Polarographic reduction of 2-carboxybenzophenone derivatives. II. Reduction of esters of 2-benzoylbenzoic acid

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The polarographic reduction of 46 esters of 2-carboxybenzophenone substituted in position 4′ was investigated. The results were correlated with Hammett σ constants in order that the effect of 4′-substituent on polarographic behaviour might be established. The polarographic properties of the compounds investigated are similar to those of other substituted benzophenones described in literature. A slight difference appears only in half-wave potentials, values of current, and transfer coefficient.

The investigation of polarographic reduction of the 2-carboxybenzophenone derivatives began with the study of nine 4′-substituded 2-carboxybenzophenones [1], for which a little different course of reduction was found when compared to benzophenone, went on and was concerned with the reduction of the esters of 4′-substituted 2-carboxybenzophenones.

The reduction of these compounds has been described only in few papers [2, 3] restricted to a compilation of half-wave potentials and numbers of electrons exchanged. Neither information on reduction scheme nor evaluation of the effect of structure on polarographic behaviour is available in literature.

The aim of this study was to examine the reducibility of 46 esters of 4′-substituted 2-carboxybenzophenones, to look into the mechanism, and to correlate the polarographic behaviour of these derivatives especially when considerable structural changes occur.

The polarographic study was performed with methyl, ethyl, propyl, *n*-butyl, and *n*-amyl esters of the compounds given in [1]. In addition, the esters of 4′-ethoxy-2-carboxybenzophenone were investigated; their behaviour was the same as that of the compounds mentioned in paper [1].

Experimental

Apparatus

The polarographic recording was performed with an LP-7 polarograph in connection with an EZ-7 recorder (Laboratorní přístroje, Prague). The polarographic analysis was carried out in a Kalousek vessel with a separated saturated calomel electrode (SCE) as a reference electrode. The capillary used had the following characteristics: $m = 3.1$ mg Hg s^{-1}, $t = 3$ s in saturated KCl solution at 0.0 V (SCE) for $h = 52$ cm.

The curves switched over were studied by means of a Kalousek commutator [4, 5] designed by *Ševčik* and *Vacek* [6] ($f = 6$ c s^{-1}).

The pH of solutions was measured on an OP-205 instrument (Radelkis) with a glass electrode OP 717−1/A (Radelkis).

Table 1

Half-wave potentials of the esters of substituted o-benzoylbenzoic acid

Compound	R	X	$E_{1/2}$ (SCE) 0.1 N-HCl	$E_{1/2}$ (SCE) pH 9.3	$E_{1/2}$ (SCE) 0.1 N-NaOH
I	CH_3	H	-0.86_5	-1.43_0	1.50_5
II		CH_3	-0.88_5	-1.46_5	-1.55_0
III		C_2H_5	-0.88_5	-1.46_5	-1.54_5
IV		Cl	-0.83_5	-1.38_0	-1.44_5
V		Br	-0.83_5	-1.37_5	-1.44_5
VI		OCH_3	-0.89_5	-1.49_5	-1.57_5
VII		$NHCOCH_3$	-0.86_5	-1.43_0	-1.51_0
VIII		$OC_6H_4CH_3$	-0.90_5	-1.50_5	-1.59_0
IX		OC_2H_5	-0.89_5	-1.49_0	-1.57_0
X	C_2H_5	H	-0.86_0	-1.43_0	-1.50_0
XI		CH_3	-0.88_5	-1.47_0	-1.54_5
XII		C_2H_5	-0.88_0	-1.46_5	-1.54_0
XIII		Cl	-0.83_0	-1.37_5	-1.44_0
XIV		Br	-0.83_0	-1.37_5	-1.44_0
XV		OCH_3	-0.89_5	-1.49_5	-1.57_5
XVI		$NHCOCH_3$	-0.86_0	-1.43_0	-1.50_0
XVII		$COOC_2H_5$	-0.80_0	-1.32_5	-1.38_0
XVIII		$OC_6H_4CH_3$	-0.90_5	-1.50_5	-1.59_0
XIX		OC_2H_5	-0.89_5	-1.49_0	-1.56_5
XX	C_3H_7	H	-0.85_0	-1.42_0	-1.49_5
XXI		CH_3	-0.87_5	-1.46_5	-1.54_0
XXII		C_2H_5	-0.87_0	-1.46_0	-1.53_5
XXIII		Cl	-0.82_0	-1.36_0	-1.43_5
XXIV		Br	-0.82_0	-1.36_0	-1.43_5
XXV		OCH_3	-0.88_5	-1.48_5	-1.56_5
XXVI		$NHCOCH_3$	-0.85_0	-1.42_0	-1.49_5
XXVII		$OC_6H_4CH_3$	-0.89_5	-1.50_0	-1.58_0
XXVIII		OC_2H_5	-0.88_5	-1.48_5	-1.56_0
XXIX	C_4H_9	H	-0.84_5	-1.41_5	-1.49_5
XXX		CH_3	-0.87_0	-1.45_5	-1.54_0
XXXI		C_2H_5	-0.86_5	-1.45_0	-1.53_5
XXXII		Cl	-0.81_5	-1.36_0	-1.43_5
XXXIII		Br	-0.81_5	-1.36_0	-1.43_5
XXXIV		OCH_3	-0.88_0	-1.48_0	-1.56_5
XXXV		$NHCOCH_3$	-0.84_5	-1.41_5	-1.49_5
XXXVI		$OC_6H_4CH_3$	-0.89_0	-1.49_5	-1.58_0
XXXVII		OC_2H_5	-0.88_0	-1.47_5	-1.56_0
XXXVIII	C_5H_{11}	H	-0.83_0	-1.41_0	-1.48_0
XXXIX		CH_3	-0.85_0	-1.45_5	-1.53_0
XL		C_2H_5	-0.85_0	-1.45_0	-1.52_5
XLI		Cl	-0.80_0	-1.35_0	-1.42_5
XLII		Br	-0.80_0	-1.35_0	-1.42_5
XLIII		OCH_3	-0.86_5	-1.48_0	-1.55_5
XLIV		$NHCOCH_3$	-0.83_0	-1.41_0	-1.48_5
XLV		$OC_6H_4CH_3$	-0.87_5	-1.49_0	-1.57_0
XLVI		OC_2H_5	-0.86_5	-1.47_5	-1.55_0

Substances

The esters were prepared from p'-substituted o-aroylbenzoic acid by the modified *Underwood* method [7] described earlier [1]. p'-Ethoxy-o-benzoylbenzoic acid prepared by the method mentioned in [1, 7] was used as a starting derivative.

The esters of 4'-substituted 2-carboxybenzophenones (I-$XLVI$) were prepared by mixing the solutions containing 100 mg of corresponding acid in 10 ml of methyl, ethyl, propyl, n-butyl, or n-amyl alcohol. The alcohols were saturated for one hour with dry hydrogen chloride beforehand. After 24 hours alcohol was distilled off *in vacuo*. The purity of preparations was checked by means of melting points and chromatographically [8].

Reduction

A 4×10^{-4} M stock solution of individual esters in absolute methyl alcohol was mixed with equal volume of 2 N-H_2SO_4, 0.2 N-HCl, 0.2 N-NaOH or Britton—Robinson buffer solution in which the ionic strength was kept constant (0.15). After bubbling through with nitrogen the polarographic record was made at the rate of 400 mV/min., chart speed 40 mm/min., and 100 mV/absc.

Results and discussion

The polarographic investigations were done with the compounds of the type
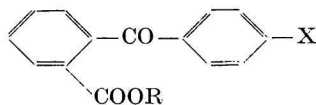
where R $= CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9, n-C_5H_{11};
X $=$ H, CH_3, C_2H_5, Cl, Br, OCH_3, $NHCOCH_3$, COOR, $OC_6H_4CH_3$, OC_2H_5.

Table 1 presents the measured half-wave potentials of these substances.

All the compounds (I—$XLVI$) listed in Table 1 are reduced in acid medium in one--electron wave of reversible character according to the general reduction scheme stated for aryl alkyl ketones by *Zuman et al.* [9, 10].

Owing to the decrease in acidity another wave appears. Its half-wave potential is pH independent so that a further decrease in acidity results in the coalescence of two one-electron waves into a single two-electron wave. In contrast to experiments described in [1], no recombination effects can appear because the substances are esters.

In slightly alkaline and alkaline region the two-electron wave decreases moderately but even in 0.1 N-NaOH it does not attain the height corresponding to the transfer of one electron which is in conformity with the literature data [1, 2, 9—12].

In order to express the effect of substituent in position 4' on the polarographic behaviour of the series of keto esters the validity of Hammett equation

$$\Delta E_{1/2} = \varrho_{\pi R} \quad \sigma_{p-x} \qquad (1)$$

was examined. In Figs. 1—3 the measured values of half-wave potentials are correlated with Hammett σ_{p-x} constants.

As obvious from all figures, the correlations are very good. Similarly as in the preceding paper [1] it was necessary to use the value of -0.33 according to *Brown* and *Okamotto* [13] for the constant $\sigma_{p-OC_6H_4CH_3}$. If the value according to *Jaffe* [14] $\sigma_{p-OC_6H_4CH_3} =$
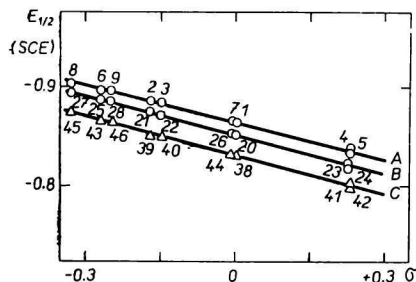
Fig. 1. Dependence of $E_{1/2}$ on σ_{p-x} in 0.1 N-HCl.

A. methyl esters; B. propyl esters; C. n-amyl esters.

The numerals denoting the points on the curves A, B, C are equal to the Roman numerals in Table 1.

$= -0.03$ was used, the esters investigated showed a deviation from the linear relationship. Since we did not succeed in fixing the values of σ_{p-x} for the groups $-COOCH_3$, $-COOC_3H_7$, $-COOC_4H_9$, $-COOC_5H_{11}$, the derivatives with these groups in 4'-position were not evaluated.

The reaction constants for 0.1 N-HCl ($\sigma_{\pi R} = +0.14$ V), for pH 9.30 ($\varrho_{\pi R} = +0.25$ V) and for 0.1 N-NaOH ($\varrho_{\pi R} = +0.26$ V) are also in agreement with the data given for substituted benzophenones [11, 12].
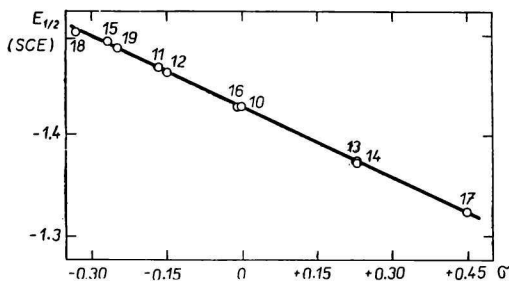

Fig. 2. Dependence of $E_{1/2}$ on σ_{p-x} at pH 9.3 for 4'-substituted ethyl esters of 2-carboxybenzophenone.

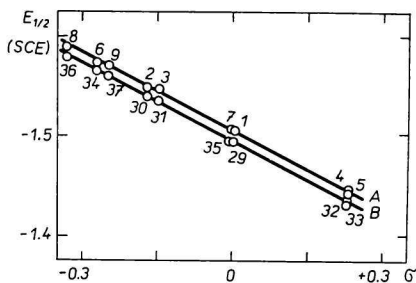The numerals denoting the points on the curve are equal to the Roman numerals in Table 1.

Fig. 3. Dependence of $E_{1/2}$ on σ_{p-x} in 0.1 N-NaOH.

A. methyl esters; B. n-butyl esters.

The numerals denoting the points on the curves A, B are equal to the Roman numerals in Table 1.

As stated above [9—12] an interaction of the radical ion with Na+ ion takes place in 0.1 N-NaOH. This interaction affects the wave height depending on substituent. Therefore the linearity of the relationship $E_{1/2} \sim \sigma_{p-x}$ might be surprising. But we have to realize, that not only the half-wave potential but also the rate of electrode process, the transfer coefficient, and the reaction rate of radical ion with alkaline ions in alkaline media depend on the structure in a similar way [12].

All the above-mentioned facts give evidence of the similarity with the reduction processes involving substituted benzophenones which have been described in literature. Therefore the general reduction scheme [9, 10] is certainly in force for all 46 substituted esters of 2-carboxybenzophenone which corroborates its accuracy and applicability for the substituted aryl alkyl ketones.

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