*Contribution from the Department of Chemistry,
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Reactivity of Vanadium(V) Polymeric and Monomeric Forms in Complex Formation with *p*-Phenetidine

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The formation of charge-transfer complex (CTC) between p-*phenetidine and vanadium(V) species existing in acid medium at low vanadium(V) concentrations was studied. It was found that while the CTC formation rate is very low for VO_2^+, it is maximal when decavanadate species are used. The results were interpreted on the ground of the electrostatic interaction between the reagents. The rate of depolymerisation of decavanadate species to VO_2^+ and $H_2VO_4^-$ was also studied and the rate constants of these processes estimated.*

Introduction

The oxidation of *p*-ethoxyaniline (*p*-phenetidine) with halates has been used for determination of traces of the catalyst vanadium(V)[1-3] and as a model reaction for many investigations on the activation of homogeneous catalytic reactions.[4-9]

Our previous investigations[8] have shown that the catalytic process proceeds in three stages:

a) formation of charge-transfer complex (CTC) between the substrate, *p*-phenetidine, and the catalyst, vanadium(V);

b) oxidation process proceeding further in this complex with the formation of a coloured reaction product and vanadium(IV);

c) oxidation of vanadium(IV) to vanadium(V) by halate and thus regeneration of the catalyst in the reaction cycle.

The rate determining stage of the overall reaction is the formation of CTC.

In water solutions vanadium(V) is present in different forms depending on the concentration and the acidity of the solution. Vanadium(V) catalyzes the oxidation of *p*-phenetidine in acid medium and for that reason it was of interest to study the complex formation between *p*-phenetidine and the vanadium(V) species present in acid solutions at relatively low concentrations. According to the diagram of Pope and Dale[10] in the concentration range 5×10^{-5}—$5 \times 10^{-3}\,M$ and pH 0-6 the following vanadium(V) forms are in equilibrium: VO_2^+, $H_2VO_{10}O_{28}^{4-}$, $HV_{10}O_{28}^{5-}$, $V_3O_9^{3-}$, $H_2VO_4^-$ and H_3VO_4 (the last two written also as VO_3^-aq and HVO_3aq).

Having in mind the differences in the charge and the structure of these forms it might be expected that their reactivity towards CTC formation with *p*-phenetidine will vary in a large extent.

The aim of the present work was to study the CTC formation between *p*-phenetidine and some of the vanadium(V) species present in acid solutions.

Experimental Section

The charge-transfer complex formed in the vanadium(V) — *p*-phenetidine interaction is not a stable one in a kinetic sense — an oxidation process proceeds further in the complex with formation of the final reaction products: vanadium(V) and N-(4-ethoxyphenyl)quinoneimine.[11] The oxidation process is favoured by increasing the temperature and lowering the acidity.

Hence, it was necessary to study the complex formation at relatively low temperature and in acid solutions in order to avoid further oxidation in the complex. For that reason all the investigations were carried out at 20°C and pH 1.8-experimentally found conditions where the oxidation process in the complex proceeds with a very low rate and could be completely neglected if the complex formation is studied during the first 10-15 min after the mixing of the reagents.

In these reaction conditions *p*-phenetidine being a very weak acid[12] ($pK_a = 5{,}25$) is present only in a protonated form $HPhen^+$.

At pH 1.8 and V^V $10^{-2}\,M$ the thermodynamically stable form of vanadium(V) is VO_2^+. Hence, the investigations with different vanadium(V) species can be carried out at pH 1.8 only if the rate of the protonation processes having as a result the formation

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of VO_2^+ is low enough not to affect the rate of CTC formation after the mixing of the reagents and of the acid, necessary to realize pH 1.8 in the reaction medium.

For the protonation processes expressed by the scheme

$$HVO_4^{2-} \xrightarrow{H^+} H_2VO_4^- \xrightarrow{H^+} H_3VO_4 \xrightarrow{H^+} VO_2^+ \qquad (1)$$

there were sufficient data in the literature[13,14,10] showing that these processes are very fast and therefore could not be used to study the activity of the different monomeric vanadate species.

As for the depolymerisation processes in acid solutions the data of many authors, summarised in[10] agree that the rate of the processes

$$V_3O_9^{3-} \xrightarrow{H^+} HV_{10}O_{28}^{5-} \qquad (2)$$

and

$$HV_{10}O_{28}^{5-} \xrightarrow{H^+} H_2V_{10}O_{28}^{4-} \qquad (3)$$

are also too fast and do not permit the investigations with the forms $V_3O_9^{3-}$ and $HV_{10}O_{28}^{5-}$ to be carried out at pH 1,8. As to the process

$$H_2V_{10}O_{28}^{4-} \longrightarrow VO_2^+ \qquad (4)$$

there were some indications in the literature[15,16] that its rate is sufficiently low and could scarcely influence in a measurable extent the concentration of $H_2V_{10}O_{28}^{4-}$ during the period of the kinetic measurements: 6-8 min.*

For that reason the first experiments in this work were based on the assumption that the depolymerisation process (4) proceeds much slower than the CTC formation and its rate was not taken into account.

The complex formation processes were studied photometrically using the intensive absorption band at 553 nm, characteristic for the charge-transfer complex between vandium(V) and *p*-phenetidine. The charge-transfer character of this band and its origin were already discussed elsewhere.[8,17,20] It must be noted here that the position of the band remained unchanged with all vanadium(V) forms studied in the limits of the experimental precision (±2-4 nm).

The rate of the complex formation was studied following the changes in the absorbance with time:

$$\text{Rate} = \frac{dC}{dt} = \frac{dA}{dt} = k \,.\, \varepsilon \,.\, l \,.\, f(c) \qquad (5)$$

where C is the concentration of the CTC in the moment t, A is the absorbance in the same moment, k is the rate constant, ε— the extinction coefficient of the CTC, l— the length of the absorbing layer, and f(c) is a function of the reagent concentration.

Because of the very high extinction coefficient of the complex[17] it was possible to study the kinetics of its formation in the initial period of the reaction, when the concentration of the complex, formed in the system, is very small in comparison with the reagent concentrations. Therefore for these conditions equation (5) changes to

$$\text{Rate} = \frac{dA}{dt} = \text{const} \qquad (6)$$

which was used to measure the reaction rate in the initial period of the CTC formation.

The reagent concentrations in the reaction system were constant in all cases: NH_4VO_3 $8\times10^{-5}\,M$ and $HPhen^+$ $1\times10^{-3}\,M$. Therefore, the differences in the complex formation rate will depend only on the different reactivity of the vanadium(V) ionic species towards $HPhen^+$.

Five sets of initial NH_4VO_3 solutions with concentrations 2×10^{-3}, 1×10^{-3}, 5×10^{-4}, 1×10^{-4} and $5\times10^{-5}\,M$ were prepared by dilution of $5\times10^{-3}\,M$ NH_4VO_3. Only when the initial $5\times10^{-5}\,M$ NH_4VO_3 solution was used its concentration in the reaction system was $4\times10^{-5}\,M$ instead of $8\times10^{-5}\,M$ as in all other experiments. The reaction rate values in this case were calculated for NH_4VO_3 concentration $8\times10^{-5}\,M$ according to the equation (5) where vanadium(V) enters on a first power.

For every initial NH_4VO_3 concentration solutions with pH in the range 1.8-6.0 were prepared by the addition of perchloric acid. The solutions were left to stand for two days and their acidity checked on a pH-meter. The establishment of the equilibrium between the different vanadium(V) forms for that period was confirmed by spectrophotometric and kinetic investigations.

Measured volumes of these solutions and of *p*-phenetidine were placed in the sections of the glass reaction vessel[17] and thermostated in separation for 15 min. The reagents were then mixed and transferred in the thermostated cell of the photometer. The total volume of the reaction system was 25.0 ml.

The ionic strength in the reaction solution was kept constant in all cases with perchloric acid, its con-

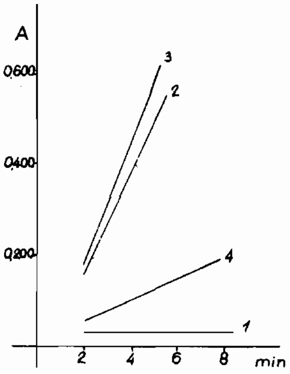

Figure 1. A Specimen Absorbance *vs.* Time Plot for the CTC formation between $HPhen^+$ and V^V Forms. Initial vanadium(V) solution: $5\times10^{-4}\,M$, 1, pH 2.3; 2, pH 2.8; 3, pH 3.4; 4, pH 2.6. Reagent concentrations in the reaction system: V^V $8\times10^{-5}\,M$, $HPhen^+$ $1\times10^{-3}\,M$, pH 1.8, t° 20.0±0.1°C.

(*) Unfortunately the considerations on the problem were only qualitative and there were not any quantitative data about the rate of the process.

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Table I. Rate of CTC Formation between $HPhen^+$ and Different V^V Forms

Conc., M	Initial V^V solution		$\frac{dA}{dt}\times 10^2$
	pH	V^V form mainly present	sec^{-1}
2.0×10^{-3}	2.0	VO_2^+	0.1
2.0×10^{-3}	2.2	$H_2V_{10}O_{28}^{4-}+VO_2^+$	1.5
2.0×10^{-3}	2.5	$H_2V_{10}O_{28}^{4-}$	10.9
2.0×10^{-3}	3.2	$H_2V_{10}O_{28}^{4-}$	12.3
2.0×10^{-3}	6	$V_3O_9^{3-}$	9.5
1.0×10^{-3}	2.3	VO_2^+	0.1
1.0×10^{-3}	2.6	$H_2V_{10}O_{28}^{4-}+VO_2^+$	4.6
1.0×10^{-3}	2.7	$H_2V_{10}O_{28}^{4-}$	11.1
1.0×10^{-3}	3.5	$H_2V_{10}O_{28}^{4-}$	12.0
1.0×10^{-3}	6	$V_3O_9^{3-}$	6.5
7.5×10^{-4}	6	$V_3O_9^{3-}$	4.7
5.0×10^{-4}	1.8	VO_2^+	0.1
5.0×10^{-4}	2.3	VO_2^+	0.1
5.0×10^{-4}	2.6	$H_2V_{10}O_{28}^{4-}+VO_2^+$	2.7
5.0×10^{-4}	2.8	$H_2V_{10}O_{28}^{4-}$	7.6
5.0×10^{-4}	3.2	$H_2V_{10}O_{28}^{4-}$	12.4
5.0×10^{-4}	3.4	$H_2V_{10}O_{28}^{4-}$	12.2
5.0×10^{-4}	3.9	$HV_{10}O_{28}^{5-}$	11.9
5.0×10^{-4}	4.5	$HV_{10}O_{28}^{5-}$	12.4
5.0×10^{-4}	5.1	$HV_{10}O_{28}^{5-}$	12.0
5.0×10^{-4}	6	$V_3O_9^{3-}$	3.3
1.0×10^{-4}	3.1	VO_2^+	0.1
1.0×10^{-4}	3.5	$H_2V_{10}O_{28}^{4-}+VO_2^+$	6.3
1.0×10^{-4}	4.0	$HV_{10}O_{28}^{5-}+H_2VO_4^-$	7.9
1.0×10^{-4}	4.6	$H_2VO_4^-+HV_{10}O_{28}^{5-}$	1.7
1.0×10^{-4}	6	$H_2VO_4^-$	0.4
5.0×10^{-5}	3.1	VO_2^+	0.1
5.0×10^{-5}	3.3	H_3VO_4	0.1
5.0×10^{-5}	4.0	$H_2VO_4^-$	0.1
5.0×10^{-5}	6	$H_2VO_4^-$	0.1

Reagent concentrations in the reaction system: NH_4VO_3 8×10^{-5} M; $HPhen^+$ 1×10^{-3} M; pH 1.8; t° 20.0±0.1°C.

centrations being at least ten times higher than that of *p*-phenetidine, which is changed only in a small extent during the period of the kinetic measurements.

All the reagent solutions were prepared from reagent grade substances and water, twice distilled in an Jena glass vessel.

The absorbance of the solution was followed with time on a FEK-photometer, cell length 50 mm (Figure 1).

Results and Discussion

The experimental data obtained in the kinetic investigations are summarized in Table I.

It can be seen that in the reaction conditions shown above the rate of the CTC formation between VO_2^+ and $HPhen^+$

$$VO_2^+ + HPhen^+ \rightleftarrows [VO_2^+ - HPhen^+] \qquad (7)$$

is practically zero. The CTC formation with VO_2^+ proceeds with a measurable rate only at higher VO_2^+ concentrations, of the same order as that of $HPhen^+$.

In the same time the data in Table I exhibit the startling fact that the CTC formation rate with the polymeric forms $HV_{10}O_{28}^{5-}$ and $H_2V_{10}O_{28}^{4-}$ is very high. As can be expected by the high rate of the process (3) there is not any difference in the CTC formation rate if $HV_{10}O_{28}^{5-}$ or $H_2V_{10}O_{28}^{4-}$ are used.

The same reasons are responsible for the negligible CTC formation rate when the monomeric ion H_2VO^{4-} is used. The high rate of the protonation of metavanadate species expressed by (1) causes a fast transformation of the metavanadates to VO_2^+ which is uneffective as a reagent in these conditions.

The lower results with initial vanadium(V) solutions with pH 6, compared with those where $H_2V_{10}O_{28}^{4-}$ is mainly present, in spite of the high rate of the protonation plrocess (2) indicate to the fact that in this case the equilibrium

$$V_3O_9^{3-}aq \rightleftarrows H_2VO_4^-(VO_3aq) \qquad (8)$$

is also of importance. The investigations of Schwarzenbach and Geier have shown[13] that this equilibrium is achieved for a very short period of time measured by several milliseconds. This fact together with the high rate of (1) is responsible for the fast elimination of a part of vanadium(V) as VO_2^+.

The fact that the decavanadate ion $H_2V_{10}O_{28}^{4-}$ shows a very high activity for complexation with $HPhen^+$ in comparison with VO_2^+ was in some extent unexpected. The investigations of Babko and Gridchina[16] have shown that the reactivity of vanadium(V) towards complexation with xylenol orange and PAR is higher for VO_2^+ and sharply decreases with the formation of polymeric forms. The observations of Sajo for the complexation between different vanadium(V) forms and EDTA are in the same direction[18] the polymeric forms also show the lowest reactivity.

We consider that the main reason for the different behaviour of vanadium(V) forms is the electrostatic interaction between the reagents. It is noteworthy that while xylenol orange, PAR, and EDTA react in the form of negatively charged ions, *p*-phenetidine in the reaction conditions we have used exists as the positive ion $HPhen^+$. This accounts satisfactorily for the inertness of $H_2V_{10}O_{28}^{4-}$, a negatively charged ion, towards the other three anionic reagents and for its reactivity in the case of $HPhen^+$. The same considerations are valid for the activity of VO_2^+ in the complex formation with the anions and its inertness towards $HPhen^+$.

The assumption for the electrostatic forces as a main reason for the different reactivity of vanadium(V) forms towards reagents with opposite charges can explain also the strong influence of 8-hydroxyquinoline on the CTC formation, estimated before.[8] In this case VO_2^+ first forms a neutral complex with oxine[19] which then react further more readily with $HPhen^+$ with the formation of a ternair complex $[ox_2-V(V)-HPhen^+]$, estimated experimentally.[20] This complex also shows the same charge-transfer band at 553 nm.

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The activation energy of the process also might serve as a criterion whether the electrostatic forces have such an important role in the process of CTC formation. It might be expected that if this is the case the activation energy should be lower when the reagents are ions with opposite charges, and higher when they are of the same sign.

Table II. Activation Energy of the CTC Formation between $HPhen^+$ and Some Vanadium(V) Forms

Reaction	E kcal/mole
$HPhen^+ + H_2V_{10}O_{28}^{4-}$	9±2
$HPhen^+ + VO_2^+$	18±2
$HPhen^+ + VO_2^+ +$ oxine	12±1

The results shown in Table II confirm this assumjtion. It can be seen that the activation energy E_a of the complex formation between VO_2^+ and $HPhen^+$ is about two times higher than in the case of $H_2V_{10}O_{28}^{4-}$ and $HPhen^+$. In the same time the presence of oxine which favours the complex formation between VO_2^+ and $HPhen^+$ leads to decrease of the activation energy with about 30%. This fact is in a good accordance with the considerations stated above, especially having in mind that oxine does not influence at all the CTC formation between $H_2V_{10}O_{28}^{4-}$ and $HPhen^+$.

The large error in the E_a values is due to the fact that the activation energy was determined for a relatively narrow temperature range (12-25°C) in order to prevent the further oxidation of the CTC. For that reason the E_a values were determined by the means of regression analysis and the less square method. The experiments of this series were carried out with a higher $HPhen^+$ concentration in order to increase the CTC formation rate in the case of $HPhen^+$—VO_2^+ and to make possible its determination.

There was also another experimental fact to be checked in order to prevent the drawing of wrong conclusions about the reactivity of vanadium(V) forms. The differences in the CTC formation rate with VO_2^+ and $H_2V_{10}O_{28}^{4-}$ might be do to a very different extinction coefficient of the CTC formed between $HPhen^+$ and vanadium(V) forms.

With this possibility in mind we studied the extinction coefficients of the CTC which $HPhen^+$ forms with $H_2V_{10}O_{28}^{4-}$ and VO_2^+.

The investigations with $H_2V_{10}O_{28}^{4-}$ were carried out with a large excess of $HPhen^+$ in order to shift the equilibrium of CTC formation to a total bonding of all vanadium(V) present in the solution. In order to check whether this is in fact realised the measurements were made with four vanadium(V) concentrations. The solutions of V^V and $HPhen^+$ were left to stand in contact untill a saturation of the absorbance curve with time was achieved and this absorbance value was used further. The fulfilment of the Bouger-Lambert-Beer law in that case (Figure 2, 1) shows that this is really the case and permits the evaluation of the extinction coefficient. The value found for the complex $H_2V_{10}O_{28}^{4-}$—$HPhen^+$ is $\varepsilon = 3.6 \times 10^3$ at $\lambda_{max} = 553$ nm. The measurements were carried out on SF-10 spectrophotometer in the following reaction conditions: $HPhen^+$ 1×10^{-2} *M*, pH 1.8 ($HClO_4$), t° 20°C, 20 mm cell.

The CTC formation rate in the case of VO_2^+ was very low even in the presence of a large excess of $HPhen^+$. On the other hand it was impossible to left the solutions for several hours to attain the equilibrium in the system because for such a long period the oxidation process in the complex also takes place in a measurable extent. For that reason we studied the extinction coefficient in this system in the presence of oxine when the CTC formation rate is much more higher. The complete bonding of vanadium(V) in the complex was checked when the CTC formation was studied at three V^V concentrations. It was found that in this case the Bouger-Lambert-Bear law is followed (Figure 2, 2). The experimental concentrations used were $HPhen^+$ 5×10^{-2} *M*, oxine 5×10^{-3} *M*, pH 1.8 ($HClO_4$), t° 20°C, 50 mm cell. The extinction coefficient thus found was 3.5×10^3 at 553 nm, which is the same as in the previous case in the limits of the experimental error (~3%).

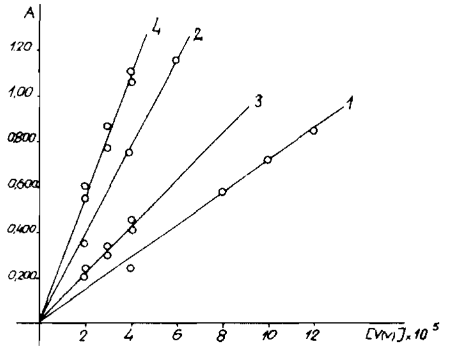

Figure 2. Fulfilment of the Bouger-Lambert-Beer Law in the case of the CTC formation with different V^V concentrations. 1, $H_2V_{10}O_{28}^{4-} + HPhen^+$. Initial V^V solution 1×10^{-3} *M*, pH 3.2. Reagent concentrations in the reaction system: $HPhen^+$ 1×10^{-2} *M*, pH 1.8 ($HClO_4$), 20°C, 20 mm cell. 2, $VO_2^+ + HPhen^+ +$ oxine. Initial V^V solution 1×10^{-3} *M*, pH 1.8 ($HClO_4$). Reagent concentrations in the reaction system: $HPhen^+$ 5×10^{-2} *M*, oxine 5×10^{-3} *M*, pH 1.8 ($HClO_4$), 20°C, 50 mm cell. 3, $VO_2^+ + HPhen^+ +$ oxine. Initial V^V solution 1×10^{-3} *M*, pH 1.8 (H_3PO_4). Reagent concentrations in the reaction system: $HPhen^+$ 5×10^{-2} *M*, oxine 5×10^{-3} *M*, pH 1.8 (H_3PO_4), 20°C, 20 mm cell. 4, like 3, cell length 50 mm.

These results show that not only the energy of the charge-transfer transition, but also its probability remains practically unchanged in the complexes of $HPhen^+$ with $H_2V_{10}O_{28}^{4-}$ and VO_2^+.

In the same time the fact that the extinction coefficient obtained for CTC in both cases is one and the same shows that probably the presence of oxine does not affect the equilibrium given by (7) but only increases the rate of its establishment.

It was of interest to compare this value of the extinction coefficient with that obtained before[8] for VO_2^+—$HPhen^+$ complex in the presence of oxine. The value 8.7×10^3 was then obtained in a buffer solution (pH 2) containing phosphoric, boric and acetic acid. It seems that the presence of phosphoric acid which easily forms complexes with vanadium(V) is responsible for this difference. In order to verify this assumption we determined the extinction coefficient in the same reaction conditions as described at Figure 2, but the necessary pH-value of 1.8 was realised using phosphoric acid instead of perchloric acid.

In this case we also obtained an increased extinction coefficient 5.5×10^3 at 553 in comparison with that received in perchloric acid medium. The results for three different vanadium(V) concentrations are shown on Figure 2 (3, 4).

All the experiments were carried at pH 1.8, where the equilibrium form of vanadium(V) is VO_2^+. Hence, there existed the possibility that the high reactivity of $H_2V_{10}O_{28}^{4-}$ might be due to a very reactive unstable vanadium(V) species, formed in the process of desintegration of the decavanadate to the monomeric form VO_2^+. In order to check this possibility we carried out experiments when the initial V^V solution contained $H_2V_{10}O_{28}^{4-}$ and after the mixing of the reagents the equilibrium V^V form is the same ion.

Because of the higher pH value in this case (2.4 instead of 1.8) the experiments were carried out at lower temperature (11.5°C) in order to prevent further oxidation in the CTC to the final reaction product. As a base for comparison we used experiments carried out in the same reaction conditions, but with pH 1.7 of the initial vanadium(V) solution and the final reaction system, the equilibrium V^V form in these conditions being VO_2^+.

These experiments have shown a very high CTC formation rate in spite of the fact that in this case there is no any transformation of vanadium(V) speciesff An example of this runs which confirmed that the reactive form is in fact $H_2V_{10}O_{28}^{4-}$ is shown on Figure 3.

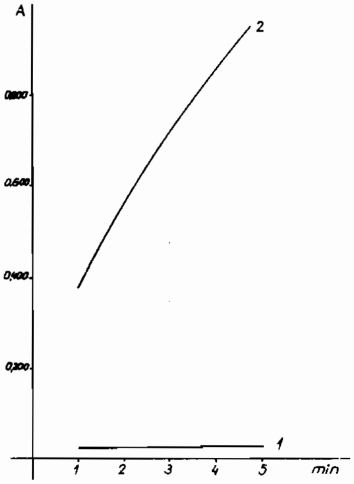

Figure 3. Dependence of the Absorbance on the Time for the CTC formation between $HPhen^+$ and V^V. NH_4VO_3 3×10^{-3} *M*, $HPhen^+$ 3×10^{-3} *M*, t° 11.5±0.1°C, 5 mm cell. 1, $VO_2^+ + HPhen^+$, pH 1.7. 2, $H_2V_{10}O_{28}^{4-} + HPhen^+$, pH 2.4.

The investigations carried out in the present work permit to estimate the rate constants of depolymerisation of decavanadates to the monomeric forms VO_2^+ and $H_2VO_4^-$.

These investigations were based on the fact that while the rate of CTC formation with decavanadates is maximal, it is practically zero with VO_2^+ in the reaction conditions used by us. Hence, the process of depolymerisation can be studied by the rate of CTC formation which is a measure for the amount of $H_2V_{10}O_{28}^{4-}$ that still remains in the solution.

Two types of depolymerisation processes were studied: caused by dilution of the solutions at constant pH value or by increasing their acidity.

The initial solution containing vanadium(V) as decavanadate was diluted or acidified. Aliquots were taken out of this solution at fixed intervals of time and the rate of CTC formation with $HPhen^+$ measured as described above.

First the rate of the depolymerisation process

$$H_2V_{10}O_{28}^{4-} \longrightarrow VO_2^+ \tag{9}$$

realised by dilution of the decavanadate solution was investigated at 20°C. The initial vanadium(V) solution (2.5×10^{-3} *M*, pH 2.6) with vanadium(V) present as $H_2V_{10}O_{28}^{4-}$ was diluted with perchloric acid solution (pH 2.6) to V^V concentration of 1×10^{-4} *M*, where V^V is present as VO_2^+. The CTC formation was studied with aliquots of this solution with $HPhen^+$ at 20.0±0.1°C and final acidity of the reaction solution pH 2.2. The reagent concentrations in the reaction solution were V^V 8×10^{-5} *M* and $HPhen^+$ 1×10^{-3} *M*, the total volume 15 ml. The absorbance was measured on a FEK photometer with 30 mm cell. The experimental data are shown on Figure 4.

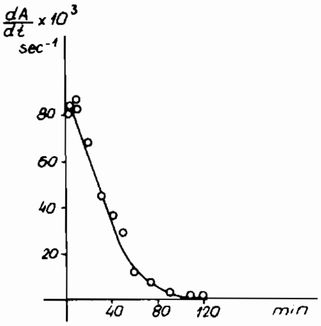

Figure 4. Kinetics of the Depolymerisation Process $H_2V_{10}O_{28}^{4-} \longrightarrow VO_2^+$. Initial V^V solution 2.5×10^{-3} *M*, with pH 2.6 diluted to 1×10^{-4} *M* (pH 2.6). Reagent concentrations in the reaction system: V^V 8×10^{-5} *M*, $HPhen^+$ 1×10^{-3} *M*, pH 2.2, t° 20.0±0.1°C.

The rate of the depolymerisation process

$$HV_{10}O_{28}^{5-} \longrightarrow H_2VO_4^- \tag{10}$$

realised by dilution was also studied. The initial vanadium(V) solution (1×10^{-3} *M*, pH 5.0) where V^V is present as $HV_{10}O_{28}^{5-}$ was diluted with water to 1×10^{-4} *M*. The dilution changed also the acidity to pH 5.5. In these conditions the stable V^V species is $H_2VO_4^-$. The depolymerisation process was studied at 20°C.

The CTC formation was followed with aliquots of this solution at 20.0±0.1°C and final acidity of the reaction solution with $HPhen^+$ pH 1.8. The results are shown on Figure 5.

The depolymerisation process (10) is a slow process which proceeds completely to the end for several days. As it was studied in the absence of buffer solutions* at low H^+ concentration (pH 5.5) the acidity was somewhat varried about this pH-value because of the absorbance of atmospheric CO_2. For that reason the reproducibility of the results in this case was not very good.

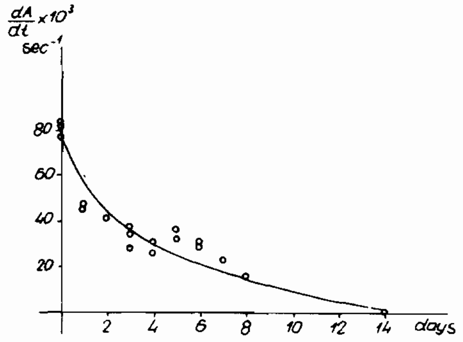

Figure 5. Kinetics of the Depolymerisation Process $HV_{10}O_{28}^{5-} \longrightarrow H_2VO_4^-$. Initial V^V solution $1 \times 10^{-3}\,M$ with pH 5.0 diluted to $1 \times 10^{-4}\,M$, (pH 5.0). Reagent concentrations in the reaction system: V^V $8 \times 10^{-5}\,M$, $HPhen^+$ $1 \times 10^{-3}\,M$, pH 1.8, t° 20.0±0.1°C.

The depolymerisation to VO_2^+ by protonation was studied with initial solutions containing V^V as $V_3O_9^{3-}$, $HV_{10}O_{28}^{5-}$ and $H_2V_{10}O_{28}^{4-}$. The following reactions take place

$$V_3O_9^{3-} \xrightarrow{H^+} HV_{10}O_{28}^{5-} \xrightarrow{H^+} H_2V_{10}O_{28}^{4-} \xrightarrow{H^+} VO_2^+ \qquad (11)$$

Three initial vanadium(V) solutions were used ($1 \times 10^{-3}\,M$) with different acidity (pH 3.1; 4.5; 6.0 resp.) which contain vanadium(V) as $H_2V_{10}O_{28}^{4-}$, $HV_{10}O_{28}^{5-}$ and $V_3O_9^{3-}$ resp. By the addition of 0.040 ml conc. $HClO_4$ their acidity was brought to pH 1.8 practically without any changes in their concentration. The depolymerisation processes were carried out at 20.0±0.1°C.

The CTC formation with the three initial V^V solutions was studied in the following reaction conditions: V^V $6.7 \times 10^{-5}\,M$, $HPhen^+$ $1 \times 10^{-3}\,M$, t° 20.0± 0.1°C, pH 1.8. The total reaction volume was 15 ml.

The experimental data present on Figure 6 show that the CTC formation rate in the three cases is one and the same. This is possible only if the rate determining stage of the depolymerisation from $V_3O_9^{3-}$ to VO_2^+ is the last step

$$H_2V_{10}O_{28}^{4-} \xrightarrow{H^+} VO_2^+ \qquad (12)$$

whose rate is in fact expressed by the data on Figure 6.

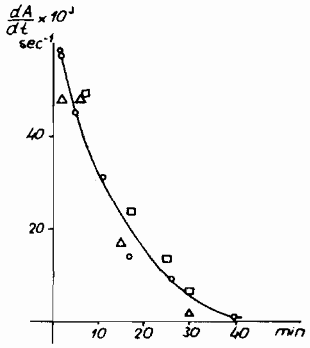

Figure 6. Kinetics of the Depolymerisation Processes: $V_3O_9^{3-} \longrightarrow VO_2^+$, $HV_{10}O_{28}^{5-} \longrightarrow VO_2^+$, and $H_2V_{10}O_{28}^{4-} \longrightarrow VO_2^+$. Initial V^V solutions $1 \times 10^{-3}\,M$, △ pH 3.1; □ pH 4.5; ○ pH 6, acidified to pH 1.8 with $HClO_4$. Reagent concentrations in the reaction system: V^V $8 \times 10^{-5}\,M$, $HPhen^+$ $1 \times 10^{-3}\,M$, pH 1.8, t° 20.0±0.1°C.

Table III. Rate Constants for the Depolymerisation Processes: $H_2V_{10}O_{28}^{4-} \longrightarrow VO_2^+$, $HV_{10}O_{28}^{5-} \longrightarrow H_2VO_4^-$ and $H_2V_{10}O_{28}^{4-} \xrightarrow{H^+} VO_2^+$

Reaction	k, sec^{-1}
$H_2V_{10}O_{28}^{4-} \longrightarrow VO_2^+$	3×10^{-4}
$HV_{10}O_{28}^{5-} \longrightarrow H_2VO_4^-$	1×10^{-6}
$H_2V_{10}O_{28}^{4-} \longrightarrow VO_2^+$	7×10^{-4}

The data from Figures 4, 5, and 6 were used for the calculation of the corresponding rate constants.

The character of the curves on Figures 4 and 6 indicates to the fact that the depolymerisation processes proceed as a first order reactions. That was confirmed by the linearity of the lg dA/dt *vs.* t graph, which permits the evaluation of the corresponding rate constants. For the reaction conditions stated above the rate constants thus found are given in Table III.

(*) We did not wish to complicate the system by the presence of other substances which might eventually interfere.