



Reduction of 4-(bromomethyl)-2-oxo-2H-chromen-7-yl acetate at carbon cathodes in dimethylformamide and acetonitrile: Lifetime of the electrogenerated radical–anion

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ABSTRACT

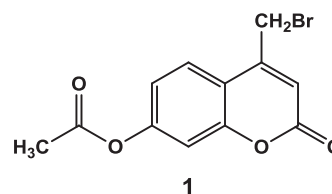
Cyclic voltammograms for reduction of 4-(bromomethyl)-2-oxo-2H-chromen-7-yl acetate (or 7-acetoxy-4-bromomethylcoumarin) (**1**) at carbon cathodes in either dimethylformamide (DMF) containing tetramethylammonium tetrafluoroborate (TMABF₄) or acetonitrile (CH₃CN) containing TMABF₄ show four irreversible cathodic peaks, the one at least negative potential being due to scission of the carbon–bromine bond. Bulk electrolysis of **1** at a reticulated vitreous carbon electrode held at potentials slightly more negative than that of the first cathodic peak afford two products: (i) a monomer, 4-methyl-2-oxo-2H-chromen-7-yl acetate (**2**), formed in yields of 18–22% in DMF–TMABF₄ and 23–24% in CH₃CN–TMABF₄ and (ii) a dimer, 4,4'-(ethane-1,2-diyl)bis(2-oxo-2H-chromene-7,4-diyl) diacetate (**3**), obtained in yields of 75–80% and 72–77%, respectively, in DMF–TMABF₄ and CH₃CN–TMABF₄. Reduction of **1** was found to conform to a classic EC mechanism; the first-order rate constant for cleavage of the carbon–bromine bond of the electrogenerated radical–anion is $2.7 \times 10^5 \text{ s}^{-1}$ in DMF–TMABF₄ and $2.5 \times 10^5 \text{ s}^{-1}$ in CH₃CN–TMABF₄. For both solvent–electrolyte systems, fast-scan cyclic voltammetry carried out with carbon-fiber ultramicroelectrodes shows that the electron-transfer process associated with formation of the radical–anion begins to exhibit reversibility at scan rates greater than 5000 V s^{-1} .

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1. Introduction

Coumarins (or 2H-chromen-2-ones) continue to be of scientific interest due to their ubiquity in nature and their photochemical, electrochemical, and biochemical properties [1]. In the biochemical arena, 7-hydroxycoumarins are well known as anticoagulants and have recently shown promise as anti-tumor and multidrug resistance reversal agents [2]. In addition, 2H-chromen-2-ones find use in various pharmacological applications: antithrombotics [3]; analgesics [4]; antibiotics, antimicrobials, enzyme inhibitors, and antifungal compounds [2]; and anti-inflammatory [5] and antiviral (including anti-HIV) agents [6,7]. Because they are a subunit of more complex natural products [8–12], coumarin derivatives are used extensively in the food, cosmetic, alcohol, and tobacco industries [13]. Due to their unique photochemical properties, coumarins are found in optical brighteners [14], in laser dyes [14], and, as a result of their high electroluminescent efficiency, in organic light-emitting devices [15]. Indeed, the subject of this report, 4-(bromomethyl)-2-oxo-2H-chromen-7-yl acetate (or 7-acetoxy-4-

bromomethylcoumarin) (**1**), is well known as a fluorescent label in thin-layer and liquid chromatography applications [16,17].



There are many studies describing the preparation of 2H-chromen-2-ones, including the one-step synthesis of 10 different coumarin derivatives from phenol and a β -keto ester [18], the palladium-catalyzed synthesis of 4-substituted coumarins [19], the preparation of fluorinated coumarin derivatives from 2,4-dihydroxybenzaldehyde [20], the platinum-promoted photodimerization of 7-allyloxycoumarin [21], and the cerium-mediated synthesis of 4-methylcoumarins [22]. At present, there is also a large body of work pertaining to the electroreduction of various coumarin derivatives. Preparative-scale bulk electrolysis has been utilized to investigate the catalytic reductions of 2H-chromen-2-one, 4-methyl-2H-chromen-2-one, and 5-methoxy-4-methyl-2H-

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chromen-2-one in the presence of tertiary amines [23,24]; the alkaloid-catalyzed enantioselective reduction of 4-methyl-2H-chromen-2-one [25,26]; and the electrosynthesis of 4-methyl-2H-chromen-2-one via cobalt(II)-catalyzed reductions of 2-acetylphenyl 2-chloroacetate and 2-acetylphenyl 2,2-dichloroacetate [27]. In addition, direct reductions of 3-nitro-2H-chromen-2-one [28], 4-methyl-2-oxo-3-[*p*-tolylidiazonyl]-2H-chromene-8-carbaldehyde [29], and 2-(7-hydroxy-4-methyl-2-oxo-2H-chromen-3-yl)diazene-sulfonamide [30] have been investigated.

Included in research dealing with 2H-chromen-2-one and its derivatives is a handful of papers concerning the electroreduction of 4-(halomethyl)-2H-chromen-2-one. Recent work in our laboratory [31] focused on the use of cyclic voltammetry and controlled-potential (bulk) electrolysis to study the electrochemical behavior of two coumarin derivatives [4-(bromomethyl)-7-methyl-2H-chromen-2-one and 4-(bromomethyl)-7-methoxy-2H-chromen-2-one] at carbon cathodes in dimethylformamide (DMF) containing tetramethylammonium tetrafluoroborate (TMAF₄). Two earlier papers that surveyed the electroreduction of **1** were authored by Kim and co-workers [32,33]; both publications deal with the use of dc and differential pulse polarography, cyclic voltammetry, and controlled-potential coulometry of **1** at mercury cathodes in acetonitrile (CH₃CN) containing tetraethylammonium perchlorate.

In the present investigation, controlled-potential (bulk) electrolysis at carbon cathodes in DMF–0.10 M TMAF₄ and in CH₃CN–0.050 M TMAF₄ has been employed to elucidate the mechanism of the reduction of **1** on the basis of coulometric *n* values and product distributions. In addition, cyclic voltammetry at glassy carbon electrodes, cyclic voltammetry in the presence of an electrogenerated homogeneous redox catalyst, and fast-scan cyclic voltammetry at carbon-fiber ultramicroelectrodes were performed in the two different solvent–electrolyte systems to determine the lifetime of the electrogenerated radical–anion of **1**. Electrolysis products formed after reductive cleavage of the carbon–bromine bond were identified with the aid of high-performance liquid chromatography–mass spectrometry (HPLC–MS), gas chromatography–high-resolution mass spectrometry (GC–HRMS), and nuclear magnetic resonance (NMR) techniques.

2. Experimental

2.1. Reagents

Each of the following chemicals, with purity and source indicated in parentheses, was purchased and used without further purification: 7-acetoxy-4-bromomethylcoumarin [4-(bromomethyl)-2-oxo-2H-chromen-7-yl acetate (**1**), 98%, TCI America], 7-acetoxy-4-methylcoumarin (**2**) (95%, Indofine Chemical Company), 4-(bromomethyl)-7-methoxy-2H-chromen-2-one (**6**) (99%, Aldrich), dichloromethane-*d*₂ (CD₂Cl₂, 99.9 atom% D, Aldrich), tetraphene-7,12-dione (benzo[*a*]anthracene-7,12-dione, 97%, Alfa Aesar), 2,5-diphenyl-*p*-benzoquinone (96%, Alfa Aesar), 1,4-benzoquinone (98%, Aldrich), 4-nitropyridine 1-oxide (97%, Alfa Aesar), and phenol-*d*₆ (99 atom% D, Aldrich). Deuterium oxide (99.9 atom% D) was obtained from Cambridge Isotope Laboratories, Inc. Tetramethylammonium tetrafluoroborate (TMAF₄, 97%, GFS Chemicals), used as the supporting electrolyte, was recrystallized from water–methanol and stored in a vacuum oven at 80 °C to remove traces of water. Dimethylformamide (DMF, ACS grade, 99.8%, Fisher) and acetonitrile (CH₃CN, Mallinckrodt AR brand) were used as solvents for cyclic voltammetry, controlled-potential (bulk) electrolysis, and fast-scan cyclic voltammetry. Deaeration of all solutions was accomplished with the aid of zero-grade argon (Air Products).

2.2. Instrumentation, cells, and electrodes

Instrumentation and procedures for cyclic voltammetry are described elsewhere [34]. For cyclic voltammetry in which scan rates did not exceed 3 V s^{−1}, a short length of 3-mm-diameter glassy carbon rod (Grade GC-20, Tokai Electrode Manufacturing Company, Tokyo, Japan) was press-fitted into a Teflon shroud to provide a planar, circular working electrode with an area of 0.077 cm². Before each cyclic voltammogram was recorded, the electrode was cleaned ultrasonically in DMF, polished with an aqueous suspension of 0.05-μm alumina on a Master-Tex (Buehler) polishing pad, rinsed ultrasonically in distilled water, and blotted dry. Cyclic voltammograms were acquired with the aid of an (a) Obbligato Objectives, Inc., Faraday MP potentiostat running Faraday MP version 1.5 software for experiments in CH₃CN or (b) a Princeton Applied Research Corporation (PARC) 2273 instrument running PowerCV[®] version 2.41 software for experiments in DMF.

Reticulated vitreous carbon disks (RVC 2X1–100S, Energy Research and Generation, Inc., Oakland, CA), approximately 2.4 cm in diameter, 0.4 cm in thickness, and 200 cm² in geometric area, were utilized as working electrodes for all controlled-potential (bulk) electrolyses. Previously established procedures [35] for fabricating, cleaning, and handling these electrodes were employed. Electrochemical cells for controlled-potential (bulk) electrolysis are described elsewhere [34,35]. We conducted controlled-potential (bulk) electrolyses by utilizing a PARC model 2273 potentiostat running PowerCorr[®] version 2.47 software. Potentials for cyclic voltammetry and controlled-potential (bulk) electrolysis are given with respect to a reference electrode consisting of a cadmium-saturated mercury amalgam in contact with DMF saturated with both cadmium chloride and sodium chloride; this electrode has a potential of −0.76 V versus the aqueous saturated calomel electrode (SCE) at 25 °C [36–38].

For fast-scan cyclic voltammetry (scan rates >10 V s^{−1}), we employed a 10-μm carbon-fiber ultramicroelectrode (Model MF2007, Bioanalytical Systems, Inc., West Lafayette, IN) as the working electrode. A rubber stopper (fitting tightly into the top of a test tube which served as the cell) accommodated the ultramicroelectrode, a silver counter-reference electrode (with a potential of −0.19 V vs. SCE), and argon inlet and outlet tubes. To generate and record the applied fast-scan potential sweeps, a Wavetek model 143 function generator was connected to both the working electrode and the A channel of a Nicolet 320 oscilloscope. Current through the counter-reference electrode was routed to an operational amplifier (Burr Brown OPA602BP) such that, in combination with a 10-MΩ precision resistor, the resulting circuit acted as a current-to-voltage converter and voltage amplifier. Then the output of this circuit was coupled to the B channel of the oscilloscope. By utilizing the *x*–*y* plotting function, we recorded cyclic voltammograms in a conventional manner.

2.3. Separation and identification of electrolysis products

On the basis of early liquid chromatographic experiments, it quickly became evident that two products arise from the electrochemical reduction of **1**. First is a monomeric species, 4-methyl-2-oxo-2H-chromen-7-yl acetate (**2**), a white compound that is commercially available and that was used without further purification for purposes of identification and quantitation. Second is 4,4'-(ethane-1,2-diyl)bis(2-oxo-2H-chromene-7,4-diyl) diacetate (**3**), a yellow material that is not commercially available and that lacks a viable synthetic route. To obtain an authentic sample of **3**, we employed the following strategy. At the conclusion of an electrolysis, the catholyte (containing dissolved **2** and solid **3**) was partitioned between CH₂Cl₂ and water; the organic layer was separated, washed with distilled water, and dried over anhydrous sodium sulfate. Then

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