

16. Alcock C.B. Vapour Pressure Equations for the Metallic Elements: 298–2500K / C.B. Alcock, V.P. Itkin, M.K. Horrigan // Can. Metall. Q. – 1984. – 23. – P. 309–315.
17. Ivanov M.I. Mixing enthalpies in liquid alloys of manganese with the lanthanides / M.I. Ivanov, V.V. Berezutski, N.I. Usenko // Int. J. Mater. Res. (formerly Z. Metallkd.). – 2011. – 102. – P. 277–281.
18. Dinsdale A.T. SGTE Data for pure elements / A.T. Dinsdale // Calphad. – 1991. – 15. – P. 317–425.

19. Bale C.W. Mathematical representation of thermodynamic properties in binary systems and solution of Gibbs Duhem equation / C.W. Bale, A.D. Pelton // Metall. Trans. – 1974. – 5. – P. 2323–2337.
20. Белобородова Е.А. Взаимодействие компонентов бинарных жидких сплавов германия с р-, d- и f-металлами периодической системы: Дис...докт. хим. наук: 02.00.04. – К., 1987. – 448 с.
21. Баталин Г. И. О применимости теории "окруженного атома" к описанию термодинамических свойств жидких алюминиевых сплавов / Баталин Г. И., Белобородова Е. А // ЖФХ. – 1971. – 45, № 8. – С. 1954.

Надійшла до редколегії 17.01.14

Н. Усенко, канд. хим. наук, Н. Котова, канд. хим. наук
КНУ імені Тараса Шевченка, Київ
М. Іванов, канд. хим. наук
Інститут проблем матеріалознавства ім. І. Н. Францевича НАНУ, Київ
Н. Головатая, канд. хим. наук
КНУ імені Тараса Шевченка, Київ

ТЕРМОХИМИЯ СПЛАВООБРАЗОВАНИЯ ЖЕЛЕЗА С ПРАЗЕОДИМОМ И НЕОДИМОМ

Методом высокотемпературной калориметрии в изопериболлическом режиме определены термохимические свойства жидких сплавов двойных систем Fe-(Pr, Nd). Исследование парциальных энтальпий смешения для лантаноидов выполнено при 1829 K и при 1550 K – для железа. Показано, что изученные жидкие сплавы этих систем образуются с незначительным выделением тепла и характеризуются очень малыми экзотермическими теплотами смешения. Энтальпии смешения в системе Fe-Pr имеют также знакопеременный характер. Эти факты свидетельствуют о слабом химическом взаимодействии между компонентами в расплавах железа с легкими лантаноидами. Энтальпии, смоделированные по модели "окруженного атома", удовлетворительно согласуются с полученными экспериментально.

Ключевые слова: железо, празеодим, неодим, высокотемпературная калориметрия, энтальпии смешения, модель "окруженного атома".

N. Usenko, PhD, N. Kotova, PhD
Taras Shevchenko National University of Kyiv, Kyiv,
M. Ivanov, PhD
I.M. Frantsevich Institute for Problems of Materials Science NAS of Ukraine, Kyiv,
N. Golovata, PhD
Taras Shevchenko National University of Kyiv, Kyiv

THERMOCHEMISTRY OF FORMATION OF Fe-Pr AND Fe-Nd ALLOYS

The thermochemical properties of binary liquid Fe-Pr and Fe-Nd alloys were determined by high-temperature isoperibolic calorimetry. The determination of partial mixing enthalpies was carried out at 1829 K for lanthanides and at 1550 K for iron in purified helium medium. It is shown that the process of alloying formation is accompanied by slight heat effects. Enthalpies of mixing in the Fe-Pr system are partially endothermic. Partial enthalpy of mixing of Pr for infinite dilution is found to be slight exothermic value of $-3.6 \pm 0.8 \text{ kJ}\cdot\text{mol}^{-1}$, whereas the first partial enthalpy of Fe is endothermic with the value of $5.4 \pm 1.8 \text{ kJ}\cdot\text{mol}^{-1}$. Enthalpies of mixing in the Fe-Nd system are completely exothermic through the whole concentration region with minimum integral enthalpy of mixing of $-1.1 \pm 0.4 \text{ kJ}\cdot\text{mol}^{-1}$ at $x_{Nd} = 0.4$. These facts indicate a weak chemical interaction between the components of investigated alloys of iron with light lanthanides due to the great size difference of the components. It is shown the complete applicability of "surrounded atom" model to description of concentration dependences of enthalpies of mixing for such systems. It is important among the possibility of further modelling predictions of thermodynamic values in still uninvestigated binary and multicomponent alloys.

Keywords: Iron; Neodymium, Praseodymium, High temperature calorimetry, Enthalpy of mixing, Model of "surrounded atom".

UDC 547.814.5 + 54.04

A. Varenikov, mgr
V.N. Karazin National University, Kharkiv,
I. Serdiuk, PhD student,
V.N. Karazin National University, Kharkiv,
University of Gdańsk, Gdańsk,
A. Roshal, Dr. hab.
V.N. Karazin National University, Kharkiv

SPECTRAL AND BASIC PROPERTIES OF FLAVONES IN THE GROUND AND EXCITED STATES

Dependence between structures of R-oxyflavones and their spectral and basic properties has been investigated. It was found that pK_a of flavones, depending on positions of hydroxy and methoxy groups, increase by 6-8 orders of magnitude upon excitation and reaches 3.7-6.6 units. Due to high pK_a^ value carbonyl group can serve as a proton acceptor in the excited-state intramolecular proton transfer as well as in the formation of phototautomers of 7- and 4'-hydroxyflavones in protic solvents.*

Key words: flavones, electronic spectroscopy, acid-base properties, protolytic equilibria

Introduction. Hydroxyflavones have been the convenient models for exploration of the intramolecular proton transfer in the excited state (ESIPT) for approximately 40 years [1]. Numerous investigations showed that the efficient proton transfer depends on three conditions, among which the most important one is high acidity of proton-donating hydroxyl group in the excited state. Lowering of 3-hydroxy group acidity upon excitation results in decrease of ESIPT rate, which, in the case of 4'-dimethylaminoflavonol in some solvents, makes possible a reverse proton transfer and the acid/base equilibrium appearance [2].

The next important factor is the presence of hydrogen bond of any strength between a donor and an acceptor of

proton. If such hydrogen bond is absent or broken, the ESIPT process is not possible. When proton-donating hydroxy group forms stronger hydrogen bond with solvent molecules, the photo dissociation process takes place, which corresponds to intermolecular proton transfer on a solvent [3, 4].

The third condition necessary for ESIPT is high basicity of proton-accepting carbonyl group in the excited state. The pK_a^* value of the carbonyl group must be higher or, at least, comparable with pK_a^* of hydroxy group. The basic properties of flavone carbonyl group in the ground and excited states were not thoroughly explored. Apparently this is so because the formation of 3-hydroxyflavone phototautomer manifests itself a high basicity of the carbonyl group in the excited

state. Some pK_a^* obtained earlier [5, 6] were not analyzed in context of the ESIPT dynamics.

The synthesis of new flavone derivatives with several carbonyl groups, for example diflavonols, which bring up the problem of a double ESIPT probability [7], or hetaryl chromones, where alternative ESIPT to the basic nitrogen atom of side heterocycle takes place [8], necessitates thorough investigations of the basicity of flavone carbonyl groups.

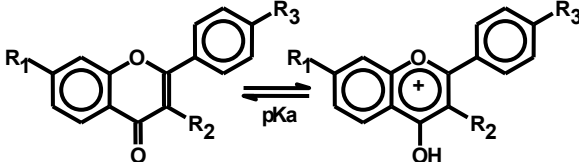
The present work is devoted to the investigations of the carbonyl group basicity for the simplest flavones, which could be able to form phototautomers. It contains the analysis of relationship between pK_a and pK_a^* and the

nature of substituents, the geometry and electronic structure of flavones in the ground and excited states. Structures of the investigated flavones are listed in table 1.

Results and discussion. Carbonyl group of flavones demonstrates weak basic properties in the ground state, its protonation takes place at $H_0 < 0$. Figure 1 shows spectral effects accompanying the protonation of flavone carbonyl group. The formation of flavylum cation results in a bathochromic shift of long-wavelength absorption band and in the most of cases to a rise of fluorescence. Spectral parameters of the neutral and cationic forms of the investigated flavones are presented in table 2.

Table 1

Structures of the investigated flavones



	R ₁	R ₂	R ₃		R ₁	R ₂	R ₃
<i>Ia</i>	OH	H	H		<i>Ila</i>	H	OH
<i>Ib</i>	OMe	H	H		<i>Ilb</i>	H	OMe
<i>Ic</i>	OH	OH	H		<i>Ilc</i>	H	OH
<i>Id</i>	OH	OMe	H		<i>Ild</i>	H	OMe
<i>Ie</i>	OMe	OH	H		<i>Ile</i>	H	OMe
<i>If</i>	OMe	OMe	H		<i>Ilf</i>	H	OMe

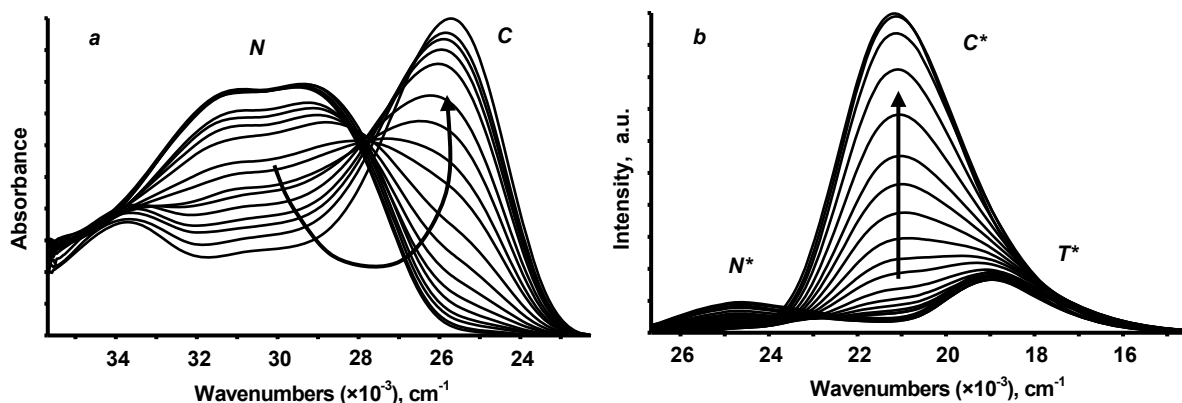


Fig. 1. Changes in absorption (a) and fluorescence (b) spectra of *Ic* upon a cation formation. N and C are a neutral form and a cation in the ground state, N* and T* are tautomers of a neutral form and C* is cation in the S₁ state

Table 2

	Neutral form				Cation			
	V _{abs} (λ _{abs})	V _{fl} (λ _{fl})	ΔV _{St}	V ₀₋₀	V _{abs} (λ _{abs})	V _{fl} (λ _{fl})	ΔV _{St}	V ₀₋₀
<i>fl</i>	32895 (304)	–	–	–	28735 (348)	24720 (405)	4015	26730
<i>Ia</i>	31700 (316)	24300 (412)	7400	28000	27020 (370)	21760 (460)	5260	24390
<i>Ib</i>	32750 (307)	24660 (406)	8090	28705	27400 (365)	22380 (447)	5020	24890
<i>Ic</i>	29500 (339)	24700 (405)	4800	27100	25770 (388)	21160 (472)	4610	23465
<i>Id</i>	31550 (317)	24000 (416)	7550	27775	26110 (383)	21340 (468)	4770	23725
<i>Ie</i>	29580 (338)	24620 (406)	4960	27100	25840 (387)	21460 (466)	4380	23650
<i>If</i>	31550 (317)	23520 (425)	8030	27535	26320 (380)	21340 (469)	4980	23830
<i>Ila</i>	30860 (324)	23820 (420)	7040	27340	26460 (378)	21500 (465)	4960	23980
<i>Ilb</i>	30670 (326)	24160 (414)	6510	27415	25970 (385)	21420 (467)	4550	23695
<i>Ilc</i>	28090 (356)	22075 (453)	6050	25080	24815 (403)	20410 (490)	4405	22610
<i>Ild</i>	29760 (336)	23000 (435)	6760	26380	25450 (393)	21060 (474)	4390	23255
<i>Ile</i>	28250 (354)	23200 (431)	5050	25725	24940 (401)	20740 (482)	4200	22840
<i>Ilf</i>	29940 (334)	23120 (433)	6820	26530	25315 (395)	20660 (484)	4655	22990

* V_{abs}, V_{fl}, λ_{abs}, λ_{fl} – positions of long-wavelength absorption and emission bands maxima (ν – in cm⁻¹ and λ – in nm), V₀₋₀ – values of 0-0 transitions (cm⁻¹), ΔV_{St} – Stokes shifts of fluorescence (cm⁻¹). *fl* – spectral parameters of unsubstituted flavone and its conjugated acid – 4-hydroxyflavylium ion [5].

The data listed in the Table 2 show that introduction of the hydroxy and methoxy groups in position 4' of the flavone moiety results in higher bathochromic shifts of long-

wavelength absorption bands (2035 cm⁻¹ and 2225 cm⁻¹) than when these groups are in position 7 (1195 cm⁻¹ and 845 cm⁻¹, correspondingly).

Introduction of the hydroxy group into position 3 results in the additional bathochromic shift in the range of 2200–2500 cm^{-1} . On the contrary, presence of the 3-methoxy group does not show any noticeable spectral effect in the case of 7-substituted flavones, and leads to some bathochromic shift (800–1100 cm^{-1}) in the case of the 4'-substituted derivatives.

Such spectral effects permit to conclude, that substituents in the side phenyl ring influence the electronic structure of flavone to a greater extent than substituents in the chromone fragment. Methylation minimizes influence of the 3-hydroxy group on spectral properties of the flavones, because of the rotation of the obtained methoxy group out of the chromone plane.

Spectral effects caused by introduction of the 4'- and 7-R-oxygroups to 4-hydroxyflavylium cations are similar to those of the neutral flavones. However, the bathochromic shifts in absorption spectra of the cations are somewhat higher than in the case of the neutral forms. For 7-OH, 7-OCH₃, 4'-OH and 4'-OCH₃ the shifts are 1715, 1565, 2275 and 2765 cm^{-1} correspondingly. Influence of the 3-hydroxy and 3-methoxy groups on spectral properties of the flavylium cations is sufficiently weaker in comparison with the neutral flavones.

The majority of the investigated flavones have a weak fluorescence band in the range 22600–24700 cm^{-1} , which does not depend on the nature and positions of substituents. 3-hydroxyflavones demonstrate two-band fluorescence spectra, where long-wavelength intense band is due to

phototautomer T* emission [1] (depicted on Figure 1). All the 4-hydroxyflavylium cations demonstrate intense one-band fluorescence in a narrow diapason of ~ 20750–21750 cm^{-1} . Positions of the band maxima are not considerably influenced by nature and positions of substituents.

The neutral forms of the majority of the investigated flavones demonstrate abnormally high Stokes shifts of fluorescence – 6760–8030 cm^{-1} , which evidences a substantial structure and solvent relaxation of these compounds in the excited states. Since flavones and especially hydroxyflavones have strong intermolecular hydrogen bonds with solvent molecules in the ground state, high Stokes shift values can be due to drastic reorganization of H-bonds upon excitation. Thus, in the case of the 3-hydroxyflavones having intramolecular hydrogen bond, H-bonding of the carbonyl fragment with solvent molecules is weakened, and Stokes shifts are significantly lower – 4800–5050 cm^{-1} . Furthermore, the high Stokes shifts can also be explained by changing of an angle between the side phenyl ring and the chromone fragment, i.e. by flattening or twisting flavone molecules in the excited state.

A typical titration curve of the flavones in H₀ region at 400 nm is depicted on Figure 2. The curve has only one inflection point, which implies one-step protonation of the investigated compounds. Dissociation constants are presented in Table 2. The obtained values are similar to pK_a determined earlier for some hydroxyflavones [5,6]. Methylation of the hydroxy groups does not substantially change pK_a values.

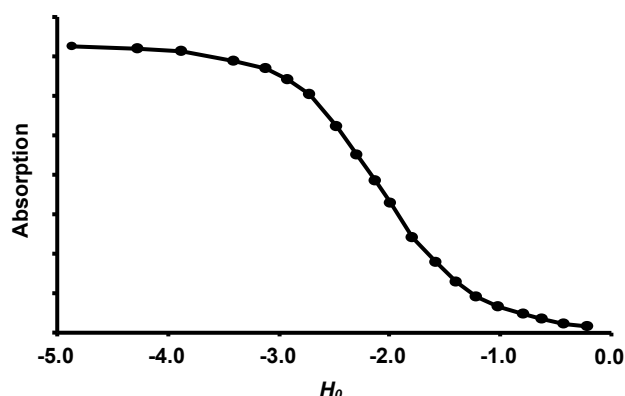


Fig. 2. Titration curve for 1c in H₀ range

Introduction of the 3-hydroxy group into hydroxyflavones decreases their basicity: pK_a of the carbonyl group diminishes on 1 order of magnitude, approximately. Methylation of the 3-hydroxy group has a negligible effect (pK_a decreases by only 0.1-0.2 units) in spite of intramolecular H-bond breakage and rotation of the obtained methoxy group.

Table 3 contains pK_a^{*} values for the excited flavones, obtained by Forster method basing on pK_a values in ground state and parameters of 0-0 transitions for the neutral forms and cations. Analysis of the pK_a^{*} values

showed that, after excitation, dissociation constants of the 7-substituted flavones increase on the average by 7.6 orders of magnitude ($\Delta\text{pK}_a = 6.8-8.5$), whereas in the case of the 4'-substituted derivatives pK_a increases by 6.7 orders of magnitude approximately ($\Delta\text{pK}_a = 6.1-7.8$). The pK_a^{*} values of the investigated flavones are in the range of 3.7-6.9 units, hence the flavones in the excited state have the basicities comparable with those of aniline and quinoline derivatives. The lowest basicity is typical for the 3-hydroxyflavones. Introduction of the 3-hydroxy group decreases pK_a^{*} value by one order of magnitude.

Dissociation (deprotonation) constants of flavones in water-methanol (2:8 v/v) mixtures at 298 K

Table 3

	pK _a	pK _a [*]		pK _a	pK _a [*]
<i>fl</i>	-1.33 [5]				
<i>la</i>	-1.01 ± 0.04 -0.79 [5]	6.6	<i>lla</i>	-0.93 ± 0.03 -0.87 [5]	5.7
<i>lb</i>	-0.72 ± 0.04	6.7	<i>llb</i>	-0.93 ± 0.04	6.9
<i>lc</i>	-2.09 ± 0.05 -2.14 [6]	5.5	<i>llc</i>	-2.21 ± 0.04 -2.15 [6]	4.1
<i>ld</i>	-2.01 ± 0.04	6.5	<i>lld</i>	-2.06 ± 0.04	4.5
<i>le</i>	-2.18 ± 0.03	4.6	<i>lle</i>	-2.37 ± 0.04	3.7
<i>lf</i>	-1.91 ± 0.04	5.9	<i>llf</i>	-2.10 ± 0.03	5.3

Conclusions. The obtained values of pK_a^* show the dramatical basicity growth in the excited state for all the investigated flavones. Taking to account that pK_a^* of the flavone hydroxy groups in the excited state may reach 0-1 [9], the explored phenomenon lies in an excellent agreement with the theory of ESIPT. Moreover, such high basicity of flavones in the excited state makes it possible to suggest a possibility of the solvent-assisted proton transfer in 7- and 4'-hydroxyflavones.

An intense emission of some flavylium cations permits also to use flavones as fluorescent indicators of medium acidity in the range from 3 to 6 pH units.

Experimental part. All the investigated flavones were obtained according known methods [10]. Structures of the flavones were confirmed by 1H and ^{13}C NMR (Mercury VX, 400MHz) and by MALDI TOF mass spectrometry (Biflex III, Bruker Daltonics). Purity of the flavones was tested by liquid chromatography (Waters 600E Multisolvant Delivery System with W2487 Dual λ Absorbance Detector and Gemini 5 μm C6 phenyl 110 column) in acetonitrile-water 60/40 v/v mixture.

Dissociation constants were determined by spectrophotometric titration of the flavones by water solutions of sulfuric acid in the acidity range from $H_0 = -4.5$ to $pH = 1.0$. Absorption and fluorescence spectra were registered on a Hitachi U3210 spectrophotometer and on a Varian Cary Eclips spectrofluorimeter.

References

1. Sengupta P.K. Excited state proton-transfer spectroscopy of 3-hydroxyflavone and quercetin / P.K. Sengupta, M. Kasha // Chem. Phys. Lett. – 1979. – V. 68. – P. 382–385.
2. Roshal A.D. Tuning the mechanism of proton-transfer in a hydroxyflavone derivative / A.D. Roshal, J.A. Organero, A. Douhal // Chem. Phys. Lett. – 2003. – V. 379. – P. 53–59.
3. McMorrow D. Intramolecular Excited-State Proton Transfer in 3-hydroxyflavone. Hydrogen-bonding solvent perturbations / D. McMorrow, M. Kasha // J. Phys. Chem. – 1984. – V. 88, № 11. – P. 2235–2243.
4. Parthenopoulos D.A. Ground state anion formation and picosecond excitation dynamics of 3-hydroxyflavone in formamide / D.A. Parthenopoulos, M. Kasha // Chem. Phys. Lett. – 1990. – V. 173, № 4. – P. 303–309.
5. Pogodaeva N.N. Ultraviolet absorption of flavonoids IV. Protonation constants of some monohydroxy flavones / N.N. Pogodaeva, N.A. Tyukavkina // Khim. Prirod. Soed. – 1972. – № 1. – P. 22–24.
6. Pogodaeva N.N. Ultraviolet absorption of flavonoids VI. Protonation constants of some dihydroxyflavones / N.N. Pogodaeva, N.A. Tyukavkina // Khim. Prirod. Soed. – 1975. – № 5. – P. 587–590.
7. Roshal A.D. Spectral and acid-base features of 3,7-dihydroxy-2,8-diphenyl-4h,6h-pyrano[3,2-g]chromene-4,6-dione (diflavonol) – a potential probe for monitoring the properties of liquid phases / A.D. Roshal, V. I. Moroz, V. G. Pivovarenko, et al. // J. Org. Chem. – 2003. – V. 68, № 15. – P. 5860–5869.
8. Svechkarev D.A. Nature of dual fluorescence in 2-(quinolin-2-yl)-3-hydroxychromone: Tuning between concurrent H-bond directions and ESIPT pathways / D.A. Svechkarev, A.O. Doroshenko, V.N. Baumer, et al. // J. Lumin. – 2011. – V. 131, № 2. – P. 253–261.
9. Roshal A.D. Flavonols as metal-ion chelators: Complex formation with Mg^{2+} and Ba^{2+} cations in the excited state / A.D. Roshal, A.V. Grigorovich, A.O. Dorochenko, et al. // J. Photochem. Photobiol. A. – 1999. – V. 127, № 1-3. – P. 89–100.
10. Shan M. De novo asymmetric syntheses of SL0101 and its analogues via a palladium-catalyzed glycosylation / M. Shan, G.A. O'Doherty // Org. Lett. – 2006. – V. 8, № 22. – P. 5149–5152.

Надійшла до редколегії 21.03.14

А. Вареников, магістр
ХНУ імені В. Н. Каразіна, Харків,
І. Сердюк, асп.
ХНУ імені В. Н. Каразіна, Харків,
Гданський університет, Гданськ,
О. Рошаль, канд. хім. наук
ХНУ імені В. Н. Каразіна, Харків

СПЕКТРАЛЬНІ ТА ОСНОВНІ ВЛАСТИВОСТІ ФЛАВОНІВ В ОСНОВНОМУ І ЗБУДЖЕНОМУ СТАНАХ

У статті досліджено залежності між структурою R-оксифлавонів, їх спектральними та основними властивостями. Було виявлено, що pK_a флавонів, в залежності від положення гідрокси та метокси груп, збільшуються на 6–8 порядків у збудженому стані і сягають значень 3.7–6.6. Завдяки високим значенням pK_a^* карбонільна група може бути акцептором протону як у реакціях внутрішньомолекулярного переносу протону у збудженому стані, так і у формуванні фототаутомерів 7- і 4'-гідроксифлавонів у протонних розчинниках.

Ключові слова: флавоони, електронна спектроскопія, кислотно-основні властивості, протолітичні рівноваги.

А. Вареников, магістр,
ХНУ імені В.Н. Каразіна, Харків,
І. Сердюк, асп.
ХНУ імені В.Н. Каразіна, Харків,
Гданський університет, Гданськ,
А. Рошаль, канд. хім. наук.
ХНУ імені В.Н. Каразіна, Харків

СПЕКТРАЛЬНЫЕ И ОСНОВНЫЕ СВОЙСТВА ФЛАВОНОВ В ОСНОВНОМ И ВОЗБУЖДЕННОМ СОСТОЯНИИ

В статье изучены зависимости между структурой R-оксифлавонов, их спектральными и основными свойствами. Было обнаружено, что в зависимости от положения гидроксильных и метоксильных групп, pK_a флавонов увеличиваются при возбуждении на 6–8 порядков и достигают значений 3.7–6.6. Благодаря высоким значениям pK_a^* карбонильная группа может быть акцептором протона как в реакции внутримолекулярного переноса протона в возбужденном состоянии, так и при образовании фототаутомеров 7- и 4'-гидроксифлавонов в протонных растворителях.

Ключевые слова: флавоны, электронная спектроскопия, кислотно-основные свойства, протолитические равновесия