PHYSICAL CHEMISTRY

V. F. Tsepalov and I. Ya. Shlyapintokh

1957

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

V. F. Tsepalov and I. Ya. Shlyapintokh

ON INTERMEDIATE PRODUCTS IN OXIDATION-REDUCTION PHOTOREACTIONS OF XANTHENE DYES

(Presented by Academician A. N. Terenin, 12 IV 1957)

The xanthene dyes eosin, erythrosin, and Bengal rose are often used as photosensitizers for oxidation and polymerization processes. According to the generally accepted point of view, in such photosensitization reactions the process is carried out by cyclic oxidation–reduction reactions of the dye with the components of the system. At the end of each cycle the dye is regenerated, while either final or active intermediate products arise in the system, in whose composition the dye is not included.

For the study of the photoreduction and photooxidation reactions of xanthene dyes, a potentiometric method was used, the applicability of which to the study of oxidation–reduction photoreactions was convincingly demonstrated in recent years by the work of the Laboratory of Photobiochemistry of the Institute of Biochemistry of the Academy of Sciences of the USSR, using as an example the photoreduction reaction of chlorophyll, its analogues, and related compounds (^1). In these works, measurements of the kinetics of the change in potential of an inert electrode immersed in the illuminated solution containing the pigment and the reducing agent, as well as measurements of photoconductivity, made it possible to establish the stagewise character of the reduction process and to detect a very active intermediate product of this reaction. In our work, measurements of the photogalvanic effect also made it possible to register the formation of intermediate products in the oxidation–reduction reactions of a number of dyes. It should also be noted that the clearly expressed stagewise nature of the process makes it possible to use, in its study, the new techniques proposed in the works of N. M. Emanuel' (^3) for investigating complex reactions (by changing the conditions and influences during the course of the process).

The experiments were carried out in a vessel with platinum electrodes, the construction of which is described in (^16). One of the knees of this vessel was darkened, while the other was illuminated by an SVDSh-250 lamp. The light of the lamp was collected by a condenser, passed through a cuvette with a solution of $CuSO_4$, a heat-protective filter SZS-14, and light filters ZhS-11, ZhS-18, and SZS-18, transmitting the region 500-550 mμ. The vessel was placed in a transparent Dewar filled with methanol, at the focus of the light source. Photopotentials were measured with a tube potentiometer of the LP-5 type.

Fig. 1

Figure 1: Fig. 1

In complete agreement with the results obtained with chlorophyll, pheophytin, and other pigments, we found that illumination of an alcoholic or pyridine solution of a xanthene dye ($C = 10^{-6}$—10^{-3} mole/l) in the presence of oxygen leads to a shift of the electrode potential in the positive direction; illumination in the presence of reducing agents (alcohol, pyridine, ascorbic acid, aldehyde) shifts the electrode potential in the negative direction. These experiments show that, in the cases investigated, the sign of the photopotential in the dye–oxygen system is determined by the oxidation products, and in the dye–reducing agent system–

products of reduction. Figure 1 shows kinetic curves of the change in the potential of a platinum electrode immersed in a pyridine solution of eosin containing ascorbic acid as a reducing agent. The measurements were carried out at different light intensities from $I = 1$ to $I = 0.08$. As is seen from the curves shown, upon illumination the electrode potential falls, reaches a certain minimum, and then rises again, returning to its initial value. By the time when the potential of the illuminated electrode again assumes its initial value, the eosin has completely faded. Switching off the light at any stage of the process of potential change leads to a shift of the potential toward positive values. The electrode potential is shifted in the same direction by the addition of oxygen. However, upon addition of oxygen the potential changes many times faster. The change in potential when the light is switched off or oxygen is added corresponds to an increase in the absorption of the original dye. Thus, both when the light is switched off and when oxygen is introduced, partial or complete reversal of the reaction is observed.

Fig. 1. Kinetics of the change in potential at different light intensities and eosin concentrations. Reducing agent–ascorbic acid ($1,2 \cdot 10$ mol/l).
1 –$I = 1,\ C_\mathrm{e} = 4 \cdot 10^{-6}$ mol/l;
2 –$I = 0.32,\ C_\mathrm{e} = 4 \cdot 10^{-6}$ mol/l;
3 –$I = 0.08,\ C_\mathrm{e} = 4 \cdot 10^{-6}$ mol/l;
4 –scales at right and bottom, $I = 1,\ C_\mathrm{e} = 4 \cdot 10^{-5}$ mol/l.

Judging from the form of the kinetic curves (Fig. 1), it could be assumed that the observed change in photopotential is connected with the existence of an intermediate product. In the first stage of the reaction, from the beginning to the minimum of the potential, there is an accumulation of an intermediate product that changes the electrode potential. At the point of the minimum, the rate of formation of the intermediate product is equal to the rate of its consumption. On the right-hand branch of the curve, owing to the decrease in the concentration of the initial dye, the rate of disappearance of the intermediate product W_2 is greater than the rate of its formation W_1, and therefore the potential gradually rises. From this point of view, the dependence of the kinetics of the potential

Fig. 2

Figure 2: Fig. 2

change on the light intensity is also understandable. As is seen from Fig. 1, the initial rate of the potential change is proportional to the intensity of the absorbed light I_{abs}. For this reason, at larger values of I_{abs}, higher concentrations of the intermediate product and, correspondingly, lower values of the potential should be reached. In addition, when the rate of formation of the intermediate product is increased and the rate constant of its consumption remains unchanged, the point of the minimum should shift toward the origin of coordinates. From Fig. 1 it is seen that this is indeed observed experimentally.

The considerations set forth also explain the dependence of the kinetics of the potential change on the concentration of the dye observed in the experiments. Increasing the concentration of eosin, which leads to an increase in the amount of absorbed light, affects the kinetics of the process in general in the same way as increasing the light intensity. A difference is observed only in the case in which much more eosin is taken than is needed for complete absorption of the light. In this case (curve 4, Fig. 1) the potential also falls rapidly, but then remains constant for a long time. If one takes into account that, at a high initial eosin concentration, so long as the solution absorbs all the incident light, the rate of formation of the intermediate product remains unchanged, then such a course of the potential can be explained by the fact that in the section *ab* a stationary concentration of the intermediate product is reached.

With decreasing temperature, the rate of return of the poten-

potential (Fig. 2). This rate remains very small even after the light is switched off. Thus, the nature of the dependence of the kinetics of the potential change on temperature clearly indicates the stepwise character of the reduction process. The stage of formation of the intermediate product is photochemical. Its rate does not depend on temperature. The second stage—the further reaction of the intermediate product—is dark and requires thermal activation. It is seen from Fig. 2 that, when the temperature is lowered, there is a strong increase in the depth of the potential drop and a shift of the minimum point toward longer times. These facts find a natural explanation within the framework of the consideration expressed above concerning the ratio of the rates of formation and consumption of the intermediate product.

Fig. 2. Kinetics of the change in potential at different temperatures in pyridine. Reducing agent—ascorbic acid ($1.2 \cdot 10^{-2}$ mol/l).
1—$C_{\text{e}} = 4 \cdot 10^{-6}$ mol/l, $t = 21°$;
2—$C_{\text{e}} = 4 \cdot 10^{-6}$ mol/l, $t = -33°$.
The arrow indicates the moment at which the light was switched off.

Experiments in which the concentration of the reducing agent was varied showed that the reducing agent participates in the reaction consuming the intermediate product. For this reason, when butyraldehyde is used—a weaker reducing agent than ascorbic acid—a slower return of the potential to its initial value after passing through the minimum is observed. The nature of the solvent has a strong effect on the rate of reaction of the intermediate product with the reducing agent. Thus, in ethanol the first stage of the photoreaction of eosin with the reducing agent proceeds as rapidly as in pyridine, while the second is many times slower. In both solvents the intermediate product reacts more rapidly with ascorbic acid than with butyraldehyde.

If a solution of eosin in ethanol is illuminated in the absence of a reducing agent and oxygen, a drop in potential is likewise observed during illumination; moreover, the process proceeds much more slowly than in the presence of a reducing agent. Under prolonged illumination, bleaching of the dye is observed. After the light is switched off, the potential returns very slowly to its initial value. If the temperature of the solution is lowered to −80, −90°, no appreciable change in potential occurs upon illumination, and the dye does not bleach. These experiments indicate that, in the absence of a reducing agent, slow photoreduction of the dye by the solvent occurs. The photochemical stage requires considerable activation energy. Similar phenomena are also observed in the pyridine—eosin system. It should also be noted that the photochemical stage of the reduction reaction of eosin by a weak reducing agent—butyraldehyde—has a significant temperature coefficient.

Figure 3 gives curves of the change in potential during the photoreduction reaction of eosin, erythrosin, and Bengal rose by butyraldehyde in pyridine solution. It is seen from Fig. 3 that the kinetic curves in the case of all three dyes prove to be similar. Therefore it may be assumed that, in the photoreduction of erythrosin and Bengal rose, as in the photoreduction of eosin, the first stage of the reaction consists in the formation of an intermediate product. The intermediate products can also be recorded by another method, namely by measuring the electrical conductivity of the solution during the course of the reaction. The corresponding curves of Fig. 3 ob—

correspond to extrema; in this case, the minimum of the potential corresponds to the maximum resistance of the solution. Consequently, the curves of change in potential and resistance describe one and the same process—the process of formation and consumption of the intermediate product.

Upon illumination of solutions of xanthene dyes in the presence of oxygen, kinetic curves without an extremum are obtained: the electrode potential gradually increases and after 20-30 min assumes a certain constant value. Measurements carried out on the reversibility of the reaction after switching off the light showed that, at short illumination times,

Fig. 3. Kinetics of changes in the potential and resistance of dye solutions in pyridine. Reducing agent—oily aldehyde (0.1 mol/l). 1, 2, 3—potential; 1′, 2′, 3′—resistance; 1, 1′—eosin; 2, 2′—erythrosin; 3, 3′—Bengal rose.

Fig. 4. Kinetics of change in the potential during photooxidation of chlorophyll

Fig. 3. Kinetics of changes in the potential and resistance of dye solutions in pyridine. Reducing agent—oily aldehyde (0.1 mol/l). 1, 2, 3—potential; 1′, 2′, 3′—resistance; 1, 1′—eosin; 2, 2′—erythrosin; 3, 3′—Bengal rose

Figure 3: Fig. 3. Kinetics of changes in the potential and resistance of dye solutions in pyridine. Reducing agent—oily aldehyde (0.1 mol/l). 1, 2, 3—potential; 1′, 2′, 3′—resistance; 1, 1′—eosin; 2, 2′—erythrosin; 3, 3′—Bengal rose

Fig. 4. Kinetics of change in the potential during photooxidation of chlorophyll by air in ethanol

Figure 4: Fig. 4. Kinetics of change in the potential during photooxidation of chlorophyll by air in ethanol

by air in ethanol.

considerable reversibility is observed, whereas at long times the system becomes practically irreversible.

We also found differences in the reversibility of the photoreaction at short and long illumination times in the photooxidation of chlorophyll a + b, during which a comparatively stable intermediate product is formed (Fig. 4). This product was previously detected by A. A. Krasnovskii by the spectral method (^{2}). Thus, from the example of the photooxidation reaction of chlorophyll, it is evident that differences in reversibility can be explained by the formation of an intermediate product. However, measurements of the reversibility of the eosin oxidation reaction, performed by the potentiometric method alone, do not unambiguously prove the existence of an intermediate product of oxidation of the dye itself, since the bleaching process is complex. It may include not only the reaction of the dye with oxygen, but also sensitized oxidation of the solvent and reactions of solvent oxidation products with the dye. Therefore, to prove the existence of intermediate products in the oxidation of xanthene dyes, further investigations are necessary.

Received7 II 1957

CITED LITERATURE

1. V. B. Evstigneev, V. A. Gavrilova, DAN, **92**, 381 (1953); **95**, 841 (1954); **96**, 1201 (1954); **98**, 1017 (1954).

2. A. A. Krasnovskii, DAN, **58**, 617 (1947).

3. N. M. Emanuel, Scientific Notes of Moscow State University, issue 174 (1955).

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