

Anodic Oxidation of Anthracenes and Related Compounds

Part II. Applications of Constant Current Coulometry

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The usefulness of constant current coulometry and preparative electrolysis in electro-organic studies was demonstrated. Precise coulometric n values were obtained for the anodic oxidation of anthracene in acetonitrile containing ethanol using three different methods for detecting the end-point. The use of low current densities was shown to result in nearly constant potentials throughout the major portion of the reaction with a sharp change in potential occurring only at the very end of the oxidation. The low cost of equipment and the ease of application of the method makes constant current electrolysis an attractive alternative to the more commonly used method, controlled potential electrolysis.

Coulometry¹ is one of the most useful electro-analytical techniques which can be applied to the study of organic electrode processes. A knowledge of the number of electrons involved in an electrochemical reaction may be of great value in suggesting possible product structures and ruling out others. The n value must be taken into account when suggesting mechanisms for electrochemical reactions.

Controlled potential coulometry has been applied extensively to the study of organic electrode reactions. Determination of n values is accomplished by integration of current-time curves either manually or by suitable electronic devices. Bard and co-workers have applied the method to determination of rates of follow-up chemical reactions.²

With the recent commercial development of moderately priced potentiostats, the number of organic electrochemical studies appearing in the literature has greatly increased. Practically all recent coulometric investigations of organic electrode processes have employed the controlled potential method. A notable exception is the constant-current coulometric determination of phenothiazine in acetonitrile solution.³ Constant current coulometric determina-

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tions, better known as amperimetric titrations, have been used extensively for analysis purposes and give very accurate analytical results.^{1a}

The purpose of this paper is to emphasize the utility of constant current methods, coulometry and macro-scale electrolysis, in the study of organic electrode processes. Highly accurate coulometric n values can be obtained using inexpensive apparatus and constant current macroscale electrolysis can be conducted in such a manner that a constant potential is also maintained. However, one gets quite a different opinion from the recent literature. In a review of anodic oxidation of organic compounds, controlled potential electrolysis carried out with a potentiostat was said to be "far more suitable and elegant" than the constant current electrolysis.⁴

Constant current coulometry and macro-scale electrolysis have been used extensively in studies of anodic oxidation of anthracene and related compounds. In this paper the method used is described in detail and examples of applications dealing with the anodic oxidation of anthracene in acetonitrile containing ethanol are given. This reaction has been shown to result in the formation of bianthrone as the major product.⁵ A more recent coulometric investigation led to the conclusion that the anode process is a two electron oxidation to 9-anthrone which is converted to bianthrone in a chemical step during isolation.⁶ This interpretation has been questioned, and the mechanism, supported by controlled potential coulometric data, was proposed to involve three electron anodic oxidation to the observed product, bianthrone.⁷

RESULTS AND DISCUSSION

In order to apply the technique of constant current coulometry it is necessary to accurately establish (1) the quantity of charge passed at the working electrode and (2) the time at which the reaction is complete. The quantity of charge passed is simply the time multiplied by the current intensity. Accurate methods of current control and measurement required for analytical application have been summarized.^{1a} It is frequently more difficult to achieve a high degree of accuracy in determination of the end point of the reaction. In this work three methods were used to determine the time at which the reaction has run to completion. The potentiometric method involved recording the potential of the working electrode (*vs.* SCE) as a function of time with a strip chart recorder. The end-point was taken as the point on the steep rising portion of the curve where the slope has the greatest value (Fig. 1). This is similar to the method used by Kuwana⁸ for measurement of chronopotentiometric transition times. The amperimetric method involved peak voltammetry at measured time intervals and extrapolating the current-time curve (Fig. 2) to zero current to determine the endpoint.* The gas chromatographic method involved withdrawing samples of the electrolysis solution at measured time intervals and extrapolating the concentration-time curve (Fig. 3) to zero concentration. All three methods applied to the oxidation of

* Attempts to record continuous current-time curves using a rotating platinum electrode were not successful for the oxidation of anthracene due to electrode filming. It is necessary to clean the electrode surface before every measurement.

anthracene (0.050 mmoles) in acetonitrile (40 ml) containing ethanol (100 mM) and sodium perchlorate (0.5 M) at a constant current of 50.0 mA are illustrated in Figs. 1–3.

Amperimetric method. The time required to pass 3.00 Faradays per mole of anthracene during the anodic oxidation of 0.05 mmoles of substrate at a constant current of 50.0 mA is 4.83 min. The electrolysis was stopped at 0.50 min intervals and the peak current at a platinum electrode during peak voltammetry was recorded. Thus, voltammograms were recorded nine times for each coulometric experiment. The coulometric n value can be determined from any one of these determinations. In effect, each coulometric experiment gave nine n values. This is in contrast to conventional controlled potential coulometry which gives only one value, that at complete reaction.* Column 4 in Table 1 gives five n values obtained from plotting the voltammetric peak current as a function of time (Fig. 2a). Excellent reproducibility for the five runs was observed (3.02 ± 0.01 Faradays/mole). The amperimetric method is a very precise and convenient method to determine the point at which reaction is complete.

Table 1. Coulometry of the anodic oxidation of anthracene.

Run	Anthracene, mmole	n_P^a	n_A^b
1	0.625	2.76	3.01
2	0.625	2.78	3.02
3	0.625	2.76	3.03
4	0.625	2.73	3.02
5	0.625	2.75	3.03

^a Potentiometric n value. ^b Amperimetric n value.

Potentiometric method. Column 3 in Table 1 gives the end-point determined from the potential-time curve for runs 1–5. Excellent reproducibility was observed with this method (2.75 ± 0.03); however, the n values are considerably lower than those determined by the amperimetric method. This difficulty can be minimized by using higher substrate concentrations. This has the effect of increasing the linear portion of the potential-time curve (Fig. 1b) without changing the shape of the rising portion. The more substrate oxidized, the less uncertainty in the end point. In this work the potentiometric method gave acceptable n values at anthracene concentrations of 1.25 mM or greater (Table 2). The potentiometric method, like controlled potential coulometry, gives single determination of n for a run. However, it has the advantage of being very convenient to apply.

* The shape of the current-time curve during controlled potential coulometry may be used to advantage to gain both qualitative and quantitative information about follow-up reactions.²

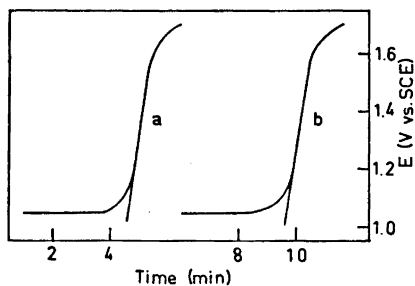


Fig. 1. Constant current coulometry using potentiometric endpoint detection. Oxidation of anthracene (a, 0.05 mmoles; b, 0.1 mmoles) in acetonitrile containing ethanol at 50.0 mA.

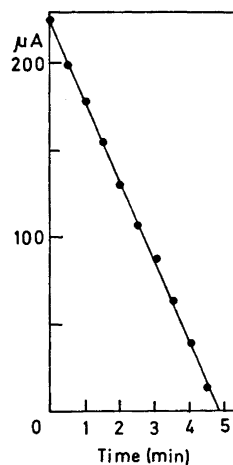


Fig. 2. Constant current coulometry using amperimetric endpoint detection. Oxidation of anthracene (0.05 mmoles) in acetonitrile containing ethanol at 50.0 mA.

Table 2. Effect of the amount of anthracene oxidized on the potentiometric end-point determination.

Run	Anthracene mm M	n_P^b	n_A^b
(1-5) Ave.	0.625	2.76	3.02
6	0.938	2.89	3.04
7	0.938	2.91	3.05
8	1.250	3.01	3.08
9	1.250	2.99	3.10
10	1.875	3.02	3.07
11	1.875	3.02	3.08

^a Potentiometric n value. ^b Amperimetric n value.

Gas chromatographic method. Any method of determining substrate concentration could be used to detect the end point of the reaction. However, many methods, such as spectral determination are not easily applied because of interference by the product of the reaction. The gas chromatographic method is of importance for at least two reasons: (1) the ready availability of gas chromatographs in organic research laboratories and (2) in some cases it allows one to follow both the decrease in substrate concentration as well as the increase in product concentration. The method applied to the anodic oxidation of anthracene (0.050 mmoles) in acetonitrile (40 ml) containing

ethanol (100 mM) gave n values of 2.84, 2.98, and 2.89. Admittedly, the reproducibility does not approach that obtained with the two voltammetric methods; however, it is as good as that obtained by manual integration of current-time curves from several controlled potential runs.⁷

The conditions chosen for the anodic oxidation of anthracene in acetonitrile are such that 3.0 electron coulometry is observed.* However, small variations of n values do occur when the conditions are changed and the reaction is not always quantitative. Therefore, we do not recommend this reaction as a coulometric standard. Two other reactions, both 1.0 electron oxidations, are more suitable as possible standards for coulometry in organic systems. They are the anodic oxidation of 9-acetoxyanthracene⁹ and 9-methoxyanthracene.¹⁰ Both compounds give quantitative yields of bianthrone on anodic oxidation in acetonitrile and the reactions are less subject to changes in conditions. Coulometry using both the potentiometric and amperimetric end-point detection methods result in n values of 1.0. These reactions are discussed in detail later.^{9,10}

Macro-scale electrolysis. Constant current electrolysis is ideally suited to preparative scale work. The combination of high substrate concentration with large anode area allows currents well below limiting values to be used. Several runs were carried out on the anodic oxidation of anthracene in acetonitrile containing ethanol. The following example is typical. Anthracene (0.534 g, 3 mmoles) in acetonitrile (200 ml) containing ethanol (100 mM) was electrolyzed at a constant current of 200 mA. The anode potential remained constant at about +1.05 V (*vs.* SCE) for 69 min and then began to rise slowly. At 70 min, the anode potential was +1.08 V and was 1.20 V at 70.8 min. A sharp increase in the anode potential occurred at 71.1 min ($n = 2.94$). The reaction was about 98 % complete before the voltammetric peak potential for anthracene was reached. Isolation and analysis of the product showed it to be identical to authentic bianthrone.

For the preparation of bianthrone from anthracene it is necessary to go to a larger cell to prepare larger quantities due to the low solubility of anthracene in acetonitrile. Anthracene (5.34 g, 30 mmoles) in acetonitrile (950 ml) containing ethanol (100 mM) and sodium perchlorate (0.5 M) was electrolyzed at a constant current of 1.00 A for 145 min (3.0 Faradays per mole). This reaction was conducted in an open 1-liter beaker without a cell divider. The product was isolated simply by dilution with water and filtration and was found to be fairly pure bianthrone. While it is more convenient to use a single compartment cell, it is not generally possible to do so because of undesirable reactions at the counter electrode.

It should be emphasized that if controlled current rather than controlled potential conditions are used for preparative electrolysis, it is necessary to observe the potential of the working electrode and be sure that conditions are such that a nearly constant potential is maintained. Constant current electrolysis has the obvious advantage of ease of measurement of the charge trans-

* As a further test of the method, several runs were conducted on the anodic oxidation of hydroquinone to benzoquinone and precise n values equal to 2.0 were observed.

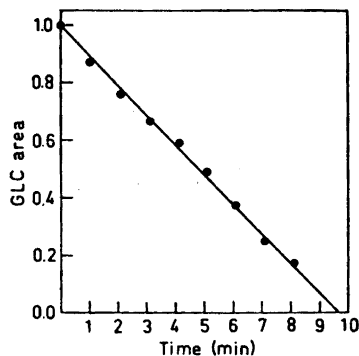


Fig. 3. Constant current coulometry using gas chromatographic end-point detection. Oxidation of anthracene (0.1 mmole) in acetonitrile containing ethanol at 50.0 mA.

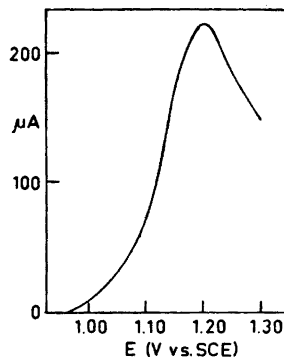


Fig. 4. Peak voltammogram for the oxidation of anthracene (1.0 mM) in acetonitrile containing ethanol (100 mM).

ferred. It also has the advantage of employing much less costly equipment than controlled potential electrolysis.

Current-potential behavior. A qualitative understanding of why the anode potential remains essentially constant during constant current electrolysis of anthracene under the conditions used in this study can be obtained by consideration of the current-potential diagram (peak voltammogram) for anthracene in this medium (Fig. 4).^{*} The peak potential measured at a voltage sweep rate of 10 V/min was found to be +1.20 V (*vs.* SCE). At anode potentials of +1.03 or less the current is 10 % of the peak current or less. Thus, if a constant current electrolysis had an initial anode potential of +1.03 V, this potential would change only slightly until 90 % of the substrate had been consumed and then rise slowly until all the anthracene was consumed at which point oxidation of the medium would be necessary in order to maintain a constant current and a sharp increase in the anode potential would occur. The same numbers naturally do not apply to the large electrode used in the coulometric experiments but the situation is qualitatively the same. This discussion is brief and qualitative but should give an approximate picture of what occurs during constant current electrolysis. A thorough treatment of current-potential behavior at solid electrodes can be found in the monograph of Adams.¹¹

EXPERIMENTAL PART

The amperioostat was of the operational amplifier type and was constructed by Mr. H. O. Martin of the Dow Chemical Research Department. The instrument is capable of maintaining a constant current of 0–2000 mA with maximum fluctuations of ± 1 %.

^{*} In a stirred solution, such as used in the coulometric studies, a limiting plateau rather than a peak is observed in the current-potential diagram. However, at potentials lower than E_p , the behavior is qualitatively the same.

The current measurement was accomplished with a Universal AVO meter with an accuracy of $\pm 1\%$. The time for the experiments using the amperimetric and gas chromatographic end-point determinations was obtained by starting an electric timer simultaneously with current by means of a single-throw, double-pole switch. When the potentiometric end-point was used, either a Varian G-11 or a Heath stripchart recorder was started simultaneously with the current. The error in time measurement is considered negligibly small.

The electrolysis vessel had a volume of 60 ml. A platinum gauze electrode (diameter of 3.5 cm) barely fit into the cell. When the cell contained 40 ml of solution the platinum electrode (height of 5.0 cm) was nearly immersed. The vessel was covered with a rubber stopper which had openings for a tube, with a sintered-glass disc on the end, which served as the auxiliary electrode compartment. The stopper also contained holes for the aqueous calomel reference electrode and for gas inlet and outlet.

A Heath EUW 19A operational amplifier with polarography module EUA-19-2 was used for voltammetric determinations. Single sweep polarograms were recorded at a Beckman platinum button (No. 39273).

Gas chromatographic determination of anthracene was performed using a Varian Series 1200 chromatograph with a flame ionization detector. A 5 ft. by 1/8 in. XE 60 column programmed from 120°C to 210°C at 6°/min was used.

Scintillator grade anthracene (K and K Laboratories) was used without further purification. Anhydrous sodium perchlorate (K and K Laboratories) or anhydrous lithium perchlorate (Alfa Inorganic Chemicals) was used as supporting electrolyte. Acetonitrile with low water content ($<4\text{mM}$) was used as solvent.¹²

The manipulations involved in a typical experiment are as follows: A solution of anthracene (17.8 mg) in acetonitrile (40 ml) containing ethanol (100 mM) and sodium perchlorate (0.5 M) was placed in the cell. The solution was purged for a few minutes with argon prior to recording the peak voltammogram. The amperostat was short-circuited and was adjusted to put out 50.0 mA current. Magnetic stirring was started and the switch thrown starting the timer and electrolysis and the recorder (recording anode potential *vs.* time) was started simultaneously. The initial anode potential was +1.03 V (*vs.* SCE). The electrolysis was stopped at 1.00 min intervals and peak voltammograms were recorded. Stirring and the argon purge were discontinued while the voltammetric measurement was being made. A sharp increase in the anode potential occurred at 9.70 min ($n_p=3.01$) and the plot of the voltammetric peak current *versus* time indicated zero current at 9.92 min ($n_A=3.08$).

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