Chemical transformations initiated by gas discharges in aqueous solutions

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Abstract. The kinetic regularities of the processes of oxidation-reduction of chromium ions under the action of a direct current discharge of atmospheric pressure in air, oxygen and argon on an aqueous solution of potassium dichromate at currents of 20–60 mA and concentrations 0.092–0.4 mmol l\(^{-1}\) are investigated. The solution served as the cathode of the discharge. It was found that the effect of a discharge in any gas on a solution stimulates the reversible \(\text{Cr}^{6+} \leftrightarrow \text{Cr}^{3+}\) reactions of oxidation-reduction of chromium ions. The apparent constants of the rates of oxidation and reduction and their dependence on the discharge current and initial concentration are found. The energy efficiency of the process is estimated. It is shown that the discharge in argon is most effective for carrying out the reduction process.

1. Introduction
In the last 10–15 years, several hundred papers have been published concerning water purification using gas discharges [1–4]. Most of these studies are associated with oxidative destruction of organic substances. However, the work of enterprises in various industries leads to water pollution and inorganic pollutants. For example, salts of heavy metals, and, in particular, salts of chromium (VI), which are strong toxicants [5]. Usually, \(\text{Cr}^{6+}\) is converted to less harmful \(\text{Cr}^{3+}\) by chemical methods [6]. The resulting oxidation-reduction reactions are reversible. Therefore, in order to achieve an acceptable degree of recovery, an excess of reducing agents is necessary, leading to secondary water pollution. At the same time, it is known that under the action of different discharges on water, particles are formed in it, possessing both oxidizing and reducing properties [7, 8]. The atoms and molecules of hydrogen, solvated electrons, have a high reducing ability, while the radicals \(\text{OH}, \text{O}, \text{HO}_2\), hydrogen peroxide are good oxidizing agents. The formation of these particles occurs without any chemical reagents, which makes the use of discharges attractive.

Studies of redox processes with the participation of chromium ions under the action of the discharge are few. In a study [9], the reduction of \(\text{Cr}^{6+}\) in a discharge called Electrolysis by a Glow Discharge was investigated at a current of 100 mA and a concentration of 100 mg l\(^{-1}\), with the addition of phenol. An increase in the concentration of phenol from 0 to 500 mg l\(^{-1}\) led to an increase in the degree of reduction of \(\text{Cr}^{6+}\) from 0.5 to 0.7 in a time of 900 s. In [10], the decomposition of phenol and the reduction of \(\text{Cr}^{6+}\) under the action of a glow discharge in air were studied. The mutual influence of the components was found – an increase in the rates of both chromium reduction and phenol decomposition.
In work [11], the redox processes in an argon discharge at a current of 40 mA and a concentration of Cr\(^{6+}\) 80 mg\(\cdot\)l\(^{-1}\) (~1.5 mmol\(\cdot\)l\(^{-1}\)) were investigated. The maximum degree of recovery 0.8 was reached during the processing time of 900 s.

Simulation of chemical transformations occurring in a solution under the action of a discharge, carried out in [12], showed that the main reactions of Cr\(^{6+}\) reduction to Cr\(^{3+}\) are reactions involving hydrogen peroxide and HO\(_2\) radicals, and the reverse reactions leading to the formation of Cr\(^{6+}\) from Cr\(^{3+}\) are reactions the latter with OH and O\(_2\). Discharges in air, oxygen and argon, burning above the surface of the water, generate significantly different concentrations of these particles. The magnitudes of cathode potential drops, which determine the energy of ions bombarding the surface of the solution, and cause chemical transformations, also differ significantly [12–15]. Since air, argon and oxygen due to their cheapness are the most used for practical purposes, the purpose of this study was to compare the efficiency of discharges in these gases with respect to redox processes involving chromium ions.

### 2. Experimental setup and measurement methods

For the experiments, a set-up was used, whose scheme is shown in figure 1. The installation included a vacuum bell-jar, inside of which there was a vessel (70 ml) containing an aqueous solution of potassium dichromate of the analytical grade of the specified concentration. The concentration range was 0.092–0.39 mmol\(\cdot\)l\(^{-1}\) for the Cr\(^{6+}\) ion. Technical oxygen (99.7%), argon of spectral purity or ambient air at a flow rate of 3 cm\(^3\)\(\cdot\)s\(^{-1}\) and atmospheric pressure was passed through a set-up. The discharge was ignited by applying a constant voltage between the metal anode and the solution (cathode). The cathode-anode distance was 10 mm. The range of discharge currents was 20–60 mA.

![Figure 1. Schematic diagram of the experimental set-up. 1 – cathode, 2 – glass bell-jar, 3 – anode, 4 – discharge, 5 – quartz window, 6 – radiation output to entrance lens of light guide, 7 – glass cell with solution, 8,9 – gas outlet and inlet, 10 – entrance lens of light guide, 11 – light guide.](image)

The electric field strength in the positive column of the discharge and the drop in potential at the electrodes were calculated from the analysis of the dependences of the voltage change at the discharge gap on the distance of the metal electrode-electrolyte surface \(d\) using the moving anode method. After ignition of the discharge and stabilization of its current, the interelectrode distance was changed by an automatic system for moving the electrode with a programmable stepping motor with a speed of \(5\times10^{-4}\) m\(\cdot\)s\(^{-1}\). During the movement, the total voltage drop across the discharge gap and the solution was measured with a True RMS Fluke 280 precision voltmeter with a frequency of 1 measurement per
second. The discharge current was kept constant. The moment when the electrode touched the solution was noted by a sharp decrease in the recorded signal, after which the movement of the electrode stopped. The magnitude of this signal is equal to the voltage drop across the solution. The difference between the total voltage drop and the voltage drop across the solution is equal to the voltage drop across the discharge itself, $U$.

The obtained values of the voltage drop across the discharge gap at different interelectrode distances $U = f(d)$ were linearly approximated. The coefficient of pair correlation was not worse than 0.98. The angular coefficient of this dependence gives the electric field strength in the positive discharge column, $E$. Extrapolating the dependence to $d = 0$ gives the sum of the values of the near-electrode potential drops (cathode and anode, $U_c$ and $U_a$, respectively). For a discharge with a liquid cathode and a metal anode, $U_c >> U_a$, and the value cut off by the linear dependence $U = f(d)$ on the ordinate axis is the cathode potential drop near the liquid electrode.

The concentration of bichromate ions was determined spectrophotometrically by absorption at a wavelength of ~ 350 nm (maximum absorption band) [16]. For measurements, the Hitachi U-2001 spectrophotometer (Japan) was used. To find the total concentration of chromium ions the same method was used. For this chromium ions with an oxidation state of less than +6 were oxidized with ammonium persulfate in an acidic medium to $\text{Cr}^{6+}$ [17].

To obtain each time point of the kinetic curve, a fresh portion of the solution was used, and at least five independent measurements were made. Random errors in determining concentrations with a confidence probability of 0.95 are shown in the corresponding figures.

3. Measurement results and discussion

The action of the discharge in any of the gases led to the reduction of $\text{Cr}^{6+}$ ions (figure 2). Their concentration in time decreased. The presence of reduction was observed and visually – the color intensity of the solution decreases (initially yellow color). No sediment is formed. Therefore, the total concentration of chromium ions is preserved (figure 2).

The form of kinetic curves (the achievement of a constant concentration at large times) indicates that the process is reversible. Along with the reduction, oxidation takes place and the achievement of the concentration limit is determined by the equality of the rates of the oxidation-reduction processes. For convenience of comparison, we can get the following expression, formally describing the kinetic curve. Suppose that the reduction of $\text{Cr}^{6+} \rightarrow \text{Cr}^{3+}$ proceeds through the reaction of the 1st kinetic order
with the rate constant \( K_R \) and the oxidation of Cr\(^{3+} \rightarrow \) Cr\(^{6+} \) also has the 1st order with the rate constant \( K_o \). Since the total concentration \([C]\_0 = [\text{Cr}^{6+}(t)] + [\text{Cr}^{3+}(t)]\) is preserved, the solution of the kinetic equation for the concentration \([\text{Cr}^{6+}(t)]\) is:

\[
[\text{Cr}^{6+}(t)] = \frac{[\text{Cr}]_0}{K_o + K_R} \times \{K_R \times \exp[-(K_R + K_o) \times t] + K_o\} \tag{1}
\]

The equation (1) well described the experimental kinetic curves (figure 2, solid lines). The coefficient of determination in all cases was not worse than \( R^2 \geq 0.98 \).

From (1) it follows that the limiting degree of reduction \( \alpha \) (as \( t \to \infty \)) is defined as

\[
\alpha(\infty) = \frac{K_R}{K_R + K_o} = \frac{[\text{Cr}^{6+}(t = \infty)]}{[\text{Cr}]_0} \tag{2}
\]

These rate constants are effective and include the concentration of active particles involved in redox processes. Therefore, they depend not only on the type of plasma-forming gas, but also on the discharge current and the initial concentration of the solution.

From the point of view of the recovery rate, the discharge in argon proved to be the most effective. Thus, for a discharge current of 40 mA and an initial concentration of 0.092 mmol\( \cdot \)l\(^{-1} \), the reduction rate constants were \((1.1 \pm 0.2) \times 10^{-2}, (2 \pm 0.4) \times 10^{-3}, \) and \((4 \pm 0.7) \times 10^{-3} \) s\(^{-1} \) for argon, oxygen and air, respectively. The same can be seen from figure 2. An increase in the discharge current had little effect on the rate constants. At the same time, an increase in the initial concentration led to a decrease in the rate constants of the recovery (figure 3).

**Figure 3.** Effective recovery rate constant at discharge in argon depending on the initial concentration. 1, 2, 3 – discharge currents 20, 40, 60 mA, respectively.

Since the change in concentration does not affect the electrical parameters of the discharge, the decrease in the rate constant is due to the fact that the rate of formation of active particles under the action of the discharge becomes the limiting stage of redox processes. The obtained data on the magnitudes of the cathode potential drops \( U_c \) and the electric field strengths \( E \) make it possible to compare the energy efficiencies \( \eta \) of discharges in different gases using the relation

\[
\eta = \frac{W \times V \times N_d}{I \times (U_c + E \times L)} \tag{3}
\]
where $W$ (mol·l$^{-1}$·s$^{-1}$) the reduction rate when $t \to 0$, $V = 0.07$ is the volume of the solution, $N_A = 6.02 \times 10^{23}$ is the Avogadro number, $I$ (A) is the discharge current, $L = 10^{-2}$ m – distance cathode anode.

For a discharge current of 40 mA, $U_c$ values were 285, 480, and 600 V, and $E = 180, 300, 600$ V·cm$^{-1}$ for argon, oxygen, and air, respectively. The calculation for an initial concentration of 0.1 mmol·l$^{-1}$ gives $\eta$ values equal to $2.6 \times 10^{15}$, $1.8 \times 10^{14}$, and $4.7 \times 10^{13}$ chromium ions per one joule of input energy for Ar, O$_2$, and air, respectively. Despite the fact that the discharge rate constants are larger in the air than in the O$_2$ discharge, the energy efficiency of the discharge in O$_2$ is higher. The reason is that in order to maintain the same current, the discharge in the air requires higher power.

The results of determining the limiting degrees of reduction by the equation (2) are shown in figure 4. An increase in the initial concentration leads to a decrease in $\alpha(\infty)$. The reasons for the decrease have already been discussed. The weak dependence on the discharge current is caused by the weak dependence of $K_R$ and $K_o$ on the current. For all plasma-forming gases studied, the values of $\alpha(\infty)$ are close, but the kinetically limiting value for the discharge in Ar is established most quickly due to the larger rate constants (the characteristic time is $(K_o + K_R)^{-1}$).

![Figure 4](image)

**Figure 4.** Dependence of the limiting degree of recovery on the initial concentration at different currents. 1, 2, 3 – discharge currents of 60, 40 and 20 mA, respectively (O$_2$). 4, 5 – Ar and air, respectively, for a current of 40 mA.

4. Conclusion

The effect of atmospheric pressure glow discharge in argon, air, and oxygen on an aqueous solution containing chromium ions stimulates the course of oxidation-reduction processes. The degrees of reduction and the rate constant depend on the initial concentration of the solution. The discharge in argon is the most efficient among the gases studied. Its application ensures the achievement of the limiting degree of reduction in a minimum time.

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