UDC 547.722

BASICITY AND STRUCTURE OF α, β-UNSATURATED HETEROCYCLIC KETONES
III. Furan Analogs of Chalcone*

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 1, No. 6, pp. 803-811, 1965

The protolytic equilibrium constants of chalcone and its furan and thiophene analogs have been measured spectrophotometrically in sulfuric acid—glacial acetic acid solution. It is shown that the furan ketones are more basic than the thiophene ones, basicity depending on the position of the carbonyl group in the conjugated chain. In the systems studied, 2-furyl exhibits an appreciably greater positive dynamical conjugation effect than 2-thienyl, but as compared with the latter it gives rise to less steric hindrance to solvation of carbonium ions.

Previous papers [1, 2] gave the results of a spectrophotometric study of the basicity of chalcone, and its thiophene analogs and nearest vinylogs in aqueous sulfuric acid solution. Continuing the study of the relationship between structures of α, β-unsaturated ketones and their proton-acceptor properties, it was decided to measure the basicity constants of furan analogs of chalcone. Further it was of interest to compare the relative effects of the furyl and thienyl groups on the protolytic equilibrium constants of the ketones, as the literature contains contradictory indications regarding the electronic characteristics of these heterocycles [3-10].

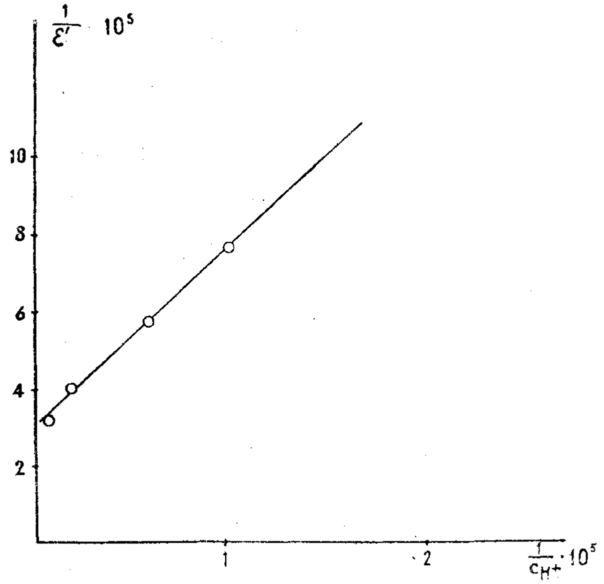

Fig. 1. Relationship between $1/\varepsilon'$ and $1/CH^+$ for 1-(thienyl-2)-3-phenylpropenone-1.

It is known that furan derivatives are acidophobic, and that this makes it impossible to determine their basicity constants in aqueous sulfuric acid solution. Two of the present authors have shown [11] that furan ketones are rather more stable in acetic acid solutions of sulfuric acid, and it was decided to carry out basicity measurements in that solvent. For comparison purposes basicity constants of chalcone and its thiophene analogs were measured in the same solvent, appropriate data being lacking in the literature.

A previous paper [1] described a method using spectrophotometric measurements and the calculation of the protolytic equilibrium constant. A graphical method was also used for preliminary evaluation of the experimental data. According to the law of mass action

$$K = \frac{x}{(c-x)CH^+}, \tag{1}$$

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*For Part II see [2].

where x is the equilibrium concentration of the ionic form of the ketone, and c the initial ketone concentration. Thence

$$c = \frac{x}{K \cdot CH^{+}} + x. \qquad (2)$$

Multiplying both sides of equation (2) by 1/D gives

$$\frac{cl}{D} = \frac{xl}{K \cdot CH^{+} \cdot D} + \frac{xl}{D}. \qquad (3)$$

But cl/D = 1/ε', and xl/D = 1/ε, so

$$\frac{1}{\varepsilon'} = \frac{1}{\varepsilon} + \frac{1}{K \cdot \varepsilon} \cdot \frac{1}{CH^{+}}, \qquad (4)$$

where ε' is the apparent molar coefficient of absorption of the ionic form; ε the real molar coefficient of absorption of the ionic form. It is obvious that equation (4) is linear, with 1/ε and 1/Kε constant coefficients, and 1/ε' and $1/CH^{+}$ quantities which can be found experimentally. As a rule the experimental values of 1/ε' and $1/CH^{+}$ fall well on a straight line (see for example Fig. 1). Points which were considerably off the straight line (mostly obtained at high sulfuric acid concentrations) were ignored for calculation purposes.

It was also useful to check whether the compounds studied behaved as Hammett indicators, i.e., gave a linear relationship between lg CBH^{+}/c_B and acid concentration. It was shown that all the compounds investigated in the present case gave straight lines parallel to one another and to the straight lines obtained by plotting literature data [12] for p-chloronitroaniline and 2, 4-dichloro-6-nitroaniline (see Fig. 2) which were used as indicators to determine the Hammett acidity constants.

The present basicity data were correlated with the characteristic IR vibration frequencies of the carbonyl group [13], as well as with the dipole moments of the compounds [14].

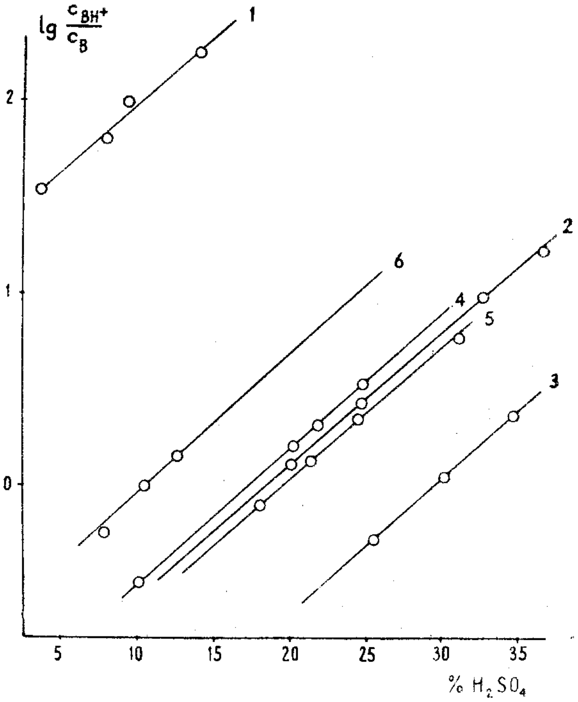

Fig. 2. Relationship between lg $(c_{BH}{}^{+}/c_B)$ and acid concentration for: 1) p-chloronitroaniline; 2) 2, 4-dichloro-6-nitroaniline; 3) chalcone; 4) 1-(furyl-2)-3-phenylpropenone-3; 5) 1-(thienyl-2)-3-phenylpropenone-3; 6) 1, 3-di(furyl-2) propenone.

Experimental

For the spectrophotometric measurements all the compounds were carefully purified by repeated recrystallization. A preliminary study was also made of the stabilities of their sulfuric acid solutions by determining the time absorption curves in the visible region using a SF-2M self-recording spectrophotometer.

Anhydrous sulfuric acid was prepared from commercial acid passing the Savall test by saturating it with sulfur trioxide,

Table 1

Spectrophotometric Measurement Data and Calculated Basicity Constants for Chalcone, and its Furan and Thiophene Analogs*

Compound number	Initial ketone concentration c · 10^5 M	% H_2SO_4 in the acetic acid, and H_0 of the solution	Optical density data for various wavelengths, D/λ, mμ				Calculated ε_{av} at the various wavelengths: ε_{av} (λ)				K ± ΔK · 10
I	3.16	34.71; −4.75 32.65; −4.63 29.72; −4.28 26.35; −4.09	0.450/390 0.400/390 0.320/390 0.240/390	0.470/395 0.410/395 0.325/395 0.245/395	0.470/400 0.410/400 0.320/400 0.240/400	0.460/405 0.400/405 0.310/405 0.230/405	17510 (390)	18390 (395)	18720 (400)	18540 (405)	6,2±0.4
II	2.00	25.18; −4.01 19.89; −3.62 16.49; −3.34 13.47; −3.14	0.510/420 0.420/420 0.340/420 0.295/420	0.520/425 0.420/425 0.340/425 0.295/425	0.490/430 0.400/430 0.300/430 0.270/430		27690 (420)	28150 (425)	27180 (430)		72±5
III	1.70	25.10; −4.00 20.58; −3.67 15.98; −3.29 10.02; −2.96	0.385/430 0.315/430 0.215/430 0.130/430	0.410/435 0.335/435 0.225/435 0.135/435	0.430/440 0.350/440 0.230/440 0.140/440	0.410/445 0.335/445 0.225/445 0.135/445	28350 (430)	30570 (435)	31980 (440)	30570 (445)	39±1
IV	1.60	14.85; −3.19 12.45; −3.08 10.28; −2.98 7.93; −2.73 6.07; −2.51	0.530/460 0.450/460 0.390/460 0.320/460 0.230/460	0.570/465 0.480/465 0.410/465 0.340/465 0.240/465	0.570/470 0.480/470 0.410/470 0.340/470 0.240/470	0.530/475 0.450/475 0.390/475 0.320/475 0.230/475	45940 (460)	50690 (465)	50690 (470)	45940 (475)	134±8
V	1.50	39.99; −5.12 35.05; −4.77 30.06; −4.31	0.430/415 0.360/415 0.265/415	0.460/420 0.375/420 0.280/420	0.460/425 0.375/425 0.280/425	0.450/430 0.370/430 0.275/430	32000 (415)	34260 (420)	34260 (425)	33510 (430)	5,7±0.5
VI	1.60	29.54; −4.26 24.53; −3.96 20.90; −3.69 17.95; −3.51	0.385/440 0.315/440 0.240/440 0.205/440	0.395/445 0.325/445 0.255/445 0.210/445	0.395/450 0.325/450 0.255/450 0.210/450	0.385/455 0.315/455 0.240/455 0.205/455	28820 (440)	29850 (445)	29850 (450)	28820 (455)	24±1
VII	1.90	23.34; −3.87 18.68; −3.55 15.50; −3.23 12.46; −3.09	0.515/465 0.425/465 0.330/465 0.250/465	0.530/470 0.435/470 0.335/470 0.255/470	0.540/475 0.435/475 0.335/475 0.250/475	0.520/480 0.420/480 0.320/480 0.240/480	33300 (465)	34450 (470)	35480 (475)	34390 (480)	55±3

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* A few independent experiments were carried out for each compound, but the table gives the results of only one.

distilled off from oleum. Generally the acid thus prepared contained a small excess of free sulfur trioxide. 100% sulfuric acid was prepared by diluting it with 98% acid, acid strength being checked by titration.

Commercial glacial acetic acid was fractionated by distillation and freezing (mp 16.3°). The mixtures of glacial acetic acid and anhydrous sulfuric acid were prepared by weighing on an analytical balance, using a vessel with a ground-glass stopper. (the acids were mixed with cooling.) The Hammett acidity constants of the solutions were derived by interpolating the data obtained [12].

Spectrophotometric measurements and calculations of the basicity constants were carried out as previously described [1]. Table 1 gives experimental data and the results of basicity calculations for chalcone I, 1-(furyl-2)-3-phenylpropenone-1 (II), 1-(furyl-2)-3-phenylpropenone-3 (III), 1, 3-di(furyl-2) propenone (IV), 1-(thienyl-2)-3-phenylpropenone-1 (V), 1-(thienyl-2-)-3-phenylpropenone-3 (VI), and 1, 3-di(thienyl-2) propenone (VII). Table 2 gives basicity constants of the compounds investigated in sulfuric—acetic acid solution, and also for comparison some basicity constants previously obtained by the present authors for solutions in aqueous sulfuric acid, along with character-

Table 2

Basicity Constants, Characteristic Vibration Frequency of the Carbonyl Group, and Dipole Moments for Chalcone and Certain of its Heterocyclic Analogs (C_4H_3O — 2-furyl; C_4H_3S — 2-thienyl)

	Compound	$K \cdot 10^5$ in acetic sulfuric acid solutions	$K \cdot 10^5$ in aqueous H_2SO_4	$\nu_{C=O}$ for the solid, cm^{-1}	Dipole moment μ, D
I	$C_6H_5—CO—CH=CH—C_6H_5$	6.2	1.4	1669	2.97
II	$C_4H_3O—CO—CH=CH—C_6H_5$	71	—	1660	3.19
III	$C_4H_3O—CH=CH—CO—C_6H_5$	39	—	1669	3.03
IV	$C_4H_3O—CO—CH=CH—C_4H_3O$	130	—	1660	3.17
V	$C_4H_3S—CO—CH=CH—C_6H_5$	5.6	3.7	1652*	3.43*
VI	$C_4H_3S—CH=CH—CO—C_6H_5$	24	6.6	1660*	3.11*
VII	$C_4H_3S—CO—CH=CH—C_4H_3S$	55	14.0	1640*	3.37*

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* Two of the present authors and V. M. Nikitchenko will later publish complete IR spectrum and dipole moment data for thiophene analogs of chalcone.

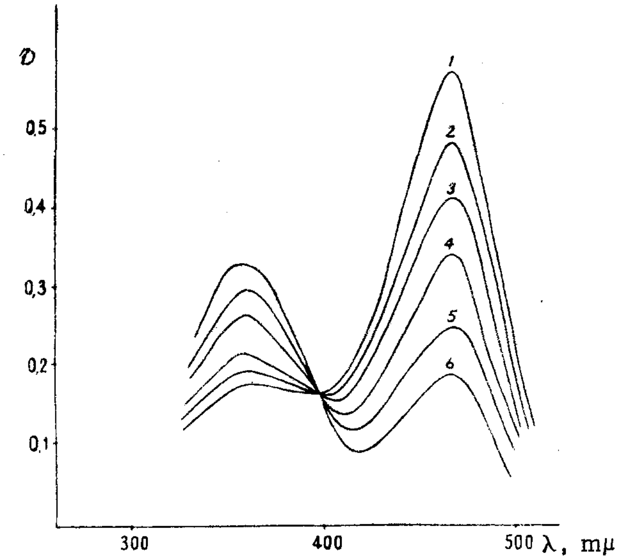

Fig. 3. Absorption curves for 1, 3-di(furyl-2) propenone in solutions containing various concentrations of sulfuric acid in glacial acetic acid: 1) 14.85%; 2) 12.45%; 3) 10.28%; 4) 7.93%; 5) 6.07%; 6) 4.96% H_2SO_4.

istic vibration frequencies $\nu_{C=O}$ for the carbonyl group, and the dipole moments of the ketones [13, 14]. Figures 3 and 4 show typical absorption curves for solutions containing various concentrations of sulfuric acid in glacial acetic acid.

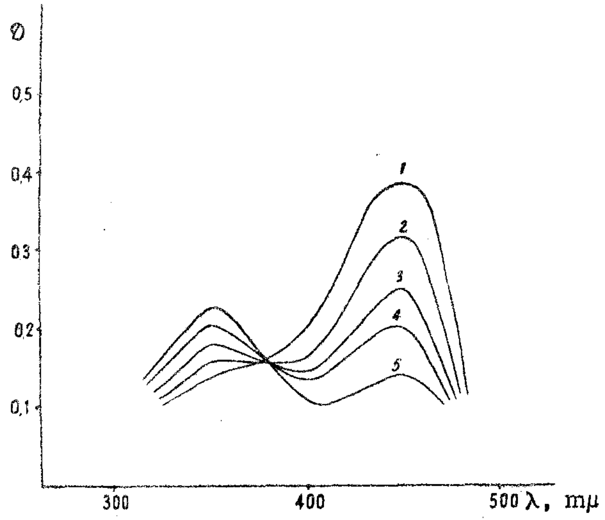

Fig. 4. Absorption curves for 1-(thienyl-2)-3-phenylpropenone-3 in solutions containing various concentrations of sulfuric acid in glacial acetic acid: 1) 29.54%; 2) 24.53%; 3) 20.90%; 4) 17.95%; 5) 14.92% H_2SO_4.

Discussion

Comparison of the basicity constants of chalcone with those of its furan analogs, shows that replacement of the benzene rings in chalcone I by furan ones always leads to a real increase in basicity. However, the increase in basicity depends on which of the two phenyls is replaced by 2-furyl, whether it is the one adjacent to the carbonyl group, or that separated from the latter by a vinyl group. In the former case the basicity is increased 12-fold (cf. I and II), but in the other case only 6-fold (cf. I and III). Thus, a furan ring, when immediately adjacent to a carbonyl group, affects the basicity more than one remote from the latter. A particularly large increase in basicity in comparison with chalcone (21-fold) is observed with 1, 3-di-(furyl-2) propenone (cf. I and IV).

Comparing the basicity constants of chalcone and its thiophene analogs in glacial acetic acid, the opposite is found, that the greater effect on basicity is exhibited by a heterocyclic ring remote from the carbonyl. Thus replacement of the phenyl remote from the carbonyl by 2-thienyl causes a 4-fold increase in basicity (cf. I and VI) while an analogous replacement effected adjacent to the carbonyl group leaves the basicity practically unchanged (cf. I and V). If both benzene rings in chalcone are replaced by thiophene ones, it leads to a 9-fold increase in basicity (cf. I and VII).

Since the increase in basicity of α,β-unsaturated ketones is due to increased electron density at the oxygen atom of the carbonyl group, the data here obtained indicate that 2-furyl, and 2-thienyl in the systems studied exert a greater electron donor effect than phenyl. The same conclusion was reached by two of the present authors from studies of UV and IR spectra and dipole moments of α, β-unsaturated ketones of the furan and thiophene series [11, 13-15].

Table 2 shows that the proton-accepting capacities of the isomeric ketones II, III and V, VI differ. There, if the more basic of two isomeric furan analogs of chalcone is the one with the carbonyl group next to the heterocyclic ring, the reverse holds for isomeric thiophene chalcones. Again previously [1, 2] when investigating basicities in aqueous sulfuric acid solutions, the present authors ascribed this difference to steric hindrance, arising through solvation of the corresponding carbonium ions arising from the direction of the adjacently situated heteroatom. So to compare the electron donor effects of 2-furyl and 2-thienyl, it is necessary to compare the basicity constants of those chalcone analogs where the carbonyl group is remote from the heterocyclic ring, for then the above-mentioned steric effect cannot have any influence. Table 2 shows that ketone III is markedly more basic than ketone VI, so that in the carbonyl protonation reaction of heterocyclic analogs of chalcone, 2-furyl exhibits a greater positive conjugated effect than does 2-thienyl.

Increase in electron density at the carbonyl group oxygen atom should not only raise the basicity, but also lower $\nu_{C=O}$, the characteristic vibration frequency of the carbonyl group, and increase the ketone's dipole moment μ. So it would appear that there is some correlation between ketone basicity constants, and the values of $\nu_{C=O}$ and μ. However, the results in Table 2 offer proof that, for example, when the carbonyl group is next to the heterocyclic ring, the thiophene analog of chalcone has a higher dipole moment than the furan one (cf. II and V). For chalcone analogs where the carbonyl group is remote from the heterocyclic ring the dipole moment is almost constant, and practically the same as that of chalcone itself (cf. I, III, and VI). Regarding the carbonyl group characteristic vibration frequency, it is always lower for the thiophene ketones than for the furan ones. Thus from the dipole moments and IR spectra it can be concluded that the thiophene ring exhibits a greater electron-donor effect than does the furan one. This apparent contradiction between $\nu_{C=O}$ and μ is evidently due to the characteristic vibration frequency of the carbonyl group and the dipole moment characterizing the molecule of a ketone in its ordinary static state, while a basicity constant characterizes carbonyl reactivity. Here it is necessary to take into account the fact that 2-furyl and 2-thienyl exhibit negative static inductive effects, the electron-accepting effect for the former being greater than for the latter [10]. This is one of the probable causes of lowering of carbonyl group vibration frequency and increased dipole moment in the case of the thiophene ketone V as compared with the furan ketone II. The lack of correlation between the above-mentioned characteristics of the ketones may further be connected with peculiarities in the behavior of the substances in solution (the presence of appreciable steric hindrance to solvation in some cases). It is peculiar that the UV spectrum data indicate practically identical bathochromic effects for 2-furyl and 2-thienyl [11, 15].

Comparisons of basicity constants for chalcone and its heterocyclic analogs for cases where the heterocyclic ring is next to the carbonyl group show that 2-thienyl does not give rise to increase in basicity here, whereas 2-furyl increases it 12-fold (cf. I and V, I and II). Obviously such a great difference indicates different degrees of steric hindrance, which the 2-furyl and 2-thienyl adjacent to the carbonyl exert in respect of solvation of carbonium ions, because the Van der Waal's radius of the sulfur atom is greater than that of the oxygen one [16]. However, the great difference between the basicities of ketones II and V cannot be ascribed only to steric hindrance, because the dynamical inductive effect of the heterocyclic groups certainly also appears in these systems.

It is of interest to compare basicity constants of thiophene ketones in glacial acetic—sulfuric acid mixtures with the constants previously obtained with aqueous sulfuric acid solutions. In all cases the ketones are more basic in the acetic acid solutions than in the aqueous ones (see Table 2), and this agrees with the results of A. M. Shkodina [17, 18], who found the strengths of weak bases to increase in acetic acid. It is important to note, at this point, that in acetic acid solution steric hindrance to solvation probably increases, as the increase in basicity on passing from aqueous solution to acetic acid solution differs for isomeric ketones. Thus with 1-(thienyl-2)-3-phenylpropenone-1 the basicity in acetic acid is only one and a half times greater than in aqueous solution, while in the case of the isomer it is 3.5 times greater. The large steric hindrance to solvation in acetic acid solution as compared with aqueous solution can be regarded as the reason for the basicity being practically unchanged when in chalcone the phenyl group adjacent to carbonyl is replaced by 2-thienyl (cf. I and V), while in aqueous solution there is a considerable difference between the basicity constants of the two compounds.

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29 June 1964

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