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Electrochemical oxidation of simple indoles at a PbO_2 anode

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Abstract

Simple indoles undergo electrolytic degradation at potentials near +1 V vs the normal hydrogen electrode at a Pb/PbO_2 anode. Oxidation is first order in both current and indole concentration. The reaction is characterized by low CO_2 yields and high TOC values, that is, most of the carbon of the starting material remained in the solution after electrolysis. Monomeric, isolable oxidation products were not found even at high conversion. These results are consistent with the intermediacy of hydroxyl radicals, which are produced at the surface of the Pb/PbO_2 anode by electrolysis of water, initiating the polymerization of the starting materials to water soluble products with high net current efficiency.

1. Introduction

Although indole and its derivatives are chemically oxidized by a variety of reagents, little is known about their electrochemical oxidation. In nonaqueous solvents such as acetonitrile, indole [1] and the 5, 6, 7 or 8-methylindoles [2] polymerized at Pt anodes; 1-, 2- and 3-methylindoles also oxidized readily [3], mostly affording small oligomers. Oxidation potentials vs Ag/Ag^+ were +0.8 V for 1-methylindole, and 0.65 V for 2- and 3-methylindoles. In aqueous solution, Tucker et al. [4] oxidized several indoles, including 3-methylindole, at mercury anodes; in these reactions the oxidized indole reacted chemically with the mercury electrode. The only reference to studies of methylindoles at nonreactive electrodes is analytical work by Malfoy and Reynaud [5] who showed that 3-methylindole oxidized at +0.8 V vs SCE at gold or carbon anodes. Tryptophan has been electrochemically oxidized in aqueous media at a variety of anodes, including graphite [6]; gold, vitreous carbon and platinum [5]; and pyrolitic and glassy carbon [7]. The primary oxidation centre was concluded to be the heterocyclic double bond, followed by rapid deprotonation at the N–H position.

The limited information in the literature therefore suggests that electrooxidation of indole derivatives in aqueous solution at easily accessible electrode potentials may be a realistic goal. In the present paper, we report the electrochemical oxidation of indole, its 1-, 2- and 3-methyl derivatives, and tryptophan at a Pb/PbO_2 anode. This study was carried out as the background to a project in which we are evaluating the prospects for electrochemical treatment of liquid hog manure as a method of reducing odour prior to land treatment; 3-methylindole (3MI), which is formed by reductive deamination and decarboxylation of tryptophan in the mammalian gut, is one of the principal odorous constituents of hog manure.

2. Experimental details

Tryptophan (98% purity) was supplied by Sigma; the remaining indoles were supplied by Aldrich: indole, >99%; 1-methylindole, >97%; 2-methylindole 98% and 3-methylindole, 98%. All samples were used as received. Solvent was water from a Millipore Milli-Q Reagent Water System, and had a resistivity of not less than 10 MΩ cm.

2.1. *Voltammetry*

All experiments were performed using an EG&G Princeton Applied Research model 273 potentiostat/galvanostat, using model 270/250 Research Electrochemistry Software, version 4.10. Data were converted to ASCII-text format, and plotted in Microsoft Excel 2000. Linear sweep and cyclic voltammetry were performed in a 20 mL open-topped glass cell. The reference electrode was Ag|AgCl, KCl (sat), which was calibrated to 200 mV; potentials are reported with respect to the normal hydrogen electrode (NHE).

Linear sweep voltammetry (LSV) was performed on 1MI, 2MI, 3MI, tryptophan and indole using platinum working (0.92 cm^2) and counter (1.26 cm^2) electrodes in unstirred bulk solutions, with 0.05 M $LiClO_4$ as supporting electrolyte. Sweep rates ranged from 2 to 200 mV s^{-1} for 1 mM solutions of each indole. 3MI was also studied at 20 mV s^{-1} over the concentration range 0.1–1 mM. Working and counter electrodes were cleaned in a flame between scans to remove any deposits. Cyclic voltammetry (CV) was performed in the same cell on 1 mM 3MI in unstirred bulk solution at Pt (0.92 cm^2), graphite (0.93 cm^2), SnO_2 on glass (2.5 cm^2), and Pb/PbO_2 (0.94 cm^2). The supporting electrolyte was 0.05 M $LiClO_4$ with the Pt, graphite and SnO_2-glass systems, and 0.05 M Na_2SO_4 with Pb/PbO_2.

2.2. *Electrolyses*

Electrolyses were run galvanostatically, with currents 0.5–500 mA programmed on the potentiostat/galvanostat. Substrate concentrations were 0.1–1 mM for all compounds; total electrolysis times ranged from 2–4 h. An open-topped, undivided cell was used except for experiments involving CO_2 collection. In either case, the anode working electrode was PbO_2, with a surface area of 39.6 cm^2, prepared by electrolysis of lead in dilute sulfuric acid. Using the open-topped cell, the cathode counter electrode was 3.38 cm^2 of Pt foil, with an external saturated Ag/AgCl reference electrode connected to the cell for measurement of cell potential. From an initial volume of 50.00 mL, 1.00 mL samples were withdrawn at intervals for analysis by HPLC or CE, and the current efficiencies were corrected for the resultant change in volume.

For the CO_2 collection experiments, the electrolysis cell contained 100.00 mL of solution, and a 7.35 cm^2 Pt cathode counter electrode. To avoid atmospheric contamination, no reference electrode was used, and no intermediate samples were taken. High purity Ar was passed through the cell to sweep out CO_2, which was collected in 50.00 mL of 5.00 mM $Ba(OH)_2$. Excess $Ba(OH)_2$ was determined by titration against 11.46 mM HCl.

HPLC analyses were done on a Waters 600E system, equipped with a model 486 variable wavelength u.v.-vis. detector set at 220 nm, and a reverse-phase Genesis C18 column, 4.6 × 250 mm, equipped with a silica precolumn guard. MeOH:H_2O (80:20), filtered with a 0.2 μm filter, was used as mobile phase, at a flow of 1.0 mL min^{-1}. Calibration samples of 3MI, 2MI, 1MI and indole, and electrolysis samples, were manually injected with a 25 μL syringe into a 5 μL sample loop, with analyses performed in triplicate. Peak areas were integrated using Millennium software (v. 1.10). Calculations of calibration curves and unknowns were performed using Microsoft Excel 2000. Calibration curves for 1MI, 2MI, 3MI and indole used concentrations 10^{-3} to 10^{-6} M. Percentage relative standard deviation (%RSD) was ~5% for 10^{-6} M solutions and <3% for more concentrated solutions.

Capillary electrophoresis was performed on a Beckman/Coulter P/ACE MDQ molecular characterization system, equipped with version 2.3 of Beckman P/ACE software, and a u.v. lamp filtered to 214 nm. Separation of tryptophan from its oxidation products was achieved using a 30 cm fused silica column. The separation method, carried out in triplicate, utilized 20 mM borate buffer, at pH 9.6 (cf. [8]). The pressure injection sequence was 2 min each of water, 100 mM NaOH, 5 mM EDTA; 5 min rinse buffer; 6 s pressure injection of analyte at 1 psi (7 kPa); then 12 min separation at 30.0 kV. The calibration curve had tryptophan concentrations 1×10^{-3} to 5×10^{-6} M. %RSD was 7.9% for the 5×10^{-6} M solution, and <3% for the more concentrated solutions.

3. Results and discussion

3.1. *Voltammetry*

At a Pt anode, the linear sweep voltammogram for 3-methylindole showed a sharp increase in current beginning at about +0.84 V, with a near plateau at 1.08 V and a second oxidation peak at 1.4 V (Figure 1). However, cyclic voltammetry showed that oxidation under these conditions was chemically irreversible, and repetitive scans showed severely decreasing current response of the anode, a phenomenon usually associated with electrode fouling [9]. Consistent with this interpretation, the activity of the Pt anode could be restored by heating it in a flame. The concurrence of electrode fouling with oxidation at Pt led us to search for anodes that were free of this problem. At Ti/TiO_2, SnO_2 on glass, and graphite anodes, linear sweep voltammetry showed peak oxidation currents that were considerably smaller than those at Pt; as at Pt, oxidation was chemically irreversible and electrode fouling was evidenced by diminishing current upon repeated scanning. By contrast, at Pb/PbO_2, prepared by anodic oxidation of lead, the magnitude of the oxidation current was not only independent of the concentration of the indole, but was identical to that obtained in blank runs without any substrate present (Figure 2). Repetitive scans of the

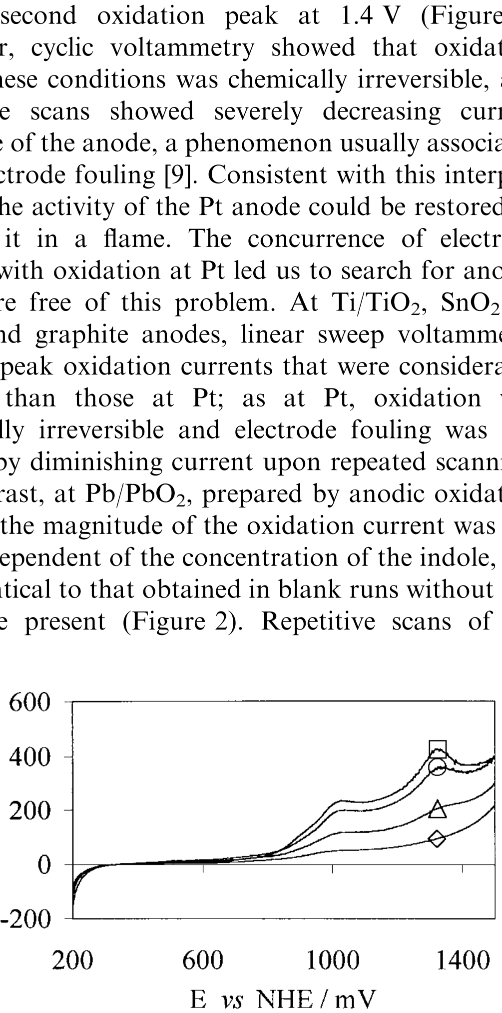

Fig. 1. Linear sweep voltammetry of 1.0 mM 3-methylindole at a Pt anode: sweep rate 20 mV s^{-1}. Symbols: (□) 0.55, (○) 0.46, (△) 0.33 and (◇) 0.10 mM.

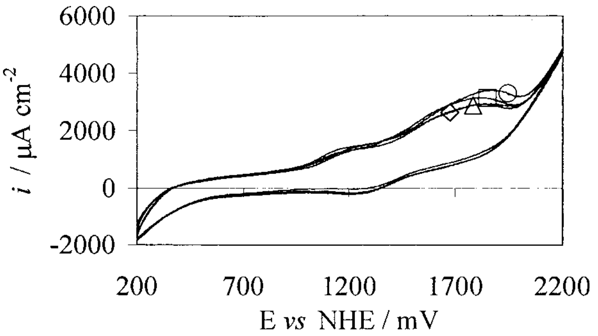

Fig. 2. Linear sweep voltammetry of 1.0 mM 3-methylindole at a Pb/PbO_2 anode: sweep rate 20 mV s^{-1}: Symbols: (□) blank, (◇) sweep 1, (△) sweep 2 and (○) sweep 3.

same solution were superimposable, suggesting that fouling of the electrode was not occurring. Possible explanations are either that no oxidation of indoles occurs at Pb/PbO_2 anodes (shown below to be incorrect), or that oxidation at this anode material is electrocatalytic, involving the reaction of the substrate with a reactive intermediate formed electrochemically at the electrode surface, rather than direct electron transfer from the substrate.

3.2. *Electrolysis at Pb/PbO₂*

Electrolyses were carried out in open-topped, undivided cells, using Pb/PbO_2 anodes prepared by anodic oxidation of lead and a Pt foil cathode with 0.05 M Na_2SO_4 as supporting electrolyte. Disappearance of the starting material was followed by HPLC (except for tryptophan, whose disappearance was followed by capillary electrophoresis); an example is shown in Figure 3. At all values of the applied current, the disappearance of the indole congeners was first order in substrate, consistent with a diffusion-limited process (Figure 4). The apparent first order rate constant was in all cases roughly proportional to the applied current (Figure 5). Because the Pb/PbO_2 anode was not susceptible to fouling, it could be used for multiple electrolyses without loss of activity. The foregoing figures all refer to 3-MI; Table 1 gives a summary of pseudo-first order rate constants for the indole congeners studied.

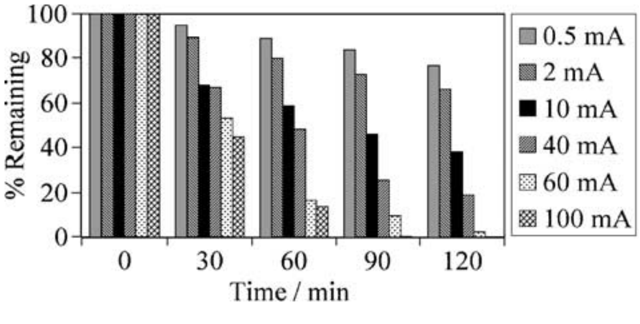

Fig. 3. Oxidation of 1.0 mM 3-methylindole at a Pb/PbO_2 anode: variation of reactivity with applied current.

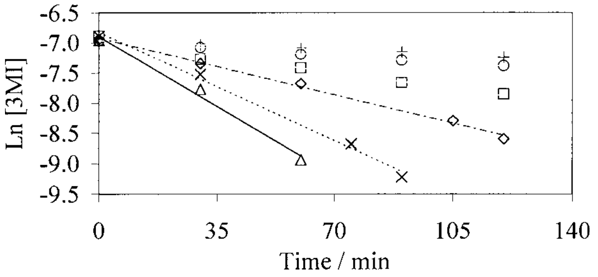

Fig. 4. Oxidation of 1.0 mM 3-methylindole at a Pb/PbO_2 anode: fit of data to pseudo-first order kinetics: ln (c_t) − ln (c_0) = $-kt$. Symbols: (+) 0.5, (○) 2, (□) 10, (◇) 40, (×) 60 and (△) 100 mA.

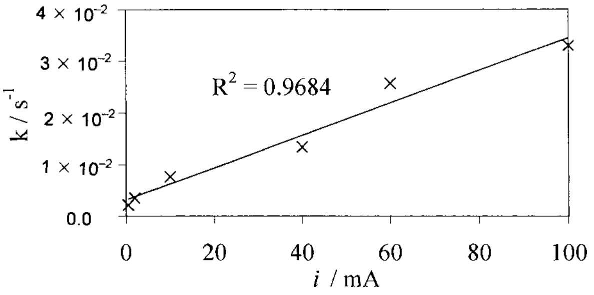

Fig. 5. Fit of pseudo-first order rate constant for the oxidation of 1.0 mM 3-methylindole at Pb/PbO_2 against applied current.

The mechanisms of oxidation at metal oxide anodes have been studied extensively, with the active oxidant being either adsorbed hydroxyl radicals or a higher metal oxide [10]:

$$MO_n \cdot H_2O \rightarrow MO_n \cdot OH + H^+ + e^- \quad (1)$$

$$MO_n + H_2O \rightarrow MO_{n+1} + 2H^+ + 2e^- \quad (2)$$

Recent work has shown that oxidations at lead dioxide involve the OH radical mechanism [11]. Thus oxidation of the substrate is a purely chemical process, and electrochemistry is involved only with the formation of adsorbed OH radicals, consistent with our voltammetric studies at PbO_2 (Figure 2). The kinetics of the reaction – first order in both current and substrate concentration – are consistent with a mechanism in which the indole diffuses to the electrode surface, where it reacts with electrogenerated hydroxyl radicals in a bimolecular reaction. As the current increases from zero, we expect to encounter the following regimes: (i) the current is too small to polarize the electrode significantly, and only ohmic heating is observed; (ii) significant amounts of the reactive intermediate are formed and the rate of oxidation increases with current; (iii) the rate of production of reactive intermediates is sufficiently fast that oxidation to form O_2 predominates, and substrate oxidation becomes less than first order in current. Our experiments appear to fall exclusively in regime (ii).

Current efficiency in an electrolysis is normally defined as the ratio (no. of moles reactant consumed/ no. of moles electrons used) × Z × 100. Here Z is the

Table 1(a). Summary of pseudo-first order rate constants for oxidation of indole congeners as a function of current, concentration 1.0 mM.

Current /mA	10^3k_{obs} for indole /s^{-1} (r^2)	10^3k_{obs} for 1MI /s^{-1} (r^2)	10^3k_{obs} for 2MI /s^{-1} (r^2)	10^3k_{obs} for 3MI /s^{-1} (r^2)	10^3k_{obs} for trp /s^{-1} (r^2)
0.5	1.4 (0.968)	4.9 (0.985)	3.7 (0.992)	2.2 (0.992)	2.4 (0.890)
2	4.8 (0.964)	6.7 (0.951)	6.3 (0.972)	3.5 (0.998)	6.6 (0.970)
10	5.9 (0.989)	8.0 (0.990)	11 (0.930)	7.7 (0.976)	8.8 (0.991)
60	17 (0.922)	16 (0.878)	29 (0.996)	25 (0.993)	12 (0.855)
100	32 (0.954)	19 (0.994)	36 (0.973)	33 (0.989)	30 (0.996)

average number of electrons used to convert 1 molecule of reactant into product(s). In the present systems, in which hydroxyl radicals are reactive intermediates, Z would be interpreted as the average number of hydroxyl radicals consumed during electrolysis of one molecule of starting material. In the absence of knowledge of the products (see below), we arbitrarily assigned $Z = 1$, tantamount to assuming consumption of one OH radical per molecule of substrate. In all cases, relative current efficiency decreased with increased conversion, lower initial substrate concentration, and higher applied current, as illustrated in Figure 6. The first two of these observations reflect the importance of mass transfer to the electrode; the third represents the effect of competition of O_2 production as the anodic polarization of the electrode increases. Limiting values of the relative current efficiency at low current and low conversion were of the same order of magnitude for all congeners: indole, 32%; 1MI, 99%; 2MI, 58%; 3MI, 27%; tryptophan, 37%. When the initial substrate concentration was varied, the first order plots lay almost parallel, and as Table 1(b) shows, the pseudo-first order rate constants were independent of the initial substrate concentration, within the precision of our experiments. This is consistent with rate-limiting diffusion of the indole derivative to the anode, where the hydroxyl radicals are produced.

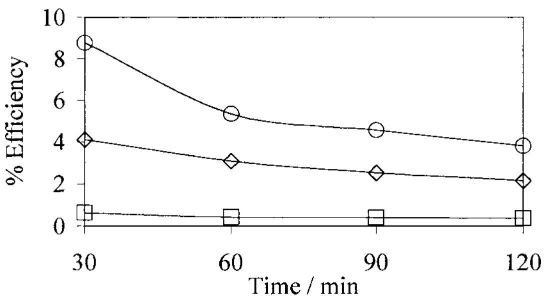

Fig. 6. Influence of current on the oxidation of 3-methylindole at Pb/PbO_2 at an applied current of 60 mA Symbols: (○) 1, (◇) 0.5 and (□) 0.1 mM.

Considerable effort was expended to identify oxidation products, particularly from 3-methylindole, but to no result. One peak was seen in each case by HPLC, its retention time indicating that it was more polar than the corresponding starting material. No useful information was obtained from either UV (strong end absorption), FTIR (no obvious functional groups), ^{1}H NMR (many small peaks at near background intensity in the unsaturation region), or LCMS (no peaks detectable by either positive or negative ion APCI). The production of carbon dioxide was examined, to check for 'electrochemical combustion' [11], by absorbing an argon stream passed through the electrolyte into baryta and titration of the excess OH^-. Although the yield of CO_2 increased with increasing applied current, in no case was it greater than 0.43 mol CO_2 per mole of methylindole consumed (i.e., <5% based on carbon). Consistent with this result, total organic carbon (TOC) analysis indicated that about 80% of the initial carbon remained in solution, even when almost all the 3-methylindole had disappeared (Table 2).

From the combined evidence of current efficiency and product analysis we suggest that electrooxidation of simple indoles proceeds by way of electroinitiated polymerization. First, electrolysis does not involve electrochemical combustion, in that CO_2 yields are low and TOC values remain high, even at high conversion. Second, in each case a UV-absorbing product remains in solution, as seen by HPLC; this product is more polar than the reactant, it contains aromatic protons according to NMR but is not susceptible to LCMS analysis. Third, current efficiencies based on $Z = 1$ seem to suggest that under conditions of low current and high concentration of starting material a very high proportion of all hydroxyl radicals are intercepted by substrate, an observation that is incompatible with the observed occurrence of the parasitic reaction of O_2 evolution at the anode. An explanation, however, is that if surface

Table 1(b). Summary of pseudo-first order rate constants for oxidation of indole congeners as a function of concentration, current 60 mA

Concentration /mM	10^3k_{obs} for indole /s^{-1}	10^3k_{obs} for 1MI /s^{-1}	10^3k_{obs} for 2MI /s^{-1}	10^3k_{obs} for 3MI /s^{-1}	10^3k_{obs} for trp /s^{-1}
0.1	7.4 ± 0.5	9.0 ± 0.8	10 ± 0.9	8.6 ± 0.5	7.6 ± 1.6
0.5	6.0 ± 0.5	9.3 ± 0.6	7.3 ± 0.6	9.9 ± 0.3	10 ± 1.9
1	5.9 ± 0.4	8.0 ± 0.5	11 ± 1.7	7.7 ± 0.7	8.8 ± 0.5

Table 2. Percentages remaining in solution of initial TOC and 3MI upon electrolysis

Time /min	60 mA		100 mA	
	% 3MI	% TOC	% 3MI	% TOC
0	100	100	100	100
30	–	–	45	81
60	18	75	14	79
120	2.4	73	0.2	61

adsorbed OH radicals added to the indole, the resulting radical intermediate could add to further substrate molecules without consumption of current. Apparent current efficiencies would then be the product of the current efficiency for addition of OH to the indole and the chain length for polymerization. The similar overall reactivity of 1-methylindole compared with the other indole congeners is consistent with attack of OH at the 2,3 position of the indole ring, as might be anticipated on chemical grounds, rather than abstraction of the N–H hydrogen. This hypothesis is also consistent with the propensity of indoles to polymerize under a variety of other conditions: under acid catalysis [12]; upon electrooxidation at Pt in acetonitrile solution [1, 2]; and in aqueous solution by direct electron transfer at a Pt anode, as shown in this work.

4. Conclusion

We have shown that although simple indoles undergo direct electron transfer at several electrodes in the potential range of water stability, this process does not appear to be a useful technique for their electrolytic degradation due to concomitant electrode fouling. At Pb/PbO_2, electrolytic oxidation occurs with high current efficiency; this reaction is proposed to involve electrochemical polymerization, in which hydroxyl radicals act as the initiating agents. These oligomers or polymers are water-soluble, and as a result anode fouling is not observed. This mechanism explains the failure to obtain discrete, isolable oxidation products, the low CO_2 yields and high TOC of the electrolysed solution, and the unexpectedly high apparent current efficiences. With reference to the overall goals of the project, namely electrochemical destruction of 3MI in liquid hog manure, the present work has shown proof of concept; future work will be directed to the electrolysis of 3MI in that matrix.

Acknowledgements

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