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Abstract

Full Text

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ABSORPTION SPECTRA OF CERTAIN FERROCENE DERIVATIVES

In published reviews ([1–3]) and elsewhere on physicochemical studies of cyclopentadienyl derivatives of various metals (in particular, ferrocene and its derivatives), it has been noted that absorption spectra in the ultraviolet and visible regions have been little studied. Recently, two reports ([4,5]) have appeared in the literature on the systematic study of the absorption spectra of ferrocene, its derivatives, and certain other cyclopentadienyl metals.

Fig. 1. Absorption spectra: **1**—ferrocene and its alkyl derivatives, **2**—ethylferrocene, *n*-propylferrocene, **3**—diethylferrocene-1,1′; di-*n*-propylferrocene-1,1′.

In Scott' s paper ([4]), the dependence of the position and intensity of the absorption bands of ferrocene and nickelocene on temperature, solvent, and various substituents in the cyclopentadienyl rings is discussed, and an attempt is made to assign the bands. However, in that work, data obtained at different times, by different authors, and on different instruments are compared. Such a comparison is hardly meaningful. In the work ([5]), data are collected on the ultraviolet and visible absorption spectra of certain metal carbonyls, cyclopentadienylmanganese tricarbonyl, ferrocene, and its derivatives. In particular, the authors noted a bathochromic shift of the 325 mμ and 440 mμ bands in ferrocene derivatives bearing electron-acceptor substituents: (CHO, $COCH_3$, COOH), phenyl and its substituted derivatives (n-$C_6H_4-NO_2$, n-$C_6H_4COOC_2H_5$, etc.).

We recorded the absorption spectra of solutions of alkyl and acyl derivatives of ferrocene in isooctane in the spectral region from 300 mμ to 700 mμ on an SF-4 photoelectric spectrophotometer, at room temperature,

in the concentration range from 10^{-2} to 10^{-4} mol/l, with different thicknesses

Fig. 2. Absorption spectra of ferrocene and its acyl derivatives

Figure 2: Fig. 2. Absorption spectra of ferrocene and its acyl derivatives

of the absorbing layer.

The products were subjected to thorough chromatographic purification. Liquid alkyl- and 1,1′-dialkylferrocenes were chromatographed on Al_2O_3 from heptane using a PRA-system flow refractometer ([6]), in the same way as was done in previous work ([7,8]). Isooctane was chosen as the solvent, since it is known from the work of Brand ([9]) that in nonpolar solvents containing a halide a charge-transfer effect occurs, which substantially affects the character of the spectrum.

The results of the investigations showed:

1. The bend at 528 mμ described in Scott' s article was not found.
2. An almost complete coincidence of the absorption spectra (region 280-600 mμ) is observed within the series:

a) of normal monosubstituted homologs of ferrocene (see Table 1, Nos. 2, 3; Fig. 1);

Table 1

No.	Substance	λ_{max}, mμ	ε, l · mol^{-1} · cm^{-1}	λ_{max}, mμ	ε, l · mol^{-1} · cm^{-1}
1	Ferrocene	440	87	325	51
2	Monoethylferrocene	438.5	95	325	57
3	Mono-*n*-propylferrocene	438.5	97	325	58
4	1,1′-Diethylferrocene	437	104	325	63
5	1,1′-Di-*n*-propylferrocene	437	105	325	63

b) of normal heteroannular disubstituted homologs of ferrocene (see Table 1, Nos. 4, 5; Fig. 1);

c) of normal monosubstituted acyl derivatives of ferrocene (see Table 2, Nos. 2, 3, 4; Fig. 2);

Fig. 2. Absorption spectra of ferrocene *(1)* and its acyl derivatives: 2 — acetylferrocene; propionylferrocene; *n*-butyrylferrocene; 3 —diacetylferrocene-1,1′; dipropionylferrocene-1,1′; 1,1′-di-*n*-butyrylferrocene;

d) of normal heteroannular diacyl derivatives of ferrocene (see Table 2, Nos. 5, 6, 7; Fig. 2).

3. The absorption spectra of heteroannular disubstituted ferrocene derivatives differ from the spectra of the corresponding monosubstituted ones both in the positions of the absorption bands and in their intensities (see Tables 1, 2; Figs. 1, 2).

4. A dependence of the absorption spectra on the nature of the substituent groups is observed:

Table 2

No.	Substance	λ_{max}, mμ	ε, l · mol^{-1} · cm^{-1}	Inflection λ, mμ	λ_{max}, mμ	ε, l · mol^{-1} · cm^{-1}
1	Ferrocene	440	87		325	51
2	Monoacetylferrocene	446	295	356	319	1120
3	Monopropionylferrocene	446	300	356	319	1120
4	Mono-*n*-butyrylferrocene	446	290	356	319	1125
5	1,1′-Diacetylferrocene	455	340	355	318	1580
6	1,1′-Dipropionylferrocene	455	350	355	318	1600
7	1,1′-Di-*n*-butyrylferrocene	455	360	355	318	1580

a) In the region investigated by us, the absorption spectra of ferrocene and the alkyl homologs of ferrocene differ little from one another. However, we observed a slight hypsochromic shift of the 440 mμ band and an increase in its intensity in the series: ferrocene—normal alkylferrocenes—normal heteroannular dialkylferrocenes;

The magnitude of the shift only slightly exceeds the sensitivity of the method, but it is invariably observed in repeated measurements on an SF-4 spectrophotometer and on a Japanese recording spectrophotometer made by Hitachi;

b) In the spectra of the ferrocene derivatives studied by us bearing electron-acceptor substituents (monoacyl and heteroannular diacyl derivatives of ferrocene), a marked bathochromic shift of the 440 mμ band and an increase in its intensity are observed in the series: ferrocene—monoacyl derivatives of ferrocene—heteroannular diacyl derivatives.

In place of the 325 mμ band of ferrocene, a band at 318 and an inflection at 356 mμ appear.

The extent to which the regularities noted above are retained for homoannular derivatives of ferrocene will be the subject of our further study.

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