Vanadium in the oxidation state +5 forms complex compounds of comparatively high stability with ethylenediaminetetraacetic acid (EDTA, $H_4A$) [1-4]. The value of the redox potential of the transition $V(V) \rightarrow V(IV)$ makes possible a redox interaction between the metal and EDTA [5]; however, this interaction was not studied in [1-4]. There are no data in the literature on complexes of $V(V)$ with diethylenetriaminepentaaacetic acid (DTPA, $H_5L$). We studied the kinetics of the oxidation of EDTA and DTPA by vanadium (V).

**EXPERIMENTAL METHOD**

The concentration of $V(V)$ was estimated according to the intensity of the absorption of light by solutions of $V(V)$ on an SF-4A spectrophotometer in the region of 240 and 260 nm [6]. As the initial preparation of $V(V)$ we used $NaVe_3\cdot2H_2O$, recrystallized twice from water. DTPA and EDTA were used in the form of dilute solutions of the sodium salts of these acids. Solutions of the complexones and $V(V)$ were prepared according to an exact weighed sample. The concentration of sodium metavanadate was determined by volumetric titration; the excess Mohr's salt added to the solution of $NaVO_3$ was titrated with $K_2Cr_2O_7$; phenylanthranilic acid was used as the indicator. The concentration of DTPA and EDTA in solutions was determined by complexometric titration [7]. To create a constant ionic strength ($\mu = 1.0$ M), sodium metavanadate and the complexones were dissolved in a 1 M solution of $NaClO_4$.

The kinetics of the oxidation of EDTA was studied at 98°, DTPA at 50°. The mixture of reagents was exposed in a constant temperature chamber for a definite time, then the redox equilibrium was "frozen" by rapid cooling of the reaction mixture with ice water. The reaction rate was estimated according to the change in the optical density ($D$) of solutions of $V(V)$ in a time ($\tau$). The reaction rate in more concentrated solutions was followed according to the change in the concentration of $V(V)$ and the complexone with time. The acidity of the solutions was monitored with an LPU-01 potentiometer.

**DISCUSSION OF RESULTS**

The kinetics of the redox interaction in the system $V(V)$—complexone was studied in two series of experiments: 1) in the presence of excess complexone; 2) under conditions in which the ratio $[V(V)] : [\text{complexone}]$ is close to the stoichiometric.

In the presence of excess complexone and a constant pH of the solutions, the logarithm of the optical density is a linear function of the time (Fig. 1). This is evidence of a first order of the reaction relative to $V(V)$

$$-\frac{d[V(V)]}{dt} = k'[V(V)]$$

where $k'$ is the observable first-order reaction rate, numerically equal to the slope of the kinetic curves ($\tan \alpha$) in a plot of $\log D$ versus $\tau$. In the presence of an excess of the complexone, the rate of the redox interaction does not depend on the concentration of the complexone (Table 1).

The kinetics of the oxidation of complexones by vanadium(V) under conditions of a small excess of vanadium in ratios $[V(V)] : [\text{complexone}]$, close to stoichiometric, was studied at higher concentrations of


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TABLE 1. Values of $k'$ for the Oxidation of Complexones by Vanadium (V)*

<table>
<thead>
<tr>
<th>$[V(V)] : [\text{complexone}]$</th>
<th>$k'_{H_A \cdot 10^4}$, sec$^{-1}$</th>
<th>$k'_{H_L \cdot 10^4}$, sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 5</td>
<td>3.62</td>
<td>1.01</td>
</tr>
<tr>
<td>1 : 6</td>
<td>3.50</td>
<td>1.04</td>
</tr>
<tr>
<td>1 : 7</td>
<td>3.45</td>
<td>1.06</td>
</tr>
<tr>
<td>1 : 8</td>
<td>3.60</td>
<td>1.02</td>
</tr>
<tr>
<td>1 : 9</td>
<td>3.60</td>
<td>1.02</td>
</tr>
<tr>
<td>1 : 10</td>
<td>3.65</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Average: $3.51 \pm 0.07$ (1.03 ± 0.02)

* $[V(V)] = 2.5 \cdot 10^{-4}$ M, $\mu = 1.0$ M, (NaClO$_4$); 1) $H_A$, pH 2.0; 2) $H_L$, pH 1.5. The order of the reaction relative to $V(V)$ and the complexone was determined simultaneously, monitoring the change in the concentrations of the two reagents with time. A linear function in the plot of log $[V(V)]_T/[\text{complexone}]$ versus $t$ for $H_L$ (Fig. 2a) and in a plot of $1/[\text{complexone}]$ versus $t$ for $H_A$ (Fig. 2b) ([$V(V)$])$_T$, [complexone]$_T$ are the concentrations of $V(V)$ and the complexone in solution at the moment of time $t$) is evidence of first order of the reaction with respect to each of the reagents

$$\frac{d[V(V)]}{dt} = k'_{[V(V)] : [\text{complexone}]},$$

where $k'$ is the observed rate constant of the second-order reaction. The values of $k'$, determined according to the slope of the kinetic curves of the second order reaction, are equal to: $k'_{H_A} = (2.16 \pm 0.15) \cdot 10^{-2}$; $k'_{H_L} = (3.39 \pm 0.25) \cdot 10^{-2}$, mole$^{-1}$, sec$^{-1}$, liter.$^\dagger$

Since complexones that are weak acids participate in the redox process, it might have been assumed that the rate of oxidation is a complex function of the acidity of the medium. Actually, the order of the oxidation of DTPA by vanadium(V) with respect to hydrogen (the slope of the straight line expressing the dependence of log$k'$ on log$[H^+]$ (Fig. 3)) varies from $-0.24$ (pH 1.0-1.2) to 1 (pH 1.5-1.9), while in the region of pH 1.2-1.5 it is equal to zero.

For the oxidation of complexones by vanadium(V) we calculated the activation energy from the temperature dependence of $k'$ (Fig. 4). The following values were obtained for the activation energies and preexponential factors: $H_A$, $E_{act} = (33.12 \pm 0.18)$ kcal/mole, $A = 3.8 \cdot 10^{18}$; $H_L$, $E_{act} = (20.05 \pm 0.10)$ kcal/mole, $A = 2.4 \cdot 10^{11}$

It is known that the oxidation of organic substances by vanadium(V) can proceed [8-10] through a step of formation of complex compounds, which then break down into derivatives of $V(IV)$ and organic radicals.

$^*$For $H_A$, treatment of the experimental data was performed in a plot of $1/[\text{complexone}]$ versus $t$ as a result of the fact that the initial concentrations of the two reagents were practically equal.

$^\dagger$The reaction kinetics was studied under the following conditions: $H_A$, pH 2.2, 98°, $\mu = 1.0$ M (NaClO$_4$); $H_L$, pH 0.96, 50°, $\mu = 1.0$ M (NaClO$_4$).

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Fig. 1. Dependence of log D on the time: 1) pH 2.0, 98°, $H_A$; 2) pH 1.5, 50°, $H_L$. $\mu = 1.0$ M (NaClO$_4$), $[V(V)] = 2.5 \cdot 10^{-4}$ M, $[V(V)] : [\text{complexone}] = 1 : 10$, $\lambda = 260$ nm.

Fig. 2. Kinetic curves of second-order reactions. a. $[V(V)] = 3.93 \cdot 10^{-2}$ M, $[H_L] = 2.40 \cdot 10^{-2}$ M, pH 0.96, $\mu = 1.0$ M (NaClO$_4$). b. $[V(V)] = 2.41 \cdot 10^{-2}$ M, $[H_A] = 2.43 \cdot 10^{-2}$ M, pH 2.2, $\mu = 1.0$ M (NaClO$_4$).