Using the method of pulse photolysis, we studied the quenching of the triplet state (TS) of a number of tetrapyrrrole molecules by complexes of Ni-, Ag-, and Fe-porphyrins in liquid solutions at a temperature of ~298 K under the conditions where the kinetics are markedly affected by the triplet-triplet annihilation of the molecules of energy donors. In the analysis of experimental data, derivatives for the time dependences of the optical density of the triplet-triplet absorption were determined. The triple-triplet annihilation process was considered for the case of the formation of excited a triplet-triplet complexes of two molecules in the triplet state. A procedure of determining the rate constant for the quenching of the triplet state by foreign molecules (K_q) under the effect of such triplet-triplet annihilation process is proposed and the values of K_q are obtained. For some donor-quencher pairs it is found that the kinetics of the triplet-state deactivation are affected by the formation of short-lived particles with lifetimes both shorter and longer than the triplet-state lifetimes. The conclusion is drawn that such particles are respectively the excited complexes of interacting molecules or ion radicals formed from such complexes in polar solvents.

Keywords: triplet-triplet annihilation, quenching of the triplet state, excited complexes.

Introduction. In [1, 2], a method is proposed for determining the rate constants for the processes that participate in the triplet-state deactivation in liquid solutions. It is based on obtaining derivatives for the time dependences that characterize a decrease in the optical density of the triplet-triplet absorption after pulse photoexcitation. Consideration was given to the triplet-state deactivation as a result of single-stage processes of the bimolecular quenching of the triplet state; it is characterized by the equation

$$\frac{dT}{dt} + k_1 [T] + k_2 [T]^2 + k_3 [T] [S] + k_4 [T] [Q] = 0,$$

where [T], [S], and [Q] are the concentrations of molecules in the lower triplet and ground states and of a foreign quencher and k_1–k_4 are rate constants for individual processes. Equation (1) can be rewritten in the form

$$\frac{d}{dt} \ln \frac{\Delta D_0}{\Delta D} = A + B \Delta D,$$

where A = k_1 + k_3[S] + k_4[Q], B = (k_2 - k_3)/(\varepsilon_T - \varepsilon_S)/l (\varepsilon_T and \varepsilon_S are the molar coefficients of extinction in the triplet and ground states, and l is the cell length), and \Delta D_0 and \Delta D are changes in the optical density of the...
solution by the instants of time $t_0$ and $t$. Having obtained a linear dependence of $\frac{d}{dt} \ln (\Delta D/\Delta D)$ on $\Delta D$, it is possible to obtain the values of $k_1 - k_4$. In [3], for solutions of chlorophylls (Chl) $a$ and $b$ and of their pheophytins in pyridine, a deviation of this dependence from the linear one was found for the region of the smallest values of $\Delta D$; it was attributed to the formation of ion radicals of the pigments and solvent as a result of electron transfer from the pyridine to the pigment molecules in the triplet state. It should be noted that the change in the slope of the dependences of $\frac{d}{dt} \ln (\Delta D/\Delta D)$ on $\Delta D$ was of the same order as the changes in the slope of the dependences of $\ln \Delta D$ on $t$, for which deviations from linearity also took place at the smallest $\Delta D$. After [3], this method was almost not used for studying the formation of short-lived photoproducts and complexes. This is possibly due to the necessity of comparing the magnitudes of changes in the slopes of the dependences of $\frac{d}{dt} \ln (\Delta D/\Delta D)$ on $\Delta D$ and $\ln \Delta D$ on $t$ in [3], which does not offer a practical advantage to the procedure with the determination of dependences (2) (while the amount of work required in determining dependences (2) is much greater than in determining the dependence of $\ln \Delta D$ on $t$). It seems, however, that the derivatives of $\ln \Delta D(t)$ are more sensitive to the formation of photoproducts and complexes than these dependences themselves. It is well known that the determination of the spectra of the derivatives of the absorption spectra permits one to detect the formation of relatively small quantities of various photoproducts or associates. Therefore, in the present study the method of derivatives was applied to the dependences $\ln \Delta D(t)$ to study a number of tetrapyrrole molecules, for which previously kinetic data were obtained that give evidence in favor of the formation of excited complexes (TQ) from molecules in the triplet state and a quencher. It is important that this method was used for determining the rate constants of bimolecular quenching by foreign molecules for the case where the triplet-triplet annihilation proceeds not in one stage, as is assumed in [1-3], but through the formation of (TT) complexes. The fact that the triplet-triplet annihilation proceeds through the reversible formation of excited (TT) complexes from two molecules in the triplet state is confirmed by the data of some works, for example, those dealing with quantum-chemical calculations for excited dimers of molecules [4, 5] and with the effect of a magnetic field on the annihilation retarded fluorescence [6]. In [7, 8], kinetic data were obtained that support the formation of long-lived (TT) complexes. Using derivatives of the dependences $\ln \Delta D(t)$, in the present work we investigated the quenching of the triplet states of a number of tetrapyrrole molecules (electron energy donors) by efficient triplet-state quenchers, which are model compounds important for biology, specifically, porphyrin complexes with iron, nickel, and silver. We considered the procedure of determining $K_q$ under conditions of the influence of triplet-triplet annihilation, which proceeds by the mechanism involving the formation of (TT) complexes, and the values of $K_q$ for a number of examined pairs of molecules were obtained.

Experimental Procedure. We investigated the kinetics of the disappearance of the triplet-triplet absorption for Zn(II)-mesotetraphenylporphin (Zn-TPhP) in toluene, Mg(II)-phthalocyanin (Mg-PhC) in dimethyl formamide (DMF), and Chl $a$ in a toluene in the presence of triplet-state quenchers and without them. As quenchers we used Ag(II)-TPhP, Ni(II)-TPhP, and Fe(III)-octaethylporphin (Fe-OEP). The concentrations of the solutions of the compounds were $9.3 \times 10^{-6}$ for Zn-TPhP, $6.3 \times 10^{-6}$ and $4.2 \times 10^{-6}$ for Mg-PhC, $2.0 \times 10^{-6}$ for Chl $a$, $(2.5-4.2) \times 10^{-5}$ for Ag-TPhP, $(0.5-4.9) \times 10^{-5}$ for Ni-TPhP, and $(0.3-1.2) \times 10^{-5}$ mole/liter for Fe-OEP. Measurements were performed at room temperature on a pulse lamp photolysis setup (the duration of the light pulse was $\tau_{1/2} \approx 20 \mu$sec and the discharge energy was $\sim 200$ J) using photoelectric recording. The investigated solutions were degassed by a standard procedure: multiple freezing-evacuation under vacuo-thawing. The triplet-triplet absorption was recorded in the regions of the maxima of its spectra. The conversion of molecules in the triplet state reached 60-80%.

Experimental Results and Their Discussion. Figure 1 shows several kinetic time dependences of the triplet-state deactivation for Zn-TPhP in toluene in the presence of a quencher (Ag-TPhP) and without it. It is established that these dependences are nonlinear. Consequently, the triplet-state deactivation follows a nonexpo-