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ASSOCIATION CONSTANTS OF SUBSTITUTED 2-ACETYLTHIOPHENES WITH PHENOL

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The association constants (K_{ass}) of a number of substituted 2-acetylthiophenes and 3-acetylthiophene with phenol in tetrachloroethylene solutions at 25, 50, and 80° were determined by IR spectroscopy. It is shown that acetylthiophenes are stronger proton acceptors than the corresponding acetophenones. The thermodynamic characteristics (ΔH and ΔS) of the association were calculated, and the presence of a compensation effect was established. It is shown on the basis of correlation of the K_{ass} values by means of the Brown, Yukawa–Tsuno, and Swain–Lupton equations that the thiophene ring is a better transmitter of the effect of substituents than the benzene ring because of the increased conductivity of the conjugation effect.

In order to characterize the effect of the thiophene ring on the proton-acceptor capacity of the carbonyl group and the efficiency of transmission of the electronic effects of substituents in this heteroaromatic system as compared with the benzene ring [1, 2], we measured the association constants (K_{ass}) of a number of substituted acetylthiophenes with phenol in tetrachloroethylene solutions at 25, 50, and 80°C and determined the thermodynamic characteristics (ΔH and ΔS) of the investigated process (Table 1).

At all of the investigated temperatures the K_{ass} values obtained for 2- and 3-acetylthiophenes (I and II) exceed the values obtained for acetophenone (X). At the same time, the previously determined $\Delta\nu_{OH}$ values for 2-acetylthiophene (196 ± 1 cm^{-1}) and acetophenone (197 ± 1 cm^{-1}) [2] do not differ. These facts are a consequence of the effect of the proton-acceptor capacity of the carbonyl group of, on the one hand, the electronic effects of the hetaryl ring bonded to it and, on the other, the steric hindrance to the formation of H bonds created by the heteroatom, which, as is well known [3, 4], is in the s-cis position relative to the oxygen atom.* When the phenyl group in acetophenone is replaced by the electron-donor 2-thienyl group [6], the effect of the above-mentioned oppositely acting factors on the $\Delta\nu_{OH}$ value is compensated and as a result does not change. However the increase in K_{ass} on passing from X to I indicates that the K_{ass} values are considerably less sensitive to steric effects, and the polarity of the carbonyl group has a greater effect on them; this is in agreement with the results obtained during a study of the proton-acceptor capacity of substituted acetophenones, 2-acetylselenophenes [2], and other carbonyl bases [7].

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*See [5] for the existence of steric hindrance between the carbonyl group and an adjacent thiophene ring.

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TABLE 1. Equilibrium Constants and Thermodynamic Characteristics of Association in Systems Involving Phenol, Tetrachloroethylene, and Ketones of the General Formula $RCOCH_3$

Compound	R	k_{ass}, liter · mole^{-1}			$-\Delta H$, kcal/mole	$-\Delta S$, eu
		25°	30°	80°		
I	2-Thienyl	11.7±0.4	5.6±0,4	2,6±0.1	5,4±0.2	13,2±0,8
II	2-Thienyl	11.4±0.5	7,7±0,1	3.0±0.1	4,8±0.2	11,1±0.1
III	5-Methyl-2-thienyl	14,6±0.9	7,0±0,9	3,2±0,2	5,5±0.3	13,0±1.0
IV	5-Chloro-2-thienyl	7.6±0,3	3,7±0,4	1,9±0,3	5.0±0,3	12,7±0,8
V	4-Bromo-2-thienyl	6,7±0,9	2,8±0,4	1,5±0,9	6.3±0,7	17,0±0,9
VI	5-Bromo-2-thienyl	8,5±0,5	4,5±0,6	2,3±0,3	4.9±0,7	12,2±0,9
VII	5-Iodo-2-thienyl	8,6±0,9	4,6±1,2	2,0±0,6	5,2±0,7	13,1±0.8
VIII	2-Nitro-2-thienyl	2,9±0,5	1.9±0,4	1,2±0.3	3,4±0.5	9,4±0,5
IX	5-Phenyl-2-thienyl	13.8±0,9	5,7±0,2	2,9±0,5	5,8±0,7	13,4±0,9
X	Phenyl	9,9±0.3	4,9±0,1	2,4±0,1	5,4±0,4	13,5±0,5

TABLE 2. Results of Correlation Analysis of the log K_{ass} Values of 2-Acetothiophenes with Respect to the Hammett, Brown, and Taft Equations*

Equation: $y = Ax + B$	k	s_A	s_B	s_{tot}	n
$\lg K_{ass} = -0,61\sigma + 1,06$	0,99	0,03	0,01	0,02	7
$\lg K_{ass} = -0,54\sigma^+ + 1,07$	0,95	0,03	0,01	0,05	7
$\lg K_{ass} = -0,64\sigma^0 + 1,13$	0,99	0,03	0,02	0,04	7

*Abbreviations: k is the correlation coefficient, s_A and s_B are the mean square errors in the A and B parameters, and s_{tot} is the total dispersion, and n is the number of points.

The considerably higher $\Delta\nu_{OH}$ value for 3-acetylthiophene (214 cm^{-1}) [2] as compared with its isomer (vis-a-vis the relatively small difference in the K_{ass} values) also evidently may be partially due to the fact that steric hindrance of the heteroatom to the formation of a hydrogen bond is removed in the first compound. In addition, the 3-thienyl group in the investigated systems has a somewhat greater electron-donor effect than the 2-thienyl group, mainly due to the smaller negative inductive effect has compared with the latter [8].

The changes in the K_{ass} values in a series of substituted 2-acetylthiophenes in general correspond to the electronic nature of the substituent, and the log K_{ass} values correlate well with the σ, σ^+, and σ^0 substituent parameters (the results of correlation analysis of the data at 25° are presented in Table 2). Considerable deviation from the correlation line is observed in all cases for the point corresponding to 5-nitro-2-acetylthiophene (VIII); this is probably due to the specific (for heterosystems) effect of the interaction of the electron-acceptor nitro group with the electron-donor heteroatom [1, 9]. It is possible that this effect also occurs to a certain degree for 3-acetylthiophene.

A comparison of the ρ reaction constants in the Brown equation* for a series of 2-acetylthiophenes ($\rho_T = -0.54$) and acetophenones ($\rho_b = 0.36$ [2]) made it possible to characterize the relative efficiency of transmission of the electronic effect of substituents by the thiophene and benzene rings in the investigated reaction: the conductivity coefficient $\gamma = \rho_T/\rho_b = 1.5$.† This confirms the previously obtained conclusion regarding the better conductivity of the electronic effects of substituents by the thiophene ring as compared with the benzene ring [1, 10].

The dependence of the log K_{ass} values of a series of 2-acetylthiophenes on the electronic effects of substituents can be also satisfactorily described by means of two-parameter equations of the Yukawa-Tsuno [11] and Swain-Lupton [12] type (in both cases correslation coefficient k = 99):

$$\lg K_{ass} = \lg K_{ass}^{H} + \rho^0\sigma^0 + \rho_R\sigma_{R^-}, \tag{1}$$

$$\lg K_{ass} = \lg K_{ass}^{H} + fF + rR, \tag{2}$$

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*A rather high correlation coefficient (k = 0.95) was obtained from the acetophenones only when the log K_{ass} values were correlated with the electrophilic σ^+ constants [2].

†The isoequilibrium temperatures for the series of acetophenones (399°K) and 2-acetylthiophenes (400°K) do not differ within the limits of experimental error and appreciably exceed the temperature (298°K) at which γ was determined.

where σ^0 are constants that characterize the inductive effect of substituted phenyl groups, σ_{R^+} characterizes the capacity of a substituent for direct polar conjugation with the reaction center, F and R are constants that characterize the so-called field and resonance effects of a substituent, and ρ^0, ρ_R, f, and r are coefficients of sensitivity to the above-indicated effects, respectively.

A comparison of the reaction constants, which characterize the sensitivity of the thiophene system to the inductive effect ($\rho^0 = -0.67$, $s_{\rho_0} = 0.11$, $f = -0.42$, and $s_f = 0.09$) and to the conjugation effect ($\rho_R = -.085$, $s_{\rho R} = 0.15$, $r = -0.57$, and $s_r = 0.11$) shows predominance of the latter in the mechanism of transmission of the electronic effects of the substituents by the thiophene ring; this is in agreement with the data obtained for thienyl acetylenic ketones [13]. It was not possible to evaluate the conductivity of the individual components of the substituent effects as compared with the benzene system, since low correlation coefficients (k = 0.88 and 0.84, respectively) were obtained in an attempt to correlate the log K_{ass} values of a series of acetophenones with respect to the data in [3] by means of Eqs. (1) and (2).

The enthalpy changes (ΔH) in the association process (Table 1) calculated from the temperature dependence log $K_{ass} - 1/T$ (T is the absolute temperature) range from −3.4 to −6.3 kcal/mole; this is characteristic for hydrogen bonds of moderate strength. The relatively large errors in the ΔH values and the entropy changes (ΔS) do not make it possible to draw rigorous conclusions relative to the effect on these values of various spectral factors. As in reaction series with the participation of acetophenones and 2-acetylselenophenes [3], the same principles as observed for the K_{ass} values are, as a rule, observed for the ΔH values of the investigated compounds. One can ascertain the presence of the compensation effect between the ΔH and ΔS values [14] that was also noted for other previously investigated carbonyl-containing bases [3, 7].

EXPERIMENTAL

The synthesis and purification of the investigated compounds were described in [1, 15, 16], and the purification of tetrachlorethylene was described in [3].

The method used to measure the association constants from the IR spectral data was described in [7].

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