ELECTRONIC SPECTRA OF THE IONIC FORMS OF α,β-UNSATURATED KETONES – INDOLE DERIVATIVES

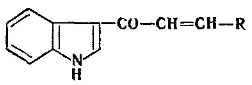
S. V. Tsukerman, A. I. Bugai,
and V. F. Lavrushin

UDC 547.756:543.422.6

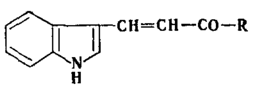
The formation of the corresponding organic cations and anions was shown on the basis of data on the electronic absorption spectra of 33 α,β-unsaturated ketones – indole derivatives – in solutions of strong acids and bases. Observations regarding the dependence of the colors of the investigated ionic forms on the chemical structure are made.

We have previously [1] reported the results of an investigation of the electronic absorption and fluorescence spectra of α,β-unsaturated ketones – indole derivatives – in alcohol and dioxane solutions. In connection with the fact that the indole ring simultaneously has weakly expressed basic and acidic properties, it seemed of interest to study the spectral characteristics of these compounds in sufficiently acidic and alkaline media, in which the corresponding organic cations and anions would be formed.

We selected the isomeric indole analogs of chalcones of the following type as the subjects of the investigation:



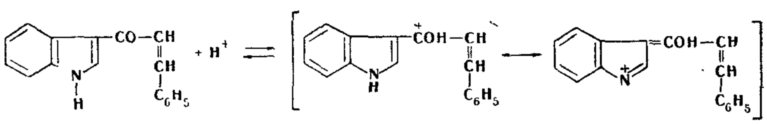
and



R is phenyl (I, II), aryl groups with different electron-donor and electron-acceptor substituents (III-XV), 2-furyl (XVI, XVII), 2-thienyl (XVIII, XIX), and N-methyl derivatives of ketones (XX-XXVI) (see Table 1).

In addition to the compounds listed above, we also investigated several ketones containing a 6-nitro-3-indolyl grouping in their molecules (XXVII-XXIX), cyclopentanone and cyclohexanone derivatives (XXX and XXXI), and indole analogs of p-dichalcones (XXXII, XXXIII) (see Table 2).

All of the investigated compounds exist in the molecular form in glacial acetic acid solutions, inasmuch as their electronic absorption spectra are practically the same as the spectra in alcohol solutions [1]. However, a halochromic coloration that vanishes as the solution is diluted with water develops when relatively small amounts of concentrated sulfuric acid (2-10%) are added to the acetic acid solutions. An isopiestic point is observed in the spectra of ketone I in solutions of various concentrations of sulfuric acid in glacial acetic acid (at a constant ketone concentration) on the absorption curves (Fig. 1); this attests to the presence of an acid-base equilibrium:



The structure of the cation, which is responsible for the appearance of a new absorption band in the visible region of the spectrum, can be represented by means of two principal limiting structures – a hydroxy carbonium ion structure and an immonium ion structure.

It follows from the data in Tables 1 and 2, in which the spectral characteristics of solutions of the investigated compounds in 30% sulfuric acid in glacial acetic acid are presented, that the long-wave absorp-

---

A. M. Gor'kii Kharkov State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 519-524, April, 1974. Original article submitted June 5, 1973.

TABLE 1. Spectral Characteristics of Acidic and Alkaline Solutions of Indole Chalcones

R	λ_{max}, nm (ε)					
	1-propenones			3-propenones		
	compound	30% solution of sulfuric acid in glacial acetic acid	2 N solution of sodium ethoxide	compound	30% solution of sulfuric acid in glacial acetic acid	2 N solution of sodium ethoxide
Phenyl	I	431 (64150), 325 (26620), 265 (25400)	397 (45000), 285 (59540)	II	477 (59670), 325 (10500), 278 (8700)	470 (89500), 285 (13500), 260 (17500)
4-Tolyl	III	437 (30900), 345 (7200), 268 (12280)	397 (22090), 287 (25090)	IV	475 (40180), 330 (7500), 265 (8700)	468 (40700), 260 (13000)
4-Anisyl	V	460 (47860), 355 (9420), 270 (21640)	392 (55160), 290 (46830)	VI	510 (80400), 345 (13300), 300 (11700), 263 (14500)	465 (85200), 288 (26600)
2,4-Dimethoxyphenyl	VII	491 (71760), 350 (10650), 275 (25950)	392 (56480), 342 (2259), 285 (33880)	VIII	518 (110500), 335 (12100), 293 (8400), 265 (12800)	447 (69280), 287 (16260)
4-Dimethylaminophenyl	IX	418 (26200), 317 (10740), 260 (13100)	410 (33570), 285 (8390), 248 (8050)			
4-Chlorophenyl	X	428 (33500), 340 (9570), 267 (1400)	406 (19900), 285 (29820)	XI	481 (38000), 335 (6200), 290 (3950)	476 (44200), 305 (9600), 263 (19200)
4-Nitrophenyl	XII	430 (35890), 367 (9300), 278 (15170)	450 (11900), 320 (14900), 295 (13100)	XIII	477 (26370), 325 (9300), 270 (9880)	520 (24700), 395 (13200), 275 (15000)
4-Diphenylyl	XIV	449 (25270), 362 (6200), 280 (10430)	405 (28670), 296	XV	508 (58600), 355 (7200), 305 (6480)	480 (42900), 290 (19140)
2-Furyl	XVI	458 (31300), 360 (5300), 270 (8790)	400 (22000), 290 (19700)	XVII	514 (45530), 345 (6200), 290 (4970), 258 (8300)	480 (45080), 285 (11800), 260 (14300)
2-Thienyl	XVIII	459 (24050), 360 (5200), 270 (11500)	407 (25700), 296 (17800)	XIX	517 (50800), 342 (6900), 287 (6500), 265 (7160)	481 (38800), 290 (11070), 265 (12400)
Phenyl*	XX	432 (65700), 330 (19600), 270 (26700)		XXI	481 (74100), 325 (13500), 280 (14000)	
4-Anisyl*	XXII	460 (34900), 353 (6500), 272 (15400)		XXIII	513 (78500), 350 (10500), 300 (10300)	
2,4-Dimethoxyphenyl*	XXIV	488 (37400), 352 (5500), 275 (13400)		XXV	522 (90300), 338 (9300), 298 (9500), 265 (13800)	
1-Methylindolyl*	XXVI	517 (49000), 342 (3200), 285 (9800)				

---

*N-Methylated compounds.

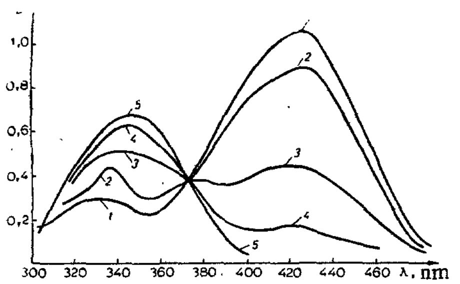


Fig. 1

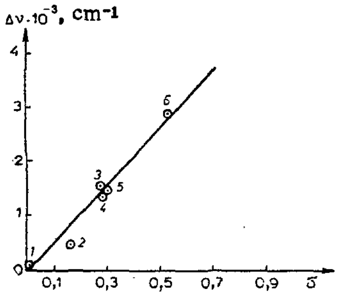


Fig. 2

Fig. 1. Absorption curves of ketone I in solutions of sulfuric acid in glacial acetic acid: 1) 3.2% H_2SO_4; 2) 2.4% H_2SO_4; 3) 1.6% H_2SO_4; 4) 0.8% H_2SO_4 in glacial acetic acid.

Fig. 2. Correction dependence between $\Delta\nu$ and the Hammett σ constants in the 1-propenone series: R = phenyl; 2) R = 4-tolyl; 3) R = 4-anisyl; 4) R = 2-furyl; 5) R = 2-thienyl; 6) R = 2,4-dimethoxyphenyl.

TABLE 2. Spectral Characteristics of Acidic and Alkaline Solutions of Some Unsaturated Ketones and Diketones Containing Indole Rings

Compound	Name	λ_{max}, nm (ε)	
		30% solution of sulfuric acid in glacial acetic acid	2 N sodium ethoxide solution
XXVII	1-(6-Nitro-3-indolyl)-3-phenyl-3-propenone	475 (42100), 320 (11400)	485 (6700), 402 (17700), 307 (28400), 260 (25700)
XXVIII	1-(6-Nitro-3-indolyl)-3-(4-chlorophenyl)-3-propenone	483 (47100), 320 (12480), 275 (9700)	494 (39260), 417 (18100), 258 (14800)
XXIX	1-(6-Nitro-3-indolyl)-3-(4-nitrophenyl)-3-propenone	478 (35700), 325 (12550), 280 (13600)	518 (26300), 357 (8900), 265 (11500)
XXX	2,5-Di(3-indolylmethylene)cyclohexanone	612 (78200), 432 (5200), 330 (5200), 278 (7300)	530 (58500), 555 (58500), 400 (6900), 290 (7100)
XXXI	2,6-Di(3-indolylmethylene)cyclohexanone	610 (31100), 460 (14000), 327 (11400), 261 (18400)	520 (20200), 452 (16300), 325 (20200), 257 (22400)
XXXII	1,4-Di[β-(3-indolyl)acrylyl]benzene	540 (45600), 337 (2300), 260 (16000)	515 (51880), 355 (8960), 270 (17000)
XXXIII	1,4-Di(α-(3-indolyl)acrylyl]benzene	538 (28100), 338 (6800), 260 (8800)	432 (41800), 317 (25300), 285 (19850)

tion band of the protonated unsaturated ketones of the indole series is shifted bathochromically as compared with the band for the analogous molecular forms by 90-130 nm (ketone IX constitutes an exception), and this shift amounts to 130-180 nm only for ketones XXX-XXXIII, which contain two indole groupings.

As compared with the analogous ketones of the pyrrole series [2], the halochromic coloration of the indole chalcones, in general, only changes slightly; this is a consequence of the approximately identical electron-donor effect of the 2-pyrrolyl and 3-indolyl groups and their N-methyl-substituted derivatives [3]. A bathochromic shift of the long-wave band of 5-15 nm is observed in acid only when the indole ring is adjacent to the carbonyl group.

The introduction of donor substituents into indole chalcones I and II and replacement of the benzene ring in them by a furan ring or thiophene ring lead to a considerable bathochromic effect; the wave numbers of the absorption maxima of the long-wave band expressed in reciprocal centimeters correlate with the σ constants (Fig. 2) according to the equation $2.3(hc/kT)(1/\lambda_H - 1/\lambda_R) = \rho\sigma$, $r = 0.98$, $\rho = 12 \pm 3$, where λ_H is the absorption maximum of I, and λ_R are the absorption maxima of ketones III, V, VII, XVI, and XVIII.

Lengthening of the conjugation chain by replacement of the phenyl group in I and II by a diphenylyl group (compare XIV and XV) also causes a bathochromic shift in the halochromic coloration. The dimethylamino group in ketone IX is protonated in acidic media and acquires acceptor properties; this leads to a hypsochromic shift. Chloro and nitro groups in both the benzene ring (X-XIII) and in the heterocyclic ring (XXVII-XXIX) do not have a substantial effect on the halochromic coloration nor does N-methylation (compare XX-XXVI).

In addition, unsaturated ketones and cyclopentanone and cyclohexanone derivatives (XXX, XXXI) which can be successfully used as indicators for very low pH values have a particularly deep and intense coloration in a solution of 30% sulfuric acid in glacial acetic acid. The indole analogs of the isomeric p-dichalcones, XXXII and XXXIII, absorb in acid solution in the longer-wave region than the corresponding monochalcones I and II; this should be ascribed to the formation of the corresponding doubly charged cations and reactions of two chromophore groupings through the benzene ring [4], but their halochromic coloration is considerably less deep than that of ketones XXX and XXXI. One should also note that the absorption maxima of the long-wave bands of 3-propenones as compared with the maxima of the analogous 1-propenones, are shifted to the red region of the spectrum; this once more attests to the strong electron-donor effect of the 3-indolyl grouping, which surpasses the effect of the 4-tolyl, 4-anisyl, 2,4-dimethoxyphenyl, 2-furyl, and 2-thienyl groups. Similar regularities are observed when the spectral characteristics of N-methylated ketones XX, XXII, XXIV, and XXVI are compared.

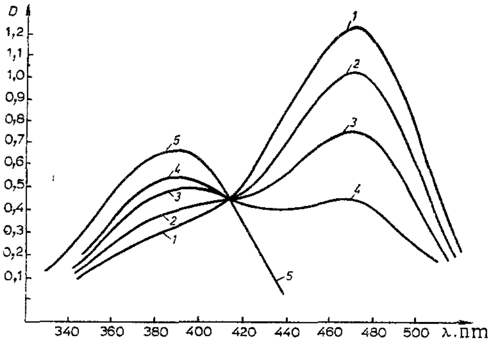
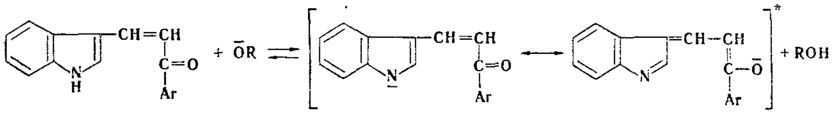


Fig. 3. Absorption curves of ketone II in alcohol solutions of sodium ethoxide: 1) 0.56% C_2H_5ONa; 2) 0.28% C_2H_5ONa; 3) 0.14% C_2H_5ONa; 4) 0.08% C_2H_5ONa; 5) in alcohol.

Halochromic coloration of ketones I-IV in 80% aqueous formic acid is not observed, but more basic compounds that contain such electron-donor groupings as 4-anisyl, 2,4-dimethoxyphenyl (V-VII), 2-furyl and 2-thienyl (XVI and XVIII) form the corresponding organic cations, the long-wave absorption maxima of which practically coincide with the analogous values in solutions of 30% sulfuric acid in glacial acetic acid. It follows from this that side processes such as sulfuration, oxidation, etc., do not occur in the latter solvent during the experiments.

Indole analogs of chalcones (unmethylated compounds) also manifest weakly acidic properties; this is reflected in the considerable bathochromic shift in their color in 2 N sodium ethoxide solution in absolute alcohol as compared with solutions in alcohol or dioxane (see [1]). An isopiestic point was detected in an investigation of the absorption spectra of ketone II in sodium ethoxide solutions of various concentrations with a constant ketone concentration (Fig. 3); this attests to an equilibrium, which, for example, for 3-propenones can be represented as follows:



It is interesting that the long-wave band undergoes a bathochromic shift of 70 nm as compared with the isomeric anions from 1-propenones for the anions formed from 3-propenones as also for analogous organic cations. However, an electron-acceptor substituent, particularly a nitro group, which in the benzene ring causes a red shift of 50-53 nm (compare XII and XIII with I and II) and in the 6-position of the heterocycle causes a shift of 15-18 nm (compare XXVII and XXVIII), has a more significant bathochromic effect on the color of the anions. Except for the dimethylamino group (IX), electron donors as a rule lead to a hypsochromic effect.

Inasmuch as the nitro group should stabilize the structure with a negative charge on the oxygen atom, it is apparently responsible for the chromaticity of the anion and is preferable.

The results of the investigation of the spectra of indole ketones make it possible to conclude that they may be used not only for the determination of the acidity functions (H_0) but also simultaneously for the determination of the H_0 values of strongly basic solutions.

EXPERIMENTAL

The electron absorption spectra of (2-4) $\cdot 10^{-5}$ M solutions were recorded with SF-4A and SF-20 spectrophotometers.

Except for III, X, XII, and XIV, which were obtained by a similar route, the synthesis of the indole derivative ketones was previously described in [5].

---

*The limiting strucures are presented in accordance with the data in [2].

1-(3-Indolyl)-3-tolyl-1-propenone (III). In contrast to the data in [6], this compound had mp 217° rather than 201°. Found: 5.6%. $C_{18}H_{15}NO$. Calculated: N 5.4%.

1-(3-Indolyl)-3-(4-chlorophenyl)-1-propenone (X). This compound was obtained in 40% yield as yellow needles with mp 256°. Found: N 5.0%. $C_{17}H_{12}ClNO$. Calculated: N 7.8%.

1-(3-Indolyl)-3-(4-nitrophenyl)-1-propenone (XII). This compound was obtained in 40% yield as orange plates with mp 251°. Found: N 9.8%. $C_{17}H_{12}N_2O_3$. Calculated: N 9.6%.

1-(3-Indolyl)-3-diphenylyl-1-propenone (XIV). A 0.05-g sample of solid potassium hydroxide was added to a solution of 1.8 g (0.01 mole) of 4-formyldiphenyl and 1.4 g (0.01 mole) of 3-acetylindole in 15 ml of ethylene glycol, and the mixture was heated at 140-160° for 20 min. It was then cooled, and the precipitated crystals were removed by filtration, washed with methanol, acidified with acetic acid, and washed with boiling alcohol to give 2.2 g (70%) of yellowish plates with mp 283°.

LITERATURE CITED

1. S. V. Tsukerman, A. I. Bugai, and V. F. Lavrushin, Khim. Geterotsikl. Soedin., 949 (1972).
2. S. V. Tsukerman, V. P. Izvekov, and V. F. Lavrushin, Khim. Geterotsikl. Soedin., 823 (1968).
3. S. V. Tsukerman, L. A. Kutulya, and V. F. Lavrushin, Khim. Geterotsikl. Soedin., 989 (1969).
4. A. I. Kiprianov and I. L. Mushkalo, Zh. Organ. Khim., 1, 744, 750 (1965).
5. S. V. Tsukerman, A. I. Bugai, V. M. Nikitchenko, and V. F. Lavrushin, Khim. Geterotsikl. Soedin., 399 (1970).
6. F. Piozzi and C. Fuganti, Ann. Chim. (Roma), 56, 1248 (1966).