The Electrochemical Reduction of $(Fe(NO)_2Cl)_2$. A Novel Route to the Catalytic Cyclodimerization of Diolefins

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The association of organotransition-metal compounds with Lewis acids or reducing reagents leads, under favorable circumstances, to catalytic systems. Two main properties can account for this catalytic behaviour: (i) the oxidation state of the central atom and (ii) the number of available coordination sites. From these two points of view, electrochemistry can be a valuable technique in order to generate such catalytic species. This technique offers several advantages related to the formation and the identification of the active species. The number of electrons transferred is easily controlled, intermediates as well as unusual oxidation states can be detected, the number of organometallic compounds present in the reaction medium is less due to the absence of cocatalysts. Although detailed electrochemical studies have been performed on transition-metal complexes [1] no systematic investigations of their catalytic properties have been reported [2].

To this regard, we are interested in the electrochemical behaviour of $(Fe(NO)_2Cl)_2$ in order to generate catalytic species. Our previous work [3] on this starting compound has shown that the one electron chemical reduction is a requisite to generate catalytic species in the selective cyclodimerization of diolefins such as norbornadiene (nbd), butadiene (bd) or isoprene (is), according to equation 1:

$$(Fe(NO)_2Cl)_2 \xrightleftharpoons{\text{solvent}} 2Fe(NO)_2SCl \xrightarrow{\text{Zn,diol.}} \text{catalytic activity} \quad (1)$$

Addition to the reaction medium of triphenylphosphine (PPh_3) or bis(1,2-diphenylphosphino)ethane (dppe) leads quantitatively to $Fe(NO)_2PPh_3$ or $Fe(NO)_2$dppe. This result indicates that the $Fe(NO)_2$ moiety is the active species. But the presence of these strong coordinating ligands (the complexes thus formed are inactive) can steer the course of the reduction reaction to the formation of compounds which are not favoured in the presence of π-ligands such as diolefins. To collect more proofs of the agency of $Fe(NO)_2$ in the catalytic cycle we have undertaken the electrochemical reduction of $(Fe(NO)_2Cl)_2$ in the presence of nbd, bd and is. It is noteworthy that this catalytic system is extremely interesting to study in order to understand the importance of the different steps which govern the selectivity. For example, in the case of the cyclodimerization of butadiene the only product obtained is vinylcyclohexene. This substrate has been claimed to be economically interesting as a precursor of styrene [4].

We wish to report here some premliminary results.

The metal–metal bond and the two chloro bridges in the dimeric μ-dichlorotetranitrosyldiiron [5] are very easily cleaved when the complex is dissolved in coordinating solvents such as tetrahydrofuran or acetonitrile. The complex then formed is the monomeric chlorodinitrosyl iron, compound *I*. The supporting pieces of evidence for its formation are (i) the ir spectrum: ν_{NO} 1775 (s) and 1710 (s) cm^{-1} *versus* 1815 (s) and 1720 (s) cm^{-1} for $(Fe(NO)_2Cl)_2$ (nujol mull), (ii) the one line esr spectrum: g=2.0375.

Compound *I* in thf, with $Bu_4N^+PF_6^-$ (0.1 *M*) as the supporting electrolyte is reduced at the mercury electrode. The polarogram exhibits three reduction waves at –0.29, –0.87 and –2.03 V and one oxidation wave at +0.54 V (*vs.* SCE). Under inert atmosphere the electrolysis at –0.5 V of the thf solution of *I* affords a solution which exhibits polarographic reduction waves at –0.87 and – 2.01 V. The polarogram of the solution obtained after electrolysis at –1.2 V shows an oxidation wave* at about –0.7 V and a reduction wave at –1.67 V. This solution is chemically unstable and evolves under inert atmosphere. Then the oxidation and reduction waves disappear simultaneously.

The solutions obtained after electrolysis are catalytically inactive: addition of nbd, bd or is leads only to traces of the organic dimers. But if the electrolysis is performed in the presence of the diolefin on the level of the first wave, catalytic activity is then observed (Table I). This result shows clearly that (i) the active species is chemically unstable and (ii) it can be generated electrochemically by reduction at –0.5 V.

As checked in Table I, the activity and the selectivity of the electrode/compound *I*/diolefin system are comparable with those of Zn/compound *I*/diolefin chemical system. This inclines us to think that the same catalytic species, probably $Fe(NO)_2$, is

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*The $E_{1/2}$ value cannot be exactly measured, because of the adsorption phenomena observed on this anodic wave.

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TABLE I. Catalytic Behaviour of Chemically and Electrochemically Reduced $(Fe(NO)_2Cl)_2$ Complex *versus* the Cyclodimerization of nbd, bd and is (thf is the solvent in all cases).

Olefin	Chemical Reduction by Zn [3]		Electrochemical Reduction at –0.5V	
	Conversion[a]	Selectivity (%)	Conversion[b]	Selectivity (%)
nbd	100	exo-*trans*-exo dimer (87)	148	exo-*trans*-exo dimer (93)
bd	100	4-vinylcyclohexene (100)	99	4-vinylcyclohexene (100)
is	74	1,4(2,4)dimethyl-4-vinylcyclohexene (96)	72	1,4(2,4)dimethyl-4-vinylcyclohexene (96)

[a] Number of dimerized olefin molecules compared with the number of iron atoms present in the solution. [b] Number of dimerized olefin molecules per Faraday.

operating in the electrochemical and in the chemical systems [3, 6].

In conclusion the chemical and electrochemical electron transfer to $(Fe(NO)_2Cl)_2$ in thf leads both to the same active complex. The polarographic behaviour has shown several reduction steps which generate the same active species (identical selectivities and activities). We are actually studying the mechanism related to these stages in order to optimize the catalytic system.

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