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Determination of the Oxidation-Reduction Potentials of *p*-Oxyphenylglycine

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There is still no generally accepted explanation of the mechanism and regularities of the photographic development process. The explanations given by the so-called "electrochemical" theory of development, unlike other theories, have not only a qualitative character but, in principle, also allow quantitative verification ([1]). For this it is necessary to know the values of the electrochemical potentials of the silver particles of the developed photographic image and the oxidation-reduction potentials of developing substances at various pH values and in the presence of the other components of the developer.

Fig. 1. Reaction vessel: **1** –saturated calomel electrode; **2** –burette; **3** –microburette; **4** –inlet for purified nitrogen; **5** –platinum electrode; **6** –stirrer with liquid seal; **7** –gas valve

Measurement of the oxidation-reduction potentials of developing substances presents considerable difficulties because of the easy oxidizability of these substances and the instability of the oxidation products. Consequently, it proves impossible to use the "mixture method" ([2],[3]), while methods based on titration with oxidants ( ) can be used only on the condition that the titration is carried out in an atmosphere of an inert gas containing minimal amounts of oxygen. Therefore, the amount of data available in the literature on the oxidation-reduction potentials of developing substances at different pH values is very limited. More complete data are available for *p*-aminophenol, methyl-*p*-aminophenol (metol), and hydroquinone (-). For limited pH intervals there are also data for several other substances ( ).

We set ourselves the goal of experimentally determining the oxidation-reduction potentials of *p*-oxyphenylglycine ("glycine") at various pH values. The choice of this substance was dictated by the fact that it is used in photographic practice and is a structural analogue of the well-studied metol and *p*-aminophenol; therefore, the data obtained could be used for comparison.

The measurements were carried out by oxidative titration with a smooth platinum electrode of 0.03 M solutions of *n*-oxyphenylglycine in an atmosphere of nitrogen, carefully purified from oxygen and other impurities. A description of the method of nitrogen purification and of the methods for checking its completeness is given in article (10). The solution being titrated was in the reaction vessel (see Fig. 1), which was placed in a water thermostat at a temperature of 25°. The potentials were measured relative to a saturated calomel electrode. *n*-Oxyphenylglycine was thoroughly purified. The constancy of pH was maintained by the presence in the solution being titrated of salts forming buffer systems. At pH from 1 to 6 a mixture of HCl, KCl, and potassium biphthalate was used; at pH from 6 to 11, a mixture of borax, HCl, and NaOH (11). The pH measurements were carried out with a glass electrode. During the titration no change in pH was observed. In an acid medium a solution of $Ce(SO_4)_2$ was used as the oxidizing agent, and in an alkaline medium a solution of $K_3[Fe(CN)_6]$.

In titration experiments with *n*-oxyphenylglycine in an acid medium it was found that the titration curve has two potential jumps: the first corresponds to 2 oxidizing equivalents of cerium(IV) sulfate, and the second, more significant one, corresponds to 4 equivalents of cerium(IV) sulfate per 1 mole of *n*-oxyphenylglycine. In back titration only one potential jump is observed, corresponding to 4 equivalents of cerium(IV) sulfate per 1 mole of *n*-oxyphenylglycine. This is explained by the fact that under these conditions the oxidation reaction proceeds in the presence of an excess of oxidizing agent. In an alkaline medium, both in direct and in back titration, only one potential jump is observed, corresponding to 4 equivalents of $K_3[Fe(CN)_6]$ per 1 mole of *n*-oxyphenylglycine.

Special experiments established that the oxidized form, both at the first and at the second stages of oxidation, remains for some time in solution without change, and that the oxidation reaction proceeds reversibly. There are grounds to suppose that the oxidation of *n*-oxyphenylglycine in an acid medium proceeds according to the scheme:

$$1)\ [p\text{-}HOC_6H_4NHCH_2COOH] + 2Ce(SO_4)_2 + H_2O = [p\text{-}C_6H_4O_2] + NH_2\text{-}CH_2\text{-}COOH + Ce_2(SO_4)_3 + H_2SO_4 \quad (1)$$

$$2)\ p\text{-}C_6H_4O_2 + NH_2\text{-}CH_2\text{-}COOH \xrightarrow{(H_2SO_4)} HO\text{-}C_6H_3(O)\text{-}NH\text{-}CH_2\text{-}COOH \longrightarrow HO\text{-}C_6H_3(OH)\text{-}NH\text{-}CH_2\text{-}COOH \quad (2)$$

3) [reaction scheme: hydroxyphenylglycine with two OH groups plus cerium sulfate forming quinonoid product plus cerium(III) sulfate and sulfuric acid]

The overall equation may be written as follows:

[overall reaction scheme: hydroxyphenylglycine plus $4Ce(SO_4)_2$ and water forming quinonoid product plus $2Ce_2(SO_4)_3$ and $2H_2SO_4$]

The obtained values of the oxidation-reduction potentials of *n*-oxyphenylglycine at various pH values are given in Table 1

Table 1

pH	1.04	1.97	2.96	4.03	4.98	6.96	8.02	9.04	9.98	10.9
E_n, mV	670.0	616.0	559.0	499.0	439.0	323.0	267.0	209.0	164.0	116.0

and in Fig. 2, where, in addition to the curve $E_n = f(\text{pH})$ for *n*-oxyphenylglycine, curves are given for *n*-aminophenol and metol. The reported values of E_n were obtained from the curves of potentiometric titrations of *n*-oxyphenylglycine at various pH values and correspond to the points $\frac{[\text{Ox}]}{[\text{Red}]} = 1$, under the condition that 4 equivalents of oxidant are consumed per 1 mole of *n*-oxyphenylglycine. From Fig. 2 it is seen that the dependence $E_n = f(\text{pH})$ for *n*-oxyphenylglycine in the pH interval from 1.0 to 9.0 is a straight line without breaks. This means that the basic dissociation constant of *n*-oxyphenylglycine is considerably smaller than the acidic one. The values of these constants cannot in this case be determined from the curve $E_n = f(\text{pH})$. Nor can they be determined by the usual methods, since the oxidized form of *n*-oxyphenylglycine cannot be isolated in pure form. Therefore we were unable to express analytically the dependence $E_n = f(\text{pH})$, as was done by Fieser (5) and Bogdanov (6,7) for *n*-aminophenol and metol.

Fig. 2. Dependence of E_n on pH for *n*-oxyphenylglycine with transfer of $4e$ (1), with transfer of $2e$ (4), metol (2), and *n*-aminophenol (3)

Fig. 3. Change in the rate of reduction of silver nitrate: 1—by *n*-oxyphenylglycine; 2—by metol; 3—by *n*-aminophenol

Comparison of the curves $E_n = f(\text{pH})$ for *n*-oxyphenylglycine, metol, and *n*-aminophenol shows that in an acidic medium the E_n of *n*-oxyphenylglycine is more negative than the E_n of metol and *n*-aminophenol, whereas in an alkaline medium it is more positive than theirs.

We found that the reduction reaction of $AgNO_3$ by *n*-oxyphenylglycine in an acidic medium proceeds faster than the reduction reaction of $AgNO_3$ by metol and *n*-aminophenol (Fig. 3). It is known from photographic practice that an alkaline glycine developer works more slowly than *n*-aminophenol and metol developers. These facts are well explained by the above-noted relationship among the E_n potentials of these substances at different pH values. Thus, experiment reveals precisely those relationships among the rates of the silver-ion reduction reaction that could be expected on the basis of the electrochemical theory of development.

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Note: Figure translations are in progress. See original paper for figures.