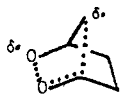
probability of achieving the appropriate conformation.[9] Such an explanation cannot be operative for decomposition of **2** since this strained bicyclic peroxide is conformationally rigid. Nevertheless, the similarity of reaction products and activation entropies suggest that the **2** → **9** rearrangement might also involve homolysis of the O-O bond with concerted β scission of a C-C bond in the transition state as indicated in **15.**



15

Geometric constraints imposed by the rigid bicyclic structure of the peroxide **2** should weaken the O-O bond owing to strain and unfavorable juxtaposition of vicinal nonbonding electron pairs on oxygen. Indeed, $\Delta H^{\ddagger}$ is considerably lower for nonpolar decomposition of **2** (21 kcal mol^{-1}) than for *tert*-butyl peroxide (38-41 kcal mol^{-1}). However, unexpectedly high thermal stability for **2**, as for **11**, is associated with an extraordinarily large negative activation entropy.

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Electrochemical Study of the Generation and Fate of Iron Dinitrosyl, a Powerful Catalyst for C-C Bond Formation from Dienes

Sir:

The building up of a selective catalyst remains a challenge to anyone interested in homogeneous catalysis. Vacant sites as well as specific ancillary ligands are needed. Reductive elimination of appropriate ligands has been proposed for the first purpose[1] and for the second one nitrosyl ligands were suggested owing to their electronic properties.[2] In this respect iron nitrosyl complexes exhibit a new selectivity toward the cyclodimerization of dienes.[3] For example $Fe(CO)_2(NO)_2$, $Fe(\eta\text{-}C_3H_5)(CO)_2NO$,[4] $[Fe(NO)_2Cl]_2$ + C_2H_5MgBr,[5] $[Fe(NO)_2Cl]_2$ + $(C_3H_5)_2Sn$,[6] $Na[Fe(CO)_3NO]$ + $[M(NO)_2X]_2$ (M = Fe, Co; X = Cl, Br, I),[7] $[Fe(NO)_2Cl]_2$ + $Ni(CO)_4$,[8] and $[Fe(NO)_2Cl]_2$ + Zn[9] convert selectivity butadiene to 4-vinylcyclohexene. The catalytic species has been claimed to be "$Fe(NO)_2$" without further characterizations owing to the complexity of the reaction medium. The generation and the identification of this moiety has retained our attention for two purposes: (i) the chemistry of dinitrosyl complexes[2c,10] and (ii) the economical importance of 4-vinylcyclohexene as a styrene precursor.[11] The complex $[Fe(NO)_2Cl]_2$ is a valuable precursor as a one-electron reduction can lead to "$Fe(NO)_2$".[12] The reduction can be achieved chemically and electrochemically. The electrochemistry, in nonaqueous solvents, of some related nitrosyl iron complexes has already been reported.[13] However, no electrochemical data on $[Fe(NO)_2Cl]_2$ are available and, more generally, connections between electrochemistry and catalysis are scarcely described.[14] We report here on the electrochemical behavior of $[Fe(NO)_2Cl]_2$ in association with catalysis in the cyclodimerization of norbornadiene (ndb), isoprene (is), and butadiene (bd). Comparison between catalytic runs performed in the electrochemical cell and by reduction with Zn definitely proves that the moiety "$Fe(NO)_2$" [12] is the active species.

All of the experiments were carried out in deoxygenated tetrahydrofuran (thf). The dissolution of the dimer $[Fe(NO)_2Cl]_2$ occurs instantaneously leading to the paramagnetic

Scheme I[a]

$$[\mathrm{Fe(NO)_2Cl}]_2 \longrightarrow 2\mathrm{Fe(NO)_2ClS}_n \tag{1}$$

$$\mathrm{Fe(NO)_2ClS}_n \rightleftharpoons [\mathrm{Fe(NO)_2S}_n]^+\mathrm{Cl}^- \tag{2}$$

oxidation

A wave:

$$2\mathrm{Fe(NO)_2ClS}_n + 2\mathrm{Hg} \xrightarrow{-4e^-} 2\mathrm{Fe}^{2+} + 4\mathrm{NO} + \mathrm{Hg_2Cl_2} \tag{3}$$

reduction

B wave:

$$\mathrm{Fe(NO)_2ClS}_n \xrightarrow{e^-} \mathrm{Fe(NO)_2S}_n + \mathrm{Cl}^- \tag{4}$$

$$\mathrm{Fe(NO)_2ClS}_n + \mathrm{Cl}^- \longrightarrow [\mathrm{Fe(NO)_2Cl_2}]^- \tag{5}$$

C wave:

$$[\mathrm{Fe(NO)_2Cl_2}]^- \xrightleftharpoons{e^-} [\mathrm{Fe(NO)_2Cl_2}]^{2-} \tag{6}$$

$$[\mathrm{Fe(NO)_2Cl_2}]^{2-} \longrightarrow \mathrm{Fe(NO)_2S}_n + 2\mathrm{Cl}^- \tag{7}$$

D wave:

$$[\mathrm{Fe(NO)_2Cl_2}]^{2-} \xrightarrow{e^-} [\mathrm{Fe(NO)_2Cl_2}]^{3-} \tag{8}$$

$$[\mathrm{Fe(NO)_2Cl_2}]^{3-} \longrightarrow [\mathrm{Fe(NO)_2S}_n]^- + 2\mathrm{Cl}^- \tag{9}$$

E wave:

$$\mathrm{Fe(NO)_2S}_n \xrightleftharpoons{e^-} [\mathrm{Fe(NO)_2S}_n]^- \tag{10}$$

[a] S_n represents molecules of tetrahydrofuran as ligands.

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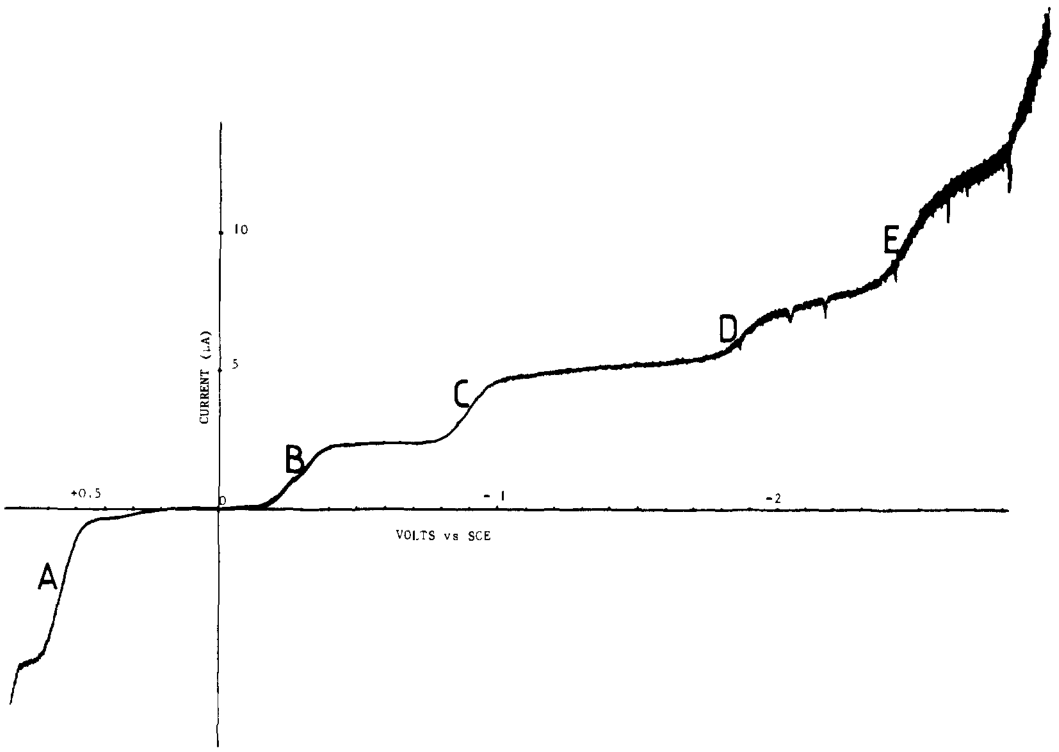

Figure 1. Polarogram of a 0.5 10^{-2} M solution of $[Fe(NO)_2Cl]_2$ in thf containing 0.1 M tetrabutylammonium hexafluorophosphate, at the dropping mercury electrode.

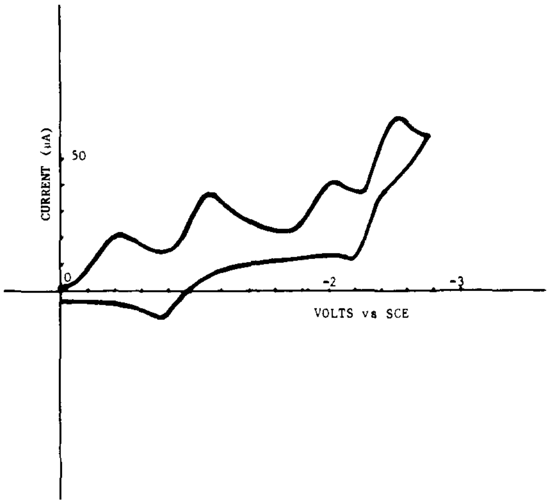

Figure 2. Voltammogram of 0.5 × 10^{-2} M solution of $[Fe(NO)_2Cl]_2$ in thf containing 0.1 M tetrabutylammonium hexafluorophosphate at the glassy carbon electrode: scanning rate, 0.1 V s^{-1}.

species $Fe(NO)_2Cl(thf)$, **1**: ν_{NO} 1780, 1714 cm^{-1}; one-line ESR signal with $g = 2.0383$, line width = 10 G at 25 °C. Upon dilution a one-line signal with $g = 2.0368$, line width = 11 G, replaces the former one. On addition of $AgBF_4$ to the reaction medium, AgCl precipitates and the cationic complex thus formed, $[Fe(NO)_2(thf)_n]^+BF_4^-$ (ν_{NO} 1810, 1730 cm^{-1}), exhibits a one-line signal with $g = 2.0359$, line width = 7 G.[15] We think that these results reveal the ion-pair character of compound **1** (Scheme I, eq 2).

The polarogram of **1** with a dropping mercury electrode shows one oxidation wave with $E_{1/2} = 0.53$ V[16] and four reduction waves, respectively, with $E_{1/2} = -0.29, -0.88, -2.03$, and -2.40 V (Figure 1). The ratio of wave heights corresponding to A, B, and C is 1:0.5:0.5 whatever the initial concentration of **1**.[17] In contrast D and E wave heights depend on this concentration. The sum is constant and equal to 1 in respect to the first set of waves, A, B, and C.

The cyclic voltammetry at a glassy carbon or a platinum electrode shows that the second and fourth reduction steps are reversible using a sweep rate of 0.1 V/s (Figure 2). Attempts to detect reversibility on the first and third reduction steps using scan rates of up to 50 V/s have failed. The oxidation step (A wave) is not detected at the platinum electrode. Therefore we must assume that mercury is oxidized to calomel in the presence of compound **1** (Scheme I, eq 3).

The controlled-potential electrolysis at +0.7 V at mercury pool electrode involves 2 faradays and leads to the disappearance of the oxidation wave, A. The detected species are only Hg_2Cl_2, which precipitates, and Fe^{2+}, with no nitrosyl ligands as shown by infrared. The oxidation experiments[18] lead us to assume that the reduction steps corresponding to the B and C waves each involve 0.5 faraday. This implies that an ECE mechanism is operative in which one species formed during the first electron transfer, namely, the chloride ion, reacts very rapidly with the starting material **1** to generate the new reducible complex $[Fe(NO)_2Cl_2]^-$ (ν_{NO} 1770, 1700 cm^{-1}; one-line ESR spectra with $g = 2.0338$, line width = 19 G at 25 °C). The successive steps are depicted in Scheme I (eq 4 and 5). We have prepared quantitatively $[Fe(NO)_2Cl_2]^-$ according to eq 5 (Scheme I) by the addition of PPN^+Cl^- to compound **1**.[19] $[Fe(NO)_2Cl_2]^-PPN^+$ exhibits a one-electron reduction wave corresponding to the C one in Figure 1.[20] This one-electron reduction is electrochemically but not chemically reversible (Scheme I, eq 6). Exhaustive electrolysis at a platinum electrode for the C wave suppresses the D wave and enhances the E wave height which corresponds then to a one-electron transfer. The electrolysis produces chloride ions in the stoichiometry 1 Cl^-:1 Fe. Moreover addition of 1,2-bis(diphenylphosphino)ethane (dppe) to the reaction medium leads to the quantitative formation of the well-known $Fe(NO)_2$dppe complex (80% yield). These results are consistent with the formulation of eq 7 (Scheme I). The D wave is logically attributed to the reduction of $[Fe(NO)_2Cl_2]^{2-}$ and the E one to that of $Fe(NO)_2(thf)_n$ (Scheme I, eq 8 and 10).

Scheme I depicts the overall electrochemical behavior of compound **1**. The multistep reduction produces neutral and anionic dinitrosyl iron complexes. Equations 4 and 7 point out

Table I. Catalytic Activity of $Fe(NO)_2(thf)_n$ Prepared Electrochemically or Chemically (T (°C), 22; reaction time, 3 h)

	reduction at −1.1 V		reduction by Zn	
diene	conversion^{a,b}	selectivity (%)	conversion^{b,c}	selectivity (%)
nbd	300	exo-trans-exo-dimer (93)^{d}	310	exo-trans-exo dimer (93)^{d}
is	750	1,4- (2,4-) dimethyl-4-vinylcyclohexene (94)^{e}	1000	1,4- (2,4-) dimethyl-4-vinylcyclohexene (94)^{e}
bd	270	4-vinylcyclohexene (100)	9500^{f}	4-vinylcyclohexene (100)

[a] Moles of diene dimerized per faraday. [b] Conversion and selectivity determined by GPC on a Chromosorb PAW–10 % SE-30 column with internal standards. The products have been identified by ^{1}H and ^{13}C NMR and mass spectrometry. [c] Moles of diene dimerized per mole of catalytic precursor; this system was not optimized. [d] Exo-trans-endo dimer, 7%. [e] 1-Methyl-5- (4-) isopropenylcyclohexene, 6%. [f] Run performed under autogenous butadiene pressure.

the formation of $Fe(NO)_2(thf)_n$. It is noteworthy that the number of moles of $Fe(NO)_2(thf)_n$ appearing after the reduction at ca. −0.7 V is half of that arising at ca. −1.1 V. Moreover the characterization of each of the reduction steps has revealed that electrochemistry is a powerful technique to generate *selectively* unsaturated iron nitrosyl complexes[12] which can be valuable candidates for catalysts. To this respect, our work was first focused on the catalytic behavior of $Fe(NO)_2(thf)_n$.

Catalytic experiments were performed with 20 mL of thf solution of **1** (10^{-2} M) containing $Bu_4N^+PF_6^-$ (0.1 M) as the supporting electrolyte and an excess of dienes (diene/Fe = 500-2000). Electrolysis was achieved either at the level of the B or C wave. After reduction at ca. −0.7 V the conversion is half of that obtained after reduction at ca. −1.1 V, thus confirming the reduction mechanism. Parallelly, chemical reduction of **1** by highly divided Zn powder was performed in the presence of dienes[21] and the catalytic activity checked. The results of typical catalytic runs are reported in Table I.

Table I shows clearly the good agreement between the two types of reduction. Norbornadiene and isoprene conversions are quite similar, whereas the discrepancy observed with butadiene is probably due to the electrochemical cell design.[22] The only products detected are the cyclodimers for every catalytic run, and, whatever the nature of the reactant, one cyclodimer is formed predominantly. The selectivity observed is specific to the iron nitrosyl complexes as stated earlier,[4-9] but in this work the activity is increased[23] 10-100-fold. Moreover, this work reports for the first time the identification and characterization, under the conditions of catalysis of the nitrosyl complex responsible for the cyclodimerization of dienes, i.e., $Fe(NO)_2(thf)_n$, a d^{10} electronic configuration according to ref 2c.

In conclusion, the electrochemical approach described in this paper outlines on one hand the catalytic properties of $Fe(NO_2(thf)_n$ in the cyclodimerization of dienes and on the other hand the possibility of preparing new unsaturated dinitrosyl transition metal complexes. Further work on this second aspect will be published in the near future.

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(16) All $E_{1/2}$ are given relative to the aqueous saturated calomel electrode.

(17) The morphology of the wave B depends on 1 concentration, the total height being equal to 1. For a 10^{-2} M concentration the wave is split into two waves at −0.22 and −0.52 V, for a 0.5×10^{-2} M concentration the wave is ill-defined at −0.29 V, and for a 0.5×10^{-3} M concentration the wave is well defined at −0.22 V. These results corroborate the ESR ones.

(18) Height comparison, in the same conditions, between the A wave and that of the system

$$Cp_2Co^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} Cp_2Co$$

shows that the A wave corresponds to a one-electron transfer. This implies the formation, on the time scale of electrolysis, of an unstable complex which evolves chemically to give a monoelectronic oxidizable species which decomposes according to

$$2Fe(NO)_2ClS_n + 2Hg \xrightarrow{-2e^-} 2Fe(NO)_2S_n{}^+ + Hg_2Cl_2$$

$$Fe(NO)_2S_n{}^+ \xrightarrow[2.\ -e^-]{1.\ \text{chemical evolution}} Fe^{2+} + 2NO$$

(19) $[Fe(NO)_2Cl_2]^-PPN^+$: ν_{NO} 1775, 1700 cm^{-1}; ESR signal with $g = 2.0339$, line width = 15 G, in agreement with data of J. Schmidt, *Transition Met. Trans. Chem.*, 1, 252 (1976), and N. G. Connelly and C. Gardner, *J. Chem. Soc., Dalton Trans.*, 1525 (1976).

(20) The reduction wave of PPN^+ hinders the waves D and E of Figure 1.

(21) The polarogram of this solution exhibits only the E reduction wave.

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Metal Binding to Four Different Sites in Adenine Ligands. Crystal Structures of 2:1 Methylmercury Complexes with Adenine and 9-Methyladenine

Sir:

Many complexes with purine and pyrimidine bases, nucleosides, and nucleotides have been investigated as model compounds for metal–nucleic acid interactions. It is generally admitted that metal ions usually bind to N-7 in N-9-substituted adenine ligands.[1] Sometimes, N-1 protonation or metalation occurs as well.[1,2] Metal coordination to N-1 exclusively has

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