Stereochemistry of the Electrolytic Reductive Coupling of Benzaldehyde

Vincent J. Puglisi,[1] **Gary L. Clapper, and Dennis H. Evans**
Department of Chemistry, University of Wisconsin, Madison, Wis. 53706

The ratios of *dl*- to *meso*-hydrobenzoin formed in the controlled potential electrolytic reductive coupling of benzaldehyde from acidic aqueous solutions are reported. Under most conditions the ratios are in the same range (1.0–1.3) as those previously reported for photochemical reduction and for electrochemical reduction using 80% ethanol as solvent. However, in the presence of adsorbed ions such as iodide and tetraethylammonium ions, it was found that relatively more *meso*-hydrobenzoin is formed. Ratios as low as 0.5 are observed. The significance of these results to the mechanism of electrolytic reductive coupling is discussed.

The products of many electrochemical reactions exist in two or more isomeric forms. One might expect that the many forces at play at the electrode–solution interface could influence the isomeric composition of the reaction products and that a comparison of isomer ratios for the electrolytic process with those for the analogous homogeneous chemical reduction or oxidation could provide useful clues concerning the molecular details of the electrode reaction. Failing this, the isomer ratio information would still retain practical significance with respect to possible stereoselective syntheses.

Nevertheless, little attention has been directed toward studies of the isomeric composition of electrolytic products (*1–4*). An important exception is the reduction of benzil (*5–7*) which is thought to proceed via *cis*- and *trans*-stilbenediol intermediates whose ratio depends on pH, solvent, potential, temperature, and composition of the supporting electrolyte. The dependence of the isomer ratio on conditions which are known to affect the electric field in the double layer has been interpreted in terms of a *trans* → *cis* isomerization in the double layer.

Stocker and coworkers have investigated the ratio of diastereoisomers (*meso* and *dl* forms) of the glycols formed by the reductive coupling of aromatic aldehydes and ketones. These workers utilized both photochemical reduction (*8–11*) and electrolysis (*12, 13*) and found very similar isomer ratios for both processes under all solution conditions and with various metals used as electrodes. Thus it would appear that the electrode surface does not play a significant role in determining the stereochemical course of the electrolytic reductive coupling of carbonyl compounds.

However, it should be noted that the above electrolyses were performed with 80% ethanol as solvent. Though little is known about the adsorption of organic species from mixed solvents, the surface excesses of reactant and intermediates are probably much lower with 80% ethanol as compared to water so that the dimerization reaction may occur primarily among species which have diffused away from the electrode–solution interface.

The present study is concerned with the isomer ratios for the electrolytic reductive coupling of benzaldehyde from aqueous solutions. The ratios have been studied under a variety of solution conditions and it has been found that with one notable exception the electrolytic ratios are the same as the photolysis ratios. The exception is found when ions which are adsorbed at the electrode–solution interface are present. Under these conditions relatively more *meso*-hydrobenzoin is formed.

EXPERIMENTAL

Reagents. Benzaldehyde was vacuum distilled and stored under nitrogen. Tetraethylammonium perchlorate (Eastman) and tetrabutylammonium perchlorate (Matheson) were used as received. Commercial preparations of hydrobenzoin were impure but gave *meso*-hydrobenzoin on recrystallization. The methods of Fieser (*14*) were employed for the preparation of *meso*- (137.4–137.9 °C from ethanol–water) and *dl*-hydrobenzoin (119.0–119.6 °C from carbon tetrachloride). All other materials were of reagent grade quality.

Electrochemical Cells. Preparative electrolyses were carried out in a 500-cc reaction kettle (Kimax, No. 33700, Owens-Illinois, Toledo, Ohio). The counter electrode (platinum wire) compartment was separated from the cathode compartment by a 10-mm medium-porosity glass frit. The working electrode was *ca.* 60-cm^2 mercury pool. The reference electrode probe was terminated by a cracked-glass seal (*15*). The total volume of cathode solution was 300 cc. All electrode compartments and gas inlets were inserted through standard taper joints in the top of the reaction kettle. Both anode and cathode compartments were deaerated with high purity nitrogen prior to and during electrolysis. Stirring was effected by a magnetic stirrer.

Controlled potential coulometry was carried out with a similar cell of smaller dimensions. The solution volume was 80 cc and the mercury pool electrode area was *ca.* 25 cm^2.

Apparatus. Either a Wenking 61 RS potentiostat (Brinkmann Instruments, Inc., Westbury, N. Y.) or a potentiostat based on a programmable regulated dc power supply (Kepco Model ABC 40-0.5M, Kepco, Inc., Flushing, N. Y.) (*16*)

---

[1] Present address, Department of Chemistry, University of Texas, Austin, Texas.

---

(1) P. J. Elving, I. Rosenthal, and A. J. Martin, *J. Amer. Chem. Soc.*, **77**, 5218 (1955).
(2) C. K. Mann, J. L. Webb and H. M. Walborsky, *Tetrahedron Lett.* **20**, 2249 (1966).
(3) R. Annino, R. E. Erickson, J. Michalovic, and B. McKay, *J. Amer. Chem. Soc.*, **88**, 4424 (1966).
(4) A. J. Fry and J. H. Newberg, *ibid.*, **89**, 6374 (1967).
(5) A. Vincenz-Chodkowska and Z. R. Grabowski, *Electrochim. Acta*, **9**, 789 (1964).
(6) E. Bauer, *J. Electroanal. Chem.*, **14**, 351 (1967).
(7) H. E. Stapelfeldt and S. P. Perone, Anal. Chem., **40**, 815 (1968).
(8) J. H. Stocker and D. H. Kern, *J. Org. Chem.*, **31**, 3755 (1966).
(9) J. H. Stocker and D. H. Kern, *ibid.*, **33**, 291 (1968).
(10) J. H. Stocker, D. H. Kern, and R. M. Jenevein, *ibid.*, **33**, 412 (1968).
(11) J. H. Stocker and D. H. Kern, *ibid.*, **33**, 1270 (1968).
(12) J. H. Stocker and R. M. Jenevein, *ibid.*, **33**, 294 (1968).
(13) *Ibid.*, p 2145.

(14) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed., D. C. Heath and Co., Boston, 1957, pp 175–90.
(15) J. J. Lingane, *J. Electroanal. Chem.*, **1**, 379 (1960).
(16) D. H. Evans and D. R. Tallant, University of Wisconsin, unpublished results, 1968.

was used for all electrolyses. For controlled potential coulometry the current was recorded on a strip-chart recorder and current–time areas were determined by planimetry.

Procedure. The following procedure is typical for a preparative electrolysis. In run No. 6, 300 cc of 0.2*M* aqueous perchloric acid was placed in the cell and deaerated until the observed current at −1.00 volt *vs.* SCE was <3 mA. A total of 371 mg of benzaldehyde was added in two portions with the first being completely electrolyzed before the second was added. This procedure was dictated by the limited solubility of benzaldehyde. The current after each addition was about 200 mA declining to <5 mA in about two hours. The final electrolysis solution contained a small amount of suspended white solid.

The solution was decanted and the cell was washed with ether. The solution was extracted with ether, all extracts were combined, dried, and the ether was evaporated yielding 360 mg of a light-yellow solid. (When alcohol-containing solutions were used, the alcohol was evaporated prior to extraction.)

A portion of the crude electrolysis product was weighed, dissolved in acetonitrile, and quantitatively transferred to an NMR tube. The NMR spectrum was obtained, the *meso* and *dl*-benzylic proton peaks were integrated, and the *dl*-to-*meso* ratio was calculated. The chemical shifts of these peaks relative to TMS in acetonitrile are 4.64 ppm for the *dl* and 4.77 ppm for the *meso*. Some analyses were performed using chloroform as solvent.

A standard addition technique was used to determine the yields. A known volume of a standard solution of *meso* hydrobenzoin was added to the sample with a syringe. The benzylic peaks were again integrated. Both the *dl* and *meso* areas were reduced by dilution, the *meso* area being reduced less because of the standard addition. The *dl* area was then normalized to its initial value and the same dilution correction factor was applied to the *meso* area. The ratio of the initial *meso* area to the corrected *meso* area from the second integration was then equated to the ratio of x, the number of grams of *meso* present initially, to $x + s$, where s is the number of grams of *meso* added. When x has been obtained, the number of grams of *dl* present may be ascertained from the original *dl*-to-*meso* ratio.

An estimation of the percentage of hydrobenzoin based on a comparison of the total benzylic proton area with the total phenyl proton area gave as much as 1.5 times that obtained by the above procedure which is considered the more reliable. The spectra showed several resonances of other minor products which were not identified. Aldehydic proton resonances were absent.

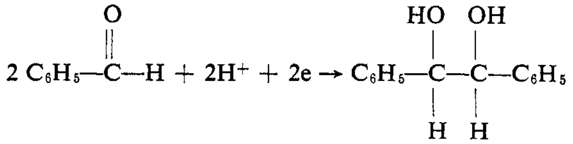
The Varian A-60 and A-60A spectrometers were used. The analytical method was tested with known ratios of *dl*-to-*meso* hydrobenzoin and it was found that the ratios could be determined in the range of 0.15 to 1.0 with an average error of ±3%.

The photolysis experiments were carried out in a Rayonet photochemical reactor using 16 Rayonet 3500-A lamps. The sample was placed in a 9- × 52-mm borosilicate glass tube and the contents were deaerated before photolysis. The tube was sealed with a rubber septum.

A Fisher–Johns melting point apparatus was used. Melting points are uncorrected.

RESULTS AND DISCUSSION

The reported polarographic behavior of benzaldehyde (*17*) was verified. One diffusion-controlled wave was found in acid media. Two waves appeared as the pH increased and they gradually merged in neutral media. The first wave is due to the one-electron electrolytic reductive coupling to form hydrobenzoin, II.



$$2\,\underset{\text{I}}{C_6H_5{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H} + 2H^+ + 2e \rightarrow \underset{\text{II}}{C_6H_5{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle HO}{|}}{C}}{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}{-}C_6H_5}$$

Controlled potential coulometry in 0.2*M* hydrochloric acid yielded an average *n*-value of 1.02 for 50% ethanol–water and 0.96 for aqueous solutions. Most of the isomer ratios were determined for electrolyses in acid media because in this pH region the polarographic wave for the reaction under study showed the maximum potential separation from succeeding processes.

Large scale electrolyses were carried out and the isomer ratios were determined by the NMR method described above. These results are summarized in Table I. In each case a polarogram of benzaldehyde in the supporting electrolyte to be studied was obtained to locate the half-wave potential and to choose an electrolysis potential for the controlled potential reduction.

The reproducibility inherent in the electrolytic and analytical procedures may be seen in runs 1, 2, and 3. These ratios, along with those of runs 4 through 7, are in excellent agreement with the 1.11–1.30 range reported by Stocker and Jenevein (*12*) for electrochemical reduction using 80% ethanol as solvent. These in turn are very similar to the ratios for photochemical reduction (*8*) which ranged from 1.01–1.22. These data clearly demonstrate that even in water as solvent the electrode surface does not appreciably influence the stereochemical course of the reaction. In agreement with Stocker and coworkers (*8*, *12*), it was found that variations in pH (run 5) and ionic composition (run 6) do not affect the ratio.

Rather large increases in ionic strength (runs 6, 8, 9, and 10) had little effect on the ratio. However, the addition of ions which are specifically adsorbed at the electrode surface causes a significant decrease in the ratio. In runs 11 and 12 a specifically adsorbed cation, tetraethylammonium ion (*18*), was present and the ratio was significantly lower than in its absence (run 6). The solution in run 11 was nearly saturated with respect to tetraethylammonium perchlorate. The more soluble chloride salt was used in run 12, permitting a substantially higher tetraethylammonium ion concentration. Run 13 shows the pronounced effect of even small concentrations of the very strongly adsorbed tetrabutylammonium ion.

Runs 14 through 16 show the effect of increasing concentrations of iodide ion. Unlike chloride, small amounts of iodide remain adsorbed at the control potential even though it is quite negative from the electrocapillary maximum (ECM) (*19*). The adsorption of a neutral species has little effect (run 17). At this concentration the surface coverage for *n*-amyl alcohol is about one (*20*).

To verify that the observed effect is not due to specific chemical interactions of these ions with the dimerizing radicals, a comparison with photochemical data was undertaken. Runs 18 and 19 represent electrolysis and photolysis, respectively, with identical solution conditions. Clearly the tetra-

---

(17) R. Pasternak, *Helv. Chim. Acta*, **31**, 753 (1948).

(18) A. N. Frumkin, in "Advances in Electrochemistry and Electrochemical Engineering," P. Delahay, Ed., Interscience, New York, Vol. 1, 1961, p 95 ff.

(19) P. Delahay, "Double Layer and Electrode Kinetics," Interscience, New York, 1965, pp 60–3.

(20) R. S. Hansen, D. J. Kelsh, and D. H. Grantham, *J. Phys. Chem.*, **67**, 2316 (1963).

Table I. Isomer Ratios in Products of Benzaldehyde Reaction

Run	Electrolysis potential[a]	Supporting electrolyte[b]	Ratio, *dl*/*meso*
1	−1.04	0.2*M* HCl	1.17
2	−1.04	0.2*M* HCl	1.19
3	−1.04	0.2*M* HCl	1.18
4	−1.04	0.6*M* HCl	1.23
5	−1.20	pH 4 phosphate–citrate buffer	1.24
6	−1.00	0.2*M* $HClO_4$	1.16
7	−0.94	0.2*M* $HClO_4$, saturated with benzaldehyde	1.00
8	−1.04	0.2*M* HCl, 0.4*M* NaCl	1.22
9	−1.04	0.2*M* HCl, 3*M* NaCl	1.08
10	−1.04	0.2*M* HCl, 5*M* NaCl	1.07
11	−1.04	0.2*M* $HClO_4$, 0.06*M* tetraethylammonium perchlorate	0.86
12	−1.04	0.2*M* HCl, 0.2*M* tetraethylammonium chloride	0.71
13	−1.04	0.2*M* $HClO_4$, $5 \times 10^{-4}M$ tetrabutylammonium perchlorate	0.48
14	−1.04	0.2*M* $HClO_4$, 0.1*M* NaI	0.98
15	−1.04	0.2*M* $HClO_4$, 0.3*M* NaI	0.78
16	−1.04	0.2*M* $HClO_4$ 0.8*M* NaI	0.48
17	−0.98	0.2*M* $HClO_4$, 0.2*M* *n*-amyl alcohol	1.10
18	−1.30	0.5*M* acetic acid 0.5*M* sodium acetate 0.15*M* tetraethylammonium perchlorate (50% 2-propanol)	1.02
19	Photolysis	0.5*M* acetic acid 0.5*M* sodium acetate 0.15*M* tetraethylammonium perchlorate (50% 2-propanol)	1.24

[a] Volts *vs.* SCE.

[b] All solutions are aqueous unless otherwise specified.

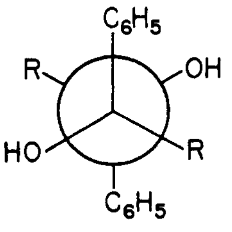
ethylammonium ion does not affect the isomer ratio for the homogeneous photolytic reaction. Its smaller effect in the electrochemical process (run 18 as compared with runs 11 and 12) may be due to the reduced adsorption of this ion from 50% 2-propanol–water. For many organic adsorbates, increased solubility signals decreased adsorption at the electrode–solution interface (*21*). The tetraalkylammonium perchlorates are distinctly more soluble in alcohol-containing solutions than in water.

Photolysis of iodide solutions gave very low yields of hydrobenzoin. Small amounts of iodine were formed and the solutions were soon opaque to the 3500-A radiation. Thus a comparison of electrochemical and photochemical results in the presence of iodide was not feasible.

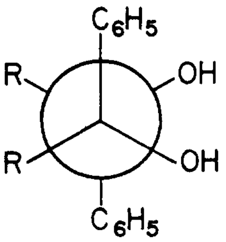
The total yield of hydrobenzoin ranged from 15–35% in these studies compared with 65–85% for electrolysis in 80% ethanol. When the work-up and analytical procedures described earlier were applied to electrolysis products from 80% ethanol, yields in the higher range were obtained indicating that the source of the lower yields is not simply in the experimental procedures. Stability and recovery of the hydrobenzoins was tested by dissolving 52.7 mg of *dl* and 54.5 mg of *meso* in 100 cc of 0.2*M* $HClO_4$. As expected, electrolysis at −1.04 volts produced no current. Work-up and analysis after 24 hours yielded 47 mg of *dl* and 48 mg of *meso*-hydrobenzoin. Thus the lower yields are not due to decomposition of the hydrobenzoins. It would appear to be more likely that electrochemical side reactions are more prevalent in electrolyses from aqueous solutions. These side reactions do not cause substantial variation in the coulometric *n*-value (see above). The identity of the electrolytic products other than the hydrobenzoins is not known, though thin-layer chromatography revealed the presence of substantial amounts of high molecular weight and/or highly polar substances in the crude product.

In any case, the excellent agreement of the "normal" ratios found in this work (runs 1–10) with the ratios found for 80% ethanol (*13*) indicates that the lower yields have not influenced the ratio—*i.e.*, the yield of each isomer is proportionally lower in water as compared to 80% ethanol. The abnormally low isomer ratios (runs 11–16) have been found only when ions which are specifically adsorbed at the control potential are present, the effect being relatively more pronounced at higher concentrations of the adsorbable ion.

The following arguments concerning steric and hydrogen-bonding control of the isomer ratios have been advanced by Stocker and coworkers (*8–13*). The formation of hydrobenzoin by both photochemical and electrochemical procedures is thought to proceed via dimerization of the neutral radicals formed by reduction and protonation of benzaldehyde. Completely random coupling would produce an isomer ratio of one. To the extent that steric factors govern the reaction, the *meso* form would predominate through preferential formation of Structure III (minimum nonbonded interaction) during dimerization. The formation of the *dl* form (Structure IV) is less likely. (R = H for benzaldehyde).



III
yields *meso*



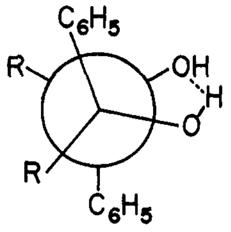
IV
yields *dl*

The slight preference for the *dl* isomer which is exhibited by benzaldehyde and many aromatic ketones (*8–13*) is probably caused by inter-radical hydrogen bonding during dimerization which, coupled with the same steric arguments as above, suggests that formation of the *dl* form (Structure V) over the *meso* form (Structure VI) is favored. Evidence for the importance of this mechanism in determining the isomer ratios is provided by the dependence of the ratio on electronic properties of the substituent in *para*-substituted acetophenones (*10*), electron-releasing groups giving relatively more *dl*-pinacol presumably by favoring hydrogen bond formation. Similarly, 2-acetylpyridine in which inter-radical hydrogen bonding is precluded by strong intra-radical hydrogen bonding gives a preponderance of the *meso*-pinacol (*22*) with *dl*/*meso* as small as 0.25.

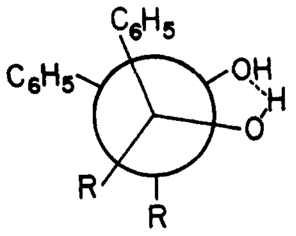
---

(21) E. Blomgren, J. O'M. Bockris, and C. Jesch, *J. Phys. Chem.*, 65, 2000 (1961).

(22) J. H. Stocker, D. H. Kern, and R. M. Jenevein, 155th National Meeting, ACS, San Francisco, April 5, 1968. Paper No. 223, Division of Organic Chemistry.



V
yields *dl*



VI
yields *meso*

In the electrochemical reduction of benzaldehyde two cases may be described. In the first, the radical intermediates are assumed to diffuse away from the electrode surface and dimerize in the bulk of the solution. If this situation pertains, it is clear that the isomer ratio must be identical to that of any process which forms the radical intermediates directly in the solution phase—*e.g.*, photolysis. In the second case it is assumed that the dimerization occurs among radicals in the immediate vicinity of the electrode–solution interface. In this case, the isomer ratio may or may not be the same as the photolysis ratio. If the conditions in the interface are not of the type or intensity to alter the course of the reaction, the isomer ratio may be unaffected. Thus the fact that the isomer ratio for electrolysis is normally the same as that for photolysis does not preclude the possibility that the electrolytic dimerization is a surface reaction.

On the other hand the stereochemical course of a surface reaction may be affected by surface conditions and the isomer ratio may be quite different from the photolytic value obtained with the same solution composition. This condition was found for the electrochemical reduction of benzaldehyde in the presence of adsorbable ions. This suggests that *at least in the presence of adsorbable ions*, the dimerization occurs in the interface.

The nature of the factors influencing the isomer ratio under these conditions is difficult to define. The studies of Blomgren, Bockris, and Jesch (*21*) indicate that the adsorption of benzaldehyde in common with other aromatic compounds occurs with the aromatic ring system parallel to the metal surface. It could be assumed that the radical intermediates are adsorbed with the same configuration. Nevertheless, if inter-radical hydrogen bonding is predominant during dimerization of surface radicals, considerations like those in Structures V and VI indicate that the *dl* form will be favored no matter what configuration of the radicals *vis a vis* the surface is assumed.

These considerations suggest that adsorbed ions may diminish the effectiveness of inter-radical hydrogen bonding and consequently favor the formation of the *meso* form. The decreased hydrogen bonding may be due to competitive orientation of the O—H bond in the high fields extant in the double layer. The field at the outer Helmholtz plane, for example, is known to be affected by the presence of specifically adsorbed ions. Nevertheless, the magnitude of the effect even at potentials quite negative from the electrocapillary maximum and the fact that both cations and anions show the same effect do not correlate well with the known effects of ion adsorption on double layer structure.

These studies are currently being extended to include other reducible aldehydes and ketones and other adsorbable ions to test the generality of the observed effect and to gain some insight into its origins.

RECEIVED for review August 28, 1968. Accepted October 28, 1968. Research supported by the Wisconsin Alumni Research Foundation and The National Science Foundation Grant GP-8350. Presented at the 156th National Meeting, ACS, September 1968, Atlantic City, N. J.

Correction

Lanthanum Hexaboride as an Electrochemical Generant of Lanthanum(III) for Titrations: Application to Determination of Nickel(II), Cobalt(II), and Zinc(II)

In this article by D. J. Curran and K. S. Fletcher III [ANAL. CHEM., **40,** 1809 (1968)] an error appears in the subtitle. The correct title appears above; however, when the article appeared in print the word "Copper(II)" was erroneously substituted for "Cobalt(II)."