

# The effect of the substituents upon the acid-base properties of benzophenone derivatives

O. KYSEL and I. JÁNY

*Polymer Institute, Slovak Academy of Sciences,  
809 34 Bratislava*

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It has been found that the protonation equilibrium constants of 2-hydroxy-5-methylbenzophenone *m*- and *p*-substituted on the phenyl group can be correlated with the  $\sigma^+$  constants according to the equation  $pK_b = -6.18 - 0.96 \sigma^+$ . The correlation between the protonation equilibrium constants of *m*- and *p*-substituted benzophenone and  $\sigma^+$  constants obeys the equation  $pK_b = -6.39 - 1.40 \sigma^+$ .

The difference in the basicity of 2-hydroxy-5-methylbenzophenone derivatives compared to benzophenone and 2-hydroxybenzophenone substituted on the 2-hydroxyphenyl group is explained by a twisted position of the phenyl group as a result of the repulsion of *o*-hydrogen atoms on this and 2-hydroxyphenyl group.

Based on the  $pK_b$  measurements of the different types of aromatic ketones it has been established that an intramolecular hydrogen bond significantly decreases the basicity of the carbonyl group and compensates the resonance effect of the *o*-hydroxyl group. It has been found that, depending on the type of the ketone, the correlation between  $pK_b$  and  $\bar{\nu}(C=O)$  of different types of ketone falls apart to give individual linear branches. The  $\bar{\nu}(C=O)$  values of different types of ketone correlate well with the  $\pi$ -electron bond order of the carbonyl group.

The fact that the protonation constants  $pK_b$  and Brown's  $\sigma^+$  constants of substituted benzaldehydes [1], acetophenones [2], benzophenones [3], and benzoic acid [4] are roughly in a linear relationship shows that a protonated carbonyl group has a nature of a carbonium ion [5]. *Stewart et al.* [6] did not find for protonated benzophenones a linear relationship between  $pK_b$  values of symmetrically *p,p'*-homodisubstituted benzophenones and  $\sigma^+$  constants. On the other hand, *Bonner and Phillips* [3] found a linear relationship between  $pK_b$  of monosubstituted benzophenone derivatives and  $\sigma^+$  constants.

We have previously described [7] the linear relationship between  $pK_b$  and  $\sigma^+$  constants for 4- and 5-substituted 2-hydroxybenzophenone derivatives. Here also the linear relationship between  $pK_b$  and  $\pi$ -electron density on the carbonyl oxygen, calculated by the semiempirical SCF method, has been described.

In the present work we describe the study of the protonation equilibria applied to 2-hydroxy-5-methylbenzophenone derivatives substituted on the benzene ring not bearing the *ortho*-hydroxyl group.

The effect of the intramolecular hydrogen bond upon the basicity of the carbonyl group is also discussed.

## Experimental

Protonation equilibrium constants of 2-hydroxy-5-methylbenzophenones (*I*) and benzophenones (*II*) bearing different substituents in the *m*- and *p*-positions to the carbonyl group were determined by measuring the absorbancy at the wavelength of the absorption maximum of the longest-wavelength band of the protonated form. Water solutions of sulfuric acid were used as the protonation medium. Hammett's acidity function  $H_0$  was taken from [8].

The equilibrium constants were determined graphically using the equation

$$\log \frac{\Delta D}{\Delta D_\infty - \Delta D} = \text{p}K_b - H_0, \quad (1)$$

where  $\Delta D$  is the difference in the absorbancy of the partially protonated and unprotonated ketone and  $\Delta D_\infty$  is the same difference in the case of complete protonation. As a result of the solvation effects the slope of the linear function (*I*) is not always equal to one.

The measurements were done at  $25 \pm 1^\circ\text{C}$  with an MOM 201 instrument.

## Results and discussion

### Basicity of benzophenone derivatives

We have found that the protonation equilibrium constants of the derivatives *I* correlate best with Brown's  $\sigma^+$  constants (Table 1). Using the least-squares method the following equation was found

$$\begin{aligned} \text{p}K_b &= -6.18 - 0.96 \sigma^+; \\ r &= 0.997, s = \pm 0.04, n = 9, \end{aligned} \quad (2)$$

Table 1

Protonation equilibrium constants of the derivatives (*I*)

No.	Substituent	$\text{p}K_b$	$m^a$	$\sigma^+$	$\text{p}K_i^b$
1	H	-6.18	0.88	0.0	10.48
2	<i>m</i> -CH <sub>3</sub>	-6.08	0.92	-0.07	10.55
3	<i>p</i> -CH <sub>3</sub>	-5.88	0.94	-0.31	10.56
4	<i>m</i> -OCH <sub>3</sub>	-6.25	1.03	0.05	10.50
5	<i>p</i> -OCH <sub>3</sub>	-5.43	0.96	-0.78	10.40
6	<i>m</i> -Cl	-6.54	1.26	0.40	10.18
7	<i>p</i> -Cl	-6.30	0.97	0.11	10.27
8	<i>m</i> -NO <sub>2</sub>	-6.90	1.03	0.67	9.92
9	<i>p</i> -NO <sub>2</sub>	-6.88	1.02	0.79	9.87

a) The values of the slopes in the relationship  $\log \frac{\Delta D}{\Delta D_\infty - \Delta D} \approx -H_0$ .

b) The values of the acidity of the 2-hydroxyl group taken from [10].

where  $r$  is the correlation coefficient,  $s$  is the standard deviation, and  $n$  is the number of points. The graphical representation of equation (2) is in Fig. 1. The correlation (2) shows that the protonated forms possess the structure of a carbonium ion, which is in agreement with the experimental data and quantum-chemical calculations of the electron spectra of the protonated forms of benzophenone derivatives [9].

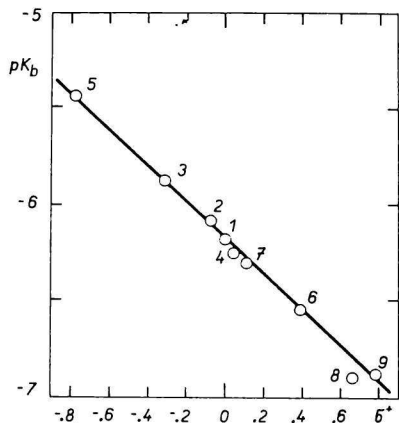


Fig. 1. Relationship between  $pK_b$  and  $\sigma^+$  constants for the derivatives of I. Numbering of points as in Table 1.

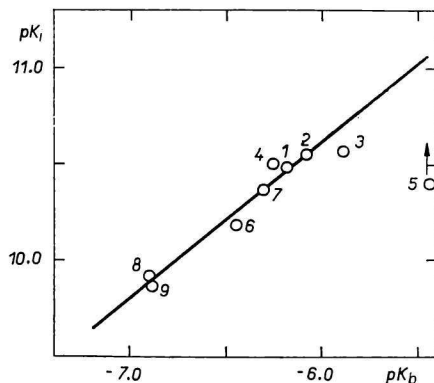


Fig. 2. Relationship between  $pK_I$  and  $pK_b$  of I. Numbering of points as in Table 1.

The protonation equilibrium constants of II are summarized in Table 2. These were again best correlated with  $\sigma^+$  constants giving the relationship

$$pK_b = -6.39 - 1.40 \sigma^+; \quad (3)$$

$$r = 0.954, s = \pm 0.12, n = 8.$$

Table 2

Protonation equilibrium constants of monosubstituted derivatives (II)

No.	Substituent	$pK_b$	$m^c$	$\sigma^{+d}$	$\bar{\nu}(C=O)^e$ [cm <sup>-1</sup> ]
1	H	-6.19	0.99	0.0	1664
2	<i>p</i> -CH <sub>3</sub>	-5.98	0.86	-0.31	1661
3	<i>p</i> -OCH <sub>3</sub>	-5.24	0.88	-0.78	1658
4	<i>p</i> -OH	-5.20	0.84	-0.92	—
5	<i>p</i> -Cl	-6.64 <sup>a</sup>	—	0.11	1666
6	<i>m</i> -Cl	-6.87 <sup>b</sup>	—	0.40	—
7	<i>m</i> -NO <sub>2</sub>	-7.52	0.86	0.67	1671 <sup>f</sup>
8	<i>p</i> -NO <sub>2</sub>	-7.42	0.87	0.79	—

a) Taken from [5]; b) taken from [3] and recalculated to fit the  $H_0$  scale according to [8]; c) slope expressed by the equation (1); d) taken from [14]; e) taken from [15]; f) taken from [16].

From the  $\rho$  values obtained using equations (2) and (3) it follows that the substituents of *I* have a less pronounced effect upon their basicity. The author [7] reports for 2-hydroxybenzophenone derivatives substituted on the 2-hydroxyphenyl ring, (*III*) a  $\rho$  value equal to  $-1.42$ . A smaller effect of the substituents upon the basicity in *I* compared to *II* or *III* may be attributed to the twisting of the phenyl group as a result of the repulsion of the *o*-hydrogen atoms of this and 2-hydroxyphenyl group. This, in turn, causes a less pronounced resonance interaction between the substituted phenyl and carbonyl group and is more pronounced in the case of the derivatives *I* compared to *II* (as a result of the 2-hydroxyphenyl group being coplanar with the plane determined by  $sp^2$  hybridization of the carbonyl carbon atom).

An attempt to correlate  $pK_b$  of the carbonyl group with acidity of the 2-hydroxyl group for 2-hydroxy-5-methylbenzophenone (*I*) is shown in Fig. 2. The point corresponding to the *p'*-methoxy derivative shows a certain deviation from the otherwise satisfactory correlation. This is obviously caused by the fact that while the effect of the *p'*-methoxy group on  $pK_b$  is expressed by a  $\sigma^+$  constant, the absolute value of which is much greater than the corresponding Hammett's  $\sigma$  constant that on  $pK_1$  involves the use of simple Hammett's  $\sigma$  constant\* [10].

*The effect of intramolecular hydrogen bond upon the basicity  
of the carbonyl group*

Table 3 shows the  $pK_b$  values of the protonation for some aromatic ketones with and without an intramolecular hydrogen bond. It has been pointed out [7] that the 2-hydroxyl group in 2-hydroxybenzophenone derivatives, due to the intramolecular hydrogen bond, decreases the basicity of the carbonyl group. On the other hand, the conjugation with the carbonyl group should increase the basicity and these two effects are roughly compensated. It can be seen from Table 3 that the 2-methoxy group, the resonance and induction

Table 3

The effect of the intramolecular hydrogen bond upon the basicity of some aromatic ketones

Ketone	$pK_b$	$\Delta pK_b$
Benzophenone (BP)	-6.19	-0.08
2-Hydroxy (BP)	-6.27 <sup>a</sup>	
4-Nitro (BP)	-7.42	-0.07
2-Hydroxy-4-nitro (BP)	-7.49 <sup>a</sup>	
Acetophenone	-5.94	-0.10
2-Hydroxyacetophenone	-6.04	
Benzaldehyde	-7.10	0.38
Salicylaldehyde	-6.72	
4,4'-Dimethoxy (BP)	-4.47 <sup>b</sup>	
2,4,4'-Trimethoxy (BP)	-3.60 <sup>b</sup>	

a) Taken from [7]; b) taken from [3] and recalculated using the  $H_0$  scale according to [8].

\* A detailed analysis of the effect of the methoxy group upon the  $pK_1$  of the 2-hydroxyl group has shown that it does not depend on  $\sigma$  constant but only on its induction component  $\sigma_I$  [11].

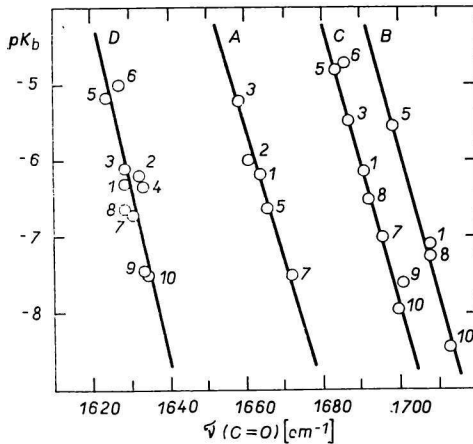


Fig. 3. Correlation between the basicity and  $\bar{\nu}(\text{C}=\text{O})$ .

A:  $\text{p}K_b$  vs.  $\bar{\nu}(\text{C}=\text{O})$  for derivatives of benzophenone.

Numbering of points as in Table 2. B, C, D:  $\text{p}K_b$  vs.  $\bar{\nu}(\text{C}=\text{O})$  of the derivatives of benzaldehyde, acetophenone, and 2-hydroxybenzophenone, respectively. The  $\bar{\nu}(\text{C}=\text{O})$  values for benzaldehyde were taken from [1], for acetophenones from [17], for 2-hydroxybenzophenones from [18,19]. 1. hydrogen; 2. *m*-methyl; 3. *p*-methyl; 4. *m*-methoxy; 5. *p*-methoxy; 6. *p*-hydroxy; 7. *m*-chloro; 8. *p*-chloro; 9. *m*-nitro; 10. *p*-nitro.

effects of which are roughly equal to those of the 2-hydroxyl group, increases the basicity by 0.87  $\text{p}K$  units. It can be seen from the data presented here that the intramolecular hydrogen bond has a considerable effect upon the basicity and, hence, that even in sulfuric acid solutions the intramolecular hydrogen bond in the neutral form of ketone predominates over the intermolecular one with the molecules of the solvent.

#### The $\text{p}K_b$ and $\bar{\nu}(\text{C}=\text{O})$ relationship

The plot of  $\text{p}K_b$  vs.  $\bar{\nu}(\text{C}=\text{O})$  (Fig. 3) for the derivatives of benzaldehyde, acetophenone, benzophenone, and 2-hydroxybenzophenone shows a good correlation only for the derivatives of the ketone of the same type. The occurrence of individual linear branches makes it obvious that  $\bar{\nu}(\text{C}=\text{O})$  values are not suitable for the comparison of the basicity of different types of ketones and can be used, if at all, only for the comparison of the relative basicity of ketones of the same type. It is worth mentioning that the linear branch of 2-hydroxybenzophenone derivatives is markedly shifted from the branch of the derivatives of benzophenone itself. Linear correlations between the stretching vibration frequencies of a certain bond and its  $\pi$ -electron bond orders have been described

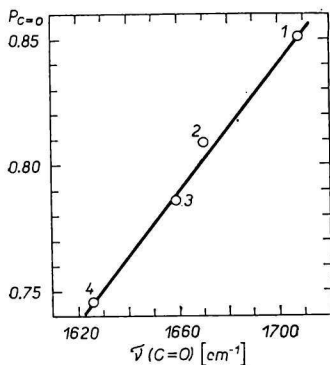


Fig. 4.  $\pi$ -Electron bond order vs.  $\bar{\nu}(\text{C}=\text{O})$ . Numbering of points as in Table 4.

in the literature. The theoretical justification of these correlations was described by Coulson and Longuet-Higgins [12]. As can be seen (Fig. 4, Table 4) there is a linear relationship between  $\bar{\nu}(\text{C}=\text{O})$  and  $\pi$ -electron bond order of  $\text{C}=\text{O}$  of different types of aromatic ketones. Thus, while the bond order determines the relative value of  $\bar{\nu}(\text{C}=\text{O})$

Table 4

The order of  $P(\text{C}=\text{O})$  and  $\bar{\nu}(\text{C}=\text{O})$  for selected types of aromatic ketones<sup>a</sup>

No.	Ketone	$P(\text{C}=\text{O})$	$\bar{\nu}(\text{C}=\text{O})$ [ $\text{cm}^{-1}$ ]
1	Benzaldehyde	0.851	1708
2	Salicylaldehyde	0.809	1670
3	Benzophenone	0.786	1659
4	2-Hydroxybenzophenone	0.746	1626

a) Taken from [13].

of different types of ketones, it cannot be used as a theoretical criterion of their relative basicity. The basicity can, however, be expressed in terms of  $\pi$ -energy of the protonation [20, 21]. For special cases, the effect of the changes in  $\sigma$ -electron systems, such as above-discussed effect of hydrogen bonds, must be also taken into account. Noticeable are also the approximately equal values of the slopes of dependences of  $\text{p}K_{\text{b}}$  upon  $\bar{\nu}(\text{C}=\text{O})$ . The explanation of this phenomenon would, however, require a deeper study.

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