Reactions of Anodically Generated Radicals with Oxygen

John E. Barry, Manuel Finkelstein, Edward A. Mayeda, and Sidney D. Ross*

Contribution from the Research and Development Center, Sprague Electric Company, North Adams, Massachusetts 01247. *Received May 3, 1976*

Abstract: When a Kolbe acid oxidation is carried out with a constant stream of oxygen passing through the solution, the electrogenerated alkyl radicals are, in part, captured by oxygen to yield dialkyl peroxides, aldehydes or ketones, and alcohols as final products. The close parallelism between the behavior of the radical intermediates in these reactions and their behavior in homogeneous autoxidation reactions suggests that the electrode is without significant influence and that the major locus of reaction is the solution rather than the electrode surface.

This work was initiated to verify a previously made suggestion[1,2] that the benzaldehyde obtained in the anodic oxidation of phenylacetic acid results from the reaction of benzyl radicals with oxygen, either dissolved in the solution or produced at the anode. A comparison of the products obtained on anodic oxidation of phenylacetic acid in an oxygen atmosphere with those obtained in a nitrogen atmosphere attested to the validity of Utley's[1,2] hypothesis. In addition, these exploratory experiments suggested that a study of other Kolbe oxidations in oxygen atmospheres would lead to useful results.

The many studies of autoxidation[3] provide an extensive body of data describing the reactions of free radicals with oxygen. The autoxidation of a hydrocarbon is a chain reaction, usually initiated by decomposition of a peroxide or an azo compound, in which the propagation steps are reactions 1 and 2 and the termination steps are reactions 3 and/or 4 and/or 5. In the Kolbe oxidation in the presence of oxygen, radicals are formed electrochemically by reaction 6. The radicals thus formed will react with oxygen as in reaction 1, but there is no hydrocarbon comparable to RH and, therefore, no reaction comparable to reaction 2. An essential chain-propagating step is lacking, and reactions 3, 4, and 5, which are still possible, may result in final products in a nonchain process.

$$\mathrm{R\cdot + O_2 \rightarrow ROO\cdot} \quad (1)$$

$$\mathrm{ROO\cdot + RH \rightarrow ROOH + R\cdot} \quad (2)$$

$$\mathrm{2ROO\cdot \rightarrow \text{nonradical products}} \quad (3)$$

$$\mathrm{ROO\cdot + R\cdot \rightarrow \text{nonradical products}} \quad (4)$$

$$\mathrm{2R\cdot \rightarrow \text{nonradical products}} \quad (5)$$

$$\mathrm{RCOO^- \rightarrow e + CO_2 + R\cdot} \quad (6)$$

The anodic oxidations in an oxygen atmosphere permit some inferences as to the probable locus of reaction of anodically generated free radicals. The question of whether these reactive intermediates are transformed into products while still adsorbed on the electrode[4] or after desorption from the electrode into the solution[5] is still controversial and incompletely resolved.

The anodic oxidation of three acids, phenylacetic acid, hexanoic acid, and 2-ethylhexanoic acid, has been studied in both nitrogen and oxygen atmospheres. The changes in product composition with changes in the gas atmosphere, in the current density and in the reaction temperature, permit some useful conclusions as to the mechanisms of the reactions involved.

Results

Table I lists the products formed in the electrolysis at platinum electrodes of 0.1 mol of phenylacetic acid in 67% methanol–33% pyridine after passage of 0.2 F of charge at a constant current of 1 A. The electrooxidations were carried out both in a solution kept saturated by a constant stream of nitrogen and in one kept saturated in similar fashion with oxygen.

The results in a nitrogen atmosphere are in essential agreement with those previously reported from these laboratories.[6] With air and oxygen excluded no benzaldehyde is formed. The two major products are bibenzyl, produced from an electrogenerated benzyl free radical, and benzyl methyl ether, a product resulting from a benzyl cation. Reactions 7 and 8 provide probable routes to both methyl phenylacetate and the benzyl alcohol obtained in the absence of oxygen.

$$\mathrm{C_6H_5CH_2^+ + C_6H_5CH_2COO^- \rightarrow C_6H_5CH_2COOCH_2C_6H_5} \quad (7)$$

$$\mathrm{C_6H_5CH_2COOCH_2C_6H_5 + CH_3OH \rightleftharpoons C_6H_5CH_2COOCH_3 + C_6H_5CH_2OH} \quad (8)$$

When the electrolysis was carried out in an oxygen atmosphere, the amount of bibenzyl produced was greatly reduced, and the major products were benzyl methyl ether, benzaldehyde, and benzyl alcohol. In this system all of the aldehyde and probably most of the alcohol result from the capture of benzyl radicals by oxygen and the further reactions of the benzylperoxy radicals so formed.

Phenylacetic acid is not a good choice of substrate for a study of the capture of anodically generated radicals by oxygen, since benzyl free radicals and benzyl cations are generated at the anode in nearly equal amounts. The electrooxidation of hexanoic acid in methanol (Table II) provides a much more straightforward example. With nitrogen passing through the solution the only significant product was *n*-decane, obtained in a yield of approximately 50%. Moreover, both the product yields and compositions are insensitive to changes in current density.

With oxygen passing through the solution the amount of *n*-decane produced was greatly diminished, and at the lowest current density studied, its formation was completely suppressed. Three new products, di-*n*-amyl peroxide, *n*-pentanal, and *n*-amyl alcohol, were obtained in amounts that varied with varying current density.

The data in Table III provide very similar results for the anodic oxidation of 2-ethylhexanoic acid in methanol. With nitrogen passing through the solution the only significant product is the dimer, 5,6-diethyldecane, formed in approximately 25% yield at all current densities studied. With oxygen passing through the solution, dimer formation is greatly diminished, and di-3-heptyl peroxide, 3-heptanone, and 3-heptanol become significant products. In this case, too, the yields

Table I. Products Formed in the Electrolysis of 0.1 mol of Phenylacetic Acid in 67% Methanol–33% Pyridine after Passage of 0.2 F of Charge at a Current of 1 A

Product	mol obtained	
	In nitrogen	In oxygen
Benzaldehyde		0.0149
Benzyl alcohol	0.0056	0.0148
Benzyl methyl ether	0.0180	0.0146
Methyl phenylacetate	0.0092	0.0057
Bibenzyl	0.0173	0.0071
Benzyl phenylacetate		0.0012

Table II. Products Formed in the Electrolysis of 0.1 mol of Hexanoic Acid in Methanol after Passage of 0.2 F of Charge

Product	mol obtained		
	At 2 A	At 1 A	At 0.2 A
A. In a Nitrogen Atmosphere			
n-Decane	0.0270	0.0255	0.0240
Methyl hexanoate	0.0015	0.0019	0.0008
B. In an Oxygen Atmosphere			
Di-*n*-amyl peroxide	0.0086	0.0120	0.0056
n-Pentanal	0.0018	0.0084	0.0426
n-Amyl alcohol	0.0057	0.0078	0.0209
n-Decane	0.0165	0.0090	
Methyl hexanoate	0.0009	0.0008	0.0014

Table III. Products Formed in the Electrolysis of 0.1 mol of 2-Ethylhexanoic Acid in Methanol after Passage of 0.2 F of Charge

Product	mol obtained			
	At 2 A	At 1 A		At 0.2 A
A. In a Nitrogen Atmosphere				
5,6-Diethyldecane	0.0129	0.0125		0.0126
3-Heptanol	0.0008	0.0009		0.0004
B. In an Oxygen Atmosphere				
		At 20 °C	At −75 °C	
Di-3-heptyl peroxide	0.0069	0.0086	0.0022	0.0017
3-Heptanone	0.0025	0.0054	0.0120	0.0342
3-Heptanol	0.0049	0.0048	0.0040	0.0141
5,6-Diethyldecane	0.0051	0.0033	0.0002	

of the three new products are strongly dependent on the current density.

With one exception, these results were obtained in a water-cooled cell in which the actual reaction temperature was approximately 20 °C. In these experiments it is at least possible that the dialkyl peroxides are the primary products and that the ketones and alcohols result from peroxide decomposition at the reaction temperature. To test the above possibility the electrolysis of 0.1 mol of 2-ethylhexanoic acid in methanol at a current of 1 A was carried out at −75 °C with oxygen passing through the solution. The result, shown in Table III, is to be compared with the result at 1A. A lesser yield of di-3-heptyl peroxide is actually obtained at the lower temperature. It may, therefore, be concluded that the peroxide is relatively stable at 20 °C and that the ketone and alcohol do not arise primarily from peroxide decomposition. It should also be noted that at the lower temperature the oxygen solubility and concentration are significantly increased.

Discussion

A comparison of the products obtained on Kolbe oxidation of carboxylate anions in nitrogen and oxygen atmospheres demonstrates that anodically generated free radicals can be captured by oxygen. In the case of phenylacetic acid (Table I) the new products that result are benzaldehyde and benzyl alcohol. With hexanoic acid (Table II) and 2-ethylhexanoic acid (Table III) the reactions with oxygen lead to dialkyl peroxides as well as aldehydes or ketones and alcohols.

The experiments in Tables II and III were carried out at three different constant currents, 2, 1, and 0.2 A. With both carboxylates the maximum yields of aldehyde or ketone and alcohol were obtained at the lowest current density and the maximum yields of dialkyl peroxides were obtained at the intermediate current density.

The maximum possible rates at which the radicals are generated in these systems are determined by the current. Assuming that the only electrode reaction is a one-electron transfer to form an alkyl radical and that this reaction is 100% efficient, the maximum rates of production of radicals are 2×10^{-5} mol s^{-1} at 2 A, 1×10^{-5} mol s^{-1} at 1 A, and 2×10^{-6} mol s^{-1} at 0.2 A. For the most part the experiments with oxygen were at approximately 20 °C in a methanol solution kept saturated with a constant stream of gas. From the known solubility of oxygen in methanol at 19 °C[7] these experiments are all at a constant oxygen concentration of approximately 7.8×10^{-3} M.

A tenfold variation in the rate of free-radical production at constant oxygen concentration results in very significant changes in the spectrum of observed products. In the anodic reactions the rate of radical production is very high, and the radicals are concentrated near the anode. Little or no chain reaction is involved. Nevertheless, the final products result from the three termination reactions, 3, 4, and 5, common to autoxidation chain reactions.

The dimers result from coupling of alkyl radicals, reaction 5; the peroxides are formed by cross-coupling of alkyl radicals with alkylperoxy radicals, reaction 4; the aldehydes or ketones and alcohols originate primarily from decomposition of alkylperoxy radicals, reaction 3.

The parallelism between the present anodic oxidations and autoxidation reactions is striking. The latter reactions have been run at constant rates of radical initiation but variable oxygen pressures.[3b] At the lowest oxygen pressure, where the ratio $[R\cdot]/[O_2]$ is highest, termination is largely by reaction 5 and dimer is a major product. At the highest oxygen pressure, the chief termination mode is reaction 3, and the final products are those resulting from decomposition of alkylperoxy radicals. At intermediate oxygen pressures reaction 4 is important, and dialkyl peroxides are formed.

In the present study the rates of alkyl radical generation were varied at constant oxygen concentration. The effect is to vary the ratio of available alkyl radicals to oxygen. The products at the highest current in the electrochemical reaction correspond to those obtained at the lowest oxygen pressure in autoxidation, at the lowest current the products arise mainly from decomposition of alkylperoxy radicals, and at intermediate currents dialkyl peroxide formation is favored.

There thus appears to be little or no distinction between the behavior of the reactive intermediates in autoxidation and the behavior of the same intermediates generated in the anodic oxidation. The electrode is without discernible influence, and the following picture of the Kolbe oxidation with oxygen passing through the solution emerges.[8] Alkyl radicals are generated at the anode either in a two-step process in which a carboxylate anion transfers an electron to give an adsorbed acyloxyl radical, which then decarboxylates and desorbs spontaneously, or in a single step in which electron transfer is

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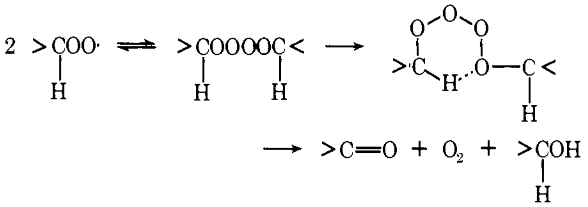
concerted with desorption and decarboxylation. The alkyl radicals, so formed, react rapidly with one another, with oxygen, or with alkylperoxy radicals. These reactions occur in the solution as the alkyl radicals are diffusing away from the anode, but because of the many rapid reactions involved, the electrogenerated alkyl radicals react before they penetrate any great distance into the solution. The most reasonable locus for the reactions of these radicals is the solution, and this is supported by the parallelisms between the behavior of radicals in the electrochemical system and in the homogeneous autoxidation reaction.

The generally accepted mechanism for the self-reaction of primary and secondary peroxy radicals is due to Russell[9] and may be represented as shown in reaction 9, where the oxygen


(9)

is in the singlet state. This mechanism has received strong support from more recent studies.[10-13] It predicts the formation of equivalent quantities of aldehyde or ketone and alcohol, but the electrochemical experiments indicate a preference for alcohol formation at the higher current densities and for aldehyde or ketone formation at the lower current densities. Control experiments indicate that the alcohol and aldehyde or ketone are neither selectively oxidized nor reduced at the various current densities. There are several possibilities to explain the variation of the product distribution with current density, but the present results do not provide a basis for choice.

Experimental Section

Materials. DPI white label phenylacetic acid was used without further purification. Hexanoic acid was distilled at the water pump, and a middle cut, bp 92 °C (10 mm), was taken. 2-Ethylhexanoic acid was distilled at the water aspirator, and a middle fraction, bp 119-120 °C (15 mm), was taken. The determined neutralization equivalent of this material was 144.7, compared to a calculated value of 144.2.

Electrolyses. The electrolysis cell for the experiments with hexanoic acid and with 2-ethylhexanoic acid was a water-jacketed cylinder, 13.5 cm long 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 2.5 cm, were sealed in a 45/50 inner joint, which could be positioned in the cell so that the electrodes extended to within 3 cm of the bottom of the cell chamber. An outer 14/20 joint was sealed to the joint holding the electrodes at a position midway between the electrodes. An 8-mm glass tube, fitted with an inner 14/20 joint, was terminated by a coarse, sintered glass bubbler, which extended to slightly below the electrodes. The 24/40 joint at the top of the cell was fitted with a condenser, and a magnetic stirrer was used to mix the electrolysis solution. In the electrolysis conducted at −75 °C the water-jacketed cell was replaced by a nonjacketed tube, 17 cm long and 4.5 cm in diameter, which had 45/50 and 24/40 joints sealed to the top. The reaction temperature was controlled by immersing the cell in a container of dry ice-acetone. The electrolysis solutions were prepared by reacting 0.5 g (0.0217 g-atom) of sodium with 100 ml of methanol and adding a solution of 0.1 mol of the carboxylic acid in 70 ml of methanol.

For the electrolysis of phenylacetic acid the cell was a water-jacketed 200-ml beaker fitted with a magnetic stirring bar and a Teflon cover to which was attached the electrode assembly. The electrodes were two pieces of platinum, 0.025 cm thick and 2.5 cm wide, immersed to a depth of 6 cm and at a separation of 2.5 cm. To permit introduction of the appropriate gas a length of 7-mm glass tubing, terminating in a coarse, sintered glass frit, was fitted through a hole in the Teflon cover midway between the electrodes. The tube, which was connected through a reducing valve to a source of gas, extended almost to the bottom of the cell. The electrolysis solution was prepared by reacting 0.5 g (0.0217 g-atom) of sodium with 100 ml of methanol and adding a solution of 0.1 mol of the carboxylic acid in 50 ml of pyridine.

In each electrolysis the appropriate gas was passed through the stirred, cooled solution for approximately 0.5 h before passage of current was initiated, and the gas stream was maintained throughout the electrolyses. At the end of the electrolysis the solution was removed from the cell and weighed, and a weighed aliquot was retained for analysis.

Analytical Methods. The oxidation products from phenylacetic acid were determined on a Varian 2720 gas chromatograph, using a thermal conductivity detector and helium as the carrier gas. The column was 6 ft × 0.25 in. stainless steel containing 10% SE30 on 60-80 mesh Chromosorb W. The equipment was programmed from 70 to 125 °C at 6 °C/min and from 125 to 225 °C at 20 °C/min and then held at 225 °C until all products were eluted. The injection port and the detector were at 240-250 °C, and the detector current was 150 mA.

The products from the electrolysis of hexanoic acid in the presence of nitrogen were analyzed on an F&M Model 720 gas chromatograph using a thermal conductivity detector with helium as the carrier gas. The column was 6 ft × 0.25 in. stainless steel containing 10% poly(*m*-phenyl ether) (six ring) on 60-80 mesh Diataport S. The column temperature was 80 °C and the injection port was at 210 °C with the detector at 225 °C. The *n*-amyl peroxide from the electrolysis in the presence of oxygen was determined on the Varian 2720 using the SE30 column at 140 °C with injection port and detector at 150 °C. The other products from these electrolyses were analyzed on the Varian 2720 using a 6 ft × 0.25 in. stainless steel column containing 10% poly(*m*-phenyl ether) (six ring) on 80-100 mesh Chromosorb W. A solution of *n*-amyl peroxide in methanol showed no decomposition to aldehyde and alcohol under these conditions.

The products from the electrolysis of 2-ethylhexanoic acid were analyzed on the Varian 2720 gas chromatograph. For the nitrogen experiments the SE30 column was used at 140 °C. For the oxygen experiments a 6 ft × 0.25 in. stainless steel column containing 10% Carbowax 20M on 80-100 mesh Chromosorb W was used at 90 °C with the injection port and detector at 150 °C. A solution of 3-heptyl peroxide in methanol showed no decomposition to ketone and alcohol under these conditions.

In all of the analyses unknowns were compared against known solutions containing weighed amounts of all of the solution components.

An appreciable amount of heptane was detected in the electrolysis solution from 2-ethylhexanoic acid. Due to its volatility and the great probability that significant amounts of it were entrained in the stream of gas passed during the electrolysis, no quantitative analyses were attempted.

Isolation of 5,6-Diethyldecane. The solutions from three separate electrolyses of 2-ethylhexanoic acid under nitrogen were combined, and the methanol was removed at atmospheric pressure, using a Vigreux column. The residue was dissolved in a large volume of water containing 5 g of sodium hydroxide and extracted twice with ether. The ether extract was dried over magnesium sulfate, and the ether was distilled at atmospheric pressure. The residue was distilled at 16 mm, and a fraction of bp 93-100 °C was retained. This was redistilled two additional times, and a main fraction, bp 120 °C (11 mm), was obtained. The infrared spectrum of this sample was identical with that of a sample of the dimer separated by preparative VPC from a solution from the electrolysis of 2-ethylhexanoic acid in the presence of oxygen.

The NMR spectrum in $CDCl_3$ was consistent with the dimer structure and showed three broad absorptions at δ 1.60, 1.25, and 0.90. The proximities of the methine and methylene adsorptions made integration difficult. The found ratio was 1/20 whereas the theoretical value is 1/14.

Di-*n*-amyl Peroxide. The synthesis and physical properties were as previously reported.[14,15] The VPC retention time and infrared spectrum were identical with that of a sample isolated by VPC from an electrolysis experiment.

Di-3-heptyl Peroxide. The synthetic method has been reported.[14,15] The yields of 3-heptyl methanesulfonate [bp 81-83 °C (0.15 mm)] and of the peroxide [bp 55 °C (0.15 mm)] were 60 and 1%, respectively. The NMR spectrum in $CDCl_3$ showed absorptions at δ 1.0 and 1.5 (14 H, multiplet) and δ 3.9 (1 H, multiplet). The chemical shifts were the same as those recorded for an authentic sample of di-*n*-butyl peroxide. The infrared spectrum, taken neat, had absorption peaks at 3.40, 6.85, 7.20, 7.50, 8.90, and 10.5 μm. The peroxide gives a positive potassium iodide test and has a VPC retention time identical with that of a sample isolated from the electrolysis of 2-ethylhexanoic acid.

The peroxide was also obtained electrochemically. Sodium (1.5 g) was reacted with 150 ml of methanol, and 2-ethylhexanoic acid (52 g) was added. The solution was continuously saturated with oxygen and subjected to anodic oxidation at 1.0 A for 16 h. Water (100 ml) was added, and the resultant solution was extracted with four 125-ml portions of hexane. The hexane was dried over magnesium sulfate. After filtration the solvent was removed, and the residue was distilled yielding 6.0 g (7.2%) of the peroxide, bp 55–57 °C (0.15 mm). Analysis by VPC on a 6 ft × 0.25 in. SE30 on Chromosorb W column indicated the sample was contaminated with approximately 5% of 5,6-diethyldecane. Nevertheless, this sample was used in preparing analytical standards for determining peroxide yields.

The peroxide was shown to yield 3-heptanone and 3-heptanol on thermal decomposition as follows. A solution obtained from the electrolysis of 2-ethylhexanoic acid in the presence of oxygen was worked up in the described manner for the isolation of 5,6-diethyldecane. The high boiling residue was analyzed on an SE30 column at 140 °C and on a Carbowax column at 80 °C and shown to contain 5,6-diethyldecane, di-3-heptyl peroxide, 3-heptanone, and 3-heptanol. The product was sealed in a heavy walled glass tube and kept at 160 °C for 18 h. Analysis by VPC on the same two columns now showed the absence of di-3-heptyl peroxide, an unchanged amount of dimer, and a large increase in the amounts of 3-heptanone and 3-heptanol.

Thermal Stabilities of the Peroxides. The thermal stabilities were investigated qualitatively using VPC. By varying both the column temperatures and injection port temperatures, it was determined that both peroxides were reasonably stable at temperatures below 150 °C. At temperatures above 150 °C there was definite conversion of peroxide to aldehyde or ketone and alcohol. All VPC analyses were performed at temperatures below 150 °C. As a further safeguard the peroxide peaks for the standard solutions were matched as closely as possible to the peaks in the electrolysis solutions. In this manner, if decomposition does occur, the same amount occurs in both the known and unknown solution.

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Plasmolysis of 2-Butene

J. G. Huntington and L. L. Miller*[1]

Contribution from the Department of Chemistry, Colorado State University,
Fort Collins, Colorado 80523.

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Abstract: The reaction of *cis*- and *trans*-2-butene in a glow discharge was studied. The discharge was sustained with a 13.6-MHz radio frequency generator. The reactant at pressures from 0.01–10 Torr was flowed through the discharge region, and the products were collected and analyzed by gas chromatography. Under conditions which produce a low conversion rate (high pressure or low power), the exclusive products from *cis*-2-butene are *trans*-2-butene and 1-butene. Under conditions which give a high extent of reactant conversion (low pressure or high power), a different reaction channel producing propylene, acetylene, and ethane becomes favorable. It is suggested that the low conversion conditions produce electronically excited 2-butene by electron impact. Under lower pressure or higher power conditions more energetic electrons are available and produce more energetic intermediates. Plasmolysis of *trans*-2-butene gave *cis*-2-butene and 1-butene at low conversions and propylene, acetylene, and ethane under conditions producing high conversion. Experiments with added helium and argon (10 Torr) gave very similar results. It is shown, however, that isomerization is more favorable under these conditions. The negligible effects of added cyclohexane, naphthalene, and triethylamine demonstrate that $C_4H_8{\cdot}^+$ is not a trappable intermediate on the reaction pathway.

Recent studies, especially those by Suhr and co-workers,[2a] have demonstrated a number of unique and moderately high yield organic reactions which take place in a radio frequency discharge. This technique is interesting to us because it promises to provide a source of unusual intermediates, e.g., ions, in quantities sufficient for synthesis applications. There is, however, so little knowledge of the mechanism of reactions under these conditions that it is difficult to explore these possibilities in a rational fashion.

The basic mechanism for sustaining a discharge is established. It is known that a plasma, an ionized gas, exists in the discharge region, and it is accepted that organic molecules are primarily activated by electron impact.[2-5] Since conditions in the plasma are sufficiently energetic to ionize molecules, a wide variety of ions, radicals, and excited species are acceptable a priori intermediates. Indeed, the major mechanistic task is to design suitably discriminatory tests to determine which of these intermediates is actually along the reaction pathway.

The present investigation pertains primarily to the origin of products from 2-butene plasmolysis. Although the product mixture was at first disappointingly complex, it is a useful system to study because considerable complementary data