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I. I. Dilung, V. E. Karpitskaya

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Abstract**Full Text**

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PHYSICAL CHEMISTRY

I. I. Dilung, V. E. Karpitskaya

PHOTOCHEMICAL OXIDATION OF CHLOROPHYLL *a* IN FROZEN SOLUTIONS

(Presented by Academician A. N. Terenin, 27 IV 1963)

At present it may be regarded as generally accepted that the basis of the photochemical oxidation of chlorophyll by oxygen is the act of interaction of triplet-excited pigment molecules with oxygen, occurring during kinetic collisions (¹). Meanwhile, for condensed systems, where favorable conditions exist for associative interactions, it may be assumed that electron transfer can also take place in a single photoact, within complexes of chlorophyll with oxygen formed under dark conditions. This type of photoreaction was described in our earlier work (²) using, as an example, the reduction of chlorophyll by stannous chloride.

To elucidate the possibility of intracomplex photooxidation, in the present work we studied the photochemical oxidation of chlorophyll by oxygen in solutions frozen at the temperature of liquid air, in which the kinetic motions of the molecules are practically completely inhibited. In addition, a spectrophotometric study was carried out of the dark interaction of chlorophyll solutions with oxygen. Chlorophyll *a* was obtained from nettle leaves by the method of Shchegl and Komar (³). Thoroughly purified and dried ethyl alcohol, benzene, toluene, chloroform, and carbon tetrachloride were used as solvents.

For carrying out photochemical experiments and recording absorption spectra at low temperatures, the cryostat shown in Fig. 1 was used. It is a transparent Dewar vessel with a duralumin block inside it. The chlorophyll solution, in a flat, elongated cuvette, was placed in the vertical channel of the block, while irradiation and recording of its absorption spectra were carried out through the horizontal through-channel. Liquid air was poured into the Dewar vessel up to a level located somewhat below the horizontal channel of the block. This level of liquid air was maintained throughout the entire experiment.

Fig. 1. Cryostat for studying the absorption spectra and photochemical properties of frozen solutions

The solution was irradiated with red light from a 1000-watt cinema lamp, focused onto the cuvette by means of a glass lens. A red light filter KS-10 was

Fig. 1. Cryostat for studying absorption spectra and photochemical properties of frozen solutions

Figure 1: Fig. 1. Cryostat for studying absorption spectra and photochemical properties of frozen solutions

Fig. 2

Figure 2: Fig. 2

used, transmitting rays with wavelengths greater than 600 m μ . To absorb infrared rays, a water filter 15 cm thick was placed between the light source and the solution under study.

Absorption spectra were recorded on a photoelectric spectrophotometer consisting of a UM-2 monochromator, an FEU-27 photomultiplier, and an I28-M tube amplifier. The solvent used was thoroughly dried—

ethanol, or its mixture with benzene or toluene in a ratio of 1 : 3, which upon slow freezing gives a transparent glassy solid mass suitable for photometric measurements. Before freezing, oxygen was passed through the solution for several minutes.

Fig. 2. Photochemical oxidation of chlorophyll *a* in a frozen alcoholic solution. 1—absorption spectrum before irradiation, 2—the same after irradiation for 6 h.

As our experiments showed, upon irradiation of frozen solutions of chlorophyll *a* a slowly proceeding photoreaction is observed, as a result of which red-colored products accumulate in the system. Figure 2 shows the absorption spectrum of the photoproduct formed.

According to all the data, the photoproduct is stable. Its absorption spectrum does not change even upon indefinitely long storage of the solution under low-temperature conditions. Thawing of the solutions likewise does not lead to substantial changes.

The absorption spectrum of the photoproduct shown in Fig. 2 consists of four bands located at λ 465, 490, 520, and 580 m μ . This makes it possible to assume that in frozen systems photooxidation is associated with dehydration of pigment molecules at positions C_7 and C_8 of the IV pyrrole ring. It should be noted that such a mechanism of photooxidation, proceeding at room temperature, has been shown for solutions of chlorophyll *a* ⁽⁴⁾ and Zn-tetraphenylchlorin ⁽⁵⁾.

Irradiation (for 5 h) of frozen chlorophyll solutions from which the air had been completely removed,* did not lead to noticeable changes in the absorption spectrum.

Thus, the data we obtained show with considerable persuasiveness that photooxidation of chlorophyll by oxygen is feasible also under those conditions where kinetic collisions of the reacting molecules are excluded. This is most readily

Fig. 3

Figure 3: Fig. 3

explained by assuming that chlorophyll *a*, already under dark conditions, forms an associate with oxygen, within which electron transfer occurs upon absorption of a light quantum.

There is information on the tendency of crystalline chlorophyll to form a molecular complex with oxygen⁽⁶⁾. Similar data for the dissolved pigment are lacking. Therefore we undertook an attempt to study the dark interactions of chlorophyll *a* with oxygen in a number of solvents. For this purpose we carried out a comparative study of the absorption spectra of a degassed solution of chlorophyll *a* and of a solution containing oxygen under a pressure of several atmospheres.

Fig. 3. Changes in the absorption spectrum of a benzene solution of chlorophyll *a* upon its interaction with oxygen.

1—absorption spectrum of the degassed solution; 2—the same after introduction of oxygen.

* Degassing of the solutions was carried out by the method described in⁽²⁾.

The experiments were carried out as follows. Chlorophyll solutions were thoroughly evacuated on a high-vacuum apparatus and their absorption spectra were recorded. The spectra were recorded in thick-walled plane-parallel cuvettes connected through a glass filter to small reservoirs containing a certain amount of KMnO_4 . After spectrophotometry, the KMnO_4 was heated until complete decomposition, and the oxygen thereby released was carefully mixed with the solution.

Figure 3 presents data on the absorption spectra of chlorophyll *a* in benzene in the presence and in the absence of oxygen. Completely analogous changes occur in toluene, carbon tetrachloride, and chloroform. In alcoholic solutions these same changes are not detected immediately, but after the solution has been stored for some time (in the presence of oxygen under dark conditions).

Attention is drawn to the fact that the observed spectral changes occur in non-polar solvents. An analogous effect was found when polar molecules were introduced into dried chlorophyll solutions⁽⁷⁾. It might therefore be supposed that the observed changes are associated with the introduction, together with oxygen, of a certain amount of moisture into the solution dried during evacuation. It should be noted, however, that in our experiments the reservoir containing KMnO_4 was, during evacuation, kept in a water bath at a temperature of 100° , which should have ensured complete removal of water adsorbed on the surface of the KMnO_4 crystals. In addition, the experiment described below confirmed that the observed spectral changes do not arise as a result of the action of moisture.

In addition to the reservoir for KMnO_4 , a second one, containing crystalline

hydrated copper sulfate, was sealed to the measuring cuvette. After the solution had been dehydrated, the copper sulfate was heated, and the water released thereby was mixed with the benzene solution. Comparison of the absorption spectrum of such a solution before the admission and after the admission of oxygen showed that the spectral changes depicted in Fig. 3 are the result of interaction with oxygen.

On the basis of the foregoing it may be concluded that chlorophyll *a* tends to enter into dark interactions with oxygen with the formation of a labile molecular complex, which apparently is responsible for the photochemical oxidation of the pigment in frozen solutions.

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

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CITED LITERATURE

¹ A. N. Terenin, *Photochemistry of Dyes*, Publishing House of the Academy of Sciences of the USSR, 1947; A. N. Terenin, *Photochemistry of Chlorophyll and Photosynthesis*, Publishing House of the Academy of Sciences of the USSR, 1951; A. A. Krasnovskii, DAN, **58**, 617 (1947); M. Calvin, G. D. Dorough, J. Am. Chem. Soc., **70**, 699 (1948); A. A. Krasnovskii, ZhFKh, **30**, 968 (1956); R. Livingston, E. Owczus, J. Am. Chem. Soc., **78**, 3301 (1956). ² I. I. Dilung, B. Ya. Dain, ZhFKh, **33**, 1740 (1959). ³ F. Cscheile, C. Comar, Bot. Gaz., **102**, 463 (1942). ⁴ I. I. Dilung, Ukr. khim. zhurn., **24**, 202 (1958). ⁵ M. Calvin, G. D. Dorough, J. Am. Chem. Soc., **70**, 609 (1948). ⁶ B. Rosenberg, I. F. Camiscoli, J. Chem. Phys., **35**, 982 (1961). ⁷ V. B. Evstigneev, V. A. Gavrilova, A. A. Krasnovskii, DAN, **70**, 261 (1950); R. Livingston, Watson, J. McArdle, J. Am. Chem. Soc., **71**, 1542 (1949).

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