Electrochemistry Communications 12 (2010) 1698–1702

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Electrochemical reduction of aliphatic conjugated dienes in the presence of carbon dioxide

Kai Zhang, Yuanjing Xiao, Yangchun Lan, Meixia Zhu, Huan Wang *, Jiaxing Lu *

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, Shanghai 200062, China

ARTICLE INFO

Article history:
Received 3 August 2010
Received in revised form 25 September 2010
Accepted 29 September 2010
Available online 8 October 2010

Keywords:
Carbon dioxide
Electrocarboxylation
Diene
Cyclic voltammogram

ABSTRACT

A voltammetric and electrolytic study involved in the electroreductive carboxylation of multi-substituted aliphatic coujugated dienes has been successfully conducted. With methyl sorbate as the modal compound, acceptable yields of carboxylation and dimerization were achieved, which were influenced by various reaction conditions such as the supporting electrolyte, cathode nature, current density, charge passed and temperature. A correlation was first established between distinct electronic effects of the dienes and the electrochemical characteristics of their reduction and the distribution law of target products.

1. Introduction

The vast abundance, nontoxicity of carbon dioxide in the nature makes it an attractive raw material for the synthesis of various organic compounds. The development of electrochemical reduction that forms C–C bonds from CO_2 has the potential to provide convenient, economical routes to functionalized products compared with classical organic synthesis, where CO_2 shows a very low reaction activity. Electrochemistry provides the possibility that CO_2 can either perform an electrophilic attack in the reaction of anionic species [1,2] or a nucleophilic one via cathodic activation to the radical anion $[CO_2]^{\cdot-}$ [3,4]. Although electrocarboxylation involving activated olefins has received much attention in recent years [5–7], rare reports are concerning the electrochemical reductive coupling reactions between conjugated dienes and CO_2. Thoroughly speaking, the addition of $[CO_2]^-$ to the unsubstituted carbon atoms of isoprene formed the regioselectively 1,4-dicarboxylated products with the help of $[CpFe(CO)_2]_2$, which could electroreduced in the presence of CO_2 to generate 1:1 adduct $[Cp(CO)_2Fe–CO_2]^-$ [8]. J.Bringmann and E.DinJus once reported that using various nickel-organic mediator systems, the electroreductive coupling between 1,3-butadiene and CO_2 resulted different preferences such as 1,4-addition production or monocarboxylation concomitant [9]. We are interested in the reactivity of more challenging dienes for the utilization of CO_2 and the product distribution law influenced by multiple substitution of diene structures.

This communication is devoted to the electroanalytical, synthetic, and mechanistic aspects of electrocarboxylation of three conjugated dienes (methyl sorbate **1**, 3-methyl-1, 3-pentadiene **2** and 2,5-dimethyl-2,4-hexadiene **3**) with CO_2 under mild conditions. We first present the electrochemical behavior of the dienes by cyclic voltammetry. Second, the influence of operative parameters and the nature of the substrate on the electrocarboxylation of conjugated dienes were investigated on a preparative scale. Then some detailed analysis about the mechanistic aspects is paid centralized attention for necessity.

2. Experimental

2.1. Apparatus and reagents

Voltammetric measurements were conducted with CHI650C electrochemical station in a conventional three-electrode cell. The working electrode was a glassy-carbon disk ($r = 1.5$ mm). The auxiliary electrode was a platinum spiral. The reference electrode was Ag/AgI/0.1 M n-Bu_4NI in DMF. Galvanostatic electrolysis was performed using a dc regulated power supply HY3002D (HYelec®, China). ^{1}HNMR spectra were recorded on an AVANCE 500 (500 MHz, Bruker, Germany) spectrometer in $CDCl_3$, with Me_4Si as an internal standard. Mass spectra were obtained on a 5973-N spectrometer connected with an HP 6890 gas chromatograph (Agilent, USA). The aliphatic conjugated dienes were used as received (TCI) without further purification.

---

* Corresponding authors. Lu is to be contacted at Tel./fax: +86 21 62233491. Wang, Tel.: +86 21 62237606; fax: +86 21 62233491.
E-mail addresses: hwang@chem.ecnu.edu.cn (H. Wang), jxlu@chem.ecnu.edu.cn (J. Lu).

1388-2481/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.elecom.2010.09.028

2.2. General electrocarboxylation experiment

A diaphragmless glass tank cell of an internal volume of 10-mL dry DMF (including 0.1-M substrate and 0.1-M TBAP) was employed equipped with a ring stainless steel (AISI304) cathode and magnesium rod sacrificial anode. Pure CO_2 was fed beforehand for 30 min and continuous bubbling was also confirmed during the whole electrolysis. At completion, the electrolyte containing the metal salts of the carboxylated products was esterified with excess methyl iodide at 60 °C for 5 h. The residue was hydrolyzed and extracted with Et_2O, and the organic layers were washed with brine, dried over $MgSO_4$, and evaporated. After isolation and identification, the product yields in methyl esters were determined by GC based on the starting materials.

2-Methyl-hex-3-enedioic acid dimethyl ester (1a) GC-MS(m/z, %): 186(M^+, 3.7), 171(2.8), 154(48.0), 127(53.7), 111(9.3), 95(15.6), 85 (100.0), 67(26.2), 59(43.3), 55(12.1), 41(15.7). ^{1}HNMR: δ1.24(3 H, d, J = 6.9 Hz, CH_3); δ3.01(2 H, d, J = 6.0 Hz, CH_2); δ3.11–3.16(1 H, m, CH); δ3.65(6 H, s, $2COOCH_3$); δ5.64-5.65(2 H, m, CH = CH).

5,6-Dimethyl-deca-3,7-dienedioic acid dimethyl ester (1b) GC–MS(m/z, %): 254(M^+, 0.3), 222(3.2), 180(4.1), 163(1.9), 127 (72.2), 95(12.8), 85(100.0), 67(16.5), 55(6.5), 41(7.2). ^{1}HNMR: δ0.92(6 H, d, J = 6.3 Hz, $2CH_3$); δ1.93–2.18(1 H, m, CH); δ2.20–2.39 (1 H, m, CH); δ3.02(2 H, d, J = 5.4 Hz, CH_2); δ3.07(2 H, d, J = 6.9 Hz, CH_2); δ3.66(6 H, s, $2COOCH_3$); δ5.36–5.52(4 H, m, 2CH = CH).

4-Methoxycarbonyl-5,6-dimethyl-deca-2,7-dienedioic acid dimethyl ester (1c) GC–MS m/z, %): 312(M^+, 0.2), 249(3.5), 217(1.6), 185(20.7), 153(6.8), 127(62.1), 111(11.6), 85(100.0), 67(20.2), 41(10.1). ^{1}HNMR: δ0.93(2 $H_{1\text{-}2}$, d, J = 6.3 Hz, $2CH_3$); δ1.18(2 $H_{3–4}$, d, J = 6.6 Hz, $2CH_3$); δ1.24(2 $H_{5–6}$, d, J = 6.3 Hz, $2CH_3$); δ2.28–2.39(1 H, m, CH); δ2.51–2.64(2 H, m, CH_2); δ3.02(1 H, d, J = 5.1 Hz, CH); δ3.14(1 H, d, J = 6.3 Hz, CH); δ3.67(6 H, s, $2COOCH_3$); δ3.71(3 H, s, $COOCH_3$); δ5.36–5.47(1 H, m, = CH); δ5.50–5.69(1 H, m, = CH); δ5.85(1 H, d, J = 15.6 Hz, = CH); δ6.82–6.92(1 H, m, = CH).

2,3-Dimethyl-hex-3-enedioic acid dimethyl ester (2a) GC-MS (m/z, %): 200(M^+, 18.1), 168(96.2), 136(93.9), 125(94.0), 109(92.0), 99(98.9), 81(100.0), 67(92.8), 59(94.8), 55(82.7). ^{1}HNMR: δ1.20 (3 H, d, J = 7.2 Hz, CH_3); δ1.58(3 H, s, CH_3); δ3.02(2 H, d, J = 6.6 Hz, CH_2); δ3.08–3.15(1 H, m, CH); δ3.60–3.62(6 H, m, $2COOCH_3$); δ5.44–5.48(1 H, m, CH).

3. Results and discussion

3.1. Electroanalytical measurements of aliphatic conjugated dienes

Fig. 1A presented the voltammetric characteristic of methyl sorbate on glassy carbon electrode in DMF–0.1 mol L^{-1} TBAP at a scan rate of 0.2 V s^{-1}. First, there was not any redox peak in the scan range without any substrate that showed a favorable potential window from −1.2 to −2.6 V (curve a). After 5.0-mmol L^{-1} methyl sorbate was added, two irreversible cathodic peaks under N_2 were observed at −1.7 V and −2.5 V (curve b), with the intensity of the second one being noticeably higher at larger scan rate. The evaluation of the number of electron involved in the first step of the diene reduction by potentiostatical electrolysis at −1.6 V under nitrogen pointed to mere dimerization happening. Consequently, this peak featured the one-electron reduction of methyl sorbate to its radical anion, which could be further reduced at more negative potential [6]. In the presence of CO_2, the current of the first reduction peak increased with its potential appreciably shifting to a more positive place (curve c) indicative of a fast chemical reaction between the racial anion of methyl sorbate and CO_2. Synchronously, the second reduction peak disappeared, whereas a new wave came up at −2.1-V probably ascribed to the reduction of the intermediate resulted from electroreductive coupling of methyl sorbate with one molecule of CO_2.

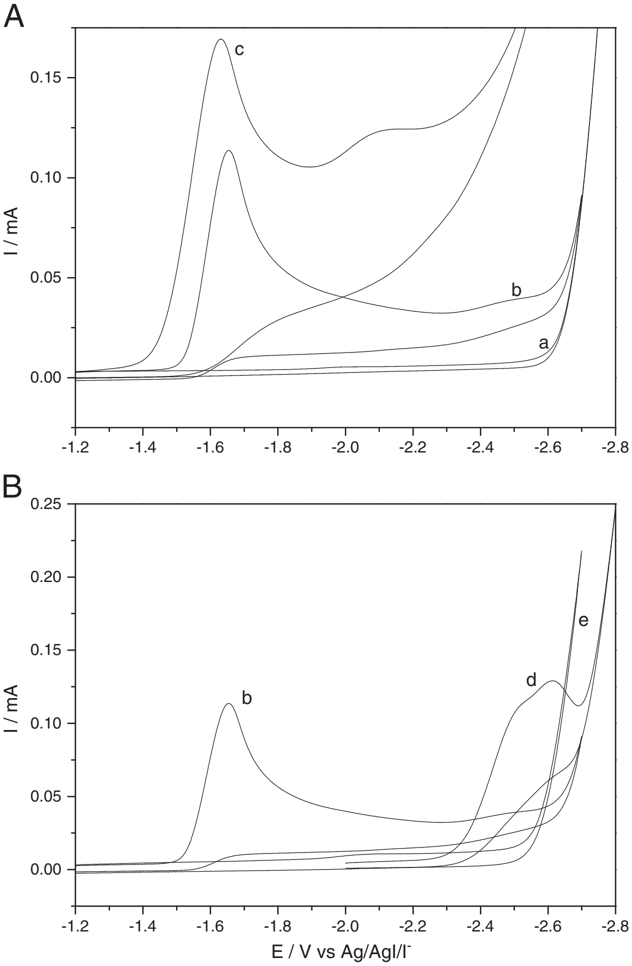

Fig. 1. Cyclic voltammograms of three conjugated dienes (5.0 mmol L^{-1}) recorded on GC electrode at 25 °C in DMF−0.1 mol L^{-1} TBAP at $v = 0.2$ V s^{-1}: a) neat solvent system; b) with methyl sorbate in the absence and c) presence of 1 atm CO_2; d) and e) electroreduction of 3-methyl-1,3-pentadiene and 2,5-dimethyl-2,4-hexadiene in the presence of N_2, respectively.

In comparison, 3-methyl-1,3-pentadiene, which bears two methyl groups on the conjugated diene structure to behave more difficulty in obtaining the electron from the cathode due to stronger electron repulsion gave two successive cathodic peaks more negatively than diene **1** correlated to the reduction of cis and trans isomer with $E_{pc1} = -2.5$ V and $E_{pc2} = -2.6$ V since single trans-diene **2** only exhibited

Table 1
Electrocarboxylation of methyl sorbate influenced by various reaction conditions.

Entry	Supporting electrolyte	Cathode	*j*/mA cm^{-2}	*Q*/F mol^{-1}	T/°C	Carboxylated yield/%	Total/% (1a:1b:1c)
1[b]	TEABr	Ss	5.0	2.0	0	16	38 (6:22:11)
2	TEABr	Ss	5.0	2.0	0	19	37 (13:18:6)
3	TEAI	Ss	5.0	2.0	0	21	45 (13:24:8)
4	$TEABF_4$	Ss	5.0	2.0	0	18	38 (11:19:7)
5	TBABr	Ss	5.0	2.0	0	19	35 (13:17:6)
6	TBAI	Ss	5.0	2.0	0	18	38 (12:21:5)
7	$TBABF_4$	Ss	5.0	2.0	0	16	29 (10:13:6)
8	TBAP	Ss	5.0	2.0	0	23	42 (17:18:7)
9	TBAP	Cu	5.0	2.0	0	18	34 (13:16:6)
10	TBAP	Ni	5.0	2.0	0	20	35 (15:15:6)
11	TBAP	Ag	5.0	2.0	0	18	36 (12:18:6)
12	TBAP	Ti	5.0	2.0	0	17	35 (13:18:5)
13	TBAP	Ss	5.0	3.0	0	15	28 (9:13:6)
14	TBAP	Ss	10.0	2.0	0	17	34 (10:17:6)
15	TBAP	Ss	10.0	4.0	0	15	29 (10:13:5)
16	TBAP	Ss	5.0	2.0	20	20	39 (14:19:6)
17	TBAP	Ss	5.0	2.0	-10	26	47 (18:21:8)

Solvent: DMF; anode: sacrificial magnesium rod; substrate concentration: 0.1 M; $pCO_2 = 1$ atm. b: the solvent was replaced by MeCN.