CHEMISTRY

=========

1965

SovietRxiv

Abstract

Full Text

CHEMISTRY

S. V. TSUKERMAN, L. A. KUTULYA, Yu. N. SUROV, V. F. LAVRUSHIN, Yu. K. YUR' EV

BASICITY OF FURAN, THIOPHENE, AND SELENOPHENE ANALOGS OF CHALCONE

(Presented by Academician A. N. Nesmeyanov, March 1, 1965)

The literature data on the electronic influence of five-membered heterocyclic radicals—furyl, thienyl, and selenienyl—on the physicochemical characteristics and reactivity of organic compounds are quite contradictory: in some systems these radicals exhibit an electron-donating character ([1–5]), while in others they behave as electron acceptors ([6,7]).

Table 1

Nos.	Ketone formula*	$(K_a \pm \Delta K_a) \cdot 10^{-2}$	$-pK_a$	$\Delta\nu_{\mathrm{OH}}$, cm^{-1}**
I	$C_6H_5-CO-CH=CH-C_6H_5$	162 ± 3	4.21	206
II	$C_4H_3O-CO-CH=CH-C_6H_5$	14.2 ± 0.5	3.15	239
III	$C_4H_3O-CH=CH-CO-C_6H_5$	25.9 ± 0.4	3.41	216
IV	$C_4H_3O-CO-CH=CH-C_4H_3O$	7.7 ± 0.3	2.89	245
V	$C_4H_3S-CO-CH=CH-C_6H_5$	185 ± 11	4.25	200
VI	$C_4H_3S-CH=CH-CO-C_6H_5$	40.8 ± 0.6	3.62	210
VII	$C_4H_3S-CO-CH=CH-C_4H_3S$	18.3 ± 0.6	3.26	214
VIII	$C_4H_3Se-CO-CH=CH-C_6H_5$	29 ± 1	3.47	206
IX	$C_4H_3Se-CH=CH-CO-C_6H_5$	33.8 ± 0.7	3.54	211
X	$C_4H_3Se-CO-CH=CH-C_4H_3Se$	11.9 ± 0.6	3.07	205

* In the ketone formulas, C_4H_3O = 2-furyl; C_4H_3S = 2-thienyl; C_4H_3Se = 2-selenienyl.

** The error in determining $\Delta\nu_{\mathrm{OH}}$, with statistical treatment of the data from 4-6 measurements, is 2 cm^{-1} for all compounds.

The change in the proton-acceptor ability of the carbonyl group of chalcone upon replacement of phenyls in it by 2-furyl, 2-thienyl, and 2-selenienyl could provide a quantitative idea of the electronic character of these heterocycles; to this end we measured spectrophotometrically the constants of the protolytic equilibrium of chalcone (I), its furan (II-IV), thiophene (V-VII), and selenophene analogs (VIII-X) in solutions of sulfuric acid (100%) in glacial acetic acid.

It turned out (see Table 1) that replacement of phenyl by a heterocyclic radical causes, as a rule, a substantial increase in basicity, which indicates their electron-donating character. At the same time, the basicity of the ketones measured depends on the position of the carbonyl group in the conjugation chain. A comparison of the K_a values for ketones of analogous structure shows that in all cases the furan chalcones are more basic than the selenophene ones, and the latter more basic than the thiophene ones. Thus, the total electron-donating influence of the radicals in these compounds decreases in the series: 2-furyl $>$ 2-selenienyl $\geq$ 2-thienyl, which is also confirmed in work ([5]). The electron-donating influence of the heterocyclic radicals considered is determined mainly by their positive conjugation effect, a correct idea of the change in 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 (III, IV, and IX). In this case the inductive influence, the field effect, and also possible steric hindrances created by the heterocyclic nucleus are eliminated. From the data in Table 1 it is clearly seen that the basicity of the furan analog of chalcone (III) is substantially greater than that of the corresponding thiophene and selenophene analogs, while the difference in the K_a values of the latter two only slightly exceeds the experimental error. Consequently, the positive conjugation effect of 2-furyl in these systems is greater than that of 2-thienyl and 2-selenienyl, while the latter two rings exert an almost identical influence. At the same time, there is nevertheless a tendency toward a somewhat greater influence of the selenophene ring in comparison with the thiophene ring, which is seen more clearly when comparing the K_a values of ketones containing two selenophene and two thiophene rings (VII and X).

Thus, the positive conjugation effect in the series of heterocycles containing oxygen, sulfur, and selenium changes nonuniformly on going from one member of the group to the next: it is greatest for oxygen, and approximately the same for sulfur and selenium. The same sequence in the change of various physical and chemical properties of organic compounds whose molecules contain atoms of oxygen, sulfur, and selenium has already been noted by a number of authors ([5], [8_13]).

The approximately identical behavior of 2-thienyl and 2-selenienyl in the systems studied is associated with the analogous electronic structure of the heteroatoms (the presence of *d*-electron orbitals) and the close values of their electronegativities (2.5 and 2.4). But, as is known, the selenophene ring should be polarized more readily than the thiophene ring, which, together with the somewhat lower electronegativity of the selenium atom, is a probable cause of the somewhat greater basicity of the selenophene ketone (IX) in comparison with its thiophene analog. Oxygen, unlike its lower neighbors in the periodic system (sulfur and selenium), has no *d*-orbitals. It follows from this that oxygen in the present case can essentially be only a supplier of an unshared pair of *p*-electrons for conjugation, whereas sulfur and selenium atoms, in addition, can exhibit the opposite effect by providing their vacant *d*-orbitals for interaction with π-electrons. Apparently, as a consequence of this dual role of sulfur and selenium in conjugation with the carbonyl, the electron-donating influence of 2-thienyl and 2-selenienyl proves to be considerably smaller than that of 2-furyl.

In the case of direct proximity of the carbonyl and the heterocyclic radical, the influence of the latter is more complex and is transmitted not only by conjugation but also by the inductive mechanism. In this connection it should be borne in mind that the inductive effect acts in the opposite direction compared with the conjugation effect ([5]). The manifestation of a field effect is not excluded either. In addition, in the case of direct proximity of the carbonyl group and the heterocyclic radical, the latter probably creates additional steric hindrances to solvation of the carbonium ions formed in an acidic medium, to which we have already drawn attention in previous works ([14]). It is possible that in the present case there are also steric effects associated with hindered approach of the proton-carrying particle $[CH_3COOH_2]^+$ to the reaction center. As is seen from a comparison of the K_a values of ketones II, V, and VIII, the basicity decreases on going from the furan ketone to the selenophene ketone and further to the thiophene ketone, with the proton-acceptor ability of the carbonyl group of ketone V being sharply reduced; it is even somewhat lower than that of chalcone. This is apparently explained, on the one hand, by the relatively large steric hindrances created by the thiophene nucleus and, on the other hand, by the fact that the positive conjugation effect of 2-thienyl has the smallest magnitude and is to a considerable extent neutralized by the negative inductive effect.

Data on the comparative basicity of furan, thiophene, and selenophene analogs of chalcone were also obtained by measuring the shift of the characteristic vibration band of the hydroxyl group of phenol ($\Delta\nu_{\mathrm{OH}}$) under the influence of hydrogen-bond formation with the carbonyl group of the compounds under study. As is known, the magnitude of this shift $\Delta\nu_{\mathrm{OH}}$ in a series of compounds of the same type is in a linear dependence on the basicity of ketones ([15,16]). In this case, there are no complicated solvation processes that occur in acid solutions during ion formation and that can distort the effects of mutual influence of atoms, in particular in the case of direct proximity of the carbonyl and the heterocycle.

Comparison of the values of $\Delta\nu_{\mathrm{OH}}$ for ketones III, VI, and IX, in which the carbonyl is remote from the heterocycle, shows that, upon formation of hydrogen bonds as well, the positive conjugation effect of 2-furyl is appreciably greater than that of 2-thienyl and 2-selenienyl, while the latter two exert the same electron-donor influence. At the same time, in the case of ketones in which the carbonyl is situated adjacent to the heterocycle (II, V, and VIII), the value of $\Delta\nu_{\mathrm{OH}}$ for the selenophene ketone is the same as for chalcone, and for its thiophene analog it has an even smaller value. The fact that 2-selenienyl and 2-thienyl in ketones V and VIII do not display an electron-donor character in the reaction of hydrogen-bond formation is due primarily to the fact that, in the process of protonation of ketones and formation of conjugated carbenium ions, a considerable shift of electron density toward the carbenium atom occurs and dynamic effects predominate, whereas in the formation of hydrogen bonds the dynamic effect should be manifested to a much smaller extent. In addition, it should be borne in mind that, in the formation of a hydrogen bond for V and VIII, steric hindrance may occur, similar to that observed in the formation of a hydrogen bond of phenol with acetophenone (^{17}).

Thus, the electronic influence of these heterocyclic radicals depends on the systems in which it is manifested and consists of a positive conjugation effect and a negative inductive effect, the total influence of which is not the same in different cases and may be complicated by steric hindrance, field effects, and manifestations of dynamic factors.

Kharkov State University
named after A. M. Gorky

Moscow State University
named after M. V. Lomonosov

Received
24 II 1965

CITED LITERATURE

1. V. F. Lavrushin, S. V. Tsukerman, I. G. Syrovatka, ZhOKh, **31**, 1275 (1961).
2. V. F. Lavrushin, S. V. Tsukerman et al., ZhOKh, **32**, 2551, 2677 (1962).
3. L. Bruzzi, J. Degani, A. Fundo, Boll. Sci. Fac. chim. industr. Bologna, **19**, 40 (1961); RZhKhim, 12B79 (1962).
4. D. Manly, E. D. Amstutz, J. Organ. Chem., **22**, 323 (1957).
5. Yu. K. Yur' ev, M. A. Gal' bershtam, A. F. Prokof' eva, Izv. Vyssh. shkoly, Khimiya, **7**, 419, 595 (1964).
6. I. I. Grandberg, A. N. Kost, ZhOKh, **32**, 3025 (1962).
7. Yu. K. Yur' ev, E. L. Zaitsev, G. G. Rozantsev, ZhOKh, **30**, 2207 (1960).
8. G. Milazzo, Gaz. chim. ital., **83**, 787 (1953); Chem. Abstrs, **49**, 2868i (1955).
9. L. Chierici, G. Pappalardo, Gaz. chim. ital., **89**, 560 (1959); Chem. Abstrs, 12108b (1960).
10. A. Bellotti, L. Chierici, Gaz. chim. ital., **90**, 1125 (1960); Chem. Abstrs, 21095b (1961).

11. L. M. Litvinenko, R. S. Chepko, ZhOKh, **30**, 3682 (1960).
12. L. M. Litvinenko, Izv. AN SSSR, OKhN, 1962, 1737.
13. M. Daniel, H. Brown, J. Organ. Chem., **23**, 420 (1958).
14. S. V. Tsukerman, L. A. Kutsulya et al., ZhOKh, **33**, 3180, 3186 (1963).
15. W. Gordy, S. Stanford, J. Chem. Phys., **8**, 175 (1940).
16. D. Noyce, M. Gorgenson, J. Amer. Chem. Soc., **84**, 4312 (1962).
17. J. W. Widom, R. J. Philippe, M. E. Hobbs, J. Amer. Chem. Soc., **79**, 1383 (1957).

Note: Figure translations are in progress. See original paper for figures.