

# Polarographic reduction of 2-carboxybenzophenone derivatives. IV. Reduction of *p*'-substituted *p*-nitro-*o*-aroylbenzoic acids

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The polarographic reduction of seven 2-carboxy-4-nitrobenzophenones substituted in position 4' was investigated. Correlation of the results obtained with Hammett constants showed both the similarity and the difference in the reduction of the derivatives without nitro group.

The study of polarographic reduction of the 2-carboxybenzophenone derivatives substituted in position 4' [1] followed by the study of their esters [2] and oximes [3] stimulated us to investigate those derivatives which contained a nitro group.

The aim of this study was to investigate the behaviour of a series of seven 4'-substituted 2-carboxy-4-nitrobenzophenones and confront the results obtained with those published earlier [1].

## Experimental

### *Apparatus*

The polarographic records including the recording of the commutated curves and pH measurements were carried out on the apparatus described earlier [2], the only difference being in the drop-time (2.95 s).

### *Substances*

The preparation of the substances under study was described elsewhere [1], 4-nitro-phthalic anhydride being employed instead of phthalic anhydride.

### *Determination of dissociation constants*

The dissociation constants of substances I—VII were determined as in [3].

### *Reduction*

The same operations as described previously [3] were performed with a  $4 \times 10^{-4}$  M stock solution of the corresponding keto acid. The values obtained are listed in Table I.

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Table 1

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

Compound	$pK_{pot}$ [mol l <sup>-1</sup> ]	$pK'_{pot}$ [mol l <sup>-1</sup> ]	$k_r$ [mol <sup>-1</sup> l s <sup>-1</sup> ]	$k_d$ [s <sup>-1</sup> ]
<i>I</i>	4.30	7.5	$1.34 \times 10^9$	$6.70 \times 10^4$
<i>II</i>	4.37	7.6	$1.73 \times 10^9$	$7.09 \times 10^4$
<i>III</i>	4.38	7.6	$1.75 \times 10^9$	$7.35 \times 10^4$
<i>IV</i>	4.00	7.2	$6.60 \times 10^8$	$6.60 \times 10^3$
<i>V</i>	4.00	7.2	$6.60 \times 10^8$	$6.60 \times 10^3$
<i>VI</i>	4.51	7.7	$2.05 \times 10^9$	$6.35 \times 10^4$
<i>VII</i>	4.50	7.7	$2.11 \times 10^9$	$6.75 \times 10^4$

### Results and discussion

2-Carboxy-4-nitrobenzophenone *I*, 2-carboxy-4-nitro-4'-methylbenzophenone *II*, 2-carboxy-4-nitro-4'-ethylbenzophenone *III*, 2-carboxy-4-nitro-4'-chlorobenzophenone *IV*, 2-carboxy-4-nitro-4'-bromobenzophenone *V*, 2-carboxy-4-nitro-4'-methoxybenzophenone *VI*, and 2-carboxy-4-nitro-4'-ethoxybenzophenone *VII* were studied polarographically.

Benzophenones *I*–*VII* give in acid medium a four-electron diffusion wave of reversible character. This wave of nitro group reduction is succeeded by a small adsorption wave the height of which is limited by  $5 \times 10^{-3}$  M concentration in the medium used. Immediately after this wave there appears a two-electron reversible diffusion wave corresponding to the reduction of carbonyl group. The presence of  $-\text{NO}_2$  group in the molecule is not able to shift the potentials  $E_1$  and  $E_2$  with respect to each other so that it is not possible to record 2 separated one-electron waves of the carbonyl group as described in literature [4, 5]. That is the first similarity with the derivatives without nitro group [1].

In neutral and slightly alkaline media the four-electron reduction to hydroxylamine is succeeded by the wave of the carbonyl group  $i_{pos}$  decreasing in the form of a dissociation curve of a weak electrolyte. Then the wave  $i_{neg}$  corresponding to the reduction of conjugated base appears while the sum of both the waves remains approximately constant. The dependence of the wave height on the square root of the reservoir height as well as the temperature dependence of the wave height indicates that the wave  $i_{pos}$  is of kinetic character. Therefore some recombination processes take place in this region. Regarding the calculated rate constants [6, 7] the recombination is assumed to be homogeneous. The half-wave potential and its pH dependence (Fig. 1) do not practically change from the break in the point corresponding to the apparent dissociation constant which is in good agreement with literature [1, 8].

In alkaline medium the reduction to hydroxylamine is a four-electron process while the reduction of carbonyl to alcohol consumes a little more than two electrons. The reason for this fact was given in preceding publications [1, 2, 4, 5].

The correlation of  $E_{1/2}$  with the Hammett constants for 0.1 N-NaOH was performed according to equation

$$E_{1/2} = \rho_{NR} \cdot \sigma_{p-x} \quad (1)$$

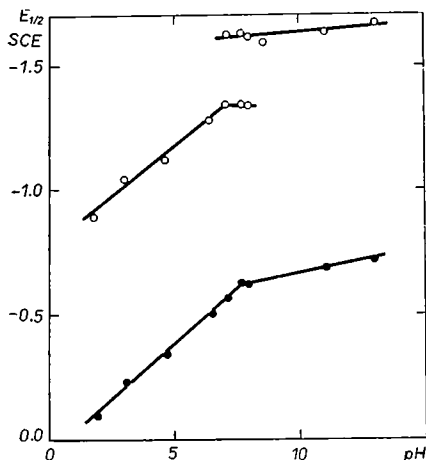


Fig. 1. Dependence of  $E_{1/2}$  on pH for benzophenone I.

Full circles correspond to the reduction of nitro group.

As obvious from Fig. 2, the correlation is good. The value of  $q_{\pi R}$  (+0.28 V) is somewhat smaller than it is in the case of the derivatives without nitro groups [1] but it is in good agreement with the data in literature [9].

The presence of nitro groups resulted in a decrease of the acid-base constants of acids I–VII (Table 1) in comparison with the values presented in paper [1] but simultaneously the apparent polarographic dissociation constants increased so that in contrast to the results given in [1] the recombinations took place in the volume phase. Nevertheless, the reducibility of the carbonyl group decreased when compared with the results of foregoing investigations [1].

Correlations of the rate constants of recombination obtained with the Hammett constants according to eqn (1) are very good (Fig. 3). Similarly, the rate constants of dissociation and the correlations  $pK_{pot} \sim \sigma_{p-x}$  and  $pK_{pol} \sim \sigma_{p-x}$  ( $q_{\pi R} = -0.86$  and  $q_{\pi R} = -0.83$  V) are in good agreement with the literature data [1].

In conclusion, it may be pointed out that the range of potentials, where the half-wave potentials non studied derivatives of the above-mentioned type could be expected, was determined. The calculation was performed by using the product

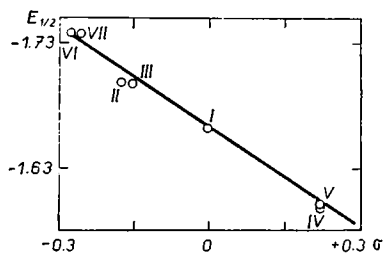


Fig. 2. Correlations of  $E_{1/2}$  with  $\sigma_{p-x}$  in 0.1 N-NaOH for the wave of carbonyl group.

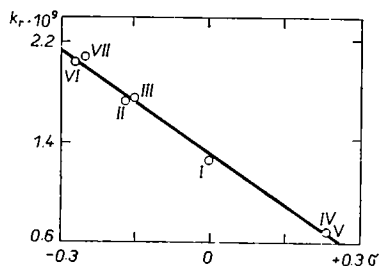


Fig. 3. Correlation of the rate constants of recombination with the Hammett constants according to eqn (1).

of the limiting values of  $\sigma_{p-\max}$  (for  $\sigma_{p-N(CH_3)_2} = -1.05$  and  $\sigma_{p-NO_2} = +1.27$ ) and the reaction constant. The value of the half-wave potential of substance *I* was added to the values thus obtained. In this way the limits of the potentials for the investigated series of substances were obtained (if the reaction mechanism did not change) in the potential range from  $-1.31$  V to  $-1.95_9$  V (SCE) for 0.1 N-NaOH.

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