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Preliminary communication

ELECTRON TRANSFER FROM d^{10} SPECIES: A POSSIBLE INITIATION FOR FREE RADICAL PATHWAYS IN OXIDATIVE ADDITIONS

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Summary

The possibility of electron transfer being the initiation step in free radical pathways in oxidative addition is probed by exposing nickel(0) and platinum(0) species to a variety of electron acceptors; one-electron transformations are found to be facile in these systems.

Oxidative addition to a variety of low valent transition metal complexes has attracted attention due to the recent elucidation of nucleophilic as well as free radical pathways [1, 2]. The latter are especially interesting since they can proceed by a chain or non-chain sequence [2, 3], but in either case the nature of the initiation process remains obscure. Although there is evidence for molecule-induced homolysis in organic systems (e.g., the addition of halogens to olefins it appeared to us that a mechanism involving an initial electron transfer [4] is an attractive alternative. According to this formulation free radicals are produced by charge transfer from the metal complex to the addend A by a process in eqn. 1 involving electron attachment or dissociative electron attachment** depending on its structure, i.e. oxygen, olefin, quinone or alkyl halide, etc.

$$L_nM + A \rightleftharpoons L_nM^+ + A^{\overline{\cdot}}, \text{ etc.} \qquad (1)$$

In order to test whether electron transfer reactions are possible, we probed for transient paramagnetic species by their electron spin resonance (ESR) spectra produced during the exposure of typical diamagnetic d^{10} species of nickel(0) and platinum(0) complexes to known one-electron acceptors***. Indeed the rapid reduction of such acceptors as tetracyanoethylene (TCNE), dichlorodicyano-*p*-

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**For electron transfer processes see ref. 5.

***Samples for ESR examination were prepared by mixing and sealing equal volumes of freshly prepared benzene solutions of the two reagents (10^{-2} *M*) in clean dry ESR tubes in an oxygen free argon atmosphere. Typically, samples were examined at ambient temperatures (25°C) within one minute of mixing.

benzoquinone (DDQ), and chloranil (CA) by a variety of nickel(0) and platinum(0) species (Table 1) is readily indicated by the immediate discharge of the colours of the metal(0) species in solution and the simultaneous appearance of the ESR spectrum of the corresponding radical anion (Table 1) [6]. In no case did we observe any metal(I) species produced during this initial rapid reaction* (^{61}Ni, $I = 3/2$, 1.3% natural abundance: ^{195}Pt, $I = 1/2$, 34% natural abundance), although on standing at room temperature a variety of other paramagnetic species were observed.

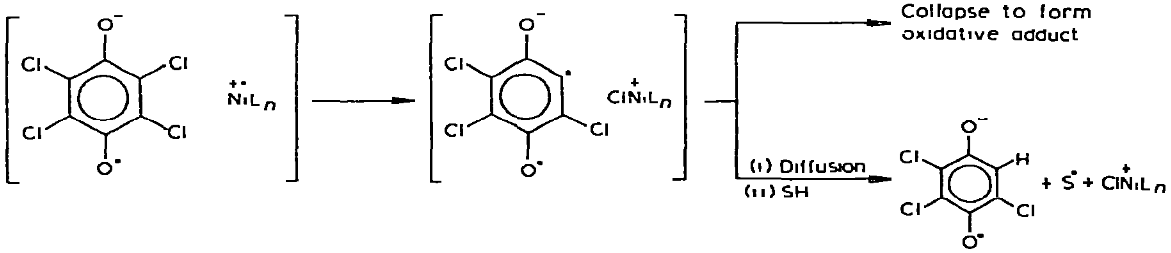
TABLE 1

PARAMAGNETIC SPECIES FROM NICKEL(0) AND PLATINUM(0) COMPLEXES

ML_n	TCNE	CA	DDQ
$Ni(PEt_3)_4$	$TCNE^{\cdot -}$ [a]	$CA^{\cdot -}$ [b], I [c]	$DDQ^{\cdot -}$ [d]
$Ni(PPh_3)_4$	$TCNE^{\cdot -}$ [e]	I	$DDQ^{\cdot -}$
$Ni(PPh_3)_3$	$TCNE^{\cdot -}$ [e]	I	$DDQ^{\cdot -}$
$Ni(diphos)_2$	$TCNE^{\cdot -}$	I	$DDQ^{\cdot -}$
$Ni(PPh_3)_2(diphos)$	$TCNE^{\cdot -}$	$CA^{\cdot -}$, I	$DDQ^{\cdot -}$
$Ni(bipy)_2$	$TCNE^{\cdot -}$	$CA^{\cdot -}$	
$Pt(PEt_3)_3$	$TCNE^{\cdot -}$	$CA^{\cdot -}$, I	

[a] $\langle a_N \rangle = 1.59$ G, $\langle g \rangle = 2.0028$ [6a].
[b] singlet, $\langle g \rangle = 2.0058$ [6b].
[c] In addition to other paramagnetic species, see text.
[d] $\langle a_N \rangle = 0.58$ G, $\langle g \rangle = 2.0057$ [6c].
[e] In addition to another paramagnetic species showing ^{15}N splittings.

In this latter regard TCNE and DDQ seemed to be less active than CA (Table 1). For example, a 10^{-2} M solution of $(Et_3P)_4Ni^0$ and 10^{-2} M CA in benzene afforded the spectrum of $CA^{\cdot -}$ in addition to two other species I and II. The intense spectrum of I consisted of a doublet splitting of 2.15 G [$\langle g \rangle = 2.0058$], which is close to that previously reported for the anion-radical of trichloro-p-benzoquinone [$\langle a_H \rangle = 2.16$ G, $\langle g \rangle = 2.0058$] [6, 9]. This behaviour is not shown by $CA^{\cdot -}$ generated from a potassium mirror in benzene. We believe that further investigation of this particular reaction will prove enlightening. Although comment on the source of such a species must necessarily remain speculative at this stage, an interesting possibility is:



Alternatively we may be observing the type of species described by Lucken et al. [12], where the differences in coupling constant and of g value arise through solvent effects.

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[*] For a nickel(I) complex see ref. 7. It is not necessary for nickel to be associated with the anion radical, compare for copper(II) ref. 8.

The spectrum of species[*], which also consists of a doublet splitting $[\langle a \rangle = 15.90$ G, $\langle g \rangle = 2.0050]$, is similar to that produced in the slower reaction between triethylphosphine and CA in the absence of nickel(0)[**]. ESR spectra were also obtained during the reaction of nickel(0) complexes with *p*-benzoquinone, but they consisted only of rather broad unresolved singlets $[\Gamma \approx 5$ G]. The facile reaction of $(Et_3P)_3Pt^0$ and CA also produces a variety of paramagnetic species including $CA^{-\cdot}$[***]. Naphthalene was thermally as well as photochemically unreactive in the presence of these nickel(0) complexes.

Our experiments demonstrate that nickel(0) and platinum(0) complexes involved in various oxidative addition reactions [1] are capable of undergoing facile one-electron transformations. The extension of this concept generally to the initiation process in oxidative additions will be strengthened by the isolation and characterization of the nickel and platinum products formed with addends used in this study. Credence for this possibility is lent by the recent studies of Balch et al., who isolated oxidative adducts of low valent metal complexes to the related *o*-quinones [10][☆]. Finally, it should be emphasized that the choice of addends examined in this study has been largely dictated by the stability of the anion-radicals for ESR study. The observation of highly transient paramagnetic species must await the development of more sophisticated flow methods presently in progress.

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Note added in proof: After this manuscript was submitted, other evidence for electron transfer in the addition of allylnickel to quinones was reported [13].

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[*] The spectra of other paramagnetic species consisted of: III: quintet with approximate binomial intensity ratio $[\langle a \rangle = 7.81$ G, $\langle g \rangle = 2.0000]$; IV: triplet $(\langle a \rangle = 6.05$ G) of doublets $[\langle a \rangle = 2.5$ G, $\langle g \rangle = 2.0051]$ with nickel splittings $[a(^{61}Ni) = 11.7$ G].

[**] Both triethylphosphine and triphenylphosphine reacted with CA to afford species whose ESR spectra were different from those reported here. α,α-Bipyridine did not react with CA.

[***] At least 3 other species were also observed. A: doublet $[\langle a \rangle = 2.54$ G, $\langle g \rangle = 2.0051]$; B: doublet $[\langle a \rangle = 15.9$ G, $\langle g \rangle = 2.0049]$; C: doublet $(\langle a \rangle = 0.50$ G) of doublets $[\langle a \rangle = 4.65$ G, $\langle g \rangle = 2.0050]$.

[☆] For complexation of Group II and III metals with semiquinones see ref. 11.

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