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Figure 1

Figure 1: Figure 1

Abstract

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CHARGE-TRANSFER COMPLEXES OF FERROCENE WITH TRINITRO DERIVATIVES OF BENZENE

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Among molecular compounds, charge-transfer complexes are of special interest; the chemistry of these complexes has begun to be developed intensively only in the last 10–15 years.

In compounds of this type, intermolecular mesomerism occurs, and in the unexcited state of the complex the equilibrium is shifted toward the nonpolar form, while in the excited state it is shifted toward the polar form (^{1})

$$\mathrm{AD} \leftrightarrow \mathrm{A}^{\ominus}\mathrm{D}^{\oplus},$$

$$\downarrow h\nu$$

$$\mathrm{A}^{\ominus}\mathrm{D}^{\oplus} \leftrightarrow \mathrm{AD},$$

where A is the acceptor and D is the donor.

An important consequence following from the theory of these compounds is the appearance, upon formation of a charge-transfer complex, of a new absorption band in the electronic spectrum, different from the absorption bands of the initial components. This absorption band is very characteristic, and if it is absent, this indicates that a charge-transfer complex is not formed (^{2}). In charge-transfer complexes the components usually occur in a ratio of $1:1$. Complexes of this kind are most often encountered among aromatic compounds, and some of them have been obtained in the crystalline state; among organometallic compounds, however, they are almost unknown. In the literature there is only one report concerning complexes of ferrocene with polyhalomethanes (^{3}).

Fig. 2. Ferrocene–symm-trinitrobenzene: $\bar{\varepsilon}$ is the formal molar extinction coefficient of the acceptor, C is the donor concentration in mole fractions (numbers at the curves are light wavelengths in millimicrons)

Figure 2: Fig. 2. Ferrocene–symm-trinitrobenzene: $\bar{\varepsilon}$ is the formal molar extinction coefficient of the acceptor, C is the donor concentration in mole fractions (numbers at the curves are light wavelengths in millimicrons)

Fig. 1. Ferrocene–sym-trinitrobenzene in 1,2-dichloroethane. ΔD–difference between the observed and calculated optical density; C–concentration of ferrocene in mole fractions in the ferrocene–sym-trinitrobenzene mixture (the numbers at the curves are wavelengths of light in millimicrons)

In the present work, ferrocene was used as the donor, and sym-trinitrobenzene, picric acid, and picryl chloride as acceptors. In recording the spectra, the solvent was mainly 1,2-dichloroethane. By applying the method of continuous variations (Job' s method) (4,5) to the change in optical density of solutions of ferrocene mixed with the indicated acceptors, it was shown that complexes with a molar ratio of components of 1 : 1 are formed (see Fig. 1). For measurements of optical density at 520 and 590 mμ, analogous results were obtained.

The complexes studied by us have a characteristic absorption band at a wavelength of 535 mμ in 1,2-dichloroethane and chloroform; this band is absent in the spectra of the initial components and in the spectrum of the ferricinium ion. The wavelength corresponding to the absorption maximum of the complexes investigated agrees well with that calculated on the basis of the Briegleb-Czekalla equation (6). This equation establishes a relation between the wavelength of the absorption maximum of a charge-transfer complex and the ionization potential of the corresponding donor for complexes in which the acceptors are sym-trinitrobenzene, iodine, and chloranil:

$$h\nu_{\max} = I - c_1 + \frac{c_2}{I - c_1},$$

where $h\nu$ is the charge-transfer energy in eV; I is the ionization potential of the donor in eV; c_1 is an empirical constant, equal for complexes with trinitrobenzene to 5.00 eV; c_2 is a constant calculated on the basis of mesomeric dipole moments and equal for complexes with trinitrobenzene to 0.70 eV; c_1 and c_2 do not depend on the nature of the donor.

The experimentally found values of $h\nu$ for complexes of trinitrobenzene with 18 different donors, for which the ionization potentials are known, agree well with those calculated on the basis of this equation (6). The ionization potential of ferrocene is 7.05 eV (7). The calculated value of $h\nu$ for the complex with symm-trinitrobenzene is 2.39 eV,

Fig. 2. Ferrocene–symm-trinitrobenzene: $\bar{\varepsilon}$ is the formal molar extinction coefficient of the acceptor, C is the donor concentration in mole fractions (numbers

at the curves are light wavelengths in millimicrons)

and the energy of light radiation corresponding to the wavelength 535 mµ is 2.32 eV. The difference between the calculated and experimentally found value is 0.07 eV, while the authors cited above allow a maximum deviation of 0.15 eV ([6]). The equilibrium constant was determined by a graphical method (see Fig. 2). The calculations were based on the Hildebrand and Benesi equation ([8]):

$$\frac{1}{\bar{\varepsilon}} = \frac{1}{\varepsilon_k} \cdot \frac{1}{K} \cdot \frac{1}{C_D} + \frac{1}{\varepsilon_k},$$

where $\bar{\varepsilon}$ is the formal molar extinction coefficient of the acceptor, K is the equilibrium constant, ε_k is the molar extinction coefficient of the complex, and C_D is the donor concentration in mole fractions.

The indicated equation, in which $1/\bar{\varepsilon} = f(1/C_D)$, is the equation of a straight line, and it is applicable for those wavelengths at which the extinction coefficients of the starting components are negligibly small in comparison with the extinction coefficient of the complex. The experimental values obtained by us—tal data obey this equation, and the plots give a bundle of straight lines. The intercepts cut off by the straight lines on the ordinate axis are equal to $1/\varepsilon_k$, and the tangent of the angle of inclination of the straight line is equal to $1/\varepsilon_k \cdot 1/K$. From the quantities found from the plot, the formation constants of the complexes were determined (Table 1).

Table 1

λ, mµ	K^* of ferrocene—symm-trinitrobenzene complexes	K^* of ferrocene—picric acid complexes	K^* of ferrocene—chlorostyrylpicryl complexes	λ, mµ	K^* of naphthalene—symm-trinitrobenzene complexes
535	2.8	2.1	2.0	425	8.7
570	2.9	2.1	2.0	430	8.5
590	2.8	2.1	2.0	435	9.1
	2.8 ± 0.1	2.1 ± 0	2.0 ± 0		8.8 ± 0.3

* Formation constant in (mole fractions)$^{-1}$.

For comparison, the formation constant of the complex of sym-trinitrobenzene with naphthalene was also found. The decrease in the formation constant on going from complexes with trinitrobenzene to complexes with chloropicryl and picric acid is caused by disruption of the coplanarity of the nitro groups and the benzene ring in the first case and by a decrease in electron-acceptor ability as a result of the electron-donor effect of the hydroxyl group in the second. For

Fig. 3

Figure 3: Fig. 3

the complexes of ferrocene with trinitrobenzene, chloropicryl, and picric acid, the molar extinction coefficients, respectively, for wavelengths of 535, 570, and 590 mμ are equal to one another. If such a dependence also exists for other wavelengths in the region 520-590 mμ, then at the given concentrations of the initial components the ratio of optical densities at a given wavelength for two different complexes will be a constant quantity (Table 2).

Fig. 3. **1** –complex of ferrocene with sym-trinitrobenzene, **2** –the same with chloropicryl, **3** –the same with picric acid (all in 1,2-dichloroethane)

Since $D = \varepsilon C l$, where D is optical density, ε is the molar extinction coefficient, C is the concentration of the complex, and l is the optical path length, then in our case $l = 1$ cm and $D = \varepsilon C$.

For two different complexes A_1 and A_2 at two different wavelengths λ_1 and λ_2, in this case we have:

$$\begin{array}{c|cc} \lambda & A_1 & A_2 \\ \hline \lambda_1 & D_a = C_1\varepsilon_1 & D_b = C_2\varepsilon_1 \\ \lambda_2 & D_c = C_1\varepsilon_2 & D_d = C_2\varepsilon_2 \end{array}$$

Thus,

$$\frac{D_a}{D_b} = \frac{D_c}{D_d} = \frac{C_1}{C_2},$$

i.e., the ratio of optical densities is equal to the ratio of the concentrations of the complexes in the solutions studied.

We give a comparison of the averaged values of the ratios of optical densities found experimentally with the ratios of the concentrations of the corresponding complexes, calculated from the formation constants determined graphically:

$\frac{D_1}{D_2}$	$\frac{C_1}{C_2}$	$\frac{D_1}{D_3}$	$\frac{C_1}{C_3}$	$\frac{D_1}{D_4}$	$\frac{C_1}{C_4}$	$\frac{D_1}{D_5}$	$\frac{C_1}{C_5}$	$\frac{D_1}{D_6}$	$\frac{C_1}{C_6}$	$\frac{D_1}{D_7}$	$\frac{C_1}{C_7}$
1.21	1.22	1.44	1.42	1.75	1.75	1.26	1.28	1.52	1.48	1.85	1.84

Here D_1-D_7 are the same as in Table 2. C_1-C_7 are the concentrations of the corresponding complexes.

Figure 3 shows the absorption curves of the ferrocene complexes. Ferrocene belongs to the superaromatic systems and is characterized by a high electron-donor ability. In this connection, it appears strange that the formation constant of the ferrocene complex with trinitrobenzene is considerably lower (by a factor of 3.1) than the constant

Table 2

λ	$\frac{D_1}{D_2}$	$\frac{D_1}{D_3}$	$\frac{D_1}{D_4}$	$\frac{D_1}{D_5}$	$\frac{D_1}{D_6}$	$\frac{D_1}{D_7}$
520	1,19	1,41	1,72	1,24	1,48	1,80
525	1,20	1,42	1,73	1,25	1,48	1,81
530	1,22	1,43	1,72	1,23	1,44	1,80
535	1,23	1,44	1,73	1,24	1,49	1,82
540	1,23	1,44	1,73	1,24	1,49	1,82
545	1,23	1,46	1,74	1,27	1,50	1,84
550	1,23	1,45	1,77	1,26	1,50	1,82
555	1,23	1,47	1,78	1,26	1,52	1,85
560	1,23	1,47	1,81	1,25	1,52	1,85
565	1,20	1,45	1,79	1,26	1,52	1,87
570	1,19	1,44	1,80	1,25	1,50	1,90
575	1,22	1,44	1,79	1,30	1,55	1,90
580	1,18	1,46	1,77	1,28	1,57	1,89
585	1,20	1,46	1,74	1,28	1,54	1,90
590	1,18	1,43	1,70	1,27	1,52	1,86
	1,21$±0, 03	1, 44±0, 03	1, 75±0, 06	1, 26±0, 04	1, 52±0, 05	1, 85±$0,05

Notes. D_1 is the optical density of the complex solution at a ferrocene concentration of $4.52 \cdot 10^{-2}$ mole fraction and a trinitrobenzene concentration of 10^{-2} mol/l.

D_2, D_3, D_4 are the optical densities of the complex solutions at ferrocene concentrations of, respectively, $4.50 \cdot 10^{-2}$, $3.81 \cdot 10^{-2}$, and $3.06 \cdot 10^{-2}$ mole fraction and a picric acid concentration of 10^{-2} mol/l.

D_5, D_6, D_7 are the optical densities of the complex solutions at ferrocene concentrations respectively as in the case of D_2, D_3, D_4 and a chloropicryl concentration of 10^{-2} mol/l.

for the formation of the corresponding naphthalene complex. This is probably connected with the location of the reaction center in the ferrocene molecule and with the mutual spatial arrangement of the components in the complex being formed. We shall return to discussion of this question after additional experimental material has been accumulated.

Experimental Part

sym-Trinitrobenzene, chloropicryl, and picric acid were purified by repeated recrystallization from ethanol and carbon tetrachloride. 1,2-Dichloroethane was purified by the method of Brand and Snedden (^{3}). The spectra were recorded on an SF-4 spectrophotometer in thermostated cuvettes at a temperature of 23°. To prepare a ferrocene solution, a weighed portion of the latter was transferred into a tared volumetric flask, which was filled with solvent to the mark and then weighed. The working solution with an acceptor concentration of 10^{-2} or $5 \cdot 10^{-3}$ mol/l was prepared from the ferrocene solution and a weighed portion of acceptor. In the spectrophotometric measurements, a ferrocene solution was used as the reference solution.

In conclusion, I express my deep gratitude to Academician A. N. Nesmeyanov for his attention to the work.

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