# BASICITY AND STRUCTURE OF α, β-UNSATURATED KETONES OF THE HETEROCYCLIC SERIES

## IV. Selenophene Analogs of Chalcone*

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The protolytic equilibrium constants of 1-(2'-selenienyl)-3-phenyl-1-propenone, 1-(2'-selenienyl)-3-phenyl-3-propenone, and 1,3-di (2'-selenienyl) propenone have been measured spectrophotometrically in solutions of sulfuric acid (monohydrate) in glacial acetic acid. The results obtained are compared with data on the basicity of chalcone and its thiophene and furan analogs. It is established that, in heterocyclic analogs of chalcone, five-membered heterocycles containing oxygen, sulfur, and selenium show an electron-donating effect which decreases in the order 2-furyl > 2-selenienyl > 2-thienyl.

In the literature, one encounters quite inconsistent information concerning the relative electronic effects of furan, thiophene, and selenophene on the physicochemical characteristics and reactivity of organic compounds. In some systems, the 2-furyl, 2-thienyl, and 2-selenienyl groups show electron-donating character [1–4]; in others, they behave as electron acceptors [5]. In many studies of the spectra of selenophene, thiophene, and furan derivatives, it is noted that a greater degree of participation of the unshared electron pair of the hetero atom in the π-electron interaction of the ring is observed in the cases of selenophene and thiophene than in the analogous furan and aromatic systems [6–8].

Table 1

Protonation Constants of Heterocyclic Analogs of Chalcone*

| Compound No. | Formula of ketone | $K \cdot 10^5$ | $K_a \cdot 10^{-2}$ | $-pK_a$ |
|---|---|---|---|---|
| I | $C_4H_3Se-CO-CH=CH-C_6H_5$ | 34 | 29.4 | 3.47 |
| II | $C_4H_3Se-CH=CH-CO-C_6H_5$ | 28.7 | 34.8 | 3.54 |
| III | $C_4H_3Se-CO-CH=CH-C_4H_3Se$ | 84 | 11.9 | 3.07 |
| IV | $C_6H_5-CO-CH=CH-C_6H_5$ | 6.2 | 161 | 4.21 |
| V | $C_4H_3S-CO-CH=CH-C_6H_5$ | 5.6 | 178 | 4.25 |
| VI | $C_4H_3S-CH=CH-CO-C_6H_5$ | 24 | 41.7 | 3.62 |
| VII | $C_4H_3S-CO-CH=CH-C_4H_3S$ | 55 | 18.2 | 3.26 |
| VIII | $C_4H_3O-CO-CH=CH-C_6H_5$ | 71 | 14.1 | 3.15 |
| IX | $C_4H_3O-CH=CH-CO-C_6H_5$ | 39 | 25.6 | 3.41 |
| X | $C_4H_3O-CO-CH=CH-C_4H_3O$ | 130 | 7.7 | 2.89 |

*K is the ketone protonation constants $B + H^+ \rightleftharpoons BH^+$; $K_a$ is the ionization constant of the corresponding conjugate acid.

There are few studies of the basicity of compounds containing heterocyclic radicals. Thus, comparison of the relative basicities of difurfurylideneacetone, difurfurylidenecyclopentanone, and the corresponding aromatic compounds [9] showed that the basicity increases roughly threefold when one goes from the aromatic ketones to their furan analogs. In a study of the acid-base properties of pyrazoles conjugated with phenyl, 2-furyl, 2-thienyl, and 2-selenienyl rings [5], the electron-accepting character of these systems relative to the pyrazole ring was established, the electron-accepting effect decreasing in the order: 2-selenienyl > 2-thienyl > 2-furyl > phenyl. A considerable electron-donating effect of the oxygen of the furan ring in α, β-unsaturated ketones has been reported [10].

We have previously reported on spectrophotometric measurements of the basicity constants of the thiophene and furan analogs of chalcone in solutions of acids [11, 12]. In this connection, it was interesting to elucidate the variation

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*For part III, see [12].

Table 2

Spectrophotometric Data and Calculated Basicity Constants of Selenophene Analogs of Chalcone

| Ketone no. | Exp. no. | Initial ketone concentration. $c \cdot 10^5$ M | Content of $H_2SO_4$ in acetic acid, %; HO of the solution | Measured optical densities at several wavelengths: $D/\lambda$, m$\mu$ | | | | | Calculated $\varepsilon_{av}$ at several wavelengths: $\varepsilon_{ax}/(\lambda)$ | $(K \pm \Delta K) \cdot 10^5$ |
|---|---|---|---|---|---|---|---|---|---|---|
| I | 1 | 2.21 | 25.02; −4.00 | 0.370/425 | 0.390/430 | 0.385/435 | 0.375/440 | | 21770 22840 22500 22450 (425) (430) (435) (440) | 34 ±2 |
| | | | 21.00; −3.70 | 0.315/425 | 0.320/430 | 0.320/435 | 0.315/440 | | | |
| | | | 17.55; −3.46 | 0.255/425 | 0.260/430 | 0.260/435 | 0.255/440 | | | |
| | | | 13.28; −3.13 | 0.145/425 | 0.150/430 | 0.140/435 | 0.130/440 | | | |
| | 2 | 2.26 | 27.48; −4.12 | 0.445/430 | 0.450/435 | 0.445/440 | 0.425/445 | | 22800 24060 24000 23100 (430) (435) (440) (445) | 35 ±2 |
| | | | 19.59; −3.60 | 0.305/430 | 0.315/435 | 0.305/440 | 0.290/445 | | | |
| | | | 15.93; −3.28 | 0.225/430 | 0.225/435 | 0.220/440 | 0.210/445 | | | |
| | | | 12.75; −3.10 | 0.160/430 | 0.155/435 | 0.155/440 | 0.140/445 | | | |
| II | 1 | 2.50 | 31.86; −4.51 | 0.620/455 | 0.635/460 | 0.640/465 | 0.630/470 | 0.620/475 | 27140 27740 28370 27980 27460 (455) (460) (465) (470) (475) | 28.9±0.8 |
| | | | 27.48; −4.12 | 0.540/455 | 0.550/460 | 0.555/465 | 0.545/470 | 0.530/475 | | |
| | | | 23.34; −3.88 | 0.470/455 | 0.475/460 | 0.475/465 | 0.470/470 | 0.460/475 | | |
| | | | 19.03; −3.57 | 0.370/455 | 0.375/460 | 0.375/465 | 0.365/470 | 0.355/475 | | |
| | | | 11.00; −3.01 | 0.165/455 | 0.165/460 | 0.160/465 | 0.155/470 | 0.150/475 | | |
| | 2 | 2.47 | 28.03; −4.14 | 0.510/450 | 0.530/455 | 0.550/460 | 0.550/465 | 0.540/470 | 24590 25590 26950 26950 26300 (450) (455) (460) (465) (470) | 28.6±0.9* |
| | | | 24.79; −3.98 | 0.445/450 | 0.460/455 | 0.475/460 | 0.475/465 | 0.465/470 | | |
| | | | 21.84; −3.77 | 0.390/450 | 0.405/455 | 0.415/460 | 0.415/465 | 0.405/470 | | |
| | | | 18.68; −3.55 | 0.320/450 | 0.330/455 | 0.335/460 | 0.335/465 | 0.330/470 | | |
| III | 1 | 1.73 | 23.33; −3.88 | 0.535/485 | 0.545/490 | 0.545/495 | 0.525/500 | | 35400 36320 36500 35640 (485) (490) (495) (500) | 85 ±5 |
| | | | 19.03; −3.57 | 0.470/485 | 0.480/490 | 0.480/495 | 0.460/500 | | | |
| | | | 15.18; −3.20 | 0.385/485 | 0.385/490 | 0.385/495 | 0.365/500 | | | |
| | | | 11.00; −3.01 | 0.270/485 | 0.275/490 | 0.270/495 | 0.250/500 | | | |
| | 2 | 1.87 | 23.34; −3.88 | 0.560/480 | 0.580/485 | 0.590/490 | 0.590/495 | 0.580/500 | 33210 34130 35020 35260 34260 (480) (485) (490) (495) (500) | 82 ±4** |
| | | | 19.96; −3.63 | 0.485/480 | 0.505/485 | 0.515/490 | 0.510/495 | 0.490/500 | | |
| | | | 18.18; −3.52 | 0.440/480 | 0.450/485 | 0.460/490 | 0.460/495 | 0.440/500 | | |
| | | | 16.07; −3.30 | 0.405/480 | 0.420/485 | 0.425/490 | 0.420/495 | 0.405/500 | | |
| | | | 12.97; −3.11 | 0.320/480 | 0.335/485 | 0.340/490 | 0.335/495 | 0.320/500 | | |

* In a separate experiment where optical saturation was employed, the value K = 28.1 ± 0.25 was obtained.

** In this experiment, optical saturation was reached at a concentration of 30% $H_2SO_4$ in glacial acetic acid.
A calculation employing optical saturation gave the value K = 85 ± 6.

of the proton-accepting capacity of the carbonyl group in a series of $\alpha$, $\beta$-unsaturated ketones containing the 2-furyl, 2-thienyl, and 2-selenienyl radicals. We have measured the protolytic equilibrium constants of 1-(2'-selenienyl)-3-phenyl-1-propenone (I), 1-(2'-selenienyl)-3-phenyl-3-propenone (II), and 1,3-di(2'-selenienyl)propenone (III) in solutions of sulfuric acid in glacial acetic acid, and have compared them with the basicity data previously obtained for chalcone (IV) and its thiophene (VI, VII) and furan (VIII–X) analogs [11, 12].

From a comparison of the basicities (see Table 1) of chalcone and the 1-(2'-selenienyl)-3-phenylpropenones, it follows that replacement of one benzene nucleus in chalcone by a 2-selenienyl group leads to a roughly fivefold increase in basicity, apart from the dependence on the position of the carbonyl group (cf. I and II with IV). When two selenophene rings are introduced into the chalcone molecule, the basicity increases 13 times (cf. III and IV). The results give unconditional evidence that, in these systems, 2-selenienyl manifests an electron-donating effect in comparison with phenyl. We reached the same conclusion earlier in regard to 2-thienyl and 2-furyl [11, 12].

Comparison of the protonation constants of ketones of analogous structure containing the selenophene, thiophene, and furan nuclei shows that, in all cases, the selenophene ketones are more basic than the thiophene and less basic than the corresponding furan ketones (cf. I, V, and VII; II, VI, and IX; III, VII, and X). This permits one to conclude that, in heterocyclic analogs of chalcone, the electron-donating effect of the radicals decreases in the order: 2-furyl > 2-selenienyl > 2-thienyl. The electron-donating effect of these heterocyclic radicals is fundamentally determined by their positive conjugative effect, a proper idea of the variation of which can be obtained by comparing the basicity constants of ketones in which the carbonyl group is separated from the heterocycle by a vinylene group (the 3-propenones). In this case, the inductive effect, the field effect, and possible steric hindrance in the heterocyclic nucleus are all eliminated. It can be clearly seen from the data of Table 1 that the difference in the basicity constants of 1-(2'-thienyl)-3-phenyl- and 1-(2'-selenienyl)-3-phenylpropenone only slightly exceeds experimental error (cf. II and VI), while on transition to the corresponding furan ketone the basicity changes more sharply (cf. II, VI, and IX). Consequently, the positive conjugative effect of 2-furyl in these systems is greater than for 2-thienyl and 2-selenienyl, the two latter rings showing almost the same effect. At the same time, there is nevertheless a tendency toward a somewhat greater influence of the selenophene than of the thiophene ring, evidence for which is also given by comparison of the protolytic equilibrium constants of the ketones containing two selenophene and two thiophene rings (cf. III and VII). Thus the positive conjugative effect in the series of heterocycles containing sixth-group hetero atoms (oxygen, sulfur, and selenium) varies discontinuously.

Similar regularities in the variation of properties have already been noted by several authors both for cyclic systems containing oxygen, sulfur, and selenium, and for systems containing these atoms in a side chain of the benzene ring or in an aliphatic chain. Thus, for example, it has been shown [13, 14] that, on the basis of decreasing electron-donating and increasing electron-accepting properties, p-substituents in the aniline molecule are arranged in the order: $C_6H_5O$ > H > $C_6H_5Se$ ~ $C_6H_5S$. The Hammett $\sigma$ constants for the substituents p-$CH_3O$, p-$CH_3S$, and p-$CH_3Se$ vary similarly [15]. In a paper by one of the authors [4] on the stabilization of a cationic center by an adjacent five-membered heterocyclic nucleus, it was established that the solvolysis rate of the chloromethyl derivatives of selenophene was lower than that for the furan derivatives but substantially higher than for the thiophenes. Similar behavior of the thiophene and selenophene rings has been noted in a number of spectroscopic studies of furan, thiophene, and selenophene derivatives [16, 17].

The nearly identical behavior of the 2-thienyl and 2-selenienyl groups in the systems in question is apparently associated with the analogous electronic structure of the hetero atoms (the presence of d-orbitals [16, 18, 19]) and their nearly equal electronegativities (2.5 and 2.4). But the selenophene ring is known to be more polarizable than the thiophene ring, which, together with the somewhat lower electronegativity of the selenium atom, is the probable cause of the greater basicity of the selenophene ketones in comparison with their thiophene analogs.

As was noted above, the electron-donating effect of 2-furyl in the present systems exceeds that of 2-thienyl and 2-selenienyl. The causes of this phenomenon are likewise to be sought in the electronic structural features of the oxygen atom of the furan ring. Because of its lack of d-orbitals, oxygen can take part in conjugation only by means of its p-electrons, while sulfur and selenium atoms may, in addition, display the reverse effect, making their empty d-orbitals available for conjugation with $\pi$-electrons. It is apparently on account of this double role of sulfur and selenium in conjugation with carbonyl that the electron-donating effect of 2-thienyl and 2-selenienyl on the carbonyl group appears less than the effect of 2-furyl.

It is asserted in the literature that the dissociation constants increase [20, 21] in the series benzoic ($K_a = 6.46 \cdot 10^{-5}$), 2-selenophenecarboxylic ($K_a = 2.6 \cdot 10^{-4}$), 2-thiophenecarboxylic ($K_a = 3.3 \cdot 10^{-4}$), and 2-furancarboxylic acids ($K_a = 7.5 \cdot 10^{-4}$), which is usually explained by the increasing electron-accepting effect of the respective heterocyclic radicals. It would seem that this contradicts the results obtained in the present study. However, it must be kept in mind that the electronic character of the radicals depends greatly on the system in which the particular mutual influence of the atoms is observed. Furthermore, the inductive effect and the ortho effect of the nearby hetero atom must play a large part in the transmission of influence from the heterocycle to the carboxyl group in these

compounds. The apparent dissociation constants of 2-furancarboxylic (pK = 4.43), 2-thiophenecarboxylic (pK = 5.96), 2-furylacrylic (pK = 6.70), and 2-thienylacrylic (pK = 6.67) acids in 80% aqueous methyl cellosolve are presented in [22]. It follows from these data that, when the effect of the nearby hetero atom is eliminated by the introduction of a vinylene group between the heterocyclic nucleus and the carboxyl group, as is the case in the acrylic acids just cited, the acid strength falls sharply, analogously to what is observed on going from o-substituted benzoic acids to o-substituted cinnamic acids [23]. Here, the difference in acidity between the corresponding furan and thiophene derivatives practically vanishes.

There remains to be discussed the question of the effect of the heterocycles under study on the proton-accepting capacity of a carbonyl located in their immediate vicinity (I, V, and VIII). In this case, the effect of the heterocyclic radical is more complicated and is transmitted not only by means of conjugation but also by an inductive mechanism. Here it must be borne in mind that the inductive effect acts in the opposite direction from the conjugative effect [4]. The appearance of a field effect is also not excluded. Moreover, in the case of direct proximity of the carbonyl group and the heterocyclic radical, the latter creates additional steric hindrance to solvation of the carbonium ions formed in the acid medium, as we have already remarked in previous communications [11, 12]. It is possible that steric effects associated with a hindered approach of the proton-bearing particle ( $[CH_3COOH_2]^+$ ) to the reaction center also occur in the 1-propenones. The protolytic equilibrium constants of the 1-propenones decrease as one goes from the furan ketone to the selenophene and on to the thiophene (cf. I, V, and VIII). The basicity of the ketone V is greatly reduced; it is even somewhat less than for chalcone. This is apparently explained, on the one hand, by the considerable steric hindrance produced by the thiophene nucleus and, on the other, by the fact that the positive conjugative effect of 2-thienyl has the smallest value of all the heterocycles examined, and is to a considerable extent neutralized by the negative inductive effect. The selenophene ring probably produces the same steric hindrance as thiophene (the dimensions of the sulfur and selenium atoms do not differ significantly), but the protolytic equilibrium constant of ketone I is greater than that of V, which can be explained by the greater conjugative effect of 2-selenienyl in comparison with 2-thienyl.

## Experimental

The basicity constants were measured spectrophotometrically in solutions of sulfuric acid (monohydrate) in glacial acetic acid at room temperature. The preparation of the monohydrate of the glacial acetic acid, and of mixtures of the two has been described in a previous communication [12]. $H_0$ values for solutions of sulfuric acid in glacial acetic acid were determined by interpolation of Hall and Spengeman's data [24].

The substances investigated were obtained according to [25, 26] and were carefully purified by repeated crystallization. In all cases, the time-stability of their halochromic solutions was studied by measuring the absorption curves in the visible region on an SF-2M spectrophotometer. All the solutions proved stable for the length of time necessary for the spectrophotometric measurements, which were made on an SF-4 apparatus. The measuring procedure and the calculation of the equilibrium constants have been previously described [11, 12]. For ketones II and III, optical saturation was reached in certain individual experiments. The basicity constants, in these cases, were calculated according to the well-known formula $K_a = \dfrac{D}{(D_\infty - D) a_H+}$ ( at the selected analytical wavelengths only the ionic form of the ketones absorbs). The experimental data obtained and the calculated average values of the molar absorption coefficients and protolytic equilibrium constants of the ketones are presented in Table 2. In the experimental range of concentrations of sulfuric acid in glacial acetic acid, the spectral curves of the selenophene analogs of chalcone are analogous to those presented in previous communications for the furan and thiophene derivatives [11, 12].

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