

Polarographic reduction of 2-carboxybenzophenone derivatives. I. Reduction of 4'-substituted aroylbenzoic acids

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The polarographic reduction of nine 2-carboxybenzophenone derivatives substituted in position 4' was investigated. The results were correlated with Hammett σ constants in order that the effect of substituent on polarographic behaviour might be established. Thus in contrast to other substituted benzophenones a different character of this reduction was revealed. A scheme of the reduction mechanism was proposed.

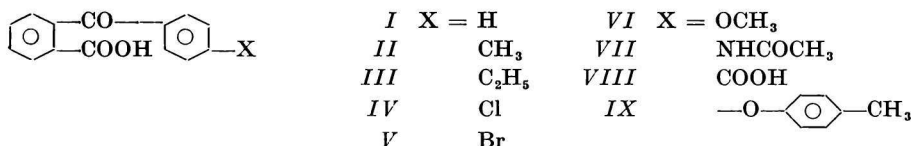
4'-Substituted 2-carboxybenzophenones (*o*-(*p*'-X-aryl)benzoic acids) appear to be prospective as morphoregulators of the white-flower varieties of flax [1]. In view of this fact, an urgent need to determine those substances quantitatively arose. Thus we began with investigating their polarographic behaviour.

There are many studies on esters and anhydrides of 2-benzoylbenzoic acid [2] and their amides available in literature [3]. In relation to these studies the derivatives of β -(*p*-bromobenzoyl)crotonic acid [4] and those of phthalic aldehydes [5] were studied. Bunyan [6] describes an interesting electrooxidation of *o*-benzoylbenzoic acid or its derivatives substituted with chlorine and bromine in *p*'-position which yields methylphenylphthalate. The conclusions of the papers [2–5] are summarized by Kolthoff in his monograph [7].

All these extensive studies are confined to the compilation of half-wave potentials, data on the values of current and transfer coefficient. Except the last two of them [5, 7], they do not present any suggestions concerning reduction schemes. The evaluation of the effect of structure and the description of recombination effects could not be presented at the time of those publications because these quantitative relationships were not known.

Furthermore, the literature lacks any data concerning the polarographic behaviour of subsequent acids though they serve as excellent derivatives in organic analysis for the identification of aromatic hydrocarbons and some substances of aromatic character [8].

From among the substances in Scheme 1 the derivatives *I*–*VII* were prepared by the Underwood modification [9] of Friedel–Crafts reaction which was adapted to semi-microscale. The derivatives *VIII* and *IX* were prepared by the oxidation of *II* with potassium permanganate [11] and by the reaction of *V* with potassium *p*-cresolate, respectively.



Scheme 1

Experimental

Compounds

The purity of preparations was tested by determining the melting point (see Ref. [8–10]) and neutralization equivalent.

4'-X-2-Carboxybenzophenones (I–VII)

Phthalic anhydride (0.01 mole) was mixed with anhydrous aluminium chloride (0.021 mole) and the corresponding excess of aromatic component. (The preparation of VII required an additional admixture of CS₂ whereupon the mixture was heated under reflux until the vapour of HCl disappeared.) After standing for several days under exclusion of air humidity the superfluous aromatic substance was steam distilled (CS₂ was evaporated *in vacuo* at room temperature). The solidified residue was dissolved in hot 10% NaHCO₃. After filtration and acidifying the separated acid was crystallized from the mixture of methyl alcohol with water (1 : 1).

4'-(p-Tolyloxy)-2-carboxybenzophenone (IX)

Potassium salt of *p*-cresol (0.011 mole) was put into a methanolic solution of V (0.01 mole) and the mixture was heated in 80% methanol under reflux for 16 hours. The solution was evaporated *in vacuo*, the residue was dissolved in water, acidified, and the separated product was crystallized from the methyl alcohol–water mixture (1 : 1). M.p. 116.5–118°C.

Apparatus

A polarograph LP 55-A (Laboratorní přístroje, Prague), in connection with a recorder EZ-2 (Laboratorní přístroje, Prague) was used for the polarographic recording of the substances I–III and VII–IX while a polarograph LP-7 with a recorder EZ-7 (Laboratorní přístroje, Prague) was used for the substances IV–VI.

The polarographic analysis was carried out in a Kalousek vessel with a separated saturated calomel electrode (SCE) as a reference electrode. For the height of mercury column of 52 cm the capillary used had the following characteristics: $m = 3.1 \text{ mg Hg s}^{-1}$, $t = 3 \text{ s}$ in saturated solution of KCl at 0.0 V (SCE).

The curves switched over were studied by means of a Kalousek commutator [12] according to the wiring diagram designed by Ševčík and Vacek [13] with $f = 6 \text{ c s}^{-1}$.

The constant potential electrolysis with a controlling system of two polarographs was performed in a Heyrovský vessel according to Zuman [14].

The pH of solutions was measured on a compensation pH meter pHK-1 (Laboratorní

přístroje, Prague) with a high-ohmic glass electrode SEV-2 for the substances *I–VI* and *VIII* and with a deflection instrument OP-205 (Radelkis) for the substances *VII* and *IX*.

The u.v. spectra of products were measured before and after electrolysis on a Spectromom 203 (MOM, Budapest) spectrophotometer.

Dissociation constants

The dissociation constants of the substances *I–IX* were determined with the above-mentioned instrument of Czechoslovak production equipped with a glass electrode OP 717-1/A (Radelkis). The 5×10^{-3} M solutions of acids in absolute methanol were prepared. Before titration 100 ml of a solution of acid was mixed with equal volume of 0.2 M- NaClO_4 . Thus the resulting content of alcohol was 50% and the concentration of sodium perchlorate which kept the ionic strength constant was 0.1 M. The titration was carried out with 0.1 N-KOH in 50% methanol. The found values are given in Table 1.

Table 1

Values of the acid-base polarographic dissociation and recombination constants for the benzophenones *I–IX*

Compound	$\text{p}K_{\text{pot}}$ [mol l ⁻¹]	$\text{p}K'_{\text{pot}}$ [mol l ⁻¹]	k_r [mol ⁻¹ l s ⁻¹]	k_d [s ⁻¹]
<i>I</i>	4.68	8.1	1.4×10^{11}	1.9×10^6
<i>II</i>	4.84	8.0	5.8×10^{10}	8.1×10^5
<i>III</i>	4.83	8.1	9.8×10^{10}	1.4×10^6
<i>IV</i>	4.39	8.4	4.4×10^{11}	1.8×10^7
<i>V</i>	4.29	8.4	5.4×10^{11}	2.7×10^7
<i>VI</i>	5.00	8.1	6.7×10^{10}	6.7×10^6
<i>VII</i>	4.74	8.3	3.0×10^{11}	2.4×10^6
<i>VIII</i>	3.72	6.3	3.2×10^3	6.1×10^4
	4.44	8.2	3.8×10^{11}	1.3×10^7
<i>IX</i>	5.12	8.1	5.1×10^{10}	3.9×10^5

Polarographic reduction

Absolute methyl alcohol was used as a solvent for the preparation of 5×10^{-4} M stock solutions of the substances *I–IX*. For a polarographic record the stock solution was mixed with equal volume of a buffer solution in which the ionic strength was kept constant at the value of 0.15. After bubbling through nitrogen the polarographic recording was done.

Results

In strongly acid medium the substances *I–IX* give a reversible wave of diffusion character which is followed by a small reduction wave corresponding to the product of the deactivation of radical. This wave is most marked in the case of benzophenones *I–III* and *VIII*. By logarithmic analysis it was found that the number of electrons exchanged was equal to 0.95. A comparison between the waves of benzophenone and benzoin corroborates the exchange of one electron. Dimerization of the product of one-

-electron reduction was proved by the shift of the half-wave potential with decreasing concentration to more positive values. In order to confirm that the dimerization really took place, the constant potential electrolysis of substance *IV* was performed. It followed from the u.v. spectra of substances taken before and after reduction in 5 N-H₂SO₄ and 0.05 N-H₂SO₄ that the products were different. This conclusion was definitely confirmed by paper chromatography of the products in five solvent systems. In strongly acid medium it could be seen that the carbonyl wave was preceded by a wave which grew evidently with increasing concentration of depolarizer. The adsorption character of this wave was demonstrated by the concentration dependence limited by 4×10^{-3} M concentration as well as by the dependence on temperature; the wave practically disappeared at about 60°C.

With decreasing acidity the wave of carbonyl gradually grew and already at about pH 0.5 a deviation from the reduction of other benzophenones described in literature [15, 16] appeared. The wave attained the height corresponding to two-electron transfer, but it was not possible to observe two separated one-electron waves.

The study of the curves switched over by means of the wiring I, where the drop was connected by turns to a measuring potentiometer and to a reference potentiometer (here the constant voltage was tapped off) showed the reversible character of waves. The half-wave potential was almost independent of pH up to the value of p*K* determined potentiometrically.

In neutral region the acids *I*–*IX* give a wave of anticlinical character i_{pcs} which falls and has a shape of dissociation curve of the weak electrolyte. In slightly alkaline region another wave i_{neg} corresponding to the reduction of conjugated base appears on this wave. The wave i_{neg} increases with the alkalinity of solution while the sum of both the waves remains constant.

The dependence of the height of wave on the square root of the height of reservoir indicates that the wave i_{pcs} is of kinetic character. Consequently, with the increasing

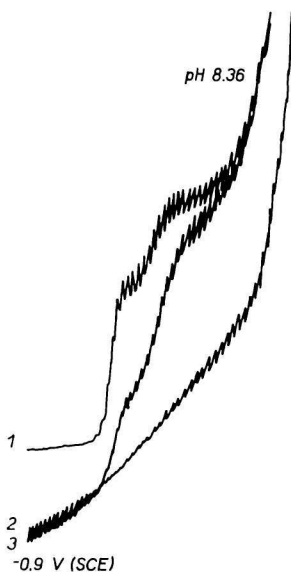


Fig. 1. Investigation of the reduction of the compound *V* by means of a Kalousek commutator. 1. normal curve; 2. commutated curve, voltage tapped off -1.3 V (SCE); 3. commutated curve of supporting electrolyte, voltage tapped off -1.3 V (SCE). 2.5×10^{-4} M 4'-bromo-2-carboxybenzophenone (*V*), pH 8.36, sensitivity 1/50, curves recorded from -0.9 V (SCE).

height of the wave i_{neg} its diffusion character becomes more and more evident. Both these facts are confirmed by the temperature dependence which shows that in neutral region the current of both waves increases exponentially while in slightly alkaline region only the wave i_{pos} increases exponentially in contrast to the height of the wave i_{neg} which changes only insignificantly with temperature.

Provided the concentration of substance *VIII* exceeds $6 \times 10^{-4} \text{ mol l}^{-1}$ a splitting of the wave i_{pos} may be observed in neutral or weakly alkaline region. $E_{1/2}$ of all substances *I*–*IX* shifts with pH to more negative values by 100 mV per unit of pH up to the value of $\text{p}K'$. The wave i_{neg} or more exactly its $E_{1/2}$ is nearly independent of pH.

Fig. 1 demonstrates that the waves in this region are of irreversible character.

On the basis of decreasing wave i_{pos} and increasing wave i_{neg} the apparent polarographic dissociation constant $\text{p}K'$ given in Table 1 was found. From these values and the values of $\text{p}K$ determined potentiometrically the rate constants of recombination

Table 2

Correlation of $E_{1/2}$ with the Hammett constants σ_{p-x} at pH 9.70 and in 0.1 N-NaOH

Compound		$E_{1/2}$ [V] (SCE)	
		pH 9.70	0.1 N-NaOH
<i>I</i>	0	–1.43 ₅	–1.48 ₀
<i>II</i>	–0.17	–1.48 ₀	–1.52 ₅
<i>III</i>	–0.15	–1.49 ₀	–1.52 ₀
<i>IV</i>	+0.23	–1.36 ₀	–1.43 ₀
<i>V</i>	+0.23	–1.35 ₀	–1.43 ₀
<i>VI</i>	–0.27	–1.53 ₀	–1.56 ₅
<i>VII</i>	–0.01	–1.45 ₀	–1.49 ₀
<i>VIII</i>	+0.13	–1.37 ₅	–1.44 ₀
<i>IX</i>	–0.33	—	–1.56 ₀

(k_r) and subsequently the rate constants of dissociation (k_d) were calculated according to literature [17, 18]. These values are also included in Table 1.

At pH > 9.5 the irreversible wave of substances *I*–*IX* slightly decreases, but even in a 0.1 N-NaOH it does not decrease to the height which would correspond to the transfer of one electron. In this region the half-wave potential does not almost change with

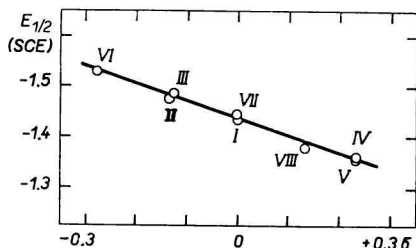


Fig. 2. Correlation of half-wave potentials with Hammett constants at pH 9.70.

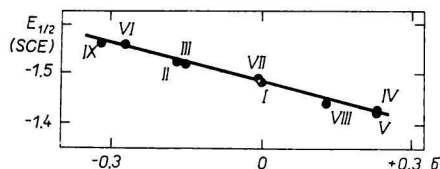


Fig. 3. Correlation of half-wave potentials with Hammett constants in 0.1 N-NaOH.

pH any more. The adsorption wave which appears in acid medium is not more observable even at highest sensitivities.

For a medium of pH 9.70 as well as 0.1 N-NaOH the correlation between the half-wave potentials and the Hammett constants was carried out according to the equation

$$\Delta E_{1/2} = \rho_{\pi R} \sigma_{p-x}.$$

Table 2 and Figs. 2 and 3 illustrate this procedure.

Discussion

With regard to the carboxyl content the polarographic behaviour of 4'-substituted 2-carboxybenzophenones (*I-IX*) differs from that of other benzophenones reducible according to the general reduction scheme [19]. Moreover, in neutral and weakly alkaline region the electrode process is controlled by a preceding chemical reaction — recombination of a proton with the anion of acid.

The compounds *I-IX* are reduced in one two-electron wave except for the strongly acid region. The fact that it is not possible to record two separated one-electron waves as in the case of other benzophenones [15] must be so explained that the potential corresponding to the reduction of $R-\dot{C}(OH)-R$ radical is at least equal or even more positive than the potential corresponding to the reduction of the protonized form $R-\overset{+}{C}(OH)-R$, i.e. $E_1 \leq E_2$. Thus it may be stated that the acceptance of the second electron proceeds immediately as a consecutive process (*B*) (see later) and limits the height of wave in this region.

In neutral region the wave of substance *VIII* present in 6×10^{-4} M concentration (i_{neg}) splits because the second carboxyl ($pK' \doteq 8.2$) also undergoes a dissociation. By raising the temperature this splitting may appear already at 2.5×10^{-4} M concentration.

From the values given in Table 1 it follows that some recombination effects occur. But in view of the values of k_r , the homogeneous recombination effects may be excluded for the substances *I-VIII*, for the second step dissociation of the substance *VIII*, and for the benzophenone *IX*.

The correlation of the data obtained for the substances *I-IX* with the Hammett constants may be carried out either in a sufficiently acid medium where the free acid is present or for $pH > 9.5$ when the substances *I-IX* exist in the form of anions and as such are reduced. The free acid is an electroactive form because it is produced, as stated before, by recombination in the neighbourhood of the electrode.

In 0.1 N-HCl, for which the correlations in acidic medium are most frequently performed, a change in the reduction mechanism takes place. The correlations of the half-wave potentials with the Hammett constants postulate that the reductions (or oxidations) should proceed according to equal mechanism. In the case of the benzophenones *I-IX* this supposition is not fulfilled and for this reason the correlations cannot be done for 0.1 N-HCl.

As obvious from Fig. 2, the correlation relationship is good. The reaction constant $\rho_{\pi} = +0.35$ V is a little higher than the value found by Zuman *et al.* ($\rho_{\pi} = +0.25$ V) [15] who correlated the data obtained with other benzophenones dissolved in borate buffer solutions of pH 9.3. The increase in the value of ρ_{π} by 100 mV is most likely due to the relative proximity of carboxyl and reaction centre. Notwithstanding, the signs of the constants are equal as it may be expected for a nucleophile attack by electron.

For 0.1 N-NaOH the correlations are very good and some slight deviations are within the range of experimental errors. According to *Brown* and *Okamoto* [20] the value $\sigma_{p-x} = -0.33$ is to be used for the substance *IX* which has the largest substituent in position 4'. This substance showed a deviation if the value $\sigma_{p-x} = -0.03$ was used. The situation is somewhat different at pH 9.70. In this case neither the value of -0.33 according to [20] nor the value of -0.03 according to *Jaffe* [21] could be used. A deviation from linear relationship occurred for the substance *IX*. It is probable that a relative proximity of the relatively voluminous tolyloxy group in position 4' may cause a change in steric energy which is then responsible for the shift of half-wave potential.

The reaction constant $q_\pi = +0.31$ V observed in 0.1 N-NaOH is again little different from that stated by *Zuman et al.* [15]. The difference of 50 mV could be explained in the above-mentioned way. However, the very close values of the constants found for pH 9.70 ($q_\pi = +0.35$ V) and for 0.1 N-NaOH ($q_\pi = +0.31$ V) evidence an identical process while the approximate value of q_π found for 0.1 N-HCl (though it is quite inadmissible for the above reasons) corroborates the difference between the electrode processes in those media. After all, that is obvious from the results of this study and the scheme which follows.

A more detailed analysis of Figs. 2 and 3 will contribute to the confirmation of the identity of the reaction mechanism at pH 9.70 and in 0.1 N-NaOH. It is obvious from both these figures that the deviations of the points from the straight line are of equal sign, only in the case of derivative *III* the deviation is a little more negative for pH 9.70.

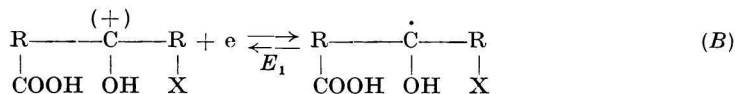
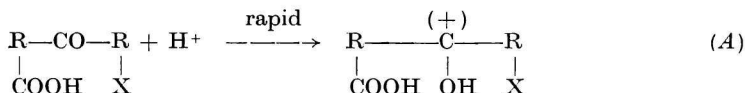
The correlation of the recombination constants k_r with the Hammett constants is good though this kind of correlation is not usual [22]. Only in the case of the compounds *IV* and *V* some deviations appear. But these deviations are within the range of errors accompanying the determination of the dissociation constants pK and pK' .

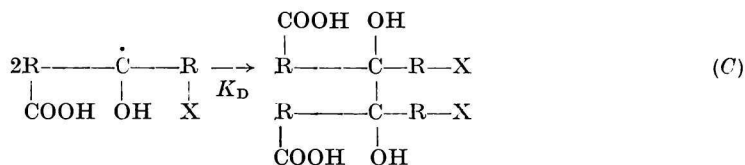
An analogous picture appears if the values of pK found potentiometrically are correlated with the values of σ_{p-x} .

On the basis of the Hammett equation it is possible to estimate the range of potentials in which the half-wave potentials of various non-studied 4'-substituted 2-carboxybenzophenones may be expected. The calculation is carried out using the product of limiting values $\sigma_{p-\max}$ (-1.05 for $\sigma_{p-N(CH_3)_2}$ and $+1.27$ for σ_{p-NO_2}) and reaction constant. To the values thus obtained the value of the half-wave potential of the unsubstituted substance *I* is added. In this way it is possible to determine the limiting potentials which may be attained in this series (assuming that the reduction mechanism does not change). Thus it has been found that the potential can vary from -1.08_0 to -1.80_5 V in 0.1 N-NaOH and from -0.99_0 to -1.80_0 V (SCE) in solutions of pH 9.70.

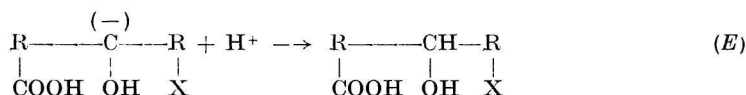
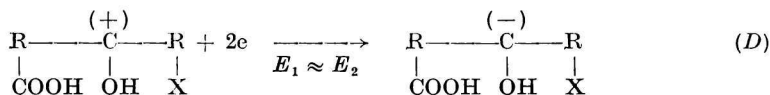
On the basis of all the above-mentioned facts a reduction pathway of 4'-substituted 2-carboxybenzophenones may be proposed.

In acid medium:

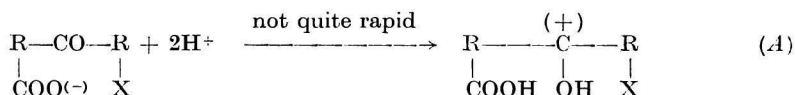




In weakly acid medium the protonation according to (A) is succeeded by the following processes:

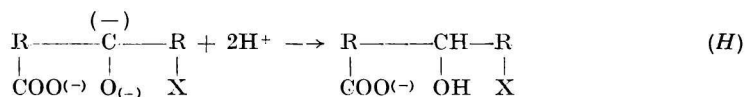
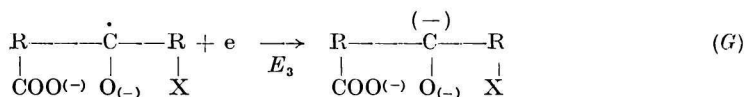
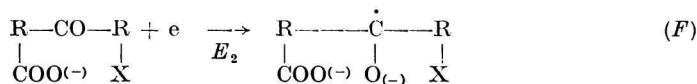


In neutral medium:



and subsequently the reactions proceed according to (D) and (E).

In alkaline medium:



This reaction scheme shows that there are four reduction mechanisms occurring in strongly acid, acid, neutral, and alkaline medium, respectively.

In strongly acid region the substance with a sextet on a carbon atom is reduced by one electron under formation of a radical that undergoes a dimerization (constant K_D) which agrees with the experimental results and the general reduction scheme [19].

In weakly acidic and neutral region the sequence of the reactions (A), (D), (E) is identical, the only difference consisting in the fact that in neutral and weakly alkaline region the electrode process is controlled by a preceding chemical reaction — recombination of proton with anion. For this reason the protonation reaction (A) is the slowest process which limits the height of polarographic wave.

In alkaline region the protonation reaction is so slow that the carbonyl cannot get protonized. Therefore the non-protonized CO group undergoes reduction according to the equation (F). The potential E_3 may be so negative that the process (G) is hidden by the wave of supporting electrolyte. At the same time the process (G) competes against the reaction with alkaline ions the potential E_4 of which is close to the potential E_2 , as assumed by Zuman for other benzophenones described in literature [15]. That is why the height of wave in 0.1 N-NaOH is somewhat smaller than it should be for the acceptance of two electrons.

With respect to this explanation it might be surprising that the half-wave potentials in alkaline region gave a linear $E_{1/2} \sim \sigma_{p-x}$ diagram. It must be taken into consideration, however, that not only the rate of the electrode process itself but also the transfer coefficient and the rate of the reaction of radical ion with alkaline ions in alkaline medium, depend on the structure in an analogous way.

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