

BASICITY AND INTRAMOLECULAR PROTON TRANSFER IN 2-HYDROXYBENZOPHENONE DERIVATIVES

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A good linear correlation has been found to exist between the estimated protonation equilibrium constants of 2-hydroxybenzophenone derivatives and Brown's σ^+ constants. The mentioned equilibrium constants also correlate quite satisfactorily with the calculated π electron densities on the carbonyl oxygen. The electron densities were calculated by means of the semiempirical SCF-LCI method. Using the Förster cycle it has been shown that, in the first excited singlet state, both the basicity of carbonyl group and the acidity of the 2-hydroxyl group in 2-hydroxybenzophenones strongly increase. The observed increase supports the supposition that proton transfer from the 2-hydroxyl group to the carbonyl group occurs in this state. It is possible that the proposed proton transfer plays an important role in the radiationless transition (probably internal conversion) from the excited state to ground state for molecules like 2-hydroxybenzophenone. An effect of the intramolecular hydrogen bond in 2-hydroxybenzophenone has to be proposed to account for the change in basicity of this compound in comparison with benzophenone.

An intramolecular proton and/or hydrogen atom transfer in the excited state of molecules has been proposed by many workers to explain the spectroscopic or photochemical behaviour of the molecules. Thus, Weller¹ studying emission spectra of methyl salicylate proposed a proton transfer in the excited state of the molecule. For this molecule the mentioned protolytic reaction equilibrium constant was estimated² to be equal to 0.1. An intramolecular hydrogen atom transfer was also postulated for the derivatives of 2-hydroxybenzophenone³⁻⁵ in order to explain the photochemical stability of these compounds. It might be worthy of note that 2-hydroxy-4,6-di-*tert*-butylbenzophenone which has the lowest excited singlet and triplet state of n, π^* type exhibits a photoreactivity which is comparable to that of 2-hydroxybenzophenone. O'Connell explained this observation by intramolecular proton transfer⁶. Merrill and Bennett showed⁷ that an intramolecular hydrogen bond in the *ortho* isomer of a 2-(aminophenyl)-2,1,3-benzotriazole is responsible for rapid deactivation of the first excited singlet state by internal conversion.

A great deal of attention has been paid to the protonation of aromatic carbonyl compounds. For substituted benzaldehydes⁸, acetophenones⁹, benzophenones¹⁰, and benzoic acids¹¹ good linear correlations between pK of protonation and Brown's σ^+ constants were generally found. A correlation between pK and σ^+ constants is usually accepted as evidence that a protonized carbonyl group possesses the character of a carbonium ion¹². In a study of the protonation of benzophenone derivatives Stewart and coworkers¹³ did not find a linear correlation between pK values and σ^+ constants for the symmetrically homodisubstituted benzophenones (mainly in *para*-position). However, Bonner and Philips¹⁰ found a good linear relationship between pK of protonation of the monosubstituted benzophenones and σ^+ constants. (Bonner and Philips¹⁰ used an other scale for H_0 than Stewart and coworkers¹³ did, however, the conclusions do not

depend on this). A quantum chemical interpretation of the protonation equilibria for conjugated carbonyl compounds was performed by Culbertson and Pettit¹⁴. They calculated the π energy of protonation by means of the perturbation theory approximation. Others have reported calculations of the protonation energy for the compounds mentioned above using the PPP method^{15,16} or the MINDO method¹⁷.

EXPERIMENTAL AND CALCULATIONS

Protonation equilibrium constants of the benzophenone derivatives have been determined spectrophotometrically using method of Davis and Geissman¹⁸ which allows for the effect associated with the change in acidity of the medium upon the absorptivity of protonized and unprotonized forms. The value of the protonation equilibrium constant has been taken as the point of inflection of the dependence $\Delta D \sim H_0$; $\Delta D = D_{\lambda_i} - D_{\lambda_u}$, where D_{λ_i} is the absorbance at wavelength λ_i where the protonized form mainly absorbs and D_{λ_u} is the absorbance at wavelength λ_u where absorption of the unprotonized form prevails. For comparison we have also used a dependence⁸ $\log \{(\Delta D_{BH^+} - \Delta D)/(\Delta D - \Delta D_B)\} \equiv \log I = pK - H_0$, where ΔD_{BH^+} is the difference in absorbance at wavelengths λ_i and λ_u for the complete protonation of a ketone and ΔD_B has a similar meaning for the neutral form of the ketone. The advantage of the latter method consists in the elimination of the subjective errors connected with finding the point of inflection. The error in pK found by both methods is ± 0.1 pK units. The spectrophotometric measurements were performed on spectrophotometer ORD/UV-5 (Jasco, Japan) at 25°C. Acidity function H_0 was taken from review by Paul and Long¹⁹. The phosphorescence spectra of 2-hydroxybenzophenones in ethanol, 96% H_2SO_4 and in 0.2M-NaOH at 77 K were measured as described earlier²⁰.

The protonation and ionization (in alkali medium) equilibrium constants in the excited states were determined according to Weller¹ using the Förster cycle²¹. For the estimation of the pK of protonation in the first excited singlet state the energy difference between the longest wavelength absorption bands of the neutral and protonized forms (measured in 0.2N- H_2SO_4 and 96% H_2SO_4) were taken. Equilibrium constants in the lowest triplet state were calculated using the energy differences between "gravity centers" of the phosphorescence bands of the corresponding forms measured in ethanol, 96% H_2SO_4 and 0.2M-NaOH. The needed spectroscopic values (except those belonging to spectra in 0.2N- H_2SO_4) were published earlier^{20,22,23}. For the preparation and purification of derivatives of 2-hydroxybenzophenone and the solvents used see refs^{20,25}.

The calculations by semiempirical SCF-LCI method in the PPP approximation were performed using the program QCPE 71 by Bloor and Gilson with an IBM 7040 computer. The semiempirical parameters published in preceding papers^{22,23} were used. The parameters were adjusted to simulate the energy of the first $\pi \rightarrow \pi^*$ absorption band of neutral, protonized and ionized derivatives. For the neutral forms of molecules we used the parameters which correctly give the value of energy of the first absorption bands of these molecules in nonpolar solvent²³.

RESULTS AND DISCUSSION

Correlations between pK Values and σ Constants or π Electron Densities

The effect of substituents in the 4- and 5-positions of 2-hydroxybenzophenone was at first interpreted by the empirical Hammett $\rho\sigma$ approach. It appears that the protonation equilibrium constants (Table I) in the ground state correlate best with Brown's

TABLE I
Equilibrium Constants of Protonation and Ionization and SCF π Electron Densities in 2-Hydroxybenzophenones

No	Substituent	pK_p	σ^{+a}	σ^a	pK_i^b	$q_{=O}^c$	$q_{=O^+H}^c$	q_{-OH}^c	$q_{-O^-}^c$
1	H	-6.27	0.00	0.00	10.83	1.4912	1.6951	1.8430	1.8111
2	4-CH ₃	-6.09	-0.31	-0.17	11.10	1.4941	1.6970	1.8422	1.8100
3	5-CH ₃	-6.18	-0.07	-0.07	11.30	1.4910	1.6950	1.8470	1.8172
4	4-OH	-4.98	-0.92	-0.37	—	1.4988	1.7000	1.8431	—
5	5-OH	-6.25	0.12	0.12	—	1.4910	1.6951	1.8400	—
6	4-OCH ₃	-5.16	-0.78	-0.27	10.86	—	—	—	1.8121
7	5-OCH ₃	-6.31	0.05	0.12	11.03	—	—	—	1.8189
8	4-Cl	-6.63	0.11	0.23	9.50	—	—	—	—
9	5-Cl	-6.68	0.40	0.37	9.80	—	—	—	—
10	4-NO ₂	-7.49	0.79	0.78	8.23	1.4781	1.6865	1.8370	1.8001
11	5-NO ₂	-7.41	0.67	0.71	6.69	1.4830	1.6900	1.8281	1.7812
12	5-COCH ₃	—	—	0.50	8.15	1.7870	—	1.8332	1.7871

^a σ^+ and σ constants are taken from review by Ritchie and Sager²⁴. ^b pK_i values are taken from paper²⁵. ^c The values of SCF π electron density on carbonyl oxygen, protonized carbonyl oxygen, 2-hydroxyl oxygen and ionized 2-hydroxyl oxygen atoms.

σ^+ constants. By the least square method the expression (1) was obtained* where

$$pK = -6.31 - 1.42\sigma^+; \quad r = 0.982, \quad s = \pm 0.169, \quad \text{and} \quad n = 11. \quad (1)$$

r stands for the correlation coefficient, s is the standard deviation and n is the number of points. The correlation is graphically represented in Fig. 1. As it was already mentioned a correlation with σ^+ constants indicates that the protonized 2-hydroxybenzophenones have also the structure of carbonium ion¹² (1).

This is in harmony with our previous theoretical and experimental studies²³ on the electronic spectroscopy of these compounds.

An interesting question is whether the strong acidic hydrogen of the protonized carbonyl group is stabilized by an interaction with free electron pair on the 2-hydroxyoxygen as proposed by Bonner¹⁰. One of the possible tests is to clear up whether the substituent effect on basicity of carbonyl group is also transmitted through the 2-hydroxyl group. The following correlation (2) including substituent effect through

$$pK = -6.26 - 1.34\sigma_1^+ - 0.20\sigma_2^-; \quad s = \pm 0.138, \quad n = 11, \quad (2)$$

* When pK value was calculated using the following equation $\log I = -mH_0 + pK$, suggested by Greig and Johnson²⁶ a surprisingly bad correlation was obtained.

two centres was obtained, where σ_1^+ is substituent constant relating to carbonyl group and σ_2^- constant is that relating to 2-hydroxyl group. According to standard deviation criterion, correlation (2) is significantly better than correlation (1) and the coefficients of the substituent constants in equation (2) are of the right sign. However, according to the statistical criterion given by Jaffé²⁷ correlation (2) cannot still be regarded as evidence for a significant transmission of the substituent effect through the two centers. However correlation (2) does not exclude the above mentioned stabilization.

An attempt to correlate the pK values of protonation with π electron density on the carbonyl oxygen calculated by SCF method assuming that the π electron energy of protonation is proportional to the π electron density, as it may be rationalized by the first order approximation derived from the simple perturbation theory, was made. A good linear correlation thus obtained is shown in Fig. 2 and demonstrates that the π electron energy of protonation correctly describes the relative change in pK values. However, the inductive effect and/or field effect, which the PPP method does not properly include, is probably also effective and roughly proportional to the π electron energy changes. In the same Fig. 2 the correlation between the protonation pK values and π electron densities on the carbonyl oxygen of the protonized forms is plotted. It is worthy of note that the strong electron donor substituents (e.g., hydroxyl group) also conform with both correlations. On the other side, the use of σ^+ constants instead of simple σ constants for the strong electron donor substituents in *para*-

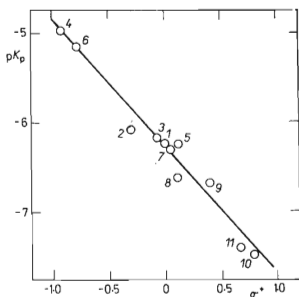


FIG. 1

Correlation of pK Values of Protonation with σ^+ Constants

For numbering see Table I.

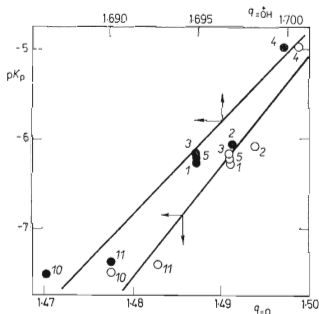


FIG. 2

Correlation of pK Values of Protonation with π Electron Density both on Protonized and Neutral Carbonyl Oxygen

For numbering see Table I.

-position is usually explained by an enhanced resonance interaction between the substituent and the protonized carbonyl group and such an enhanced resonance interaction was proposed to take place either in reagent or in product but not in both²⁶. Correlations in Fig. 2 show that the enhanced resonance interaction takes place both in the product and the reagent.

The correlation between pK of ionization of 2-hydroxyl group (in alkali medium) and π electron density on the 2-hydroxyl oxygen in the neutral form and on that in the ionized form is shown in Fig. 3. Again, strong electron acceptor groups (nitro and acetyl) in *para*-position towards 2-hydroxyl group decrease the π electron densities on the hydroxyl oxygen both in neutral and ionized forms in accordance with the change in pK_i . As it is well-known for such strong electron acceptor substituents in *para*-position we have to use σ^- constant if we correlate pK_i with substituent constants. It is claimed (*e.g.* see review by Ritchie and Sager²⁴) that in such a case the substituent may be in strong resonance interaction with reaction center either in product or in reagent but not in both. Conversely, our results show that the mentioned resonance interaction takes place both in product and reagent.

Relationship between Acidity and Basicity

The exploration of the relationship between acidity and basicity in 2-hydroxybenzophenone derivatives is quite attractive because of the simultaneous presence of both the acidic 2-hydroxyl group and the basic carbonyl group within the same molecule.

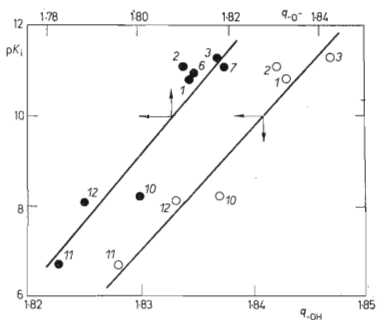


FIG. 3

Correlation of pK Values of Ionization with π Electron Density on both the Neutral 2-Hydroxyl Oxygen and Ionized 2-Hydroxyl Oxygen
For Numbering see Table I.

In Fig. 4 the correlation between acidity and basicity is shown. From the expression for acidity given in the literature²⁵ (equation (3)) and from that for basicity (equation (1)),

$$pK_i = 10.77 - 3.32\sigma^- \quad (3)$$

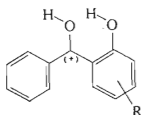
the following relation can be obtained

$$pK_i = 25.52 + 2.34 pK_p \quad (4)$$

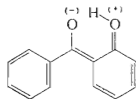
Eq. (4) was derived under a very rough approximation according to which the equivalence between σ^- and σ^+ constants for both *meta*- and *para*-positions was assumed. This "theoretical" straight line drawn in Fig. 4 is very close to all experimental points except for the strong electron donor methoxy group in the 4-position and the strong electron acceptor nitro group in the 5-position, which is quite understandable because of a large difference between σ_p^- , σ_p^+ and σ_m constants for each of these substituents.

Basicity, Acidity and Proton Transfer in the Excited States

In Fig. 5 the dependences of protonation and ionization equilibrium constants in the ground and the lowest excited singlet state on σ^+ and σ^- constants are plotted. These results show striking changes in the acid-base properties in the excited state in comparison with the ground state. Thus, both the acidity of the hydroxyl group and the basicity of the carbonyl group are strongly enhanced in the excited singlet state so that in some cases the protonized carbonyl group is even less acidic than the 2-hydroxyl group. The pK values of protonation and ionization for the lowest triplet state lie between those for the ground and the lowest excited singlet states (Table II). The large change in acid-base properties for the excited state can be accounted for by the assumption that π electron densities on the atoms, on which particular protolytic reaction takes place, are responsible for the changes in acid-base properties. From Table II it may be seen that for the first excited singlet state there is a significant increase in π electron density on the carbonyl oxygen and a strong decrease in that on the 2-hydroxyl oxygen. In our previous studies^{20,22,23} on the electronic spectro-



I



II

scopy of 2-hydroxybenzophenones it has been shown that in the first excited singlet state there is a considerable transfer of the π electron density from both the hydroxyl oxygen and the phenyl group of the 2-hydroxyphenyl group to the carbonyl group, and that the structure (II) is very important in the lowest excited singlet state. It is worthy of note that when we draw a structure like II as a representative for the excited singlet state we mean that structure II has the most important contribution among all other structures except that of the ground state, which, of course, usually still prevails since the excitation of one of sixteen electrons does not change very strongly the overall structure of the ground state.

The π electron densities for the lowest triplet state lie between those for the ground and the first excited singlet state. As to the $\rho\sigma$ correlations for the excited states, pK values of protonation for the lowest excited singlet and triplet states do not correlate with substituent constants. The failure might be due to both experimental errors and non-validity of $\rho\sigma$ correlation for the excited states. Except the causes of experimental errors in establishing pK values given by Jaffé²⁸ we should also take into consideration the differences in the solvent effect (96% H_2SO_4 and 0.2N- H_2SO_4) on the electronic absorption spectra which probably do not correlate with the electronic structure of the derivatives. On the other side, a good linear relationship between pK of ionization and σ^- constants was found for the lowest excited singlet

TABLE II

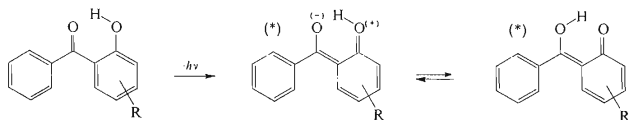
Acid-Base Properties and SCF π Electron Densities in the Excited States of 2-Hydroxybenzophenones

No	Substituent	pK_p^{*a}	$pK_1^{*a,c}$	pK_p^{Tb}	pK_1^{Tb}	$q_{=0}^*{}^a$	$q_{-OH}^*{}^a$	$q_{=0}^T{}^b$	$q_{-OH}^T{}^b$
1	H	1.43	3.78	-2.57	4.13	1.6271	1.5600	1.5202	1.6381
2	4-CH ₃	0.61	4.20	-4.94	5.13	1.6330	1.5682	1.5201	1.6663
3	5-CH ₃	3.64	3.70	-0.73	4.18	1.6322	1.5750	1.5479	1.6350
4	4-OH	2.12	—	-4.77	—	1.6309	1.5028	1.5411	1.6991
5	5-OH	2.67	—	-6.46	—	1.6400	1.6341	1.5380	1.6679
6	4-OCH ₃	2.69	2.70	-1.81	5.41	—	—	—	—
7	5-OCH ₃	0.71	5.59	-2.54	6.60	—	—	—	—
8	4-Cl	2.63	0.93	-2.44	4.80	—	—	—	—
9	5-Cl	4.09	2.14	-0.61	2.78	—	—	—	—
10	4-NO ₂	0.09	-3.54	-7.49	— ^d	1.5521	1.5230	1.5162	1.5511
11	5-NO ₂	4.22	-8.36	-9.50	2.50	1.6030	1.5379	1.4491	1.6700
12	5-COCH ₃	—	-0.75 ^c	—	2.70	1.6209	1.5771	1.4799	1.6772

^a By asterisk the values in the lowest excited singlet state are designated. ^b Symbol T stands for the lowest triplet state. ^c Data taken from ref.²⁵. ^d No phosphorescence observed in ethanol.

^e This is a corrected value obtained after determination of correct position of the first absorption band corresponding to ionized form of 5-acetyl derivative as estimated in ref.²³.

state (Fig. 5) and even for the lowest triplet state (Fig. 6). The ρ value of -3.0 for the lowest triplet state comparable with that for the ground state (-3.32) was observed, while ρ value of the just mentioned correlation for the excited singlet state is about three times greater than that for the ground state²⁵.



We believe that the change in acidity and basicity in the lowest excited singlet state favours the following proton transfer reaction (A) in all of the 2-hydroxybenzophenone derivatives. Such a protolytic reaction was proposed by some authors as it is mentioned in the introduction. Considering the acid-base data it is clear that the mentioned reaction involves namely proton transfer and not hydrogen atom transfer. To classify an equilibrium constant of the intramolecular proton transfer reaction we may use as a relative measure the values of $pK_{is}^* = p(K_i^*/K_p^*)$ given in Table III. The higher K_{is}^* the greater is the equilibrium constant for proton transfer reaction. The pK_{is}^* values change a great deal depending on the electron donor-acceptor property of substituent. The molecules with electron acceptor substituents show greater "readiness" for the proton transfer reaction than those with electron donor substituents. On the other side, similar proton transfer reaction may be also considered in the lowest triplet (pK_{is}^T) and even in the ground (pK_{is}) state, though

TABLE III

Data for Proton Transfer Reaction in the First Excited Singlet, the Lowest Triplet, and the Ground States of the 2-Hydroxybenzophenone Derivatives

No	Substituent	pK_{is}^*	pK_{is}^T	pK_{is}
1	H	2.35	6.70	17.10
2	4-CH ₃	3.59	10.07	17.19
3	5-CH ₃	0.06	4.91	17.48
4	4-OCH ₃	0.01	7.22	16.20
5	5-OCH ₃	4.88	9.14	17.34
6	4-Cl	-1.70	7.12	16.13
7	5-Cl	-1.95	3.39	16.48
8	4-NO ₂	-3.63	—	15.72
9	5-NO ₂	-12.58	12.00	14.10

with less probability (Table III). As to the pK_{is} values in the ground state, they probably indicate the relative strength of intramolecular hydrogen bond. The higher the basicity of carbonyl group and acidity of 2-hydroxyl group the stronger is hydrogen bond.

We believe that the just discussed data on proton transfer reaction in the excited state as well as those in the ground state are of some importance for explanation of the complex photostabilizing mechanism of molecules of 2-hydroxybenzophenone type. While the data on proton transfer reaction in the excited state may be related

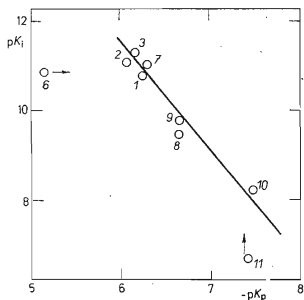


FIG. 4

Relationship between Basicity and Acidity of 2-Hydroxybenzophenones

The line stands for a "theoretical" straight line drawn according to Eq. (4). For numbering see Table I.

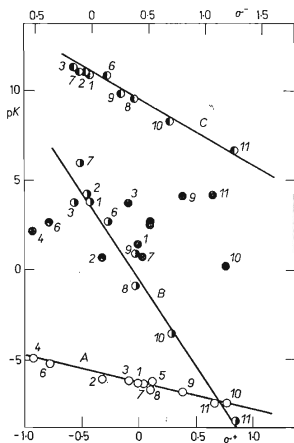


FIG. 5

Relationship between pK Values of Protonation and Ionization in the Ground and the Lowest Excited Singlet State for 2-Hydroxybenzophenone Derivatives and σ Constants *A* Protonation equilibrium constants in the ground state, *B* Ionization equilibrium constants in the excited singlet state. *C* Ionization equilibrium constants in the ground state. ● Points marking pK_p in the excited singlet state. Numbering of the points on the lines *A* and *C* according to Table I, those on the lines *B* and the points ● according to Table II.

TABLE IV

The Influence of *ortho*-Substitution on the Basicity of Benzophenone Derivatives

Substituent	pK_p	ΔpK_p	Substituent	pK_p	ΔpK_p
H	-6.16		4-CH ₃	-5.91 ^a	-0.18
2-OH	-6.27	-0.11	2-OH-4-CH ₃	-6.09	
2,2'-(OH) ₂	-6.66	-0.39	4-NO ₂	-7.42	
4-OH	-4.86		2-OH-4-NO ₂	-7.49	-0.07
2,4-(OH) ₂	-4.98	-0.12	4,4'-(OCH ₃) ₂	-4.47 ^b	
4-OCH ₃	-5.10		2,4,4'-(OCH ₃) ₃	-3.60 ^b	-0.87
2-OH-4-OCH ₃	-5.16	-0.06			
2,2'-(OH) ₂ -4-OCH ₃	-5.52	-0.36			

^a The value taken from ref.³⁰. ^b Data taken from ref.¹⁰ after transformation into the H₀ scale given in ref.¹⁹

to the effectiveness of radiationless processes from the excited to the ground state, the pK_{1s} values for the ground state, as a supposed measure of relative strength of intramolecular hydrogen bond, also express the relative probabilities of formation of the intermolecular hydrogen bond between 2-hydroxyphenyl group and basic group in, e.g., polymer or in solvent. Lamola and Sharp²⁹ showed that the phosphorescent intensity of 2-hydroxybenzophenone derivatives in different solvents depends on the "fraction" of molecules where intramolecular hydrogen bond is "replaced" by intermolecular one. The molecule of 2-hydroxybenzophenone in which intramolecular hydrogen bond was "replaced" by intermolecular one are supposed, by the authors, to be capable of producing relatively long-lived triplet states which could sensitize photochemical reactions. To characterize an intramolecular hydrogen bond in the 2-hydroxybenzophenone derivatives in more detail, a study by NMR and electronic spectroscopy is now being performed by the author.

The Energy of Intramolecular Hydrogen Bond in 2-Hydroxybenzophenones

The basicity data in Table IV show only a small influence of the 2-hydroxy substitution on the pK of protonation. The average change in pK due to such a substitution is of about -0.1 pK units towards lower basicity. The second *ortho* hydroxyl group decreases basicity even more (about 0.4 pK units approx.). The decrease in basicity due to *ortho* hydroxy substitution is somewhat unexpected since the resonance effect of *ortho* hydroxyl group should be approximatively equal to that of *para* hydro-

xyl group.* As it has already been mentioned, the hydroxyl group in *ortho* position probably also stabilizes acidic hydrogen of protonated carbonyl group through hydrogen bond. All these facts would predict an enhanced basicity of 2-hydroxybenzophenone. The difference between pK values of protonation of 2,4,4'-trimethoxybenzophenone and 4,4'-dimethoxybenzophenone shows that methoxy group in *ortho* position enhances basicity by 0.87 pK units. It seems that the unexpected low value of the basicity of 2-hydroxybenzophenone in comparison with that of benzophenone, can be accounted for by the effect of intramolecular hydrogen bond between the 2-hydroxyl group and the carbonyl group in the neutral form of this molecule which approximatively compensates the resonance effect between 2-hydroxyl and carbonyl groups and stabilization *via* hydrogen bond in the protonized form. As a rough estimation of the energy of intramolecular hydrogen bond in neutral form of 2-hydroxybenzophenone the value of 1.3 kcal/mol was found.** This value was determined on the supposition that the decrease in basicity due to *ortho*-hydroxy substitution in comparison with *ortho*-methoxy substitution is caused only by intramolecular hydrogen bond, and the change in pK due to *ortho*-

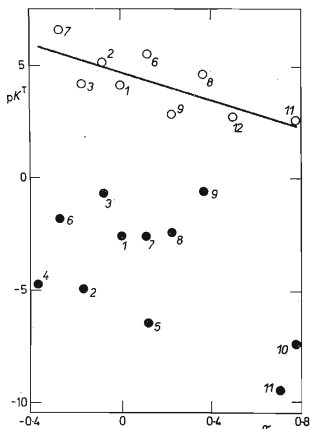


FIG. 6
Correlation of pK Values of Protonation (●) and Ionization (○) in the Lowest Triplet State with σ Constants
For numbering see Table II.

* SCF calculations performed by the author show indeed even a little higher value of π electron density on carbonyl oxygen for *ortho* in comparison with *para* derivative.

** This value can be probably regarded as difference between the energy of intermolecular hydrogen bond in 2-hydroxybenzophenone and that of intermolecular one formed by carbonyl oxygen with solution of sulphuric acid.

-methoxy substitution was taken as equal to 0.87 pK units and that due to *ortho*-hydroxy substitution as equal to -0.1 pK units. The assumption of equal change in entropy of protonation of both benzophenone with 2-hydroxy and that with 2-methoxy group was employed.

Basicity data for other substituted 2-hydroxybenzophenones show approximatively the same effect of *ortho* hydroxy substitution (about -0.1 pK units) regardless the substituent.

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REFERENCES

1. Weller A. in the book: *Progress in Reaction Kinetics* (G. Porter, Ed.), p. 187, Vol. I. Pergamon Press, London 1961.
2. Beens H., Grellman K. H., Gurr M., Weller A. H.: *Discussions Faraday Soc.* 39, 183 (1965).
3. Hammond G. S., Turro N. J., Leermakers P. A.: *J. Phys. Chem.* 66, 1144 (1962).
4. Pitts J. N., jr, Johnson H. W., jr, Kuwana T.: *J. Phys. Chem.* 66, 2456 (1962).
5. Porter G., Suppan P.: *Proc. Chem. Soc.* 1964, 191.
6. O'Connell E. J., jr: *J. Am. Chem. Soc.* 90, 6550 (1968).
7. Merrill J. R., Bennett R. G.: *J. Chem. Phys.* 43, 1410 (1965).
8. Yates K., Stewart R.: *Can. J. Chem.* 37, 664 (1959).
9. Stewart R., Yates K.: *J. Am. Chem. Soc.* 82, 4059 (1960).
10. Bonner T. G., Phillips J.: *J. Chem. Soc. (B)* 1966, 650.
11. Stewart R., Granger M. R.: *Can. J. Chem.* 39, 2508 (1961).
12. Arnett E. M. in the book: *Progress in Physical Organic Chemistry* (S. G. Cohen, A. Streitwieser, jr, R. W. Taft, Eds), p. 301, Vol. I. Interscience, New York 1963.
13. Stewart R., Granger M. R., Moodie R. B., Muenster L. J.: *Can. J. Chem.* 41, 1065 (1963).
14. Culbertson G., Pettit R.: *J. Am. Chem. Soc.* 85, 741 (1963).
15. Kende A. in the book: *Advances in Chemical Physics* (R. Daudel, Ed.), p. 138, Vol. VIII. Interscience, London 1965.
16. Zahradnik R., Tichý M., Reid D. H.: *Tetrahedron* 24, 3001 (1968).
17. Dewar M. J. S., Morita T.: *J. Am. Chem. Soc.* 91, 802 (1969).
18. Davis Ch. T., Geissman T. A.: *J. Am. Chem. Soc.* 76, 3507 (1954).
19. Paul M. A., Long F. A.: *Chem. Rev.* 57, 1 (1957).
20. Kysel' O., Zahradnik R., Pakula B.: *This Journal* 35, 3020 (1970).
21. Förster T.: *Z. Elektrochem.* 54, 42 (1950).
22. Kysel' O., Zahradnik R.: *This Journal* 35, 3030 (1970).
23. Kysel' O., Zahradnik R., Belluš D., Sticzay T.: *This Journal* 35, 3191 (1970).
24. Ritchie C. D., Sager W. F. in the book: *Progress in Physical Organic Chemistry* (S. G. Cohen, A. Streitwieser jr, R. W. Taft, Eds), p. 327, Vol. 2. Wiley, New York 1964.
25. Hrdlovič P., Belluš D., Lazár M.: *This Journal* 33, 59 (1968).
26. Greig C. C., Johnson C. D.: *J. Am. Chem. Soc.* 90, 6453 (1968).
27. Jaffé H. H.: *J. Am. Chem. Soc.* 76, 4261 (1954).
28. Jaffé H. H., Jones H. L.: *J. Org. Chem.* 30, 964 (1965).
29. Lamola A. A., Sharp L. J.: *J. Phys. Chem.* 70, 2634 (1966).
30. Fischer A., Grigor B. A., Packer J., Vaughan J.: *J. Am. Chem. Soc.* 83, 4208 (1961).