Chemistry

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1965

SovietRxiv

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Abstract

Full Text

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Absorption Spectra of Some Ferrocene Derivatives

The present work is a continuation of the systematic study we have begun of the absorption and refraction spectra of ferrocene and its derivatives ([1,2,11]). Despite the extreme importance of reliable and systematic spectral data, they are still clearly insufficient. In addition to the works ([3–7,9]) mentioned by us in the preceding paper, the authors know only the article by Rosenblum ([8]).

In the preceding work, devoted to the study of the absorption spectra of ferrocene and its alkyl and acyl derivatives in the region 300-600 mμ, an almost complete coincidence of spectra within homologous series of monosubstituted ferrocenes and homologous series of heteroannular disubstituted ferrocenes was established, with a marked difference between the spectra of ferrocene and mono- and heteroannular disubstituted ferrocenes.

In the present work we investigated the absorption spectra of alkyl esters of ferrocenecarboxylic and 1,1′-ferrocenedicarboxylic acids in the region 180-600 mμ and extended the spectral range of the derivatives we had studied earlier to the region 180-220 mμ (vacuum UV). Measurements in the region 220-600 mμ were carried out on an SF-4 photoelectric spectrophotometer and on a Japanese recording spectrophotometer manufactured by Hitachi. In the region 180-230 mμ they were made on an apparatus built on the basis of the SP-41 double monochromator.* Isooctane was used as the solvent. The short-wavelength boundary of the spectrum investigated is limited by the absorption of isooctane. The products were carefully purified ([1]).

Fig. 1. Absorption spectra of ferrocene and its alkyl derivatives: 1—ferrocene, 2—ethylferrocene, 4—1,1′-diethylferrocene.

No changes in the spectra of the substances studied were observed during the course of the measurements.

* The authors are grateful to Prof. P. P. Shorygin and V. A. Petukhov for the

opportunity they provided to record spectra on the SP-41.

Table 1

Absorption spectra of alkyl derivatives of ferrocene of the type $R_1—C_{10}H_8Fe—R_2$

No.	R_1	R_2	λ_{max}, mμ	ε, l·mol^{-1}·cm^{-1}	f·10^3	λ_{max}, mμ	ε, l·mol^{-1}·cm^{-1}	f·10^3	λ^*, mμ	ε, l·mol^{-1}·cm^{-1}	λ^*, mμ	ε, l·mol^{-1}·cm^{-1}	λ_{max}, mμ	ε, l·mol^{-1}·cm^{-1}	f·10^3
1	H	H	440	87	1,5	325	51	0,6	265	1700	230	4400	200	49000	820
2	C_2H_5	H	438	95	1,7	325	57	0,7	265	2000	235	4500	203	42000	760
3	*n*-C_3H_7	H	438	97	1,7	325	58	0,7	265	2000	235	4600	203	42000	760
4	C_2H_5	C_2H_5	437	104	1,9	325	63	0,8	265	2600	235	5000	206	38000	680
5	*n*-C_3H_7	*n*-C_3H_7	437	105	1,9	325	63	0,8	265	2600	235	5000	206	38000	680
6	*n*-C_4H_9	*n*-C_4H_9	437	104	1,9	325	64	0,8	265	2600	235	5000	206	38000	680

* Wavelength of the midpoint of the inflection.

Table 2

Absorption spectra of acyl and alkyl esters of carboxylic acids, derivatives of ferrocene of the type $R_1—C_{10}H_8Fe—R_2$

No.	R_1	R_2	λ_{max}, mμ	ε, l·mol^{-1}·cm^{-1}	f·10^3	λ^*, mμ	ε, l·mol^{-1}·cm^{-1}	λ_{max}, mμ	ε, l·mol^{-1}·cm^{-1}	f·10^3	λ_{max}, mμ	ε, l·mol^{-1}·cm^{-1}	f·10^3	λ_{max}, mμ	ε, l·mol^{-1}·cm^{-1}	f·10^3	λ_{max}, mμ	ε, l·mol^{-1}·cm^{-1}	f·10^3
7	$COCH_3$	H	446	300	5	356	500	319	1100	21	267	5300	80	220	22500	320	198	32000	750
8	COC_2H_5	H	446	290	5	356	500	319	1140	21	267	5300	80	220	22000	320	198	32000	750
9	COC_3H_7-*n*	H	446	300	5	356	500	319	1140	21	267	5300	80	220	22000	320	198	32000	750
10	$COCH_3$	$COCH_3$	455	350	5,7	350	700	318	1600	32	260	10400	183	224	26000	328	196	25000	670
11	COC_2H_5	COC_2H_5	455	350	5,7	350	690	318	1600	32	260	10400	183	224	26000	328	196	24000	660
12	COC_3H_7-*n*	COC_3H_7-*n*	455	360	5,7	350	690	318	1600	32	260	10400	183	224	26000	328	196	24000	660
13	$COOCH_3$	H	444	180	2,9	335	260	304	860	10	264	4100	52	212	35000	490	196	31000	720
14	$COOC_2H_5$	H	444	180	2,9	335	260	304	870	10	264	4100	52	212	35000	490	196	32000	720
15	$COOCH_3$	$COOCH_3$	420	220	3,5	342	280	300*	1200	—	255	8000	173	218	37000	415	193	26500	660
16	$COOC_2H_5$	$COOC_2H_5$	420	220	3,5	342	280	300*	1200	—	255	8000	173	218	37000	415	193	27000	660

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

* See footnote to Table 1.

The results of the study, presented in Table 1 and Figs. 1, 2, 3*, confirmed our observations that the spectrum of ferrocene itself differs from the spectra of its derivatives, especially in the case of derivatives bearing electron-acceptor substituents (acyl and carboalkoxy groups). The spectra of monosubstituted derivatives differ from the spectra of the corresponding heteroannular disubstituted derivatives both in the positions of the bands and in their intensities over the entire wavelength range; within the homologous series of derivatives studied, the spectra coincide almost completely.

Fig. 2. Absorption spectra of ferrocene and its acyl derivatives: **1** —ferrocene, **7** —acetylferrocene, **10** —1,1′-diacetylferrocene, **12** —1,1′-dibutyrylferrocene.

Fig. 3a, b. Absorption spectra of ferrocene and alkyl esters of ferrocenecarboxylic and 1,1′-ferrocenedicarboxylic acids: **1** —ferrocene, **13** —methyl ester of ferrocenecarboxylic acid, **14** —ethyl ester of ferrocenecarboxylic acid, **15** —dimethyl ester of 1,1′-ferrocenedicarboxylic acid, **16** —diethyl ester of 1,1′-ferrocenedicarboxylic acid.

It is interesting that, when comparing the spectra of mono- and heteroannular derivatives of arylferrocenes (region 220-600 mμ), presented in work (8), an increase in the intensity of the bands can also be found in the series: ferrocene —monosubstituted —heteroannular disubstituted ferrocenes.

In the region of 230 and 265 mμ, the spectra of ferrocene and its alkyl homologs have an inflection; in the spectra of derivatives with electron-acceptor substituents, comparatively strong bands are observed in the region 212-220 and 255-267 mμ. The regularities in the change of the intensities of these bands are the same as in the case of the bands lying in the 220-600 mμ region.

All the substances have a strong band at about 200 mμ. The intensity of this band exceeds the intensity of the bands at about 440 mμ and 325 mμ by 2-3 orders of magnitude.

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* The numbers of the curves in the figures correspond to the numbers in Tables 1 and 2.

If in the 600-220 mμ region the intensity of the bands increases in the series ferrocene—monosubstituted—heteroannular disubstituted, then in the 220-180 mμ region directly opposite regularities are observed. The bands of substances with alkyl substituents are shifted bathochromically, while the bands of substances with electron-acceptor substituents are shifted hypsochromically in comparison with the band in the spectrum of ferrocene.

Table 1 gives the oscillator strengths of all the observed bands for each of the substances studied, calculated by formula (10),

$$f = \frac{9n}{(n^2+2)^2} 4.32 \cdot 10^{-9} \int \varepsilon_\nu d\nu,$$

where n is the refractive index of isooctane, ε_ν is the molar extinction coefficient.

The value of the oscillator strength of the 200 mμ band is considerably greater than the corresponding value for the 440 and 325 mμ bands.

This circumstance, as well as the decrease in intensity in the series ferrocene—monosubstituted—heteroannular derivatives, confirms the assignment of the 200 mμ band to $\pi - \pi^*$ of the ring (^{5}).

The coincidence of the spectra noted above within the homologous series of derivatives studied confirms the additivity of molecular refraction for monosubstituted homologs of ferrocene that we observed earlier and permits one to assert the existence of additivity of refraction within homologous series of ferrocene derivatives.

A comparison of the spectra and refraction of ferrocene, its monosubstituted and heteroannular disubstituted derivatives will be the subject of the next communication.

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Received
10 VII 1964

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