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Abstract

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TEMPERATURE DEPENDENCE OF THE DEACTIVATION OF THE METASTABLE STATE OF CHLOROPHYLL

(Presented by Academician A. P. Vinogradov on July 20, 1963)

It is known ([1–4]) that the rate of radiationless deactivation of the metastable (triplet) state of chlorophyll in solution can be represented as the sum of the rates of monomolecular and bimolecular deactivation processes

$$-\frac{d[C^*]}{dt} = K_1[C^*] + K_2[C^*]^2 + K_3[C^*][C_g], \tag{1}$$

where

$$K_1 = K_0 + \sum_i K_{Q_i}[Q_i], \tag{2}$$

where K_0, K_1, K_2, K_3, and K_{Q_i} are the rate constants of monomolecular and bimolecular processes of decomposition of metastable pigment molecules.

Fig. 1. Typical oscillograms of spectral changes ($\lambda = 520$ mμ) of chlorophyll a+b solutions in toluene (concentration $1.7 \cdot 10^{-5}$ g-mol/l) under pulsed illumination. Solution temperatures $+20^\circ$ (a), -50° (b). Time-marker interval 10^{-4} sec.

One of the paths of deactivation of the metastable state may be a chemical reaction of the long-lived, electron-excited pigment molecules in solution, leading to the formation of a number of intermediate states (radicals, etc.). It may be supposed that the deactivation of different states proceeds by different mechanisms with different activation energies.

In this connection, it was of interest to investigate the mechanism of deactivation of the metastable (triplet) state of chlorophyll in solution at different temperatures.

Fig. 2. Dependence of $\frac{d}{dt}\ln\frac{\Delta D_0}{\Delta D}$ on ΔD at various temperatures ($\lambda = 520$ mμ)

Figure 2: Fig. 2. Dependence of $\frac{d}{dt}\ln\frac{\Delta D_0}{\Delta D}$ on ΔD at various temperatures ($\lambda = 520$ mμ)

The measurements were carried out by the method of flash photolysis [4] with solutions of chlorophyll $a + b$* in toluene (concentrations 10^{-5}–10^{-6} g-mol/l) in the interval $+20^\circ \div -50^\circ$, and also in an ether–isopentane–alcohol mixture at -196° (concentration $5 \cdot 10^{-5}$ g-mol/l).

The distinctive features of the present experiment consisted in the use of a special quartz vacuum cuvette [5] (optical path length 150 mm), provided with a jacket for a circulating thermostated liquid (alcohol cooled by a mixture of dry ice and acetone), which was placed between the solution under study and an outer jacket evacuated to a high vacuum. The source of powerful short-duration illumination was flash lamps of the IFK-2000 type. The greater part of the experiment was carried out with a flash energy of 300 joules [4]. Individual measurements were made with a flash energy of 120 joules and a duration of $1 \cdot 10^{-5}$ sec, measured at half the light amplitude. The recording of the spectral changes in time was performed with a cathode oscillograph IO-4 or S1-8 (UO-1M). Typical oscillograms are presented in Fig. 1.

It is assumed that the spectral changes of solutions of chlorophylls a and b in toluene [4], and, consequently, also of their natural mixture $a+b$, under powerful short-duration light irradiation are associated with the accumulation of pigment molecules at a metastable (possibly triplet) electron-excited level. Equation (1) for the rate of deactivation of the metastable state of the pigment can be reduced to the form convenient for graphical representation of the experimental data

Fig. 2. Dependence of $\frac{d}{dt}\ln\frac{\Delta D_0}{\Delta D}$ on ΔD at various temperatures ($\lambda = 520$ mμ)

$$\frac{d}{dt}\ln\frac{\Delta D_0}{\Delta D} = K_1 + K_3 C_0 + \frac{K_2 - K_3}{(\varepsilon_T - \varepsilon_S)l}(\Delta D), \tag{3}$$

where ΔD_0 is the change in the optical density of the pigment solution upon excitation by a light pulse, referred to an arbitrary zero time t_0; ΔD has the same meaning provided it is referred to the subsequent time $(t - t_0)$; C_0 is the concentration of the pigment solution in g-mol/l; ε_S and ε_T are the corresponding molar extinction coefficients of the molecules in the singlet and triplet states. In the coordinates ΔD and $\frac{d}{dt}\ln\frac{\Delta D_0}{\Delta D}$, equation (3) is, evidently, the equation of a straight line.

Typical results of measurements carried out with a solution of chlorophyll $a+b$ in the region 430–520 mμ at temperatures $+20^\circ \div -50^\circ$ are presented in Fig. 2. As

Fig. 3

Figure 3: Fig. 3

follows from the figure, the dependences under consideration are well described by straight lines, which indicates the validity of equation (1) in the indicated temperature interval and, consequently, the existence under these conditions of a single metastable state. It follows from Fig. 2 that lowering the temperature of the system under study leads to a decrease in the slope of the straight lines to the abscissa axis and to a decrease in the intercepts $A_i = K_1 + K_3 C_0$,

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cut off by straight lines on the ordinate axis. It may be thought that these regularities are the result of the dependence of the rate constants of the bimolecular deactivation reactions K_2, K_3, K_{Q_i} on temperature. Of the three values K_2, K_3, and K_{Q_i}, the temperature dependence of the rate constant can be studied reliably for K_2. Since $K_2 \gg K_3$ (4), it follows from equation (3) that

$$K_2 \simeq \operatorname{tg}\varphi\,(\varepsilon_T - \varepsilon_S)\,l, \tag{4}$$

where φ is the angle of inclination of the straight line to the abscissa axis (for the given temperature).

Fig. 3. Dependence of $\ln \operatorname{tg}\varphi$ on $1/T$ for pigment solutions. Concentration: $1.7 \cdot 10^{-5}$ g-mol/l (1); $1.7 \cdot 10^{-6}$ g-mol/l (2)

Assuming an Arrhenius dependence for K_2,

$$K_2 = K_{20} e^{-E/RT}, \tag{5}$$

where E is the activation energy of the process of deactivation of two metastable molecules, from equations (4) and (5) we obtain

$$\ln \operatorname{tg}\varphi = -E/RT + \text{const}. \tag{6}$$

Figure 3 presents the corresponding results of measurements of pigment solutions. As follows from the figure, the dependences considered are well described by straight lines, which confirms the assumption of an Arrhenius dependence of the deactivation rate constant. From the slope of the straight lines to the abscissa axis it is not difficult to determine the activation energy

$$E = 2.6 \pm 0.4 \text{ kcal/mol},$$

Fig. 4

Figure 4: Fig. 4

and finally for the rate constant we obtain

$$K_2 = 10^{11} e^{-2600/RT}.$$

From equation (2) it follows that the apparent rate constant K_1 of the monomolecular decay of the metastable state differs from the true constant K_0 by the amount $\sum_i K_{Q_i}[Q_i]$, where $[Q_i]$ is the concentration of extraneous quencher molecules (traces of O_2, impurities of chemical compounds, etc.). The value K_1 is very "sensitive" to the experimental conditions (purity of the solvent, method of degassing the solution, etc.), and therefore determination of the true value $K_0 = K_1$ is very difficult. However, if equality of the activation energies in the expressions for the constants K_2, K_3, and K_{Q_i} is assumed, then the value of K_0 can be estimated. After simple transformations we obtain

$$K_0 = \frac{A_i e^{E/RT} - A_i e^{E/RT_j}}{e^{E/RT_i} - e^{E/RT_j}}.$$

Fig. 4. Dependence of $\lg \dfrac{\Delta D_0}{\Delta D}$ on time $(t - t_0)$ for a chlorophyll solution in a mixture of ether–iso-pentane–alcohol at -196°

The mean value of K_0, calculated for the temperature range $+20^\circ \div -50^\circ$, is $K_0 = 500 \pm 150$ s^{-1}, whereas $K_1 = 600 \pm 200$ s^{-1}.

The value K_0 can also be determined from an experiment with an extremely viscous medium–a solid matrix. In this case equation (1) for the rate

deactivation will be written in the form

$$-\frac{d[C^*]}{dt} = K_0[C^*]. \qquad (1')$$

The results of measurements performed with a solution of the pigment in a mixture of ether–isopentane–alcohol at -196° (solid glass) are presented in Fig. 4. As follows from the figure, the dependence $\lg \frac{\Delta D_0}{\Delta D}$ on $t - t_0$ is described by a straight line, from whose slope to the abscissa axis the value $K_0 = 350 \pm 50$ sec^{-1} is determined. Similar measurements at room temperature (polymer matrix–polystyrene) could not be carried out because of the instability of chlorophyll in the styrene medium during polymerization. However, it may be thought that the transition from liquid-nitrogen temperature to room temperature has little effect[6] on the value of K_0.

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