I. S. Shchegoleva, A. V. Egunov, T. S. Glikman, V. Ya. Dain

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I. S. Shchegoleva, A. V. Egunov, T. S. Glikman, V. Ya. Dain

PHOTOCHEMICAL AND RADIATION-CHEMICAL REDUCTION OF SILVER PERCHLORATE IN THE PRESENCE OF ORGANIC SUBSTANCES

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It is known that the yields of certain radiation-chemical reactions in aqueous solutions can be increased by introducing extraneous additives. The action of these additives is usually explained by their ability to bind the "radical" products of water radiolysis—free hydroxyls or hydrogen atoms. It is of interest, however, that such an effect of additives is also observed in certain photochemical processes, to which the above explanation cannot be extended. Thus, for example, salts of silver, mercury, and trivalent iron, which under ordinary conditions are only slightly sensitive to light in aqueous solutions, readily undergo photochemical reduction in the presence of a number of organic substances. It has been suggested that this increase in sensitivity to light is caused by complex formation, as a result of which new compounds capable of photochemical transformations arise in the system ([1]). However, this hypothesis, applicable only to photoprocesses, has not yet been tested by direct methods.

In order to determine whether there is anything common in these photochemical and radiation-chemical effects, we undertook a parallel study of the action of light and of X-radiation on solutions of silver perchlorate in the presence of a number of organic substances and in their absence. The photochemical experiments were carried out in a cylindrical glass vessel with a quartz upper base. The light source was a PRK-7 mercury lamp operating in a steady regime. The light was filtered through a 0.02 M NaOH solution, which cut off the short-wavelength part of the spectrum below 2000 Å, thereby excluding the possibility of direct photochemical decomposition of water. The experiments were conducted under conditions of practically complete absorption of the active ultraviolet radiation.

The source of ionizing radiation was an X-ray installation with a BKhV-80 tube ([2]), operating at a voltage of 70 kV and a current of 100 mA. The irradiated solution was in a cuvette made of molybdenum glass, one wall of which, directed toward the source, was a thin glass membrane. The dose rate of the absorbed radiation, determined with a ferrosulfate dosimeter, was in all experiments equal to $5.6 \cdot 10^{16}$ eV/ml · sec. In both the photochemical and the radiation-chemical

Fig. 1

Figure 1: Fig. 1

experiments, a stream of argon was bubbled through the solution during irradiation and, before it, for 20 min in order to remove dissolved oxygen.

Irradiation, under the described conditions, of an aqueous solution of $AgClO_4$ ($C = 0.035\,M$) with ultraviolet light, as well as with X-radiation, does not lead to noticeable reduction of Ag^+ ions in the absence of additives. However, the introduction into the solution of even insignificant amounts of methanol makes it sensitive both to ionizing radiation and to the light of the mercury source. At higher concentrations of the additive, comparable with the concentration of the silver salt, already distinct radiation and photochemical reactions of silver reduction are observed. The amount of formed

formed during the radiolysis of silver is proportional to the dose, which made it possible to determine the values of G for this reaction. The experiments showed that these values depend strongly on the concentration of methanol, increasing noticeably as it is increased. At an alcohol concentration of $0.25\,M$ per liter, G already reaches a value of 6.8. With further increase in concentration, the growth of the yields slows greatly and even at $C_{CH_3OH} = 3M$ does not exceed 8 atoms per 100 eV. It remains approximately the same in a purely alcoholic solution. The dependence of the process yield on the methanol concentration is illustrated in Fig. 1, *I*.

Fig. 1. Dependence of the yields of the radiation-chemical (I) and photochemical (II) reduction reactions of $AgClO_4$ on the concentration of methyl alcohol.

Other alcohols (ethanol, butanol, ethylene glycol, glycerin), as well as urea, exert a "sensitizing" action analogous to that of methanol. The pattern of increase of the G values with increasing concentration of these additives is the same as for methanol. Table 1 compares the values of G for various additives at the same concentration ($0.5\,M$ per liter).

It is interesting that all additives "sensitizing" the radiation-chemical process are also capable of inducing the photochemical reduction reaction. As characteristics of the photoprocesses, data were used on the number of g-atoms of silver formed during 30 min of irradiation—L. With the source constant and the active light practically completely absorbed, these values for various additives are proportional to the corresponding quantum yields*. Experiments showed that the yields of the photochemical reactions increase with increasing concentrations of additives according to the same law as was noted above for the radiation-chemical reactions, namely: a rapid rise at low concentrations and a slow rise, dying away at high concentrations (see curve II, Fig. 1). In this case as well, the maximum yield, attained at approximately a concentration of $1\,M$, is retained in a purely alcoholic solution.

Table 1

Additive	G	$L \cdot 10^3$
Methanol	7.6	6.5
Ethanol	6.5	5.8
Butanol	6.3	5.1
Ethylene glycol	5.8	4.8
Glycerin	5.0	3.3
Urea	2.8	1.0

The analogy between the photochemical and radiation reactions goes so far that even the activity series of the additives coincide for both types of irradiation. This is clearly seen from comparison of the data in Table 1. The values of L in Table 1 are given without corrections for internal filtration of light by the additives. Since, owing to the strong absorption of light by Ag^+ ions, the reaction proceeds in the thinnest layer, the effect of internal filtration for all additives (except urea) proves to be so small that it may be neglected.

Figure 2 gives the absorption spectra of $AgClO_4$ in water and in several alcohols. Their comparison leads to the conclusion that replacement in the ion environment of water molecules by alcohols has a pronounced effect on the spectra. Nevertheless, this cannot explain the increased photosensitivity of the alcohol-water solutions. The latter is already clearly observed at rather low alcohol concentrations (see Fig. 1). Meanwhile, as separate measurements have shown even at ethyl alcohol concentrations in an alcohol-water mixture on the order of 7 moles per liter, the spectrum of $AgClO_4$ remains in all respects similar to its spectrum in aqueous solution. It follows from this that the displacement of water by alcohol in the environment of the Ag^+ ion takes place with difficulty, and the primary photochemical act is carried out, over a wide range of concentrations in our experiments, on hydrated ions.

The absorption band of Ag^+ ions in aqueous solution, with a maximum at 210 mμ, belongs to the type of charge-transfer spectra (3). This means that excitation of the ion as a result of absorption of a quantum of light leads to a partial displacement of an electron from the hydration environment of the ion to the central Ag^+ ion

$$Ag^+,\ H_2O \xrightarrow{h\nu} Ag,\ H_2O^+\cdot\,. \tag{1}$$

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* Using a monochloroacetic actinometer, we estimated the quantum yield of the photoreaction at concentrations of $AgClO_4$ and ethanol of $0.035\,M$ and $0.5\,M$, respectively. It proved to be 0.067.

This elementary act must necessarily be accompanied by the reverse process (2), associated with the release of energy:

$$\mathrm{Ag},\ \mathrm{H_2O^+} \rightarrow \mathrm{Ag}^+,\ \mathrm{H_2O}. \tag{2}$$

There is a certain probability that the primary act will be followed by an act of decomposition of the complex Ag, H_2O^+

$$\mathrm{Ag},\ \mathrm{H_2O^+} \rightarrow \mathrm{Ag} + \mathrm{H^+} + \mathrm{OH}. \tag{3}$$

However, process (3) is practically completely suppressed by process (4), which proceeds inside the solution “cage” and is therefore very effective,

$$\mathrm{Ag} + \mathrm{H^+} + \mathrm{OH} \rightarrow \mathrm{A^+},\ \mathrm{H_2O}. \tag{4}$$

This explains why, in the absence of additives, reduction of silver does not take place. The introduction of additives—electron donors—sharply changes the situation, since secondary processes then arise, schematically represented by equations (5) and (6):

Fig. 2. Absorption spectra of $AgClO_4$.
1 —in water; 2 —in ethyl alcohol; 3 —in methyl alcohol; 4 —in ethylene glycol; 5 —in glycerol

and

$$\mathrm{Ag},\ \mathrm{H_2O^+} + \mathrm{D} \rightarrow \mathrm{Ag} + \mathrm{D}'\ (+\mathrm{H_2O}) \tag{5}$$

$$\mathrm{OH} + \mathrm{D} \rightarrow \mathrm{D}' + \mathrm{OH}^-. \tag{6}$$

Here D and D′ conventionally denote the molecules of the additives and the products of their destruction.

If the reaction (6), which cannot compete with reaction (4), proceeding inside the solution “cage,” is neglected, then we arrive at the kinetic equation:

$$\frac{d\,\mathrm{Ag}}{dt} = \frac{k_1 k_5 I[\mathrm{D}]}{k_2 + k_3 + k_5[\mathrm{D}]}. \tag{7}$$

With a certain ratio of the values of the constants, this equation corresponds to the experimental data, reflecting a rapid increase in yield at low concentrations and a slow, decaying increase at higher concentrations of additives.

Along with the mechanism described, another mechanism, not associated with kinetic collisions, must also play a certain role. The appearance of a charge defect in the hydration shell of the excited ion as a result of the primary act (1) can readily be compensated by charge displacement from the introduced donor. This will reduce the probability of the reverse process (2) and will lead to the reduction of silver and to destructive oxidation of the additive. For

For such charge displacement there is no need for direct contact of the excited ion with the electron donor. It will occur through a series of water molecules along a chain of hydrogen and sigma bonds (4) and, by virtue of the Franck-Condon principle, constitutes an instantaneous elementary act unified with the act of excitation. Ultimately, its result will be electron transfer from the additive molecule to the Ag^+ ion.

The probability of such a charge-displacement act will depend on a number of factors and, in particular, on the concentrations and spatial coordination of the additives. Thus, an increase in the yield must reach a limit when the coordination most favorable for charge transfer has been achieved in the system. According to all the data, such optimal conditions are created long before all coordination sites around the Ag^+ ions are replaced by molecules of the organic substance. This explains the fact that at high alcohol concentrations the yield is almost the same as in a purely alcoholic solution. As this state is approached, the increase in yield gradually slows. The mechanism of the radiation-chemical reaction is more difficult to analyze. Undoubtedly, it must vary strongly depending on the concentration of the organic substance, since with an increase in the latter the probability of its direct interaction with the products of water radiolysis will increase, as will the effect of direct action and the possibility of formation and participation of organic radicals in the reaction. It is interesting, however, that despite all the possible diversity of mechanisms in this case, the activity series of organic additives and the general regularity of the growth of yield with their concentration coincide for the photochemical and radiation-chemical reactions. This gives grounds to suppose that the radiation-chemical processes in the systems under consideration arise not only with the participation of solvent radicals, but also, to a considerable extent, as a result of excitation of silver ions. The possibility of formation of excited states of a dissolved substance under the action of ionizing radiation on aqueous solutions has already been noted repeatedly (5).

Institute of Physical Chemistry
named after L. V. Pisarzhevskii
Academy of Sciences of the Ukrainian SSR

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