

Electrochemical behavior of 3-chloro-2,4-pentanedione in the presence of cobalt salen

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Abstract

We have studied the catalytic two-electron reduction of 3-chloro-2,4-pentanedione by cobalt(I) salen electrogenerated at a glassy carbon cathode in acetonitrile containing tetramethylammonium tetrafluoroborate. When cobalt(I) salen is electrogenerated at -0.65 V (a potential that is 30 mV more negative than the peak potential for the reversible one-electron reduction of cobalt(II) salen), the carbon-chlorine bond of 3-chloro-2,4-pentanedione is catalytically cleaved to form 2,4-pentanedion-3-ate; this anion can be protonated either by adventitious water or by a deliberately added proton donor to produce 2,4-pentanedione, or the anion can be trapped with iodoethane to give 3-ethyl-2,4-pentanedione. However, when cobalt(I) salen is electrogenerated at -0.40 V (a potential at which the rate of generation of cobalt(I) salen is relatively small), the 2,4-pentanedion-3-ate, resulting from the catalytic two-electron cleavage described above, can deprotonate unreduced starting material to form 3-chloro-2,4-pentanedion-3-ate and 2,4-pentanedione. In further work, we have found that 2,4-pentanedion-3-ate can be oxidized directly to form the corresponding radical which couples to yield 3,4-diacetyl-2,5-hexanedione. Chemically produced 2,4-pentanedion-3-ate reacts with electrogenerated cobalt(III) salen to give a dionylcobalt(III) salen species which undergoes a one-electron reduction to liberate cobalt(II) salen and the dionate. In addition, cobalt(II) salen reacts with molecular oxygen to give cobalt(III) salen and superoxide, and the latter reduces 3-chloro-2,4-pentanedione to form chloride ion, the 2,4-pentanedion-3-yl radical, and molecular oxygen. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Electrochemical reduction; Cobalt salen; Glassy carbon cathodes; 3-Chloro-2,4-pentanedione

1. Introduction

Considerable research has been published concerning the chemical and electrochemical behavior of cobalt(II) salen. In particular, there has been interest over the past 25 years in the use of

electrogenerated cobalt(I) salen for the reduction of halogenated organic compounds [1–10]. Costa et al. [1–3] have studied the rate of the catalytic reduction of alkyl bromides and alkyl chlorides with electrogenerated cobalt(I) salen as well as the electroreduction of some alkylcobalt(III) salen complexes, and Bedioui et al. [4] have used zeolite-encapsulated cobalt(I) salen to reduce benzyl bromide. In addition, cobalt(I) salen has been

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employed by Fry et al. [5–7] for the reduction of benzal chloride to stilbene and by Kaufman et al. [8] for the tricatalytic reduction of benzotrichloride to diphenylacetylene. Bicontinuous micro-emulsions have been utilized by Zhou et al. [9,10] as an alternative solvent system for cobalt(I) salen-catalyzed reductions of alkyl bromides.

In the present study, we have employed cyclic voltammetry, controlled-potential electrolysis, and various spectroscopic techniques to investigate the catalytic reduction of 3-chloro-2,4-pentanedione by cobalt(I) salen, electrogenerated at carbon cathodes in acetonitrile containing tetramethylammonium tetrafluoroborate, and to explore how the mechanism for the catalytic reduction differs from that for the direct reduction of 3-chloro-2,4-pentanedione [11]. In addition, we discovered that direct anodic oxidation of chemically formed 2,4-pentanedion-3-ate, which is the final product of the catalytic reduction, can occur to give the 2,4-pentanedion-3-yl radical, which couples to yield 3,4-diacetyl-2,5-hexanedione. Furthermore, reaction of chemically generated 2,4-pentanedion-3-ate with electrogenerated cobalt(III) salen leads to a stable dionylcobalt(III) salen species which can undergo a one-electron reduction. Finally, cobalt(II) salen interacts chemically with dissolved molecular oxygen to give cobalt(III) salen and superoxide, and superoxide reacts with 3-chloro-2,4-pentanedione to yield chloride ion, the 2,4-pentanedion-3-yl radical, and molecular oxygen.

2. Experimental

2.1. Reagents

Each of the following reagents was used as received: [[2,2'-[1,2-ethanediyl]bis(nitrilomethylidyne)]bis[phenolato]]-*N,N',O,O'*]cobalt(II) hydrate (cobalt(II) salen, Aldrich, 97%), 3-chloro-2,4-pentanedione (Aldrich, 98%), 2,4-pentanedione (Fisher, 99%), iodoethane (Aldrich, 99%), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, Aldrich, 99.8 + %), and *n*-tetradecane (Aldrich, 99%). We synthesized 2,4-pentanedion-3-ate via the reaction of stoichiometric amounts of 2,4-pentanedione and sodium *tert*-butoxide (Aldrich, 97%) in ace-

tonitrile; the resulting salt was filtered and washed with diethyl ether. Acetonitrile (CH₃CN, Aldrich, 99.5%), employed as the solvent for all electrochemical experiments, was continuously refluxed over calcium hydride to remove water. Tetramethylammonium tetrafluoroborate (TMA-BF₄, Aldrich, 98%), used as the supporting electrolyte, was stored in a vacuum oven at 60°C prior to use. All deaeration procedures were accomplished with Air Products zero-grade argon.

2.2. Cells, electrodes, instrumentation and procedures

The cells for cyclic voltammetry [12] and controlled-potential electrolysis [13] have been described previously. For cyclic voltammetric experiments, a short length of 3 mm diameter glassy carbon rod (Grade GC-20, Tokai Electrode, Tokyo, Japan) was press-fitted into a shroud of Teflon to provide a planar, circular working electrode with an area of 0.077 cm². For controlled-potential electrolyses, reticulated vitreous carbon disks (RVC 2X1-100S, Energy Research and Generation, Oakland, CA) with geometric surface areas of approximately 200 cm² were used as working cathodes; these disks were prepared and cleaned according to a procedure described elsewhere [14]. All potentials are quoted with respect to a reference electrode consisting of a cadmium-saturated mercury amalgam in contact with dimethylformamide saturated with both cadmium chloride and sodium chloride [15,16]; this electrode has a potential of –0.76 V versus the aqueous saturated calomel electrode (SCE) at 25°C.

Cyclic voltammograms were obtained with the aid of a Princeton Applied Research Corporation (PARC) model 175 Universal Programmer coupled to a PARC model 173 potentiostat-galvanostat and were recorded with a Yokogawa model 3023 *X–Y* plotter. Controlled-potential electrolyses were performed with the aid of the potentiostat-galvanostat equipped with a PARC model 176 current-to-voltage converter. Electrolyses were programmed and current–time curves were acquired, stored, and integrated by means of lo-

cally written software, which controlled a Tecmar data acquisition board installed in an IBM personal computer.

Ultraviolet–visible spectra were obtained with either a Perkin Elmer (PE) model 552 scanning spectrophotometer equipped with a PE model 561 chart recorder or a Hewlett Packard (HP) model 8450A diode-array spectrophotometer equipped with an HP model 7550A graphics plotter. A pair of matched quartz cells with path lengths of 1.00 cm was used.

Electrolysis products were identified with the aid of gas chromatography–mass spectrometry (GC–MS); an HP model 5890 series II gas chromatograph in tandem with an HP model 5971 mass-selective detector (operating at 70 eV) was used. Quantitation of all products was accomplished by means of gas chromatography; samples of an electrolyzed solution were injected directly into an HP model 5890 series II dual-channel instrument equipped with flame-ionization detectors and coupled to an HP 3392A integrator. A 30 m × 0.53 mm capillary column (AT-35, Alltech Associates) with a stationary phase of poly(phenylmethylsiloxane) was employed. A known quantity of an electroinactive internal standard (*n*-tetradecane) was added to each solution prior to the start of an electrolysis. A gas chromatographic response factor was determined experimentally (with respect to *n*-tetradecane) for each electrolysis product. All yields reported represent the absolute percentage of starting material incorporated into a particular species.

2.3. Product identification

We identified the adduct obtained from the reaction of iodoethane with a previously electrolyzed solution of cobalt(II) salen and 3-chloro-2,4-pentanedione as 3-ethyl-2,4-pentanedione by means of GC–MS: *m/z* 128, M^+ (2%); 100, $C_5H_8O_2^+$ (8%); 86, $C_5H_{10}O^+$ (36%); 71, $C_4H_7O^+$ (68%); 43, $C_2H_3O^+$ (100%). To obtain a pure sample of 3,4-diacetyl-2,5-hexanedione, the dimer that is formed by direct oxidation of 2,4-pentanedione-3-ate, four electrolyzed solutions (each with a volume of 50 ml) were combined and stripped of solvent by means of rotary evaporation to give a

solid consisting of a mixture of the desired dimer and the supporting electrolyte. This solid was treated with diethyl ether to dissolve only the dimer, the mixture was filtered to remove the insoluble supporting electrolyte, the ether was removed by rotary evaporation, and the recovered dimer was purified by recrystallization from ethanol. Using 1H NMR spectrometry, we verified the identity of the dimer as 3,4-diacetyl-2,5-hexanedione: δ ($CDCl_3$), 2.02 (s, 12H, CH_3), 16.78 (s, 2H, OH).

3. Results and discussion

3.1. Cyclic voltammometric behavior of 3-chloro-2,4-pentanedione in the presence of cobalt(II) salen

Fig. 1 shows a cyclic voltammogram for the reversible, one-electron reduction of 1.0 mM cobalt(II) salen (curve A) recorded at 100 mV s^{-1}

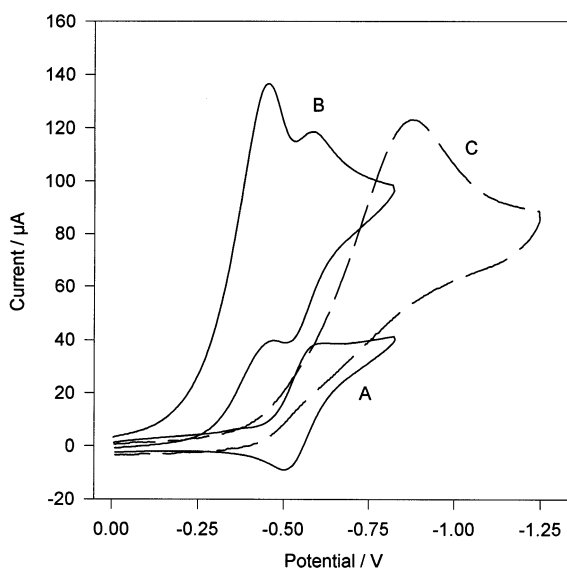


Fig. 1. Cyclic voltammograms recorded at 100 mV s^{-1} for the reduction of 1.0 mM cobalt(II) salen (curve A), for the reduction of 5.0 mM 3-chloro-2,4-pentanedione in the presence of 1.0 mM cobalt(II) salen (curve B), and for reduction of 5.0 mM 3-chloro-2,4-pentanedione (curve C) at a glassy carbon cathode (area, 0.077 cm^2) in CH_3CN containing 0.050 M TMBF₄.

Table 1

Coulometric data and product distributions for controlled-potential electrolyses of 20 mM 3-chloro-2,4-pentanedione by cobalt(I) salen electrogenerated at -0.65 V and under various conditions at carbon cathodes in CH_3CN containing 0.050 M TMABF_4

Entry	Conditions		<i>n</i>	Product distribution (%)			
	Co(II) salen (mM)	Added reagent (mM)		2,4-Pentanedione	3-Ethyl-2,4-pentanedione	3-Chloro-3-ethyl-2,4-pentanedione	Total ^b
1	2.00	—	2.01	55	—	—	55
2	1.00	—	1.94	65	—	—	65
3	0.50	—	1.95	60	—	—	60
4	1.00	Water (100)	1.86	80 ^c	—	—	80
5	1.00	HFIP (100)	2.01	105	—	—	105
6	2.00	Iodoethane (100) ^a	2.01	13	70	6	89
7	1.00	Iodoethane (100) ^a	2.02	7	68	7	82
8	0.50	Iodoethane (100) ^a	1.95	7	71	7	85

^a Added after completion of the electrolysis.

^b Remaining product is the tetramethylammonium salt of 2,4-pentanedion-3-ate.

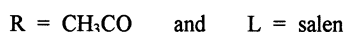
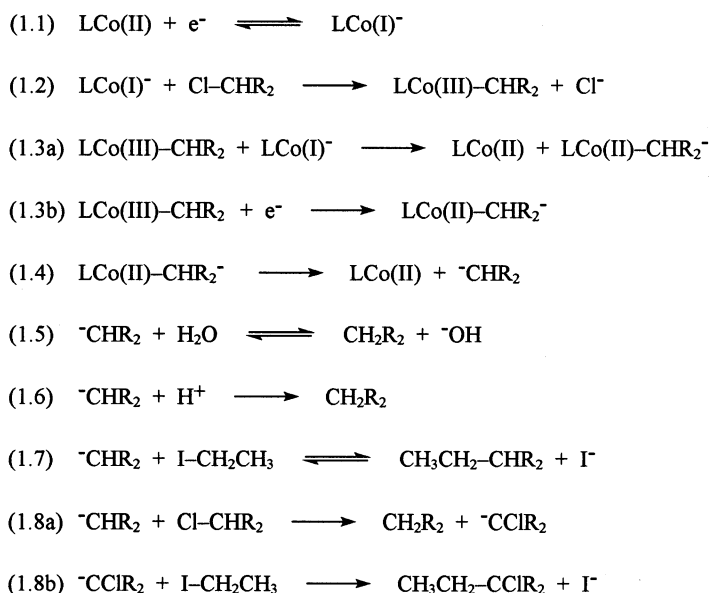
^c Average for water concentrations ranging from 100 mM to 1 M.

with a glassy carbon cathode in CH_3CN containing 0.050 M TMABF_4 . Curve C depicts a cyclic voltammogram for the direct, irreversible reduction of 5.0 mM 3-chloro-2,4-pentanedione under similar conditions. For a solution containing 5.0 mM 3-chloro-2,4-pentanedione and 1.0 mM cobalt(II) salen, the voltammogram appears as illustrated in curve B of Fig. 1. We attribute the first wave in curve B to the virtually simultaneous occurrence of three events: (a) one-electron electrogeneration of cobalt(I) salen, (b) its very fast reaction with a molecule of 3-chloro-2,4-pentanedione to form a dionylcobalt(III) complex, and (c) one-electron reduction of the complex to form cobalt(II) salen and the 2,4-pentanedion-3-ate anion. Reversible one-electron reduction of cobalt(II) salen, liberated by the reduction of the dionylcobalt(III) species, is responsible for the second wave of curve B. Increasing the concentration of 3-chloro-2,4-pentanedione from 5.0 to 15.0 mM, while the concentration of cobalt(II) salen is kept at 1.0 mM, causes the height of the first wave to increase, whereas the height of the second wave remains constant.

3.2. Controlled-potential reduction of 3-chloro-2,4-pentanedione by cobalt(I) salen electrogenerated at -0.65 V

Compiled in Table 1 are coulometric data and

product distributions, averaged from at least three replicate experiments, for controlled-potential reductions of 3-chloro-2,4-pentanedione by cobalt(I) salen electrogenerated at -0.65 V at reticulated vitreous carbon cathodes in CH_3CN containing 0.050 M TMABF_4 under a variety of conditions. Coulometric *n* values are reproducible to ± 0.1 and product yields agree to $\pm 3\%$ absolute. In the absence of a deliberately added proton donor, as entries 1–3 reveal, catalytic reduction of the starting material is a net two-electron process, and 2,4-pentanedione is obtained in approximately a 60% yield; changes in the initial concentration of cobalt(II) salen have no significant effect on the *n* value or the yield of 2,4-pentanedione. As shown by entry 4, the presence of deliberately added water during electrolysis causes the yield of 2,4-pentanedione to increase to 80%. Performing controlled-potential electrolyses in the presence of a 5-fold excess of HFIP, a proton donor that is stronger than water, causes no change in the measured *n* value, but the yield of 2,4-pentanedione increases to essentially 100% (entry 5). In the presence of a 5-fold excess of isopropanol-2-*d*, an excellent deuterium atom donor, no incorporation of deuterium into 2,4-pentanedione was detected, a result indicating that a radical is not produced by the catalytic reduction of the starting material. If an excess of iodoethane is added to the solution after the



Scheme 1.

completion of electrolysis, the observed major product is 3-ethyl-2,4-pentanedione, along with 2,4-pentanedione and 3-chloro-3-ethyl-2,4-pentanedione (entries 6–8).

On the basis of the preceding information and the previously described cyclic voltammetric investigations, we believe that, when cobalt(I) salen is electrogenerated at -0.65 V, 3-chloro-2,4-pentanedione undergoes catalytic reduction as described in Scheme 1. Reaction 1.1 shows the reversible one-electron reduction of cobalt(II) salen to cobalt(I) salen which reacts rapidly with a molecule of starting material to displace chloride ion and to form a dionylcobalt(III) salen complex (reaction 1.2). Our attempts to isolate and characterize the dionylcobalt(III) salen species proved unsuccessful due to the apparent reduction of this complex by electrogenerated cobalt(I) salen (reaction 1.3a); indeed, the reaction of stoichiometric amounts of cobalt(I) salen and 3-chloro-2,4-pentanedione yields cobalt(II) salen and approxi-

mately half the amount of starting material. Thus, the dionylcobalt(III) salen species appears to undergo easy one-electron reduction, either indirectly (reaction 1.3a) or directly (reaction 1.3b), to give an unstable dionylcobalt(II) salen complex, which breaks apart as shown in reaction 1.4 to give cobalt(II) salen and 2,4-pentanedion-3-ate.

After reaction 1.4 takes place, the chemistry of the system is dictated solely by the behavior of 2,4-pentanedion-3-ate. In the absence of an added proton donor, the products are the aforementioned 2,4-pentanedione and 2,4-pentanedion-3-ate (which is present in solution as the tetramethylammonium salt). It is important to note that the solvent-supporting electrolyte contains adventitious (35 mM) water and that protonation of 2,4-pentanedion-3-ate by this water is responsible for the formation of 2,4-pentanedione in approximately a 60% yield (reaction 1.5); when the concentration of water is increased (100 mM or higher), 2,4-pentanedione is obtained in essen-

tially a 100% yield, but if the system were perfectly dry we would expect 2,4-pentanedion-3-ate to be the only product. However, addition of a 5-fold excess of HFIP causes complete conversion of 2,4-pentanedion-3-ate to 2,4-pentanedione (reaction 1.6). In three separate experiments, a 5-fold excess of iodoethane was added to a previously electrolyzed solution of 3-chloro-2,4-pentanedione in an effort to trap the 2,4-pentanedion-3-ate anion. We observed that a new product, 3-ethyl-2,4-pentanedione, is formed in approximately a 70% yield and that there is an accompanying decrease in the yield of 2,4-pentanedione, which can be attributed to a set of equilibria (reactions 1.5 and 1.7) describing the reactions of 2,4-pentanedion-3-ate. As the concentration of the anion is depleted due to reaction with iodoethane (reaction 1.7), 2,4-pentanedione is deprotonated by hydroxide ion to maintain equilibrium (reaction 1.5), which accounts for the decrease in the yield of 2,4-pentanedione shown in Table 1, entries 6–8. Furthermore, 2,4-pentanedion-3-ate can deprotonate the starting material to form 2,4-pentanedione and 3-chloro-2,4-pentanedion-3-ate (reaction 1.8a) which, when trapped by iodoethane, will yield 3-chloro-3-ethyl-2,4-pentanedione (reaction 1.8b).

3.3. Controlled-potential reduction of 3-chloro-2,4-pentanedione by cobalt(I) salen electrogenerated at -0.40 V

A previous study [17] of the catalytic reduction of iodoethane by electrogenerated cobalt(I) salen revealed that the peak potential for reduction of cobalt(II) salen shifts 130 mV in the positive direction in the presence of excess substrate due to the exceedingly large second-order rate constant (5×10^6 l mol⁻¹ s⁻¹) for the catalyst–substrate reaction. Since the cathodic peak potential for the first wave of curve B in Fig. 1 is 170 mV more positive than that for curve A, the reaction between electrogenerated cobalt(I) salen and 3-chloro-2,4-pentanedione to form the dionylcobalt(III) salen intermediate as well as the ensuing one-electron reduction of this intermediate must be easier than the cobalt(I) salen-iodoethane reaction. Accordingly, we were interested in exploring the behavior of the present system under

conditions where the rate of generation of cobalt(I) salen is lower than for the experiments carried out at -0.65 V.

Table 2 lists coulometric data and product distributions obtained from reductions of 3-chloro-2,4-pentanedione by cobalt(I) salen electrogenerated at -0.40 V. Entries 1, 3, and 5 show results of cobalt(I) salen-catalyzed reductions of starting material with catalyst to substrate ratios of 1:5, 1:20, and 1:40, respectively, whereas entries 2, 4, and 6 show data for the same experiments except that excess iodoethane was added to each solution after completion of electrolysis. Two important differences are seen when the results in Tables 1 and 2 are compared. First, the coulometric n values listed in Table 2 are less than the expected value of 2 (Table 1) and approach 1 as the ratio of catalyst to substrate decreases. Second, the major product obtained from the trapping experiments with iodoethane changes from 3-ethyl-2,4-pentanedione (Table 1) to 3-chloro-3-ethyl-2,4-pentanedione (Table 2).

Since the rate of reduction of cobalt(II) salen is small, the reaction between cobalt(I) salen and 3-chloro-2,4-pentanedione proceeds more slowly to yield the 2,4-pentanedion-3-ate anion. Thus, the concentration of unreduced 3-chloro-2,4-pentanedione remains comparatively high, allowing deprotonation of the starting material by 2,4-pentanedion-3-ate (reaction 1.8a) to become the dominant pathway for the consumption of 3-chloro-2,4-pentanedione, and causing the n value to be less than 2. Then, in the subsequent trapping experiments with iodoethane, 3-chloro-3-ethyl-2,4-pentanedione is formed in a higher yield (reaction 1.8b) than is seen in Table 1.

3.4. Direct electrochemical oxidation of 2,4-pentanedion-3-ate

Shown in Fig. 2, curve A, is a cyclic voltammogram recorded at 200 mV s⁻¹ for the direct oxidation of 5.0 mM 2,4-pentanedion-3-ate at a glassy carbon anode in CH₃CN containing 0.050 M TBABF₄. Direct oxidation of this anion gives rise to a single irreversible wave with a peak potential of +1.30 V and, on the basis of controlled-potential coulometry, involves the transfer

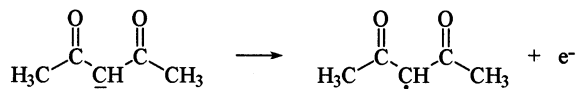
Table 2
Coulometric data and product distributions for controlled-potential electrolyses of 3-chloro-2,4-pentanedione by electrogenerated cobalt(II) salen at -0.40 V and under various conditions at carbon cathodes in CH_3CN containing 0.050 M TMABF_4

Entry	Conditions		n	Product distribution (%)				
	Co(II) salen (mM)	Starting material (mM)		Iodoethane ^a (mM)	2,4-Pentanedione	Starting material	3-Ethyl-2,4-pentanedione	3-Chloro-3-ethyl-2,4-pentanedione
1	2.00	10.0	—	61	0	—	—	61
2	2.00	10.0	100.0	52	0	15	21	88
3	1.00	20.0	—	55	4	—	—	59
4	1.00	20.0	100.0	55	4	6	31	96
5	0.50	20.0	—	65	0	—	—	65
6	0.50	20.0	100.0	56	0	5	31	92

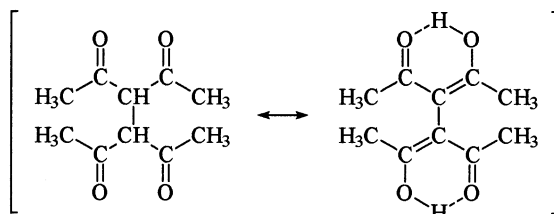
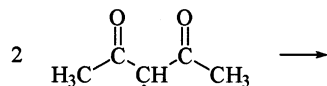
^a Added after completion of the electrolysis.

^b Remaining product is the tetramethylammonium salt of 3-chloro-2,4-pentanedione-3-ate.

of one electron to afford the 2,4-pentanedion-3-yl radical:

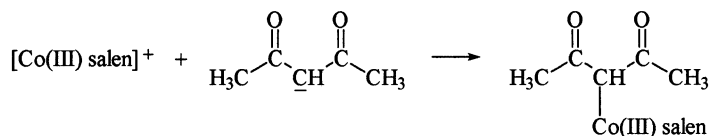
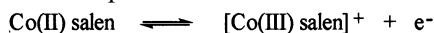


Upon being formed, the radical dimerizes to give 3,4-diacetyl-2,5-hexanedione, which exists in the enol form as evidenced by ^1H NMR data that we obtained and that appears in the literature [18]:



3.5. Electrochemical formation and behavior of the dionylcobalt(III) salen complex

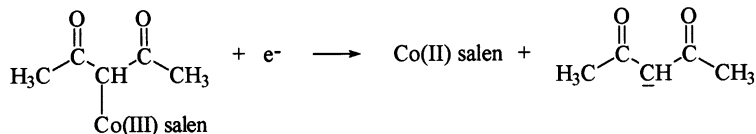
Evidence for the formation of a complex between electrogenerated cobalt(III) salen and 2,4-pentanedion-3-ate is provided in Fig. 2, curve B, which depicts a cyclic voltammogram obtained at a carbon electrode in CH_3CN containing 0.050 M TMABF_4 for the oxidation of 5 mM 2,4-pentanedion-3-ate in the presence of 1.0 mM cobalt(II) salen. Wave 1, with a peak potential of +0.87 V, corresponds to the reversible oxidation of cobalt(II) salen to cobalt(III) salen in the presence of 2,4-pentanedion-3-ate, this potential is roughly 100 mV more negative than for the irreversible oxidation of cobalt(II) salen alone (illustrated by the dashed line in curve B). These observations indicate the formation of a neutral dionylcobalt(III) salen complex:



We believe that this dionylcobalt(III) salen species is identical to that formed during the catalytic reduction of 3-chloro-2,4-pentanedione by electro-generated cobalt(I) salen.

As the potential for the experiment denoted by curve B in Fig. 2 is scanned in the positive direction beyond wave 1, one sees wave 2 with a peak potential of +1.36 V which we attribute to direct oxidation of the anion. Notice, however, that the peak current for wave 2 is approximately 80% of

the value measured for direct oxidation of 2,4-pentanedion-3-ate at the same concentration (curve A, Fig. 2); this result is due to complexation of 1.0 mM 2,4-pentanedion-3-ate by the 1.0 mM cobalt(III) salen, leaving 4.0 mM dionate (80% of the original amount) free to be oxidized directly. When the direction of the positive-going scan is reversed at +1.60 V and the potential is swept in the negative direction, one observes wave 3 (with a peak potential of approximately -0.1 V) which represents the irreversible one-electron reduction of the dionylcobalt(III) salen complex to yield 2,4-pentanedion-3-ate and cobalt(II) salen:



Digital simulations of this mechanistic picture for the formation and reduction of the dionylcobalt(III) species produce a cyclic voltammogram, shown by curve C in Fig. 2, similar to that shown in curve B, with the simulated peak currents and peak potentials for the three waves being within 3% of the experimental values. Parameters for the simulation were taken, in part, from work done previously in our laboratory [17] for the cobalt(II) salen–iodoethane system.

Additional evidence for the existence of the dionylcobalt(III) salen complex can be seen in

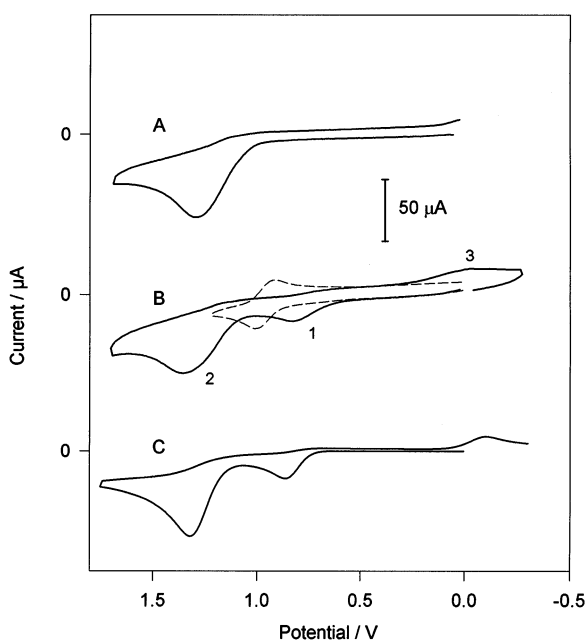


Fig. 2. Cyclic voltammograms recorded at 200 mV s^{-1} for the direct oxidation of 5.0 mM 2,4-pentanedion-3-ate (curve A) and for the oxidation of 5.0 mM 2,4-pentanedion-3-ate in the presence of 1.0 mM cobalt(II) salen (curve B) at a glassy carbon cathode (area, 0.077 cm^2) in CH_3CN containing 0.050 M TMABF_4 . For both curves A and B, the potential scan was initiated in the positive direction starting from 0 V . The dashed curve shows the reversible one-electron oxidation of cobalt(II) salen to cobalt(III) salen. Curve C is a simulated voltammogram that corresponds to curve B.

Fig. 3, which portrays ultraviolet–visible spectra for cobalt(II) salen (curve A), cobalt(III) salen (curve B), and the dionylcobalt(III) salen complex (curve C). To obtain the spectrum of cobalt(III) salen, we carried out a controlled-potential oxidation of cobalt(II) salen in an electrolysis cell fitted with delivery tubes and a peristaltic pump so that the resulting cobalt(III) salen could be circulated through a quartz flow-through spectrophotometer cell. We obtained the spectrum of dionylcobalt(III) salen in a similar fashion by electro-generating cobalt(III) salen and then adding a slight excess of chemically prepared 2,4-pentanedion-3-ate to form the complex. In the vicinity of 400 nm are charge-transfer (CT) bands; with respect to the CT band for cobalt(III) salen, the CT bands for both cobalt(II) salen and the dionylcobalt(III) salen species are shifted toward longer

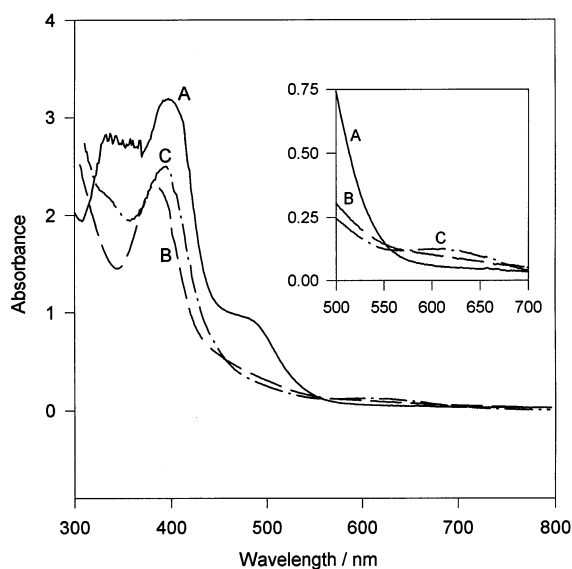


Fig. 3. Ultraviolet–visible spectra obtained in CH_3CN for (A) cobalt(II) salen, (B) cobalt(III) salen, and (C) the dionylcobalt(III) salen complex; each species was at a concentration of 0.50 mM in a 1.00 cm quartz spectrophotometer cell. For these spectra, the values of λ_{max} for the CT bands are as follows: 397 nm (curve A), 381 nm (curve B), and 393 nm (curve C).

Table 3

Initial conditions and final concentrations of 3-chloro-2,4-pentanedione for the reaction of cobalt(II) salen with molecular oxygen to facilitate reduction of 3-chloro-2,4-pentanedione

Initial concentration		Final concentration of 3-chloro-2,4-pentanedione		
Co(II) salen (mM)	3-Chloro-2,4-pentanedione (mM)	Expected (mM)	Found (mM)	Difference (%)
2.43	10.0	7.57	7.15	-5.5
0.98	10.0	9.0	9.2	2.2
0.49	10.0	9.5	9.3	-2.1
0.20	10.0	9.8	9.6	-2.0

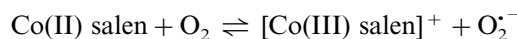
wavelengths (lower energies). We expect this behavior on the basis of the facts that: (a) formation of cobalt(II) salen by addition of one electron to cobalt(III) salen causes the CT energy gap to decrease, and (b) donation of electron density to cobalt(III) through its complexation with 2,4-pentanedion-3-ate decreases the CT energy gap. In the inset of Fig. 3, showing the wavelength region from 500 to 700 nm, a new absorption maximum can be seen only for the dionylcobalt(III) salen complex, which indicates the strong interaction of the anion with the metal.

3.6. Chemical reduction of 3-chloro-2,4-pentanedione by superoxide formed by the reaction between cobalt(II) salen and dissolved molecular oxygen

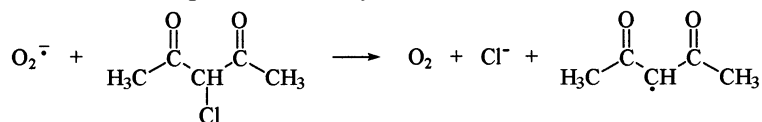
While studying the electrochemical behavior of 3-chloro-2,4-pentanedione in the presence of either cobalt(I) salen or cobalt(III) salen, we detected a reaction involving cobalt(II) salen, the chlorodione, and dissolved molecular oxygen. Shown in Table 3

cobalt(II) salen was 0.49 mM (Table 3), we found that the ultraviolet–visible spectrum changed from that of cobalt(II) salen before the start of the reaction to that of cobalt(III) salen after the reaction had proceeded for 24 h. In addition, we performed a potentiometric titration (with standard silver nitrate solution) of the chloride released during the reaction of 10.0 mM cobalt(II) salen with 10.0 mM 3-chloro-2,4-pentanedione in air-saturated CH_3CN ; we found the chloride concentration to be 9.8 mM. Finally, no reaction was observed when the cobalt(II) salen solution was deaerated with argon prior to addition of 3-chloro-2,4-pentanedione.

On the basis of the preceding information, we believe that dissolved molecular oxygen oxidizes cobalt(II) salen to form cobalt(III) salen and superoxide:



In turn, superoxide can reduce 3-chloro-2,4-pentanedione to form oxygen, chloride, and the 2,4-pentanedion-3-yl radical:



are product distributions obtained after 24 h for the reaction of 10.0 mM 3-chloro-2,4-pentanedione with different initial concentrations of cobalt(II) salen in air-saturated CH_3CN . Assuming that the reaction involves one-to-one stoichiometry, we noticed that in all experiments the quantity of 3-chloro-2,4-pentanedione decreased by the amount of cobalt(II) salen initially present. For the experiment in which the initial concentration of

and the radical can dimerize to form 3,4-diacetyl-2,5-hexanedione, as described earlier.

Conceivably, if the potential of an electrode in air-saturated CH_3CN containing cobalt(II) salen and 3-chloro-2,4-pentanedione is held at 0 V, complete catalytic reduction of the starting material would eventually occur with 3,4-diacetyl-2,5-hexanedione and cobalt(II) salen as the major products.

4. Conclusions

Catalytic reduction of 3-chloro-2,4-pentanedione by electrogenerated cobalt(I) salen occurs through a pair of one-electron transfers to afford 2,4-pentanedion-3-ate. Protonating the anion with water or trapping the anion with iodoethane yields 2,4-pentanedione or 3-ethyl-2,4-pentanedione, respectively, as the major product. Virtually no chlorinated species are detected among the products. These findings differ dramatically from what is known about the direct reduction of 3-chloro-2,4-pentanedione [11]. Most likely, the absence of chlorinated products is due to the fact that formation of the dionylcobalt(III) salen intermediate takes place preferentially to the deprotonation of 3-chloro-2,4-pentanedione by the generated 2,4-pentanedion-3-ate; the latter process occurs when 3-chloro-2,4-pentanedione is reduced directly. In addition, electrochemical oxidation of 2,4-pentanedion-3-ate leads to a different kind of dimer from that obtained via the direct oxidation of 3-chloro-2,4-pentanedion-3-ate. As seen in the present investigation, when the former anion undergoes one-electron oxidation, the resulting 2,4-pentanedion-3-yl radical dimerizes by the formation of a carbon–carbon bond; however, when the latter anion undergoes one-electron oxidation, the resulting 3-chloro-2,4-pentanedion-3-yl radical forms a dimer with a vinyl–ether linkage [11].

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