The Mechanism of the Electroreduction of Benzyltriethylammonium Nitrate in Dimethylformamide at Aluminum and Platinum Cathodes

Sidney D. Ross, Manuel Finkelstein, and Raymond C. Petersen

Contribution from the Research and Development Center,
Sprague Electric Company, North Adams, Massachusetts 01247.
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Abstract: The electroreduction of benzyltriethylammonium nitrate in dimethylformamide at an aluminum cathode results in bibenzyl and toluene. The bibenzyl is the coupling product of benzyl radicals, generated at the cathode. The toluene arises primarily from benzyl carbanions, which are generated at the electrode and which can be trapped with carbon dioxide. A second demonstrated source of toluene, especially when water is added, is the cross-coupling of benzyl radicals and hydrogen atoms, generated simultaneously at the cathode. At a platinum electrode bibenzyl production is almost negligible, and toluene is the major product. An overall, two-electron electrode transfer to form a benzyl carbanion accounts for more than 95% of the toluene formed.

The electroreduction at an aluminum cathode in dimethylformamide (DMF) of quaternary ammonium compounds containing benzyl, fluorenyl, cinnamyl, *p*-methoxybenzyl, or α-phenylethyl groups yields the coupling products of these radicals. This coupling reaction involves the generation and dimerization of free radicals, formed in a one-electron transfer at the cathode, as indicated by the fact that *d*-α-phenylethyltrimethylammonium nitrate gives optically inactive products, *meso*- and *dl*-2,3-diphenylbutane.[1]

Mayell and Bard[2] studied the electroreduction of benzyldimethylanilinium bromide both polarographically and coulometrically. Application of Koutecky's treatment for irreversible polarographic waves indicated that a one-electron rate-determining step was involved, but the apparent number of Faradays per mole for the coulometric reduction in water, acetonitrile, and DMF varied between 1.4 and 2.0. In water and in DMF at a mercury cathode, the products were dimethylaniline and toluene. In acetonitrile, bibenzyl was also a product. In spite of the coulometric results, the authors proposed that the mechanism of this reaction involves the primary formation of benzyl free radicals, which either abstract hydrogen atoms to give toluene or couple to give bibenzyl. Mechanisms involving either benzyl carbanions or a benzylmercury intermediate were considered but deemed less probable.

The reduction of a benzyl quaternary ammonium compound at an aluminum cathode, with DMF as solvent leads to significant amounts of toluene (25–40%), in addition to the major product, bibenzyl.[3] As will be shown in the present work, with some cathode materials, toluene is the major or sole product. This attaches greater significance to the mechanism by which toluene is formed. The available evidence does not eliminate the possibility that toluene arises from a benzyl carbanion, and, as suggested by Perrin,[4] Bard's coulometric result[2] makes this pathway relatively probable. In addition, other sources of toluene, *e.g.*, the simultaneous generation and cross-coupling of benzyl radicals and hydrogen atoms, are possible and need to be explored.

The present work is addressed to the question of the mechanism or mechanisms by which toluene is formed. The electroreduction of benzyltriethylammonium compounds in DMF was screened for products formed at a variety of cathode materials and studied in more detail at platinum and aluminum. Carbanions, formed in these reductions, were trapped by carrying out the electrolyses in solutions saturated with carbon dioxide and maintained at the saturation level with a continuous stream of carbon dioxide. This diagnostic technique has been used successfully to demonstrate the intermediacy of both carbanions and carbanion radicals in electrochemical reductions.[5–8] In addition, the rates of hydrogen evolution during the course of these reductions were measured, and the effect of added water on the course of these reactions was studied.

Results

The results obtained in screening experiments with six different cathode materials are assembled in Table I. In all of these experiments 2 or more faradays of charge per mol of the salt were passed through the solution and

Table I. Products Obtained in the Electroreduction of 0.05 Mol of Benzyltriethylammonium Nitrate[a]

Cathode	Charge passed, faraday	Moles of product	
		Toluene	Bibenzyl
Al	0.104	0.0128	0.0105
Mg	0.200	0.0181	0.0103
Ta	0.200	0.0265	0.0082
C	0.300	0.0287	
Hg	0.104	0.0207	
Pt	0.201	0.0328	

[a] In dimethylformamide at a current of 2.0 A.

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a substantial fraction of the salt was converted to products. Triethylamine is also a product of this reaction, but our work-up focused only on the fate of the benzyl moiety of the salt. A tenfold decrease in the current with an aluminum cathode and a fourfold decrease in the current at platinum were without significant effect on the products obtained. These experiments were carried out before the importance of water content in the solvent, DMF, became apparent. The DMF used had been dried over magnesium sulfate and distilled. Analysis by vpc indicated that it contained as much as 0.1% water. In all subsequent experiments the DMF was heated with calcium hydride and distilled from the hydride.

The three cathode materials which result in bibenzyl formation are metals which normally have an oxide coating, which might be retained, in whole or in part, even under cathodic conditions. To explore the possibility that these oxide coatings might be relevant to the observed bibenzyl formation, aluminum cathodes were preoxidized by treatment with boiling water for 30 min and by anodizing them to 25, 50, and 75 V in an ammonium pentaborate–glycol electrolyte.[9] All four of these cathodes gave results which were essentially the same as that shown in Table I.

Of the cathodes explored in Table I, aluminum and platinum were chosen for more detailed study. When electrolyses were carried out in solutions kept saturated with carbon dioxide, less toluene was obtained at both platinum and aluminum electrodes, and significant amounts of phenylacetic acid were formed. These results are shown in Table II. As long as the electrolysis solution is initially saturated with carbon dioxide, the formation of phenylacetic acid is not controlled by the rate of carbon dioxide diffusion and is independent of the rate at which the gas is passed through the solution. This was demonstrated by a series of experiments in which the carbon dioxide input was varied almost tenfold, from 70 ml/min to 640 ml/min. The amount of phenylacetic acid obtained was essentially constant, but the amount of toluene found did decrease noticeably as the rate of gas addition increased, almost certainly due to entrainment of this latter product by the gas stream.

Table II. Products Obtained in the Electroreduction of 0.05 Mol of Benzyltriethylammonium Nitrate[a]

Cathode	Charge passed, faraday	Moles of product: Toluene	Bibenzyl	Phenylacetic acid
Pt	0.104	0.00113		0.0266
Al	0.104	0.00456	0.0105	0.0116
Al	0.104	0.00326	0.0109	0.0115
Al[b]	0.098	0.0315	0.00225	

[a] At a current of 2.0 A; in dimethylformamide kept saturated with carbon dioxide. [b] In dimethylformamide containing 10% water.

At an aluminum cathode in anhydrous DMF saturated with carbon dioxide, phenylacetic acid is obtained at the expense of the toluene, but the amount of observed bibenzyl is not diminished. This is in accord with expectations, since carbon dioxide will trap a benzyl carbanion but does not react with a benzyl radical. When, as shown in the last experiment in Table II, 10% water is added to the DMF, no phenylacetic acid is obtained, the amount of bibenzyl formed is greatly decreased, and the major product is toluene. That water in relatively high concentration can compete successfully with carbon dioxide for a carbanion is not surprising, but it is significant that, in this experiment, there is also a large decrease in the amount of bibenzyl obtained.

This last observation made it desirable to determine the effect of added water on the course of this electroreduction at both aluminum and platinum. The results from this study are shown in Table III. At an aluminum cathode with increasing amounts of water added, there is a steady decrease in the amount of bibenzyl formed and an accompanying steady increase in the amount of toluene obtained. At platinum, where bibenzyl is never more than a very minor product, small additions of water (up to 3.0%) are without significant effect. With the addition of 6.0% water, the amount of toluene obtained is greatly decreased, and with the addition of 9.0% water, only 3.3% of the salt has been converted to product, despite the fact that enough charge has been passed to convert all of the salt to toluene and triethylamine.

Table III. Effect of Water on the Products Obtained from the Electroreduction of 0.05 Mol of Benzyltriethylammonium Nitrate[a]

Cathode	% water	Charge passed, faraday	Moles of product: Toluene	Bibenzyl
Al	0	0.0808	0.0072	0.0112
Al	1.5	0.0510	0.0167	0.00576
Al	5.0	0.0634	0.0207	0.00466
Al	7.5	0.0796	0.0301	0.00280
Al	10.0	0.0808	0.0321	0.00132
Pt	0	0.104	0.0239	0.00035
Pt	1.5	0.104	0.0264	
Pt	3.0	0.104	0.0252	
Pt	6.0	0.104	0.0158	
Pt	9.0	0.104	0.00163	

[a] In dimethylformamide at a current of 2.0 A.

This large decrease in the conversion of salt to product with ≥6% water added demands that there be a competing cathodic reaction. The most probable such reaction is hydrogen evolution. Rates of hydrogen evolution from these solutions, as a function of added water, were, therefore, determined with both platinum and aluminum cathodes. Aliquots of the total gas evolved during the course of these reductions were taken at appropriate times and analyzed by vpc. The only gas found was hydrogen, the evolution of which followed an unusual pattern.

At a platinum cathode, in anhydrous DMF, the rate of gas evolution is initially low, increases steadily to 215 ml/hr at 0.5 hr, 315 ml/hr at 1.0 hr, and 400 ml/hr at 1.55 hr. As a point of reference it should be noted that, for a constant current of 2.0 A, a hydrogen evolution rate of approximately 950 ml/hr would represent 100% hydrogen generation at the cathode. With 1.3% added water gassing is again slow at the beginning and increases to 245 ml/hr at 0.5 hr, 515 ml/hr at 0.9 hr, and

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(9) Solutions of boric acid and its salts in hydroxylic solvents are commonly used in the anodic formation of oxide films on aluminum. The ammonium pentaborate–glycol combination is especially common.

770 ml/hr at 1.6 hr. With 3.1% added water gassing is initially fast (about 835 ml/hr), decreases to a minimum of 365 ml/hr at 0.25 hr, then increases to 500 ml/hr at 0.75 hr and 660 ml/hr at 1.3 hr. With 9.4% added water, gassing is fast at the start (about 960 ml/hr) and decreases very gradually to 915 ml/hr at 1.0 hr.

At an aluminum cathode, without added water, the rate of hydrogen evolution remains at or near zero for 0.35 hr, then increases to 170 ml/hr at 0.85 hr, then decreases to 70 ml/hr at 1.75 hr. With 2% added water there is little or no gassing for 0.55 hr. Gassing then increases rapidly to 570 ml/hr at 0.70 hr. With 10% added water gassing begins immediately but remains constant at 130 ml/hr for at least 0.45 hr and then rises to 490 ml/hr at 1.0 hr.

The hydrogen evolution behavior is, thus, both complex and varying with time at both cathodes, but it is, at least, clear that a significant amount of the charge passed results in hydrogen generation under all conditions. For example at aluminum, with 10% water added to the DMF, approximately 13.7% of the charge is used in hydrogen generation during the first 0.45 hr (the time required to pass 0.034 faraday of charge). Coulombic yields, based on a two-electron change, for the formation of both toluene and bibenzyl were determined in this system as a function of the charge passed. Total yield (per cent) of these two products decreases somewhat as total charge increases. This is consistent with the observed gassing behavior, and the total product, toluene, bibenzyl, and hydrogen, accounts for all of the charge passed, within a reasonable estimate of experimental error.

In systems containing added water the source of the observed hydrogen poses no problem. In DMF, dried over and distilled from calcium hydride, it is clear that some of the hydrogen arises from a source other than water. Triethylamine is formed in the reduction reaction. Oxidation of this product at the anode leads to alkylammonium ions,[10,11] which are possible precursors of the observed hydrogen.

Finally, the effect of varying the anion of the benzyltriethylammonium salt was explored briefly, using fluoroborate, nitrate, and bromide. The course of this reduction is essentially independent of the anion.

Experimental Section

Materials. The preparation of benzyltriethylammonium nitrate has been described.[12] Benzyltriethylammonium fluoroborate was prepared by treating an aqueous solution of the bromide with 50% fluoroboric acid. The precipitate which formed was crystallized from acetone–ether; mp 113–115°. *Anal.* Calcd for $C_{13}H_{22}BF_4N$: N, 5.02. Found: N, 4.99. DPI, white-label DMF was stirred with anhydrous magnesium sulfate and distilled at water-pump pressure. A middle cut, bp 44° at 10 mm, was used. To effect further drying, the above DMF was stirred with calcium hydride at 70–80° for 2 hr and distilled from the calcium hydride at water–pump pressure, a middle cut being taken.

Electrolyses. The electrolysis cell for the experiments in Tables I and II was a water-jacketed, 200-ml beaker fitted with a magnetic stirring bar, a thermometer, and a Teflon cover to which was attached the appropriate electrode assembly. In the experiments with a platinum cathode, the electrodes were two pieces of platinum, 0.025 cm thick and 2.5 cm wide immersed to a depth of 5 cm and at a separation of 2 cm. When an aluminum cathode was used, the platinum electrode was replaced with an aluminum one, made from 0.02-in. 99.999% super Raffinal aluminum from AIAG Metals, Inc., Zurich, Switzerland, and having the same dimensions and separation from the anode. The same procedure was used for magnesium and tantalum cathodes. When a carbon cathode was used, the above two platinum electrodes were interconnected to form a dual anode, and a carbon rod (a spectroscopic electrode from National Carbon Company), 0.6 cm in diameter and immersed to a depth of 5 cm, was placed between them as the cathode. The mercury cathode was a 0.5-in. pool of mercury placed at the bottom of the electrolysis cell. Electrical connection was made *via* a small piece of platinum sealed in glass. The accompanying anode was a 0.04-in. diameter platinum wire dipped into the solution. When the electrolysis was conducted in a solution saturated with carbon dioxide, the gas was admitted through a capillary tube adjacent to the cathode. In each experiment, benzyltriethylammonium nitrate (12.7 g; 0.05 mol) in DMF (150 ml) was electrolyzed at the currents and for the times indicated in Tables I and II. Current was provided by a variable-voltage power supply.

For the aluminum experiments in Table III the cell described above was used. For the experiments shown in Table III using a platinum cathode, the electrolysis cell was a water-jacketed cylinder, 13.5 cm in length and 4.5 cm in diameter. Two outer joints, one 45/50 and one 24/40, were sealed to the top of the cell chamber. Two platinum electrodes, 9 × 3 cm at a separation of 1.5 cm, were sealed in a 45/50 inner joint and positioned in the cell such that the electrodes extended to within 2.5 cm of the bottom of the cell chamber. A gas inlet tube, with a fritted glass disk at the bottom to disperse the gas, was sealed into this same joint and positioned between the two electrodes. The 24/40 joint was fitted with an efficient, glass-coil reflux condenser, and a magnetic stirrer was used to mix the electrolysis solution.

In determining the products, the electrolysis solution was taken up in water (1 l.), NaCl and concentrated hydrochloric acid (100 ml) were added, and the solution was extracted with four 250-ml portions of ether. The combined ether extracts were washed with two 100-ml portions of water, then with saturated sodium bicarbonate solution (200 ml) and finally dried over magnesium sulfate. The ether solution was concentrated to 50 ml for analysis, and toluene was determined, both in this solution and in the ether distillate obtained in preparing it.

In the experiments with carbon dioxide added, the bicarbonate wash was omitted, and three additional 100-ml water washes were substituted. The ether solution was concentrated to 50 ml as before and analyzed for toluene and bibenzyl. The ether and toluene were then removed with the water pump. The residue was taken up in ether (200 ml) and extracted three times with 100-ml portions of 5% sodium hydroxide solution. The basic extract was washed with ether, acidified with concentrated hydrochloric acid (50 ml), and extracted with three 150-ml portions of ether. The ether solution was dried, the ether was removed, and the residue was crystallized from hexane to give phenylacetic acid; mp 72–74°. A mixture melting point with authentic acid showed no depression. The infrared spectrum of this material was identical with that of authentic phenylacetic acid.

The vpc analyses for toluene and bibenzyl were made using a Perkin-Elmer large diameter Golay column of 0.06 in. i.d. and 300-ft length in which the stationary phase was Ucon polyglycol LB-550-X. The unknown solutions were compared with standards prepared from the identified components.

Gas Measurements. Rates of gas formation were measured using both aluminum and platinum cathodes in solutions of various water concentrations. The previously described water-jacketed 200-ml beaker and water-jacketed large cylinder were used as cells for these measurements. The 200-ml beaker was used with aluminium cathodes and had a large rubber stopper fitted with the aluminum cathode, a platinum anode, and a glass capillary tube which was connected to a gas buret. The 2.5-cm wide electrodes were immersed to a depth of 6 cm. For experiments with platinum cathodes, the larger cylinder was used, with the same 9 cm × 3 cm electrodes described previously. This cell had an outlet through which gas could be led to the buret.

All electrolyses were conducted at 2.0 A, all solutions contained 12.7 g (0.05 mol) of benzyltriethylammonium nitrate, and the total volume of solvent (water and DMF) was either 150 ml (with aluminum) or 160 ml (with platinum). The gas collected was analyzed by vpc using a silica gel column and nitrogen carrier gas.

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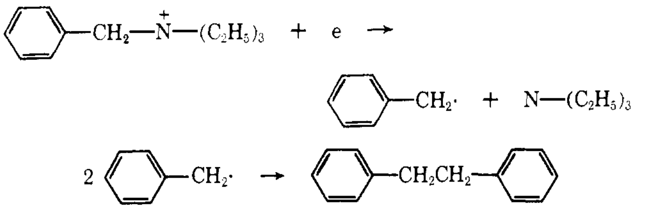
Discussion

Depending on the choice of cathode metal, the electroreduction of benzyltriethylammonium nitrate in DMF follows one of two reaction modes. In the first, exemplified by the reaction at platinum, the major product is toluene, and no more than trace amounts of bibenzyl are obtained. In the second reaction mode, of which the reaction at aluminum is an example, bibenzyl is the chief product, but toluene is also formed in significant amounts.

The mechanism by which bibenzyl is obtained, in the reaction at aluminum, is straightforward. This product can arise only from coupling of benzyl radicals, generated in the primary electrode process.[1] The reactions are as shown below.



The toluene obtained in this reaction is not *all* formed by benzyl radicals abstracting hydrogen atoms from either solvent or substrate.[2] When the same reduction is effected in a solution kept saturated with carbon dioxide, there is no decrease in the amount of bibenzyl obtained (*cf.* results in Tables I and II), but the amount of toluene produced decreases by at least 64%, and phenylacetic acid is formed in its stead. This formation of a carboxylic acid during an electroreduction in the presence of carbon dioxide is diagnostic of a carbanionic intermediate,[5–8] since, while carbon dioxide will trap a carbanion, it will not react with a benzyl radical, as evidenced by the failure to observe any diminution in the amount of bibenzyl obtained in the reaction with carbon dioxide present. It follows, therefore, that most of the observed toluene has its genesis in a benzyl carbanion, generated at the cathode either by a single two-electron transfer or two consecutive one-electron transfers.

The toluene obtained in the reaction with carbon dioxide present, which represents as much as 36% of the amount observed in the absence of carbon dioxide, may also arise from a benzyl carbanion, which could abstract a proton from the salt, the solvent, or traces of water present in the system. This is, however, not certain, and it is possible that this toluene has its origin in a benzyl radical, which abstracts a hydrogen atom from the solvent or the salt.

The experiments with water added (Table III) point to another, perhaps more probable, source for this toluene. As increasing amounts of water are added in the reaction at aluminum, more and more toluene and less and less bibenzyl are obtained. Moreover, with 10% water added in a solution kept saturated with carbon dioxide, no phenylacetic acid is formed. This last result is not surprising, since water, in relatively high concentration, would be expected to compete favorably with carbon dioxide for a carbanion. The progressive decrease in bibenzyl as the water concentration increases is significant. This cannot be due to hydrogen abstraction from water by benzyl radicals, since such abstraction would be energetically unfavorable compared to hydrogen atom abstraction from either the solvent or the cation. These reductions are accompanied by some hydrogen evolution at the cathode, and the rate of this hydrogen evolution increases with increasing water concentration. It, therefore, follows, with considerable probability, that the observed decrease in bibenzyl production and increase in toluene formation are the results of cross-coupling of benzyl radicals and hydrogen atoms, generated simultaneously at the cathode. Furthermore, since hydrogen evolution is significant even in systems containing no added water, it is highly probable that some of the toluene obtained in these relatively anhydrous reactions is also due to this cross-coupling reaction.

In the reaction at a platinum cathode, the amount of bibenzyl produced is virtually negligible, and toluene is the major product. When the reduction is carried out in a solution kept saturated with carbon dioxide, less than 5% of the amount of toluene observed in the absence of carbon dioxide is obtained, and the major product is phenylacetic acid. At platinum the predominant reactive species generated in the initial electrode process is the benzyl carbanion. With increasing additions of water less and less toluene is produced, until, with 9.0% water added, less than 5% of the charge passed is used in reducing the quaternary ammonium cation. At this electrode, in the presence of water, there is competition between reduction of the benzyltriethylammonium cation and the hydrogen evolution reaction, and at water concentrations above 3% the hydrogen evolution reaction is favored.