the Eyring equation for various temperatures (Table 1). The kinetics of the studied reaction was also investigated spectrophotometrically. In the presence of sodium azide the absorption maximum of the Mn(III) ions shifts from the original value of $\lambda_{\text{max}} = 490 \text{ nm}$ to the value of $\lambda_{\text{max}} = 432 \text{ nm}$. During the reaction the absorbance of the Mn(III) ions decreases according to the first order kinetics while the position of λ_{max} does not change (Fig. 6).

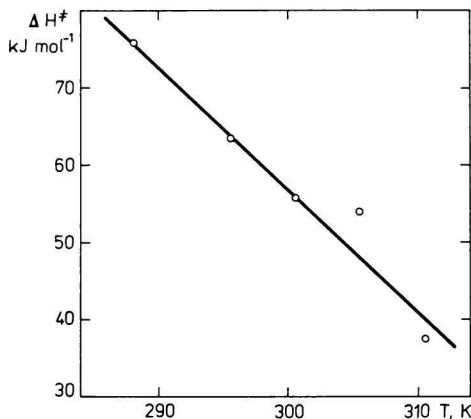


Fig. 5. Variation of the activation enthalpy with temperature.

Experimental conditions see in Fig. 1.

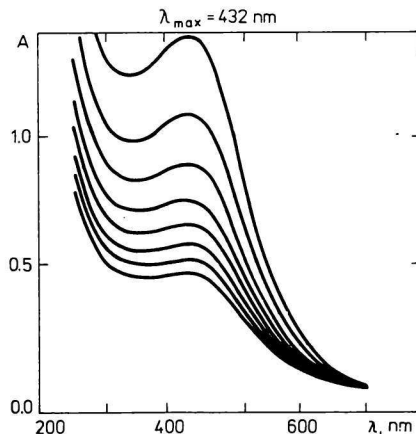


Fig. 6. Time dependence of the absorption spectrum of the Mn(III) ions.

Experimental conditions see in Fig. 1 ;
 $T = 303.16$ K. The curves were taken
 in 9 minutes' intervals.

Table 1

Dependence of the activation entropy on temperature
 2×10^{-3} M-Mn(III), 2×10^{-1} M-NaN₃, 54% CH₃COOH, 0.08 M-CH₃COONa

ΔS^\ddagger J mol ⁻¹ K ⁻¹	T, K
42.7	288.16
85.0	295.66
110.5	300.66
114.3	305.66
169.5	310.66

Discussion

For the region of lower concentrations of sodium azide (from 0.1 to 0.225 M) a simple rate equation of the reaction studied may be put forward

$$-\frac{d[\text{Mn(III)}]}{dt} = k [\text{Mn(III)}] [\text{NaN}_3]$$

where [Mn(III)] stands for the total concentration of the Mn(III) ions and [NaN₃] is the total concentration of sodium azide. It may be assumed that the reactive form of sodium azide in acidic medium is a molecule of HN₃. The increase in the rate constant with concentration of H₃O⁺ ions may be explained in the main by a shift in

tion ratio of both reactants as well, it may be assumed that the reaction proceeds through an intermediary 1 : 1 complex while the higher complex $\text{Mn}(\text{HN}_3)_2(\text{Ac})_2^+$ reacts substantially slower.

The values of activation parameters ΔH^* and ΔS^* of the reaction studied depend considerably on temperature. The value of the activation heat capacity $\Delta C_p^\ddagger = (-\partial\Delta H^*/\partial T)_p = 1569 \text{ J mol}^{-1} \text{ K}^{-1}$. It is substantially higher than the value of ΔC_p^\ddagger which was measured for the reaction of the Mn(III) ions with oxalic acid in a solution of 70% acetic acid ($\Delta C_p^\ddagger = 699 \text{ J mol}^{-1} \text{ K}^{-1}$) [15]. It is probable that the considerable temperature dependence of activation parameters is also related with the physicochemical properties of the solvent used. If a higher value of ΔC_p^\ddagger occurred in other redox reactions taking place in a given solvent (mixture of solvents) too, it would be easier, in contrast to purely aqueous solutions, to find out correlations between this activation quantity and different types of reaction mechanism.

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