

# Polarographic Reduction of 2-Hydroxybenzophenone Derivatives

N. SCHUBERTOVÁ and P. HRDLOVIČ

*Institute of Polymers, Slovak Academy of Sciences, Bratislava 9*

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In this study the polarographic reduction of ten 2-hydroxybenzophenone derivatives substituted on positions 4 and 5 (*I*), six 2-hydroxy-5-methylbenzophenone derivatives substituted on positions 3' and 4' (*II*), and seven 2-hydroxy-6-methylbenzophenone derivatives substituted on positions 3, 4 and 5 (*III*), has been investigated. This reduction has been investigated in 0.1 M-HCl and 0.1 M-NaOH containing 50 volume % of methanol and in acetate buffer solution containing 40 volume % of methanol.

The half-wave potentials of the derivatives (*I*) and (*II*) have been correlated to  $\sigma$  constants. For each of these two types, the different correlation straight lines were obtained. The steric effect of the methyl group on position 6 of derivatives (*III*) has become effective by the shift of half-wave potential to more negative values.

A considerable attention has been given to the polarographic reduction of benzophenone and its derivatives. Recently, a fundamental article of Zuman, Exner, Rekker and Nauta [1] was published where a critical review of the papers dealing with this topic up to now was presented. The general mechanism for the polarographic reduction of aryl alkyl ketones in various range of pH was suggested by Zuman [2].

In this paper, the polarographic reduction of 2-hydroxybenzophenone derivatives (*I*) substituted on positions 4 and 5, 2-hydroxy-5-methylbenzophenone derivatives (*II*) substituted on positions 3' and 4', and 2-hydroxy-6-methylbenzophenone derivatives substituted on positions 3, 4 and 5 (*III*), has been investigated. The 2-hydroxybenzophenone derivatives are efficient light stabilizers [3] and from this point of view the study of their polarographic behaviour is very useful. At the same time, the number of benzophenone derivatives previously described [1] has extended for several derivatives with constant substituents on positions 2 and 6 and variable substituents on positions 3, 3', 4, 4' and 5. The purpose of this study has been the correlation of half-wave potentials to structure. Considering the general mechanism of aryl alkyl ketones reduction [2], the medium of 0.1 M-HCl and 0.1 M-NaOH has been applied. For comparison of our results to those of Brockman and Pearson [4], the acetate buffer solution has been chosen though a change of reduction mechanism [2] occurs in this medium.

## Experimental

### Compounds

The preparation of derivatives (*I*) has been described in literature [5]. The 2-hydroxy-5-methylbenzophenone derivatives (*II*), prepared by Fries rearrangement of *p*-cresol esters of benzoic acids substituted on *meta* or *para* positions will be described elsewhere. The solvents used were chemical grade and made in Czechoslovakia.

## Equipment

The polarographic curves were recorded by means of the recording polarograph LP 60 (Laboratorní přístroje, Prague). The measurements were carried out by using a Kalousek vessel with a separated, saturated calomel electrode (SCE). The drop-time was 3.7 sec. and the flow-rate 2.1 mg/sec. The pH values of the buffer solutions used were measured by means of the pH-meter PHM-4 (Radiometer, Copenhagen) with a glass electrode G 200 B.

## Procedure

From the 0.005 M stock solution of respective derivative dissolved in methanol, 1 ml was pipetted. Then 5 ml of 0.2 M-HCl or 0.2 M-NaOH were added and made up to 10 ml with methanol. The methanol content was 50 volume %. In the second case, 4.0 ml of acetate buffer solution, 1 ml of 1 M-KCl and 1 ml of 0.2% gelatine were added to 1 ml of 0.005 M stock solution. The methanol content was 40 volume %. The solutions got rid of oxygen by a stream of bubbling nitrogen.

Table 1

Half-wave potentials of 2-hydroxybenzophenone derivatives

No.	R	$\sigma^a$	$-E_{1/2}$	$-E_{1/2}$	$-E_{1/2}$
			0.1 M-HCl [V]	Buffer solution [V]	0.1 M-NaOH [V]
(I)					
1	H	0.00	0.912	1.13	1.50
2	5-COCH <sub>3</sub>	0.31 <sup>b</sup>	0.850	1.052	<sup>d</sup>
3	5-Cl	0.39	0.83	1.046	1.445
4	5-CH <sub>3</sub>	-0.10	0.915	1.12	1.497
5	5-CH(CH <sub>3</sub> ) <sub>2</sub>	(-0.05) <sup>c</sup>	0.908	1.125	1.503
6	5-OCH <sub>3</sub>	0.12	0.884	1.106	1.476
7	4-Cl	0.22	0.872	1.067	1.495
8	4-CH <sub>3</sub>	-0.14	0.940	1.139	1.52
9	4-OCH <sub>3</sub>	-0.26	0.973	1.177	1.566
10	4-OH	-0.33	1.017	1.21	1.695 <sup>e</sup>
(II)					
11	4'-Cl	0.22	0.865	1.062	1.453
12	4'-CH <sub>3</sub>	-0.14	0.932	1.126	1.517
13	4'-OCH <sub>3</sub>	-0.26	0.939	1.163	1.539
14	3'-Cl	0.39	0.842	1.036	1.425
15	3'-CH <sub>3</sub>	-0.10	0.90	1.104	1.496
16	3'-OCH <sub>3</sub>	0.12 <sup>b</sup>	0.918	1.096	- <sup>d</sup>
(III)					
17	4-CH <sub>3</sub>		1.01	1.162	1.646
18	3-CH(CH <sub>3</sub> ) <sub>2</sub>		0.965	1.137	1.644
19	3-C(CH <sub>3</sub> ) <sub>3</sub>		0.963	1.114	1.593
20	3-C <sub>5</sub> H <sub>11</sub>		0.987	1.118	1.568
21	3-CH(CH <sub>3</sub> ) <sub>2</sub> , 5-Br		0.946	1.091	1.592
22	3-C(CH <sub>3</sub> ) <sub>3</sub> , 5CH <sub>3</sub>		0.965	1.128	1.55
23	3-C-H <sub>11</sub> , 5-CH <sub>3</sub>		0.955	1.13	1.569

<sup>a</sup>) Taken from literature [1]; <sup>b</sup>) taken from literature [5]; <sup>c</sup>) an estimated value; <sup>d</sup>) the first wave poorly developed; <sup>e</sup>) value for O<sup>-</sup> = -0.71<sup>b</sup>.

The polarographic curves were registered under these conditions: polarization range 0–2 V, polarization rate 100 mV/min., rate of paper movement 40 mm/min., sensitivity of recorder  $3.6 \times 10^{-10}$  A/mm. The half-wave potentials were determined graphically by means of two recorded curves. The determination accuracy was  $\pm 3-4$  mV, but it decreased to  $\pm 5-10$  mV in case of vague and poorly distinguishable double-waves.

### Results and Discussion

The polarographic potentials of all 2-hydroxybenzophenone derivatives are summarized in Table 1. In order to express the effects of *meta* and *para* substituents on mono- and disubstituted derivatives the validity of equation (1) has been tested

$$\Delta E_{1/2} = \rho \sigma. \quad (1)$$

In case of the derivatives of type (I) the correlation between half-wave potentials of one-electron wave in acid medium and  $\sigma$  constants (Fig. 1, curve A) has been good. The reduction in acid medium runs in two one-electron waves. The first one-electron wave in acid medium arises from the reduction of protonized carbonyl group [2]. Quite a good correlation has also been obtained in acetate buffer solution though a transition of two one-electron waves into one one-electron wave occurs at the involved pH [2]. In acetate buffer solution, the correlation between  $\sigma$  constants and half-wave potential of the two-electron wave has been made. The ionization constants of hydroxyl groups on position 2 exclude the use of buffer solution with pH 9.00 [1]. The part of derivatives with electron-acceptor substituents would be ionized while the part with electron-donor substituents would not [5]. The hydro-

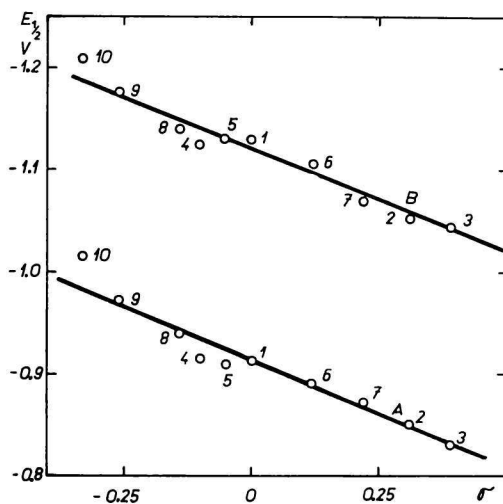


Fig. 1. Dependence of  $E_{1/2}$  on  $\sigma$  for the derivatives (I) in 0.1 M-HCl and in acetate buffer solution.

A. 0.1 M-HCl; correlation constants calculated by the least square method, slope  $\rho = 0.22$  V, correlation coefficient  $r = 0.980$ , standard deviation  $s = \pm 0.011$ .

B. Acetate buffer solution;  $\rho = 0.20$  V,  $r = 0.967$ ,  $s = \pm 0.014$ .

yl group of all derivatives is ionized in alkaline medium of 0.1 M-NaOH. In this case, the reduction of carbonyl group runs in two separated one-electron waves [2]. The first one-electron wave corresponds to the reduction of a free carbonyl group [1, 2]. The correlation in this medium is, however, not good (Fig. 2).

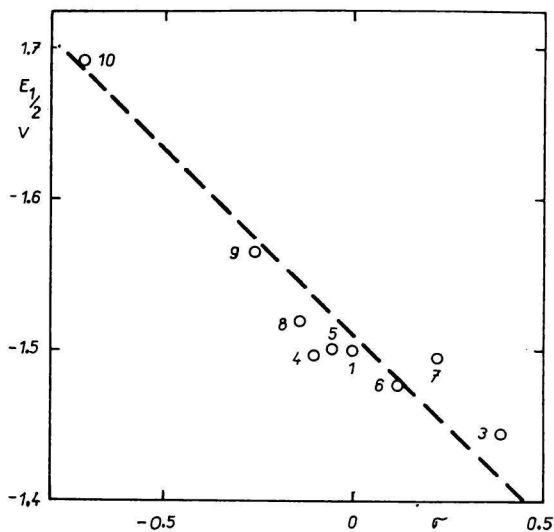


Fig. 2. Dependence of  $E_{1/2}$  on  $\sigma$  for the derivatives (I) in 0.1 M-NaOH.  
 $\varrho = 0.24$  V,  $r = 0.77$ ,  $s = \pm 0.050$ .

With benzophenone derivatives, substituted on both benzene rings, the additivity of their effect on half-wave potentials has been proved [1, 4]. For the derivatives (I) and (II), no consistent correlation has been obtained by adding the substituent effects if 2-hydroxybenzophenone has been taken for the basic compound. A satis-

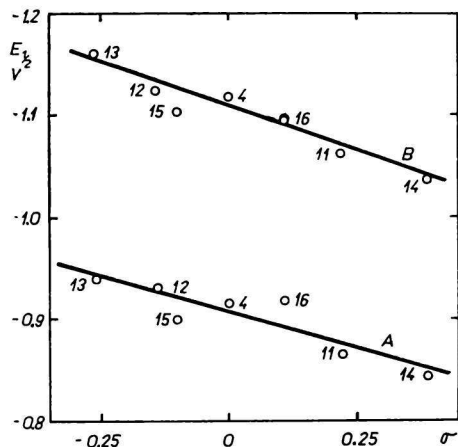


Fig. 3. Dependence of  $E_{1/2}$  on  $\sigma$  for the derivatives (II) in 0.1 M-HCl and in acetate buffer solution.

A. 0.1 M-HCl;  $\varrho = 0.14$  V,  $r = 0.866$ ,  
 $s = \pm 0.036$ .

B. Acetate buffer solution;  $\varrho = 0.17$  V,  
 $r = 0.921$ ,  $s = \pm 0.015$ .

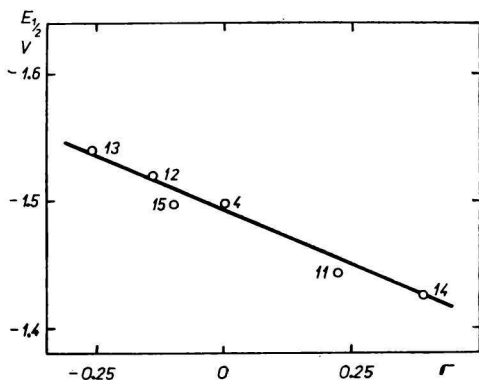


Fig. 4. Dependence of  $E_{1/2}$  on  $\sigma$  for the derivatives (II) in 0.1 M-NaOH.

$$\rho = 0.17 \text{ V}, r = 0.94,$$

$$s = \pm 0.012.$$

factory correlation can be obtained in every medium for the derivatives (II) in case 2-hydroxy-5-methylbenzophenone is taken to be the basic derivative (Figs. 3 and 4).

The ineffectiveness of additivity manifests itself by different slopes of the correlation relationship for benzophenone [1] and derivatives (I) and (II). The correlation slope for benzophenone is in acid medium  $\rho = 0.15 \text{ V}$  and in alkaline medium  $\rho = 0.26 \text{ V}$ . The correlation slopes of derivatives (I) and (II) fluctuate in this range. For instance, the derivatives (I) show  $\rho = 0.22 \text{ V}$  in acid and  $\rho = 0.24 \text{ V}$  in alkaline medium while the corresponding values for derivatives (II) are  $\rho = 0.14 \text{ V}$  and  $\rho = 0.17 \text{ V}$ , respectively. These data demonstrate that the effect of substituents on both benzene rings of the symmetrical benzophenone is equal while this effect is different in case of an asymmetrical 2-hydroxybenzophenone.

The values of half-wave potentials in acid medium ( $E_{1/2} = -0.86 \text{ V}$  for benzophenone,  $E_{1/2} = -0.912 \text{ V}$  for 2-hydroxybenzophenone and  $E_{1/2} = -0.968 \text{ V}$  for 4-hydroxybenzophenone) [1] show that the intramolecular hydrogen bond of these derivatives [5, 8] has no principal influence on their polarographic reduction. An analogous comparison in alkaline medium show that the order of half-wave potentials is the same ( $E_{1/2} = -1.497 \text{ V}$  for benzophenone,  $E_{1/2} = -1.500 \text{ V}$  for 2-hydroxybenzophenone and  $E_{1/2} = -1.735 \text{ V}$  for 4-hydroxybenzophenone) what means that the electronic effect of the ionized and non-ionized hydroxyl group is smaller on position 2 than on position 4.

Because of a small variety, it has not been possible to correlate the half-wave potentials of the derivatives (III) to corresponding  $\sigma$  constants. Nevertheless, these values are of great use for drawing some conclusions. The half-wave potential difference of derivatives 8 and 17 (Table 1) in 0.1 M-HCl is  $\Delta E_{1/2} = -0.07 \text{ V}$  what agrees with the calculation of Pfister and Bonastre [6] who computed the *ortho* effect of methyl group on the carbonyl group reduction. This calculation can not, however, be tested with other derivatives.

The polarographic behaviour of 2-hydroxybenzophenone derivatives is very much alike the behaviour of benzophenone derivatives. The substitution of hydroxyl group on position 2 and of methyl group on position 6 changes the polarographic properties very little in comparison to benzophenone derivatives. On the other hand, this substitution results in a great change in spectral [7, 8] and photochemical [9] properties of these derivatives.

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