

Preliminary communication

REACTION OF MOLECULAR OXYGEN WITH PARAMAGNETIC ORGANOMETALLIC CLUSTER ANIONS

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Summary

Electrochemically generated paramagnetic cobalt or iron cluster anions bearing μ_1 , μ_2 or μ_3 organic ligands react with oxygen with fragmentation and extrusion of the organic ligands.

Paramagnetic clusters are neutral species bearing an odd electron number [1] or anions generated by reversible one-electron reduction of the parent neutral diamagnetic compounds [2, 3]. Up to now the ready access to these anion radicals has only been utilized to perform electrocatalytic replacement of carbon monoxide by other ligands through an $S_{RN}1$ mechanism [4–6]. During the course of our investigation on the reactivity of such transient species we have looked for reactions other than electron-transfer and we now report our results concerning the reactions of paramagnetic cluster anions with molecular oxygen. It is well-known that reduced metal complexes react with molecular oxygen, but to our knowledge this reaction has been studied only in cases in which the potentials are such that electron transfer to O_2 occurs in the first step. We have studied a new situation: the metal complexes chosen show a first reversible one-electron reduction at a potential lower than the monoelectronic reduction of oxygen in aprotic solvents so that the paramagnetic species can be electrogenerated in situ in the presence of O_2 , thus avoiding, in principle, a thermodynamically disfavored electron transfer occurring by an outer-sphere mechanism.

The cluster complexes I [7] (Ia: $R^1 = C_6H_{11}$, $R^2 = C_6H_5$; Ib: $R^1 = \alpha$ -cholestan-1-yl, $R^2 = C_6H_5$), II [8] ($R = CO_2Me$), and III, (p -MeOC₆H₄C(Co)₃(CO)₉) [9],

are appropriate substrates because the redox potential for cluster + $e^- \rightleftharpoons$ cluster $^-$, in the range -0.58 to -0.73 V SCE in dimethylformamide (DMF) is less negative [10,11] than that corresponding to $O_2 + e^- \rightleftharpoons O_2^-$ (-0.85 V SCE in DMF). In addition the clusters studied contain μ_1, μ_2 or μ_3 organic ligand, which enables useful information to be obtained about the course of the reaction.

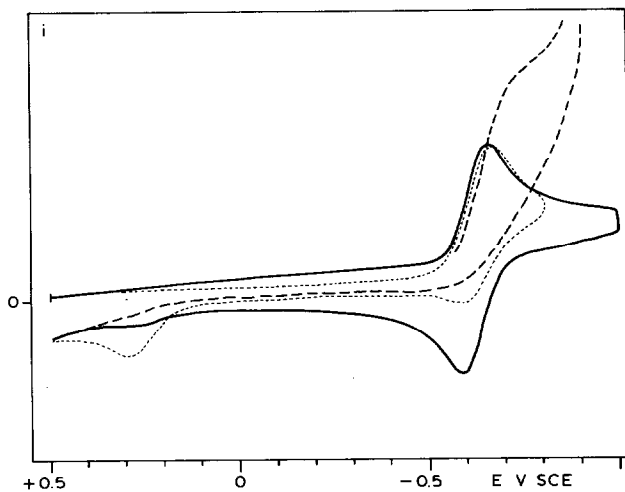
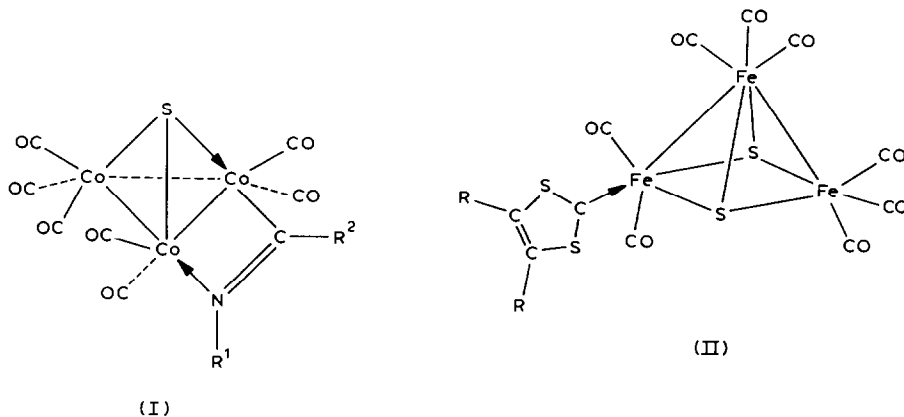


Fig. 1. Cyclic voltammetry of cluster Ia (10^{-3} M) in dimethyl formamide/ 0.1 M $Bu_4N^+ BF_4^-$, on platinum electrode; scan rate 0.2 V s^{-1} . — under nitrogen (1 atm.); ... in an aerated solution; ---- under oxygen (1 atm.).

As shown in Fig. 1 the voltammetric curve is markedly changed when oxygen is passed through the solution. At low concentration of O_2 the cathodic peak remains unchanged but the reversibility is lost, and the $Co(CO)_4^-$ fragment is identified by its irreversible oxidation at $E_p = +0.30$ Volt SCE. With an excess of oxygen $Co(CO)_4^-$ is not observed, and the cathodic current increases in agreement with a catalytic reduction of oxygen. Since all the starting materials are air-stable, these results indicate that there is a reaction between oxygen and the cluster anion. Additional informations are obtained after controlled

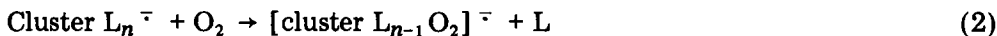
potential electrolysis of I, II and III under O₂ (0.2 atm.) at a mercury electrode in dimethyl formamide. The coulometric data were inaccurate because of the close proximity of the oxygen reduction, but in every case the organic ligands were recovered after abstraction of sulfur or incorporation of oxygen, as the thioamides IV, R¹NHC(S)R² (IVa: R¹ = C₆H₁₁, R² = C₆H₅; IVb: R¹ = α -cholestanyl, R² = C₆H₅), the dicarbomethoxy 1,3-dithiole-2-thione, V, or to the carboxylic acid, VI, (*p*-MeOC₆H₄CO₂H); these were isolated in good yield after conventional treatment and chromatography on silica (Table 1).

TABLE 1

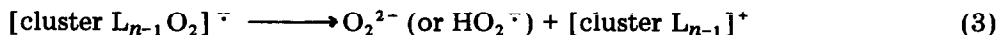
Cluster ^a	Potential (volt SCE)	Electricity used ^b	Product % ^d
Ia	-0.8	1.35	IVa (76)
Ib	-0.7	—	IVb (78)
II	-0.7	4 ^c	V (57)
III	-0.5	0.78	VI (73)

^a 5 × 10⁻⁴ mole of cluster in 150 ml of DMF 0.1 M Bu₄NBF₄ at 25°C in the dark. ^b In mole of electrons per mole of cluster. ^c The electrolysis was stopped after consumption of 4e⁻ per mole; unidentified electroactive products catalysed the reduction of oxygen. ^d Yields of pure products identified by mass spectroscopy and comparison with authentic samples (IR, ¹H NMR, mixed m.p.).

It is noteworthy that the reaction of O₂ with the anion radicals of clusters I and II regenerated the thioamides IV and the thione V, which are the ligands used to prepare the cluster complexes by reaction with Co₂(CO)₈ [7] or Fe₂(CO)₉ [8]. Destruction of complex III results in the incorporation of one molecule of oxygen per molecule of cluster, but the final product, VI, is at the same oxidation level as the starting materials from which it is made (RC(S)SME or RCCl₃) [9]. In addition to the organic products the solution contains cobaltous or ferrous salts, which may explain why no hydrogen peroxide could be detected in the solution. These results suggest the occurrence of a stepwise fragmentation, and can be rationalized by assuming that the first step is either the redox equilibrium 1 or the ligand substitution reaction 2.



Reaction 1 is not thermodynamically favored and, since in the medium used, the protonation of O₂⁻ is excluded the equilibrium is not displaced by further dismutation of HO₂⁻. The reaction can thus be interpreted as a regio-selective radical-radical interaction between oxygen and the metal atoms of the paramagnetic cluster in which the unpaired electron occupies antibonding orbitals of high metal character [1, 3]. But in view of recent results [4-6] showing that the rate of ligand substitution is markedly enhanced when paramagnetic species are involved, reaction 2 seems more likely. Intramolecular electron-transfer to coordinated oxygen may then give O₂²⁻ or HO₂⁻ and a cluster cation, as in equation 3.



Cluster cations are not stable enough to bring about catalytic reduction of oxygen, and they undergo stepwise fragmentation leading to the release of the organic components and to organometallic fragments such as $\text{Co}(\text{CO})_4^-$ and ultimately to inorganic salts of low oxidation states. Under high concentration of oxygen more than one molecule can interact with the cluster anions leading to a rapid destruction of the metallic framework and deposition of metal at the electrode surface. This accounts for the catalytic reduction of oxygen and we have observed the multi-electron reduction of O_2 at a cobalt electrode, in agreement with similar observations recently reported for other metallic electrodes [12].

Our results reveal that O_2 regio-selectively destroys the metal framework of the paramagnetic cluster anions and that is accompanied by extrusion of the organic ligand. The observations are of particular interest in the case of clusters I and II which provide models of an intermediate step in the well-known desulfurization reaction of sulfur-containing molecules by organometallic reagents [7]. Since clusters can be viewed as microscopic models of metal surfaces we are now studying the scope and limitations of these reactions, which may be relevant to the regeneration of catalysts used in the desulfurization of fuels and coals [13] and to the problem of oxygen reduction at metallic electrodes [14].

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