

Deactivation of the reduction product of *p*-benzoylbenzaldehyde

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The reduction of *p*-benzoylbenzaldehyde has been investigated. This reduction is different from that of benzaldehyde, benzophenone, or the mixtures of these substances, but it resembles the reduction of *p*-diacetylbenzene. In spite of a certain similarity, some differences appear in the cathodic reduction of both these compounds.

Of the compounds with two electroactive centres which behave in the reduction differently from the compounds with a single group, *p*-diacetylbenzene was given particular attention [1–4].

The aim of this study was to investigate *p*-benzoylbenzaldehyde, appreciate its reducibility, or find out anomalies in its polarographic behaviour.

Experimental

Apparatus

The polarographic records were performed with an LP-60 polarograph in connection with an EZ-2 line recorder (Laboratorní přístroje, Prague). Polarographic analysis was carried out in a Kalousek vessel with a separated saturated calomel electrode (SCE) as reference electrode. At the height of reservoir $h = 60$ cm the dropping mercury electrode showed the following properties: $m = 2.9$ mg Hg s⁻¹, $t = 3$ s in 1 N-KCl at the potential of 0.0 V (SCE).

The commutated curves were studied by means of a Kalousek commutator [5, 6] constructed by Ševčík and Vacek [7] ($f = 6$ c s⁻¹).

Controlled potential electrolysis based on a controlling system of two polarographs was carried out with a mercury drop in a Novák vessel according to Manoušek and Zuman [8] up to the disappearing of the wave. It was proved by a blank test that the disappearance of wave was caused by the electroreduction and not by the reaction of the substance with solution.

The u.v. spectra of products before and after electrolysis were taken on a Spectromom 202 (MOM, Budapest) spectrophotometer.

The pH of solutions was measured on a PHM-4 (Radiometer, Copenhagen) instrument.

Substances

p-Benzoylbenzaldehyde was prepared according to Bourcet [9]. The purity of preparation was tested by means of melting point and chromatographically [10].

p-Methylbenzophenone and *p*-toluylaldehyde were commercial preparations.

Reduction

Stock solutions (concentration 4×10^{-4} M) of the investigated substances were prepared in 60% ethyl alcohol. The stock solution was mixed with equal volume of 10 N-H₂SO₄, 2 N-H₂SO₄, 0.2 N-NaOH, or Britton—Robinson buffer solution. The polarographic records were made after bubbling through with nitrogen purified by passing through an alkaline solution of pyrogallol.

Results

p-Benzoylbenzaldehyde (I) is reduced in two main reduction steps (Fig. 1). The total height of the first step i^1 decreases significantly at pH > 5 and it splits into two waves i_A^1 and i_B^1 (Fig. 1 and Table 1) at pH > 7. The total height of the second reduction step i^2 :

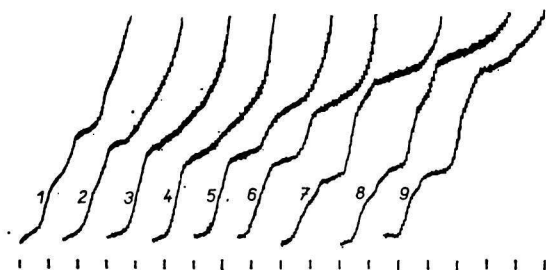


Fig. 1. Polarographic reduction of *p*-benzoylbenzaldehyde.

1. from -0.1 V (SCE) in 5 N-H₂SO₄; 2. from -0.2 V (SCE) in 1 N-H₂SO₄; 3. from -0.3 V (SCE) in Britton—Robinson buffer at pH 2.40; 4. from -0.4 V (SCE) in Britton—Robinson buffer at pH 3.04; 5. from -0.5 V (SCE) in Britton—Robinson buffer at pH 4.30; 6. from -0.6 V (SCE) in Britton—Robinson buffer at pH 5.38; 7. from -0.65 V (SCE) in Britton—Robinson buffer at pH 7.01; 8. from -0.7 V (SCE) in Britton—Robinson buffer at pH 8.55; 9. from -0.8 V (SCE) in Britton—Robinson buffer at pH 11.27.

Concentration of depolarizer 2×10^{-4} M, sensitivity 1/7, 200 mV/absc.

increases in acid media (pH < 1) and at pH > 3 until it reaches the limiting value at pH 9 (Table 1). At pH > 7 the wave i^2 also splits into two waves i_A^2 and i_B^2 the height of which is pH dependent in the shape of a polarographic curve with $pK'_2 \approx 9.3$, similarly as is the case with the wave i^1 .

The half-wave potentials of the wave i_A^1 are shifted to more negative values with increasing pH (Table 1). The dependence of $E_{1/2}$ on pH shows a change in slope at pH 5.6, which indicates the presence of two poorly separated waves, i_{AA}^1 at pH < 5.6 and i_A^1 at pH between 5.6 and 10.5. The half-wave potential of the more negative wave i_B^1 is pH independent at pH > 9.3. Wave i_A^2 is also shifted to more negative values while the half-wave potential of i_B^2 is pH independent.

Table 1
Half-wave potentials and currents of the reduction of *p*-benzoylbenzaldehyde

pH	i_A^1	i_n^1	$E_{1/2}$ [V]	i_A^2	i_n^2	i_A^1	i_n^1	i_A^2	i_n^2	$i_1 + i_2$
								[μA]		
10 N-H ₂ SO ₄			-0.70	0.47	0.60	0.29				0.76
5 N-H ₂ SO ₄	-0.26	-0.46	-0.73	0.46	0.60	0.19				0.65
1 N-H ₂ SO ₄	-0.43		-0.75	0.60		0.07				0.67
2.15	-0.53			0.57		0.03				0.60
2.99	-0.60			0.57		0.04				0.61
3.56	-0.63		-0.96	0.59		0.07				0.66
4.40	-0.68		-1.03	0.59		0.16				0.75
5.12	-0.72		-1.07	0.54		0.21				0.75
5.55	-0.75		-1.09	0.49		0.26				0.75
6.35	-0.79		-1.13	0.43		0.43		0.10	0.53	0.96
7.22	-0.79		-1.13	0.39		0.51		0.13	0.64	1.03
7.78	-0.81	-0.90	-1.16	0.30	0.11	0.49	0.41	0.17	0.66	1.07
8.27	-0.85	-0.93	-1.19	0.24	0.16	0.46	0.40	0.21	0.67	1.07
9.10	-0.88	-0.96	-1.21	0.24	0.19	0.40	0.43	0.29	0.69	1.12
9.80	-0.90	-0.99	-1.23	0.20	0.24	0.19	0.44	0.44	0.74	1.18
10.38		-0.98	-1.25	0.11	0.37	0.18	0.48	0.53	0.71	1.19
10.81		-0.96			0.46		0.46	0.74	0.74	1.20
10.39		-0.96			0.44		0.44	0.71	0.71	1.18
11.90		-0.96			0.41		0.41	0.71	0.71	1.12
0.1 N-NaOH		-0.97			0.36		0.36	0.74	0.74	1.10

The anodic wave obtained by means of a Kalousek commutator [5, 7] indicates a reversible electrode process as illustrated in Figs. 2 and 3. The anodic wave attains its maximum in the pH region between 0 and 4. The shift to higher or lower pH value is attributed in conformity with literature [1, 3, 4] to the deactivation of the primary reduction product

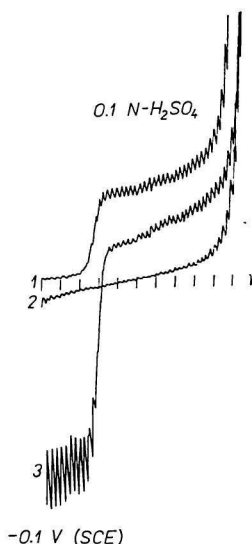


Fig. 2. Curves of *p*-benzoylbenzaldehyde switched over by means of wiring I [5, 7]; 0.1 N-H₂SO₄.

1. curve recorded without commutator;
2. curve recorded with commutator (supporting electrolyte), auxiliary potential -0.6 V (SCE);
3. with commutator, auxiliary potential -0.6 V (SCE).

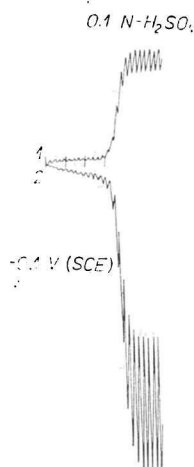


Fig. 3. Curve of *p*-benzoylbenzaldehyde switched over by means of wiring II [5, 7]; 0.1 N-H₂SO₄.

1. curve recorded without commutator;
2. with commutator, auxiliary potential -0.1 V (SCE).

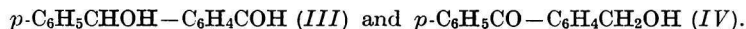
which is acid-base catalyzed. This fact is proved by the change in the height of cathodic waves: in the pH region where the primary reduction product is stable (pH 0–4), the total reduction current corresponds to somewhat more than two electrons. Provided the product of deactivation may be further reduced, the total current reaches the values corresponding to four-electron reduction in that pH region where the deactivation is too rapid and practically all the primary product may be transformed. The graph expressing the difference between the current corresponding to four-electron reduction and the total limiting current found experimentally as a function of pH resembles very much the diagram of anodic current.

The reduction of *p*-benzoylbenzaldehyde was carried out in both cases with 5×10^{-4} M solutions in Britton–Robinson buffer of pH 7.82 at -0.9 V. In either case it was found that simultaneously with the decrease in the first wave the second wave also disappeared. The absorbance of solution disappeared in the whole measurable region linearly with the decrease of both waves.

Discussion

The polarographic behaviour of *p*-benzoylbenzaldehyde (*I*) resembles therefore that of *p*-diacetylbenzene (*II*). This similarity manifests itself in the existence of a single two-electron reversible wave at low pH values with the rise of the more negative wave at increasing as well as decreasing pH values with respect to the pH region where the reversible process prevails. The difference between diketone (*II*) and keto aldehyde (*I*) appears outside the region where the process is reversible. The height of the first reduction wave of *p*-diacetylbenzene is pH independent and corresponds to the uptake of more than two electrons while the height of wave i^1 of *p*-benzoylbenzaldehyde reaches the maximum at pH 7.5 and decreases at pH > 10. If wave i^1 of *p*-benzoylbenzaldehyde decreases, i^2 is higher than i^1 and the limiting current of wave i^2 corresponds to the uptake of more than two electrons. On the other hand, the second wave of *p*-diacetylbenzene is never higher than the first one and reaches the maximum corresponding just to the uptake of two electrons. Moreover, no such splitting of waves into i^1 and i^2 was observed in the case of *p*-diacetylbenzene.

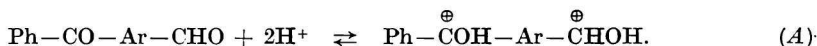
The deactivation of the primary reduction product of *p*-benzoylbenzaldehyde on an electrode may yield two alcohols:



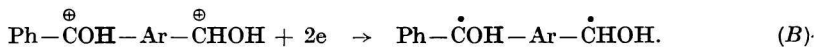
A comparison of the half-wave potentials of wave i^2 with the potentials of *p*-methylbenzophenone and *p*-toluylbenzaldehyde as well as the results of the controlled potential electrolysis indicates that the most probable intermediate is substance *IV*.

The separation of waves i_A and i_B ascertains the presence of at least two forms which are protonized to different degrees. The fact that the half-wave potentials of waves i_B^1 and i_B^2 are pH independent gives evidence that these waves correspond to the reduction of the unprotonized form of a substance. It is assumed in the literature [1] that the diprotonized form may undergo a reversible reduction. The jump in the relationship between $E_{1/2}$ and pH demonstrates that the monoprotionized form can be reduced in the pH region between 7 and 10. Finally, the decrease in the wave i_B^1 at pH > 10 is attributed to an attenuation of the protonation of the radical anion which has been produced by accepting a primary electron. It is thus in analogy with other carbonyl compounds [11, 12].

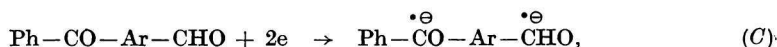
In the proximity of a drop, substance *I* is thus protonized owing to recombination according to summary eqn (A)



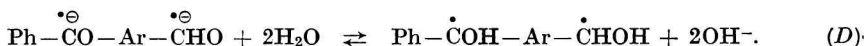
In acid medium the two-electron reduction takes place and a biradical is formed according to eqn (B).



In alkaline medium the reduction takes place under the formation of an anion radical



which is able to recombine with solvent



Between both the extremes the reduction of monoprotionized form occurs.

In the case of the electrolysis at constant potential the biradical being formed diffuses into solution where it is deactivated under the formation of inactive form. With the increasing potential of the drop the biradical is either reduced to alcohol on the drops in the potential range corresponding to the reduction of benzophenone or is isomerized to (IV) owing to the specific conditions on a double layer with subsequent reduction of the keto group. The latter alternative seems more likely because of good agreement between potentials of the first wave and those of benzophenone.

References

1. Kargin, Yu., Manoušek, O., and Zuman, P., *J. Electroanal. Chem.* **12**, 443 (1966).
2. Philip, R. H., Jr., Flury, R. L., and Day, R. A., Jr., *J. Electrochem. Soc.* **111**, 328 (1964).
3. Fisher, O., Kišová, L., and Štěpánek, J., *J. Electroanal. Chem.* **17**, 233 (1968).
4. Zuman, P., Manoušek, O., and Wig, S. K., *J. Electroanal. Chem.* **19**, 147 (1968).
5. Kalousek, M., *Collect. Czech. Chem. Commun.* **13**, 105 (1948).
6. Rálek, M. and Novák, L., *Collect. Czech. Chem. Commun.* **21**, 248 (1956).
7. Ševčík, J. and Vacek, K., *Chem. Zvesti* **23**, 501 (1969).
8. Manoušek, O. and Zuman, P., *Collect. Czech. Chem. Commun.* **29**, 1718 (1964).
9. Bourcet, P. M., *Bull. Soc. Chim. Fr.* [3] **15**, 940 (1896).
10. Mollin, J. and Marek, V., unpublished results.
11. Zuman, P., *Collect. Czech. Chem. Commun.* **33**, 2548 (1968) and other references cited therein.
12. Zuman, P., Barnes, D., and Ryvolová, A., *Disc. Faraday Soc.* **45**, 202 (1968) and other references cited therein.

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