UV SPECTRA OF CARBONYL-CONTAINING FURAN COMPOUNDS

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UDC 547.724:543.422.6

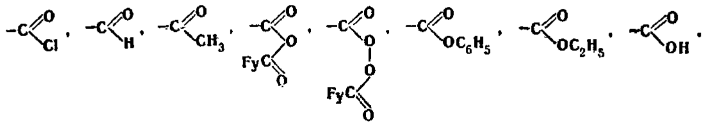
The optical absorption maxima in the UV spectra of furan aldehydes, ketones, acids and their derivatives – acid chlorides, anhydrides, esters, and diacyl peroxides – can be arranged in an order similar to the order of reactivities of the carbonyl groups. The effect of a solvent on the position of λ_{max} was examined.

We have synthesized a number of furan diacyl peroxides with various substituents in the 5 position of the furan ring. The spectra of the peroxide compounds obtained are interesting from the point of view of the identification of peroxides detected in the reaction mixture during the autooxidation of various furan derivatives and also in the examination of the effect of the substituting groups on the position of the optical absorption maxima. The UV spectra of the diacyl peroxides have not received sufficient study, and the spectral characteristics of furan peroxides have not up to now been examined at all. It was of interest to compare the UV spectra of furoyl peroxides with the spectra of carbonyl-containing compounds with a non-peroxide structure, primarily the anhydrides and esters of furan-2-carboxylic acids.

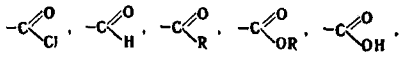
All of the investigated furan compounds give an optical absorption maximum in the UV portion of the spectrum, which is caused by the furan ring in conjugation with the carbonyl group (the FyC = O chromophore, in which Fy is furyl, C_4H_3O). The spectral characteristics of the examined compounds are presented in Table 1.

The introduction of both electron-donor and electron-acceptor substituents into the 5 position of the furan ring leads to a bathochromic shift of the optical absorption maximum.

The absorption maxima (when the substituent in the 5 position is the same) are shifted regularly hypsochromically on passing from the acid chlorides to the acids. This corresponds to a gradual decrease in the acceptor activity in the order



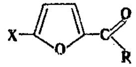
It is known that the carbonyl groups are arranged in the following order [1] with respect to decreasing reactivity in nucleophilic addition reactions:



Thus the electronic spectra of carbonyl-containing compounds of the furan series to a certain degree reflect their reactivities; thus, judging from the spectra, the carbonyl groups of acid anhydrides and diacyl peroxides should occupy an intermediate position, in the order of reactivities, between ketones and esters.

We also recorded the UV spectra of benzoyl chloride, benzaldehyde, acetophenone, benzoic anhydride, benzoyl peroxide, phenyl benzoate, ethyl benzoate, and benzoic acid (λ_{max}, nm, respectively: 243, 241, 239, 232, 231, 229, and 228), i.e., a gradual hypsochromic shift of λ_{max} is also observed for this series of compounds. Thus the described regularity is not limited to the furan series and is of general character.

Krasnodar Polytechnic Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 590-594, May, 1973. Original article submitted June 5, 1972.

TABLE 1. UV Spectra* of Furan Carbonyl-Containing Compounds of the  Type

X \ R	Acid chlorides, Cl	Aldehydes, H	Ketones, CH_3	Anhydrides, $O-\overset{O}{\overset{\|}{C}}-Fy$	Peroxides, $O-O-\overset{O}{\overset{\|}{C}}-Fy$	Esters OC_6H_5	Esters OC_2H_5	Acids, OH
	λ_{max} (lg ε)							
CH_3	288 (4,26)	282 (4,23)	280 (4,29)	279 (4,47)	278 (4,66)	266 (4,62)	261 (4,31)	256 (4,15)
H	272 (4,16)	268 (4,13)	265 (4,19)	264 (4,42)	262 (4,50)	254 (4,49)	249 (4,22)	246 (4,10)
Cl	285 (4,25)	280 (4,17)	278 (4,27)	— —	276 (4,60)	263 (4,58)	257 (4,29)	254 (4,22)
Br	288 (4,23)	282 (4,20)	280 (4,28)	279 (4,55)	278 (4,60)	267 (4,60)	261 (4,30)	256 (4,24)
I	295 (4,27)	291 (4,20)	282 (4,30)	— —	285 (4,59)	272 (4,63)	267 (4,33)	264 (4,20)
NO_2	299 (4,06)	302 (4,06)	— —	299 (4,27)	294 (4,43)	297 (4,40)	298 (4,10)	299 (4,04)

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* The spectra were recorded in dioxane.

TABLE 2. Effect of Solvents on the Position of the Absorption Maximum in the UV Spectra of Carbonyl-Containing Compounds of the Furan Series*

X \ R	Acid chlorides, Cl		Aldehydes, H				Ketones, CH_3				Anhydrides, $O-\overset{O}{\overset{\|}{C}}-Fy$		Peroxides, $O-O-\overset{O}{\overset{\|}{C}}-Fy$			Esters								Acids, OH			
																OC_6H_5				OC_2H_5							
	λ_{max}, nm																										
	n-heptane	dioxane	n-heptane	dioxane	ethanol	water	n-heptane	dioxane	ethanol	water	n-heptane	dioxane	n-heptane	dioxane	ethanol	n-heptane	dioxane	ethanol†	water†	n-heptane	dioxane	ethanol	water	n-heptane	dioxane	water	ethanol
CH_3	280	288	277	282	284	292	272	280	283	289	276	279	271	278	276	262	266	268	270	258	261	262	265	264	256	256	250
H	268	272	265	268	272	278	262	265	269	273	260	264	256	262	261	252	254	256	259	248	249	251	254	250	246	245	241
Cl	275	285	273	280	282	288	272	278	280	285	—	—	269	276	276	264	263	—	—	255	257	258	263	261	254	253	248
Br	284	288	275	282	285	290	273	280	281	286	277	279	271	278	278	267	267	—	—	259	261	262	266	263	256	256	250
I	290	295	283	281	296	299	275	282	285	292	—	—	274	285	281	269	272	—	—	264	267	267	269	269	264	259	253
NO_2	286	299	292	302	310	310	—	—	—	—	286	299	286	294	296	290	297	300	—	291	298	295	310	289	209	315	314

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*λ_{max} for the corresponding carbonyl-containing derivatives of benzene (nm): 241, 243; 240, 242, 245; 237, 239, 241; 232, 232; 231, 232, 234; 227, 228, 228; 227, 228, 228; 229, 228, 227 (in ethanol).

† Halogen-substituted phenyl furoates undergo esterification in ethanol and are hydrolyzed to acids in water.

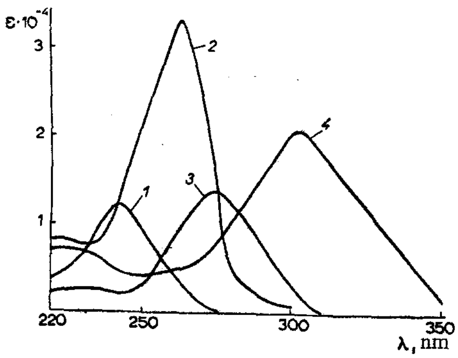

Fig. 1. UV spectra in ethanol: 1) furan-2-carboxylic acids; 2) furoyl peroxide; 3) furfural; 4) furyl.

Nitro compounds should be placed in a special group. While in all the other cases Δλ is ~ 30 nm on passing from the acid chloride to the acid itself, all of the nitro compounds absorb at 296 ± 4 nm, and the extinction is somewhat lowered as compared with unsubstituted furans. These peculiarities of the spectra of nitrofurans are explained by "competition" between two electron-acceptor groups – the carbonyl group and the nitro group – and this leads to a certain weakening of the conjugation in the system [2]. The effect of the nitro group as a stronger acceptor prevails.

The furoyl peroxides absorb at 262-285 nm. The extinction is about twice that of aldehydes, since the peroxide molecule consists of two FyC = O chromophores joined by an oxygen–oxygen bridge.

The closest analogs of diacyl peroxides are the anhydrides of the corresponding acids. The absorption maxima of the anhydrides of furan-2-carboxylic acids are only slightly bathochromically shifted as compared with the spectra of the furoyl peroxides. The extinction is somewhat lower than for peroxides. A similar pattern was observed for benzoyl peroxide and benzoic anhydride, p-toluyl peroxide, and the corresponding anhydride [3]. This may be explained by the higher possibility of conjugation between the two FyC = O groups through one oxygen atom than through the peroxide bridge.

In connection with the discussed problem of the interaction of the chromophore groups in the molecule, it was of interest to compare the UV spectra of furoyl peroxides and anhydrides of furan-2-carboxylic acids with the spectra of difuroyl – a diketone that has two FyC = O chromophores directly connected to one another (Fig. 1). Difuroyl absorbs at 302 nm (log ε 4.32). In this case, the intramolecular interaction between the chromophore groups leads to an appreciable shift to the longer-wavelength side with a simultaneous increase in the absorption intensity as compared with the isolated chromophore.

The fact that the presence of two chromophores in the molecules of the furoyl peroxides and anhydrides does not cause a large shift in λ_{max} to the long-wavelength region and the molar extinction is approximately equal to the sum of the extinctions of the isolated FyC = O groups makes it possible to assume that the interaction between the chromophore groups in these compounds is minimal [4].

The unshared p electrons of oxygen in the molecules of the ethyl esters and in the molecules of the acids participate in conjugation with the chromophore. The positive inductive effect of the alkyl group somewhat facilitates the shift of the p electrons of the ester oxygen. The degree of conjugation in the molecules of the ethyl furoates is therefore greater than that observed for molecules of the acids; this is expressed in the bathochromic shift of λ_{max}. In addition, the state of oxygen in the phenyl furoates somewhat recalls the anhydride oxygen – the unshared p electrons of oxygen are conjugated simultaneously with the carbonyl group and the benzene ring, and, in the case of the anhydrides, with two carbonyl groups.

We also examined the effect of a solvent on the position of λ_{max} of carbonyl-containing furans, for which we recorded their UV spectra in n-heptane, dioxane, ethanol, and water (Table 2). A bathochromic shift of the absorption band on passing from n-heptane to ethanol and water, i.e., in the order of increasing dielectric constant of the solvent, is observed for all of the investigated compounds except the acids. A particularly large solvatochromic effect is observed for nitrofurans; this attests to considerable polarization of these compounds and redistribution of the electron density as the dielectric permeability of the medium changes.

A hypsochromic shift of the absorption maximum in the series of solvents n-heptane–dioxane–water–ethanol is observed in the case of furan-2-carboxylic acids. This is apparently explained by the existence of the acids in nonpolar media as a mixture of monomeric and dimeric unsolvated molecules, while in water and alcohols the formation of hydrogen bonds with the solvent, which leads to stabilization of the acid molecules primarily in the monomeric form, is possible.

The carbonyl-containing benzene derivatives absorb over a much narrower range of the spectrum (229-241) than furans (241-272 nm) and are less subject to the effect of the solvent: Δλ for transition from n-heptane to ethanol is 1-3 nm compared with 3-9 nm for furans. This again confirms that the furan system is more labile and is to a greater degree capable of transmitting electronic effects [5].

EXPERIMENTAL

The furoyl peroxides were synthesized for the first time (except for the previously known furoyl peroxide) via the method in [6]. The degree of purity of the preparations obtained, which was determined iodimetrically, was no less than 98%. The anhydrides of furan-2-carboxylic acids were obtained by transdehydration with acetic anhydride [7].

The ethyl esters of furan-2-carboxylic acids were obtained by reaction of the appropriate acid chlorides with ethanol, while the phenyl esters were obtained by reaction of the acid chlorides with phenol in dioxane.

The UV spectra in n-heptane, dioxane, ethanol, and water were recorded with an SF-4A spectrophotometer in 1-cm-thick quartz cuvettes.

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