

Formation of $\text{Fe}_3(\text{CO})_{12}^-$ and $\text{Fe}_3(\text{CO})_{12}^{2-}$ during the Electrochemical Reduction of Triiron Dodecacarbonyl

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Though the electrochemical behaviour of $\text{Fe}_3(\text{CO})_{12}$ was reported by several investigators [1–3] not even in the most recent paper [3] has the overall mechanism of the reduction of $\text{Fe}_3(\text{CO})_{12}$ been described. Whereas the first reduction step was studied in some detail, although not fully conclusively [2, 3], not much attention was paid to the second reduction, especially as regards the nature of the products. In this short note we would like to describe new experiments giving conclusive information on the nature of the first reduction product as well as on the mechanism of the second reduction step.

To avoid the interference of the solvent-assisted reactions, which seem to be the reason of discrepancies in the behaviour as described by various workers, all the investigations described were carried out in dry dichloromethane with tetrabutylhexafluorophosphate as base electrolyte under conditions excluding atmospheric moisture and oxygen.

$\text{Fe}_3(\text{CO})_{12}$ shows at mercury as well as platinum electrode two 1 electron reduction steps (determined by comparison with pilot ion and coulometrically) (${}_1E_{1/2} = -0.44$ V, ${}_2E_{1/2} = -0.83$ V vs. SCE) both using the classical dc polarography or single sweep cyclic voltammetry.

The first reduction step is electrochemically as well as chemically fully reversible (shown by Kalousek commutator and cyclic voltammetry). The preparative electrolysis at low temperatures ($T = 180$ K) at the potential of the limiting current of the first reduction wave gives a product, the ESR spectrum of which shows only one line (A) with $g_A = 2.0043$ (see Fig. 1, curve 1). The heating of the solution up to $T = 243$ K or more gives rise to traces of other two paramagnetic species (curve 2), the ESR signal of which is not changed by back cooling (curve 3). When the electrolysis is carried out at room temperature the two lines B and C arise a few seconds after appearance of the line A. The g -factors of the new observed species are $g_B = 2.054$ and $g_C = 2.051$. Lines B and C are obviously due to decomposition products and not to forms which were in equilibrium with species giving the line A, as was deduced by Peake and collaborators [3a].

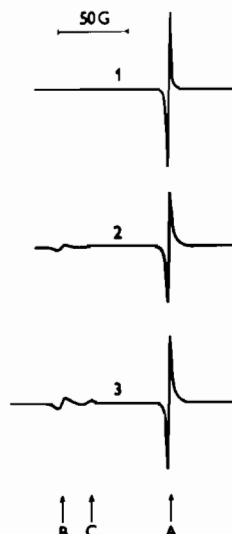


Figure 1. ESR spectra of radicals generated electrochemically from $\text{Fe}_3(\text{CO})_{12}$ at the potential $E = -0.5$ V vs. (SCE) at low temperature. (1) $T = 180$ K; (2) after heating up to $T = 243$ K; (3) the same solution cooled to $T = 180$ K.

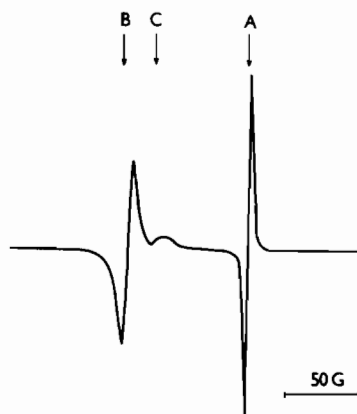


Figure 2. ESR spectra of the solution of $\text{Fe}_3(\text{CO})_{12}$ during electrolyses at $E = -0.5$ V (vs. SCE) at room temperature ($g_A = 2.0043$, $g_B = 2.054$, $g_C = 2.052$).

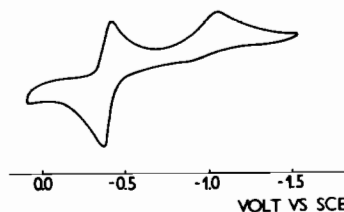


Figure 3. Dc cyclic voltammogram at platinum of $\text{Fe}_3(\text{CO})_{12}$ in dichloromethane; scan rate 8 V s^{-1} .

The electrochemical and chemical reversibility of the process point to the conclusion that the line A is due to the monoanion radical, $\text{Fe}_3(\text{CO})_{12}^-$, which decomposes in rather complicated way.

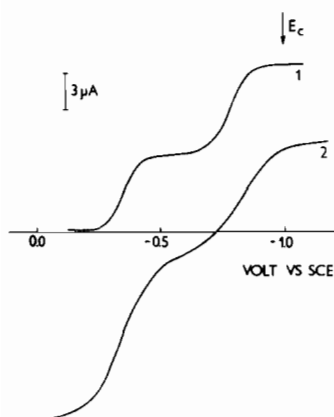


Figure 4. Dc polarogram (1) and curve recorded by Kalousek commutator (2) of $\text{Fe}_3(\text{CO})_{12}$ at DME in dichloromethane. Auxiliary potential $E_C = -1.0$ V (vs. SCE), drop time 2s, commutating frequency 12.5 s^{-1} .

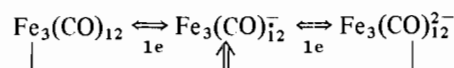
The second reduction step is electrochemically not fully reversible ($\alpha = 0.83$) nor any product oxidizable at the potential of the second step has been detected. However, the product of the overall reduction is oxidized at the potential of the first step as can be deduced from the cyclic voltammetry curves (see Fig. 3) and especially from the experiments with Kalousek commutator (see Fig. 4). The latter one shows that the product formed at -1.0 V (*i.e.* at the potential of the limiting current of the second reduction step) is converted rapidly into a product reversibly oxidized at the potential of the first step, *i.e.* $\text{Fe}_3(\text{CO})_{12}^-$. In the early stages of electrolysis with ESR control at the potential of the second reduction step (*i.e.* when 2 electrons are consumed per one $\text{Fe}_3(\text{CO})_{12}$ particle) only line A is observed, *i.e.* $\text{Fe}_3(\text{CO})_{12}$ is formed as the only product. Lines B

and C arise again after a few seconds as the result of follow up reactions.

This behaviour points to the conclusion that the primary product of the second reduction step is $\text{Fe}_3(\text{CO})_{12}^{2-}$ which reacts very rapidly with $\text{Fe}_3(\text{CO})_{12}$ with formation of the monoanion radical. As only line A is primarily observed it can be concluded that this reaction is faster than any reaction splitting off CO from the dianion.

However, in the presence of proton donating solvents direct abstraction of hydrogen from the solvation shell seems to occur transforming $\text{Fe}_3(\text{CO})_{12}^{2-}$ into a hydride species, reducible at the same potential and causing thus an increase of electron consumption in the overall reduction over 2 per one $\text{Fe}_3(\text{CO})_{12}$ molecule.

In summary, the electrode reaction can be described by the scheme:



The scheme omits slower reactions of $\text{Fe}_3(\text{CO})_{12}^-$ and $\text{Fe}_3(\text{CO})_{12}^{2-}$ resulting in splitting off of CO as the existence of these reactions is only indicated but cannot be studied in detail by electrochemical methods.

References

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