PROTON-ACCEPTOR CAPACITIES OF ALLYL ESTERS OF FURAN-2-CARBOXYLIC ACIDS

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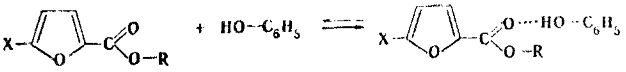
The basicities of 5-substituted allyl 2-furoates with respect to phenol and pentachlorophenol were investigated by IR spectroscopic methods. Measurements of the $\Delta\nu_{OH}$ values of phenols were made in CCl_4 and C_2Cl_4. The energy of the intermolecular H bond is 13-16 kJ/mole. The vinyl group of the allyl grouping in the allyl furoates retains its electron-acceptor character.

Considerable information is available from studies [1-6] of the proton-acceptor capacities of esters of aliphatic and aromatic acids and compounds containing a 2-furoyl group. It is known that esters [1-4], 2-acetylfurans [5], and furan analogs of chalcones [6] are weak organic bases that are capable of forming complexes with a hydrogen bond, the energy of which ranges from 10 to 30 kJ/mole, with proton donors of the OH acid type. The magnitude of the enthalpy of the intermolecular H bond in complexes of this type depends on the chemical structure of the proton-acceptor molecule and its polarizability, the acidity of the proton donor, the character of the solvent, and the temperature. Little study has been devoted to esters of furancarboxylic acids from the point of view of the relationship between the chemical structure of the molecules and their reactivities. The results of chemical and some spectral studies of vinyl esters of furan-2-carboxylic acids are known [7]. In this connection, it seemed of interest to us to study the proton-acceptor capacities of some esters of furan-2-carboxylic acids by comparison of the energies of the intermolecular hydrogen bonds of complexes of esters I-IV with OH acids of the phenol type (V, VI):



I-IV V, VI

I X=H, R=CH_2–CH=CH_2; II X=CH_3, R=CH_2–CH=CH_2; III X=Br, R=CH_2–CH=CH_2;
IV X=H, R=CH_2–CH_2–CH_3; V Ph=C_6H_5; VI Ph=C_6Cl_5

Measurements of the shift of the IR absorption band of the hydroxyl group of phenols V-VI ($\Delta\nu_{OH}$) were made in two aprotic solvents – carbon tetrachloride and tetrachloroethylene. Self-association of the proton donors was virtually excluded at selected concentrations of the donors. The absence of self-association was verified by recording the IR spectra of the phenols in CCl_4 or C_2HCl_4 at 3300-3700 cm^{-1}. The no less than tenfold excess of the proton-acceptor with respect to the concentration of the phenol in the "ester—phenol—solvent" ternary system was due to the necessity for the production of the most convenient (for graphical measurements) IR spectra of the bands of the associated hydroxyl group ($\nu_{OH...}$) of the OH acids. The maximum of the $\nu_{OH...}$ absorption bands was determined graphically by a method described in [8].

The furan-2-carboxylic acid ester molecule contains three different types of bonds involving an oxygen atom that are potential basicity centers.

It is known that the energy of the intermolecular H bond of furan with phenol in CCl_4 is 3.22 kJ/mole [9], while esters of carboxylic acids of the aliphatic and aromatic series react with phenols in the same solvent to give complexes with considerably higher H bond energies [2, 3, 9, 10]. Consequently, the oxygen atoms of the ester group are more basic than the oxygen atom in the furan ring.

The observed absence of any distortions on the high-frequency side of the $\nu_{OH...}$ IR bands makes it possible to assume that in the allyl furoate molecules intermolecular hydrogen bonds are not formed with centers that are less basic than the ester group.

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TABLE 1. Characteristics of the Intermolecular Hydrogen Bond of Allyl Furoates with Phenol and Pentachlorophenol

Compound*	Solvent	$\Delta\nu_{OH}$, cm^{-1}, V* (pK_a = 9.95)†	ΔH, kJ/mole	$\Delta\nu_{OH}$, cm^{-1}, phenol VI* (pK_a = 4.50)†	ΔH, kJ/mole
I	CCl_4	146±2	14,3±0,1	153±2	14,8±0,1
II		165±2	15,5±0,1	172±2	15,9±0,1
III		138±2	13,7±0,1	148±2	14,4±0,1
IV		160±2	15,2±0,1	165±2	15,5±0,1
I	C_2Cl_4	140±3	13,9±0,2	152±2	14,7±0,1
II		154±3	14,6±0,1	171±3	15,9±0,1
III		133±2	13,4±0,1	148±2	14,4±0,1
IV		153±3	14,6±0,1	164±2	15,4±0,1

*The numbering of the compounds corresponds to the numbering in the scheme.

†These data were taken from [17].

Levchenko and co-workers [3], in a study of the proton-acceptor capacities of allyl benzoates, concluded that "the formation of H complexes in the ester—phenol—CCl_4 system proceeds exclusively at the carbonyl group of the esters." The same thing is also asserted in [9], although there are also other opinions relative to the site of association of OH acids [10, 11] and other organic acids [12] with esters of carboxylic acids. The shift of the IR absorption band of the stretching vibrations of the carbonyl oxygen atom ($\nu_{C=O}$) to the low-frequency region in the reaction of I-IV with phenols V-VI confirms the fact of the association of OH acids with furoates only with the carbonyl oxygen atom.

The energy of formation of the intermolecular hydrogen bond was calculated from the formula [13]

$$(\Delta H)^2 = 1.926(\Delta\nu_{OH} - 40) \text{ kJ/mole}$$

The results of the measurements and calculations, which were treated by statistical methods with a confidence probability coefficient of 0.95, are presented in Table 1.

In analyzing the data in Table 1 one's attention is drawn to the fact that $\Delta\nu_{OH}$ of phenol V is somewhat lower in tetrachloroethylene solution than in carbon tetrachloride solution. This is in agreement with the analogous results obtained in [9, 14]. However, when phenol VI was used as the proton donor, we did not observe the above-indicated effect. In this case the specific interaction of the solvent with the OH acid is evidently reduced to a minimum.

The change in the energy of the H bond of the complexes of allyl furoates with OH acids is in agreement with the character of the substituents in the 5 position of the furan ring: The methyl group promotes an increase in the basicity of the carbonyl oxygen atom, whereas halogen has the opposite effect.

During a study of allyl benzoates, Levchenko and co-workers [3] concluded that the vinyl group in the allyl grouping of the alcohol portion of the ester retains its electron-acceptor properties. It seemed of interest to ascertain whether the acceptor character of the vinyl group is retained in allyl furoates. It follows from Table 1 that the energy of the intermolecular H bond is 0.8 kJ/mole higher in propyl furoate than in allyl furoate. This makes it possible to conclude that the allyl grouping has electron-acceptor character as compared with the propyl group in the alcohol portion of the furoates. In our opinion, this effect is due both to partial retention of the conjugation between the alkoxy oxygen atom of the ester group and the terminal double bond and to the manifestation of a negative inductive effect of the sp^2-hydridized β-carbon atom of the alcohol portion of the allyl furoates. The above-indicated factors increase the total electron-acceptor effect of the ester oxygen atom on the C=O bond even more, thereby lowering the basicity of the carbonyl oxygen atom.

One should also note the fact that $\Delta\nu_{OH}$ values that we obtained for unsubstituted allyl and propyl furoates are lower than the corresponding values for unsubstituted allyl and propyl benzoates [3]; this would seem to contradict the literature data on the electron-donor character of the furyl group in acetylfurans [5] and furan analogs of chalcones [6]. We will present the results of a more detailed study of this fact in subsequent papers.

EXPERIMENTAL

The IR spectra of the compounds in cylindrical cuvettes with KBr windows and an absorbing-layer thickness of 0.5 cm were recorded at 25°C with an IKS-14 double-beam IR spectrometer at 3300-3700 cm^{-1} (LiF prism). The scanning rate was 37 cm^{-1} min, the recording scale was 6 mm/min, and the slit width was 11 divisions of the micrometric screw.

The furan-2-carboxylic acid esters were synthesized by methods similar to those presented in [15]; the allyl esters were obtained for the first time in the present research.

To investigate the proton-acceptor capacities of the esters we prepared solutions of the esters and phenols with the following concentrations: 0.2 mole/liter of the ester plus 0.02 mole/liter of phenol V in CCl_4 or C_2Cl_4, and 0.3 mole/liter of the ester plus 0.005 mole/liter of phenol VI in CCl_4 or C_2Cl_4, as well as solutions of the esters in CCl_4 and C_2Cl_4 with the same concentrations as in the ternary systems (for the comparison cuvettes).

Analytical-grade carbon tetrachloride was dried for 24 h over calcined $CaCl_2$, after which it was refluxed over P_2O_5 for 3 h and fractionated with a 48-cm long fractionating column of the rod-and-disk type, as a result of which the solvent had bp 76.8°C. Tetrachloroethylene was purified by the method in [16]; it was dried with $CaCl_2$ and fractionated twice in a dry box, as a result of which a solvent with bp 121°C was obtained. The phenol and pentachlorophenol were purified as described in [2].

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