6,7-Dimethoxy-2-naphthol (VIII, $C_{12}H_{12}O_3$). To a suspension of 0.22 g (1 mmole) of the aldehydoketone (IIc) [6] in 4 ml of ethanol was added 4 ml of 5% KOH, and the mixture heated for 10 min. After cooling, the mixture was diluted with 15 ml of cold water and acidified with 15% HCl. The resulting precipitate was extracted with ether (3 × 5 ml), and the extracts evaporated to give 0.20 g (90%) of colorless product, mp 154°C (from hexane—benzene, 2:1), R_f 0.33. IR spectrum: 3460, 1640, 1620, 1593 cm^{-1}. PMR spectrum ($CDCl_3$): 3.70 (s, OCH_3); 3.75 (s, OCH_3); 5.20 (br.s, 1H, OH); 6.67-7.37 ppm (m, $5H_{arom}$).

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DISSOCIATION OF THE (4H-FLAVEN-4-YL)TRIPHENYLPHOSPHONIUM CATION IN ACETONITRILE

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The thermodynamic and kinetic parameters of the reversible dissociation of (4H-flaven-4-yl)triphenylphosphonium perchlorate in acetonitrile were determined.

In the study of the electrochemical properties of phosphonium salts — the pyrylium derivatives were first described by S. V. Krivun in [1] — we found that some of them can dissociate into the initial components: the corresponding pyrylium cation and the phosphine. Thus, the peaks, for which the values of the potentials correspond to the reduction of the flavylium cation (F) [2] and the oxidation of triphenylphosphine (T) [3], are observed on the cyclic voltamperograms of the flavenylphosphonium salt (FT) in dilute solutions of acetonitrile. The temperature of the medium significantly, but completely reversibly, influences the ratio of the peak heights of all three components of the equilibrium (1) (Fig. 1, a, b).
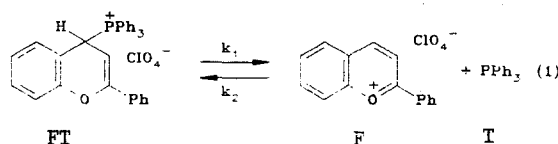
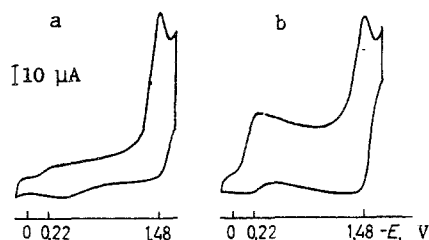$$ FT \underset{k_2}{\overset{k_1}{\rightleftarrows}} F + PPh_3 \quad (1) $$

Fig. 1. The cyclic voltamperograms of (4H-flaven-4-yl)-triphenylphosphonium perchlorate in acetonitrile (c = 5·10⁻³ M) at the temperature of 20°C (a) and 40°C (b).

TABLE 1. Thermodynamic Characteristics of the Equilibrium (1) at Different Temperatures

No. of experiment	T, °C	ε	$K_e \pm 5.0$, M	ΔG, kJ/mole
1	25	33 895	$6{,}92 \cdot 10^{-7}$	35
2	30	36 939	$1{,}15 \cdot 10^{-6}$	34,4
3	35	33 025	$1{,}76 \cdot 10^{-6}$	33,9
4	40	27 788	$2{,}83 \cdot 10^{-6}$	32,7
5	45	25 304	$4{,}90 \cdot 10^{-6}$	32,3

The reverse reaction — the formation of the phosphonium salt — is the reaction of the addition of the nucleophile to the free carbocation. The physicochemical parameters of similar reactions have been intensively studied recently [4-6]. However, with rare exception, the equilibrium constants are lacking, since the majority of the reactions proceeds irreversibly.

We employed a spectrophotometric method to determine the thermodynamic parameters of the equilibrium (1), since the values of the maximal currents in the cyclic voltamperometry for the compounds formed as the result of chemical processes preceding the stages of the charge transfer bear a kinetic character in this case, and are not proportional to the volume concentrations of these compounds (the concentrations of the flavylium and the triphenylphosphine in the given case). In fact, the characteristics of the reduction currents of the flavylium formed as a result of dissociation are altered by comparison with the electrochemical characteristics of the flavylium reduced in the absence of triphenylphosphine. The temperature coefficient of the current increases from 0.26 to 1.68; this corresponds with the change in the energy of activation of 7.2 to 32.4 kJ. The dependence of the current on the height of the mercury stem, measured in logarithmic coordinates ($\Delta\log i_{lim}/\Delta\log h$), decreases from 0.69 to 0.37. In the case of the utilization of voltamperometry with the linear scanning of the potential, the $\Delta\log i/\Delta\log v$ ratio decreases from 0.56 to 0.24. The dependence of the limiting current on the initial concentration of the phosphonium salt bears a curvilinear character. Such changes of the electrochemical characteristics of the limiting (maximal) currents permit the reduction of the flavylium cation in the presence of triphenylphosphine to be considered as a process limited by the kinetics of the preceding dissociation reaction (1) [7] (p. 288), [8] (p. 282), [9] (p. 186).

The experimental determination of the equilibrium constant (K_e) of the reaction (1) from the absorption spectra proved to be convenient. Of the three reaction components, only the flavylium possesses absorption in the visible spectral region (the absorption maximum is at 395 nm). Its equilibrium concentration c_F was measured from the optical density (D), and K was calculated according to the law of mass action from the formula:

$$K = c_F^2/(c_{FT}^0 - c_F), \qquad (2)$$
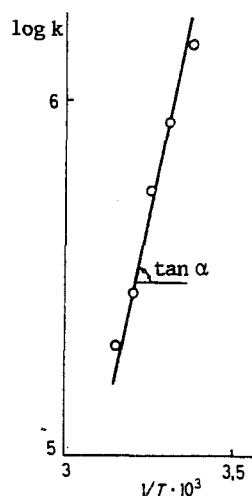
where c_{FT}^0 is the initial concentration of FT.

Fig. 2. The dependence of the logarithm of the equilibrium constant of (1) on the reciprocal of the temperature. $\tan \alpha = 4834$; $\Delta H = -2.303 \ R \tan \alpha$.

TABLE 2. Spectrophotometric Characteristics of Flavinylphosphonium at Different Temperatures

No. of experiment	$c \cdot 10^{-4}$, M	D				
		25 °C	30 °C	35 °C	40 °C	45 °C
1	1,35	0,294	0,410	0,487	0,442	0,562
2	2,01	0,392	0,496	0,540	0,607	0,751
3	2,48	0,410	0,502	0,654	0,695	0,799
4	2,90	0,465	0,645	0,739	0,772	0,903
5	3,23	0,542	0,657	0,796	0,808	0,984

The measurements of c_F were performed at different temperatures (Table 1); therefore the extinction (ε) of the flavylium in acetonitrile was first determined at the corresponding temperatures. Judging from the mean values of the equilibrium constants (Table 1), the equilibrium (1) is displaced, to a significant degree, in favor of the formation of the flavenyl-phosphonium. The free energy calculated for the temperature of the experiment (Table 1) allows the evaluation of the enthalpy and entropy of the reaction (1) (Fig. 2). The values $\Delta H = 91.9$ kJ/mole and $\Delta S = 177.4$ J/(mole·K) in comparison with the literature data indicate the strong donor—acceptor interaction, which is evidently accompanied by the complete transfer of charge from the triphenylphosphine to the flavylium cation. The equilibrium (1) is characterized by the significant value of the free energy ($\Delta G = 32-35$ kJ/mole), which is encountered relatively rarely for the donor—acceptor interactions [10] (p. 99).

The flavenylphosphonium perchlorate at the concentration of 0.05 M at 70°C (in CD_3CN) and 110°C (in dimethylacetamide) exists in the pyran form according to the PMR spectral data; this is indicated by the presence of signals of the CH group (δ 5.83 ppm). This corresponds to the value of the equilibrium constant of (1); the FT taken at the initial concentration of 0.05 M occurs virtually completely in the form of the phosphonium cation.

The constants of the rate of reaction (1) at T = 298°K were determined according to the limiting kinetic polarographic waves of the reduction of the flavylium cation in the solutions with the different initial concentration of the FT in acetonitrile. In conformity with the value of K_e, even a small excess of triphenylphosphine leads to a significant shift of equilibrium of the reaction (1) in favor of the formation of the FT salt. The reduction wave of the F thereby decreases sharply, and the measurement of the kinetic current becomes impossible with the excess of the T. Consequently, it is impossible to employ the usual method of calculation pertaining to the pseudo first-order reaction (see, for example, [8]). In connection with this, we employed the method proposed in the work

[11] for the calculation of the kinetic parameters of the studied second order reaction (1) from the polarographic currents, where the equation relating the limiting kinetic current i_k to the reaction rate constants was obtained:

$$i_\kappa/i_d = (3/7\pi\tau k_2)^{1/3}(c_T^0)^{1/3}[1 - c_F^0/c_{FT}^0(i_\kappa/i_d - 1)]^{2/3}, \qquad (3)$$

where $i_d = \varkappa c_F^0$ (the diffusion current of the reduction of the flavylium), κ is the Ilkovic constant for the flavylium, τ is the dropping period of the mercury drop, and k_2 is the rate constant of the interaction of the F and the T.

The results of the measurement of i_k in the solutions of the FT of differing concentration were plotted in the coordinates $i_k/i_d - (c_T^0)^{1/3}[1 - c_F^0/c_{FT}^0(i_k/i_d - 1)]^{2/3}$ and the $k_2 = 5.4 \cdot 10^7$ liters/(mole·sec) was determined from the slope of the plot, and then the $k_1 = 37$ sec^{-1} was determined with the utilization of K (Table 2).

EXPERIMENTAL

The UV spectra were registered on a Specord M-40 instrument using a quartz cuvette of thickness 1 cm. The PMR spectra were taken on a Tesla BS-487 C (80 MHz) spectrometer.

The classical polarograms were taken on the OH-105 polarograph having the dropping mercury electrode with the blade; the dropping period $\tau = 0.40$ cm^{-1}. The base level was provided by tetraethylammonium perchlorate; the comparison electrode was the aqueous saturated calomel electrode with the diaphragm of asbestos-aluminum hydroxide [14]. The acetonitrile was purified by multiple distillation over calcium hydride.

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