Polarographic reduction of 2-carboxybenzophenone derivatives. III. Reduction of oximes of *o*-benzoylbenzoic acid

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The polarographic reduction of seven oximes of 2-carboxybenzophenone substituted in position 4′ has been investigated. The results have been correlated with Hammett σ_{p-x} constants in order that the effect of 4′-substituents on the polarographic behaviour might be established. On the basis of the reduction scheme and linear relationship between $E_{1/2}$ and σ_{p-x} it has been stated that the above oximes behave like the oximes described in literature.

The polarographic reduction of oximes was studied from two points of view. Firstly, the data for a general reduction scheme were gathered by means of classical polarography. Secondly, the results were utilized for the analytical polarographic determination of carbonyl compounds or those oximes which were important as analytical reagents.

Therefore it took time before *Souchay* and *Ser* [1] on the basis of a generalization of the results obtained with the reduction of oximes up to 1952 and *Lund* [2] on the basis of macroreductions on a large-surface electrode were able to throw light upon the suggestions [3] concerning the reduction scheme. The reduction of the azomethine substances of the type $RR'-C=N-Y-R$ depends on the character of Y. Provided Y is equal to C or H, a two-electron reduction to amine can be observed while a four-electron reduction is observed if Y is equal to N or O [2, 4]. The reduction of oximes has been reviewed by *Perrin* [5] up to 1965.

Only few papers are concerned, besides the reduction mechanism, also with the effect of the structure of oximes on their polarographic reduction [6, 7].

The aim of this paper was to continue in the study of the derivatives of 2-carboxybenzophenone [8, 9] and elucidate the polarographic behaviour of the oximes of 2-carboxybenzophenone substituted in position 4′. Furthermore, we tried to assign the results to a general reduction scheme and correlate them with the Hammett constants in order to find out the effect of substituents on the polarographic behaviour of these substances.

Experimental

Apparatus

The polarographic experiments as well as pH measurements were carried out on the apparatus described earlier [9].

Substances

The *p*′-substituted *o*-aroylbenzoic acids the preparation of which by the modified Underwood procedure [10] had been described earlier [8] were used for the preparation of oximes.

The oximes of 4′-substituted 2-carboxybenzophenones *I*—*VII* were prepared as follows: ethyl alcohol (5 ml) and pyridine (5 ml) were added to the corresponding keto acid (0.01 mole) and $NH_2OH \cdot HCl$ (0.011 mole). The mixture was heated under reflux for 2 hrs. Then the solvents were distilled off *in vacuo* and the residue, usually crystalline, was washed with redistilled water and recrystallized from methyl alcohol—water (3 : 1). The purity of preparations was checked by means of melting points and chromatographically [11].

Determination of dissociation constants

Determination of the dissociation constants of substances *I*—*VII* was performed on an OP-205 (Radelkis) pH-meter with a glass electrode, type OP 717-1/A (Radelkis). Acids (1×10^{-3} M) were prepared in absolute methanol. A solution of the acid (150 ml) was mixed with redistilled water (50 ml) and used for titration. The titration was performed with 0.1 N-KOH solution in 75% methyl alcohol. The values obtained are listed in Table 1.

Table 1

Values of the acid-base constants for acids *I*—*VII*

Oxime	pK_{pot} [mol l^{-1}]
I	10.19
II	10.14
III	10.20
IV	10.30
V	10.19
VI	10.15
VII	10.19

Reduction

A 1×10^{-3} M stock solution of the respective oximes (*I*—*VII*) in absolute methyl alcohol was mixed in the ratio 3 : 1 with 4 N-H_2SO_4, 0.4 N-H_2SO_4, 0.4 N-NaOH, or Britton—Robinson buffer solution. Further procedure was as described earlier [9].

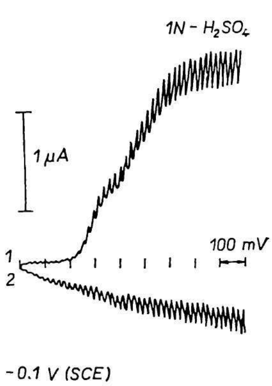
Results and discussion

The oximes of 2-carboxybenzophenone (*I*), 4′-methyl-2-carboxybenzophenone (*II*), 4′-ethyl-2-carboxybenzophenone (*III*), 4′-chloro-2-carboxybenzophenone (*IV*), 4′-bromo-2-carboxybenzophenone (*V*), 4′-methoxy-2-carboxybenzophenone (*VI*), and 4′-tolyloxy-2-carboxybenzophenone (*VII*) were studied polarographically.

The oximes *I*—*VII* give two two-electron diffuse waves of irreversible character at pH < 4 (Fig. 1). Since the half-wave potentials of the second wave, i_2, are almost pH independent both waves merge into a single four-electron wave at about pH 4.

In neutral region between pH 6.6 and 8.0 where the rate of protonation reaction is already low, the compounds *IV* and *V* yield a wave of anticlinal character decreasing in the shape of a dissociation curve of a weak electrolyte, the value of pK' being 7.3 for

Fig. 1. Polarographic curves of the oxime of 4′-bromo-2-carboxybenzophenone in 1 N-H_2SO_4.
1. curve recorded without commutator; *2.* commutated curve, auxiliary potential −0.1 V, f = 12 c/s.

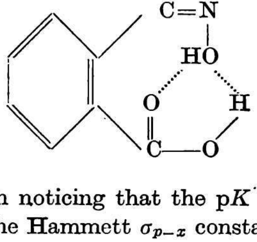


both oximes. After this wave, i_{pos}, another wave, i_{neg}, corresponding to conjugated base appears while the sum of both the waves remains approximately constant. The dependence of the wave height on the square root of the reservoir height indicates that the character of i_{pos} is kinetic in this region. This fact is also confirmed by the temperature dependence because the current of wave i_{pos} increases exponentially with temperature whereas the current of i_{neg} increases only slightly.

The remaining oximes (*I*—*III*, *VI*, and *VII*) behave differently. The rate of the protonation reaction of these compounds (negative values of σ_{p-x} correspond to the substituents except oxime *I*) is of such character that both the waves merge into a single wave in this region. The recombination processes may be thus revealed by means of classical polarography only in the case of oximes *IV* and *V*. The dissociation constants found potentiometrically indicate that no recombination of COO^- group with protons takes place. Thus the recombination of oxime group with H^+ ions appears.

At pH > 9 the protonation reaction is so slow that no recombination processes typical of reducible organic acid [8, 12] can proceed. The height of the four-electron wave decreases and oximes *I*—*VII* are not reducible in 0.1 N-NaOH. The half-wave potentials after the break in slightly alkaline region are already pH independent.

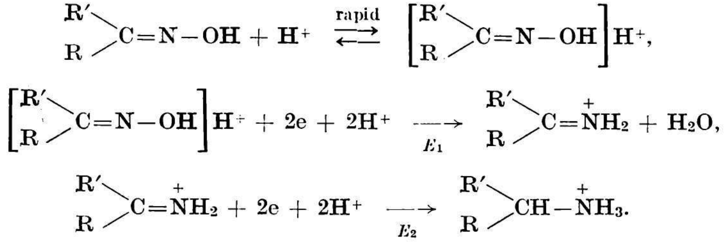
A substantial decrease in the acidity of acids, when compared with those described in [8], accompanying the conversion of carbonyl to oxime may be accounted for by the formation of the hydrogen bonds [13] in the compound



In this connection it is worth noticing that the pK values found potentiometrically are in linear relationship with the Hammett σ_{p-x} constants.

On the basis of these facts the reduction can be explained by means of the following scheme:

In acid medium:

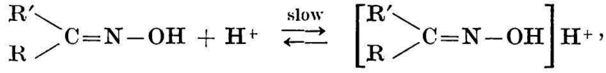


$$\left.{}^{R'}_{R}\!\right>C=N-OH + H^+ \overset{\text{rapid}}{\rightleftarrows} \left[\left.{}^{R'}_{R}\!\right>C=N-OH\right]H^+, \qquad (A)$$

$$\left[\left.{}^{R'}_{R}\!\right>C=N-OH\right]H^+ + 2e + 2H^+ \xrightarrow[E_1]{} \left.{}^{R'}_{R}\!\right>C=\overset{+}{N}H_2 + H_2O, \qquad (B)$$

$$\left.{}^{R'}_{R}\!\right>C=\overset{+}{N}H_2 + 2e + 2H^+ \xrightarrow[E_2]{} \left.{}^{R'}_{R}\!\right>CH-\overset{+}{N}H_3. \qquad (C)$$

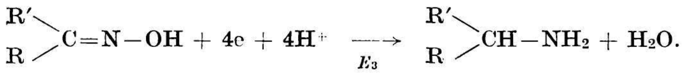
In neutral medium:



$$\left.{}^{R'}_{R}\!\right>C=N-OH + H^+ \overset{\text{slow}}{\rightleftarrows} \left[\left.{}^{R'}_{R}\!\right>C=N-OH\right]H^+, \qquad (D)$$

and further reaction steps according to eqns (*B*) and (*C*) assuming $E_1 = E_2$.

In slightly alkaline medium:



$$\left.{}^{R'}_{R}\!\right>C=N-OH + 4e + 4H^+ \xrightarrow[E_3]{} \left.{}^{R'}_{R}\!\right>CH-NH_2 + H_2O. \qquad (E)$$

It follows from this scheme that the protonized oxime (*A*) can be reduced in acid medium in the first two-electron wave to imine (*B*) which may be caught by means of macroreduction as an intermediate [2]. In step (*C*) imine is reduced to amine. In neutral region the electrode process is controlled by the chemical reaction, *i.e.* protonation of oxime group which limits the height of wave i_{pos} in this region (*D*). In weakly alkaline medium the oxime is reduced directly to amine, but it is not possible to catch imine (*E*). In alkaline medium oxime is non-reducible.

The above scheme is in good agreement with the literature data [2, 4, 5] and thus proves their correctness. Moreover, it confirms the similarity between the behaviour of oximes *I*—*VII* and that of other oximes described in literature.

Correlations of half-wave potentials with the Hammett constants according to equation

$$E_{1/2} = \varrho_{\pi R} \cdot \sigma_{p\text{-}x}$$

were carried out in 1 N-H_2SO_4 for i_2 and at pH 9.45 for establishing the substituent effect on the polarographic behaviour. As obvious from Figs. 2 and 3 the correlations are relatively good. In both media oximes *VI* and *VII* show deviations from linear relationship. It is interesting that the deviation for oxime *VI* is on the average 110 mV in both media while oxime *VII* shows the deviation of 50 mV both in 1 N-H_2SO_4, and at pH 9.45. We did not succeed in finding out the cause of deviations. The deviation appearing with oxime *VI* is in conformity with the data reported in [7] concerning the oximes of 4′-substituted benzophenones. According to these data, the derivative with the substituent $-OCH_3$ in position 4′ also exhibits a deviation. It is also worth mentioning that the reaction constant of oximes *I*—*VII* (+0.08 V in 1 N-H_2SO_4) is in accordance with the value of reaction constant of the oximes substituted in the 4′ position [7] (in acetate buffer); the good agreement between the constant $\varrho_{\pi R}$ (+0.11 V) and the *Brockman*'s data [6] is also remarkable. It follows from the reaction constants in both media that the effect of structure on the polarographic behaviour of oximes *I*—*V* is relatively small.

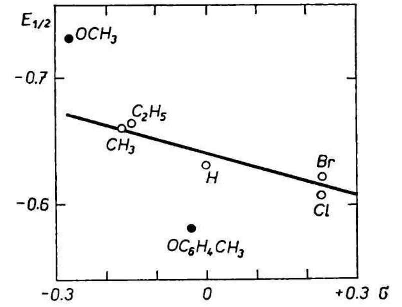


Fig. 2. Correlations of $E_{1/2}$ with the Hammett $\sigma_{p\text{-}x}$ constants for the second wave in 1 N-H_2SO_4; $\varrho_{\pi R} = +0.08$ V. Full circle denotes a deviation.

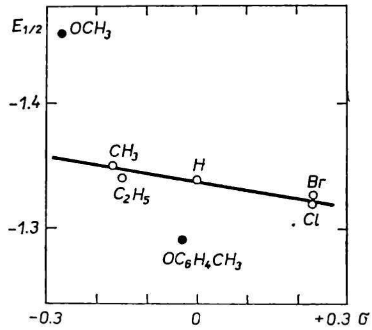


Fig. 3. Correlations of $E_{1/2}$ with the Hammett $\sigma_{p\text{-}x}$ constants at pH 9.45; $\varrho_{\pi R} = +0.11$ V. Full circle denotes a deviation.

References

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