Journal of Organometallic Chemistry, 241 (1983) C41—C44
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

REACTIONS OF ANIONIC NITROGEN HETEROCYCLES WITH IRON CARBONYLS

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(Received October 5th, 1982)

Summary

Redox disproportionation of iron carbonyls to carbonylferrate anions and Fe^{+}, Fe^{2+} compounds occurs during the reaction of these carbonyls with both free azoles and their sodium salts. It is assumed that coordination of azole anion to iron carbonyl takes place and that the species formed acts as a one-electron reducing agent towards iron, iron carbonyl anion-radicals, detected by ESR, being formed on the initial stage of the reaction.

Azole anions are known to act as nucleophilic reagents substituting carbonyl or halogen ligands in reactions with carbonyls and π-cyclopentadienyl complexes of transition metals [1—3]. Under these conditions there is no change in the oxidation state of the central atom. However, we have shown recently that anions of pyrazole, imidazole and vicinal triazoles (as their sodium salts) are able to react as a one-electron reducing agent towards nitroso-compounds and organoiron compounds, viz., ferricinium salts, π-allyltricarbonylhalides and certain iron carbonyls [4—7], with azole anions being transformed into free radicals. In the present paper we wish to report on the reactions of iron carbonyls, $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, with the sodium salts of azoles (AzNa).

The interaction of sodium pyrazolide (PzNa) with $Fe_3(CO)_{12}$ at —80°C in THF results in signals appearing in the ESR spectra with a g factor equal to 2.0023 due to $Fe_3(CO)_{12}^{\overset{\cdot}{-}}$ anion-radicals. Further, the accumulation of these signals and emergence of other signals due to $Fe_3(CO)_{11}^{\overset{\cdot}{-}}$ anion-radicals with $g = 2.0484$ (see Fig. 1) take place. The latter seem to be a metal-centered radical in contrast to the ligand-centered $Fe_3(CO)_{12}^{\overset{\cdot}{-}}$, whose g factor values are close to the purely electronic ones. On further reaction, signals with g

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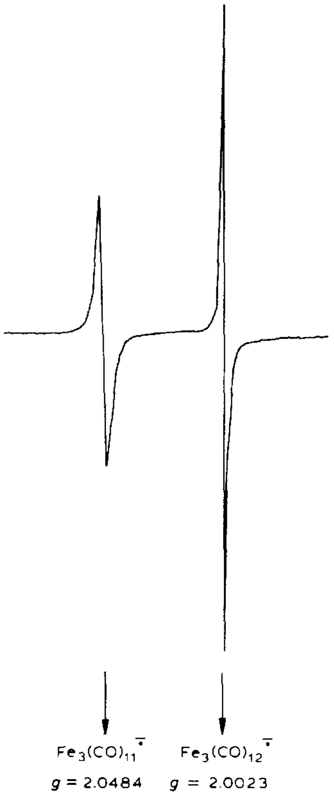

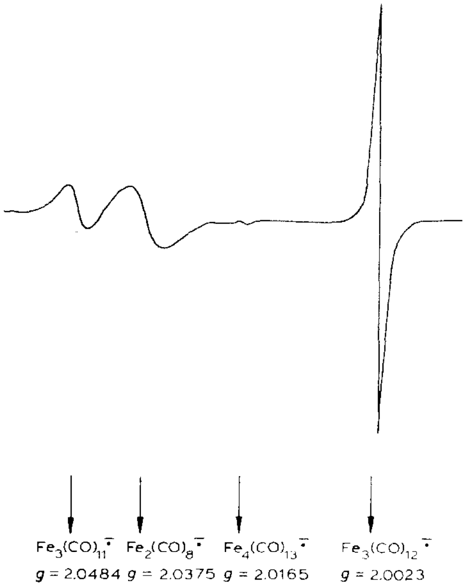

Fig. 1. ESR spectrum for the reaction PzNa + $Fe_3(CO)_{12}$ (1:1) in a spectrometer cell recorded 3 min after sample preparation. Solvent: THF; temperature: —80°C.

Fig. 2. ESR spectrum for the reaction PzNa + $Fe(CO)_5$ (1:1) in a spectrometer cell recorded 15—20 min after sample preparation. Solvent: THF; temperature: —80°C.

values equal to 2.0375 and 2.0165 emerge due to the anion-radicals $Fe_2(CO)_8^{\dot{-}}$ and $Fe_4(CO)_{13}^{\dot{-}}$, respectively (see Fig. 2). The assignment of signals for anion-radical species was made by comparison of our data with reported spectra [8,9].

It may be assumed that one-electron reduction of $Fe_3(CO)_{12}$ by azole anions takes place first. The $Fe_3(CO)_{12}^{\dot{-}}$ anion-radicals thus formed then undergo decarbonylation and are converted into $Fe_3(CO)_{11}^{\dot{-}}$.

$$Az^- + Fe_3(CO)_{12} \rightarrow Fe_3(CO)_{12}^{\dot{-}} + Az^{\cdot}$$

$$Fe_3(CO)_{12}^{\dot{-}} \rightarrow Fe_3(CO)_{11}^{\dot{-}} + CO$$

In this case, however, it is not possible to detect by spin trapping the formation of azolyl radicals, in contrast to the reduction of ferricinium salts [4,5]. This may be related to the fast consumption of the radicals. Nevertheless, it seems more probable that the actual reducing agents in these systems are not azolyl anions but their iron-carbonyl complexes:

$$Az^- + Fe_3(CO)_{12} \rightarrow [AzFe_3(CO)_{12}]^-$$

$$[AzFe_3(CO)_{12}]^- + Fe_3(CO)_{12} \rightarrow \underset{\text{oxidized products, Fe}^+\text{, Fe}^{2+}}{\underset{\downarrow}{[AzFe_3(CO)_{12}]^{\cdot}}} + Fe_3(CO)_{12}^{\overset{\cdot}{-}}$$

The reactions of azole salts with $Fe(CO)_5$ also occur rapidly, even at −80°C. In contrast, the reaction with $Fe(CO)_5$ of the heterocycles themselves occurs only under irradiation [10]. First, the broadened signal of the $Fe_2(CO)_8^{\overset{\cdot}{-}}$ anion-radical appears ($g = 2.0375$); however we did not manage to observe the $Fe(CO)_4^{\overset{\cdot}{-}}$ signals. Further, $Fe_3(CO)_{12}^{\overset{\cdot}{-}}$ is formed and then $Fe_4(CO)_{13}^{\overset{\cdot}{-}}$ and $Fe_3(CO)_{11}^{\overset{\cdot}{-}}$. Thus, the final set of paramagnetic species is the same as in the reduction of $Fe_3(CO)_{12}$. In this case, a gradual aggregation of paramagnetic clusters possibly takes place by addition of $Fe(CO)_5$ and decarbonylation. The interaction of azole anions with $Fe_2(CO)_9$ produces a set of anion-radicals analogous to the series obtained in the reactions with $Fe(CO)_5$ and $Fe_3(CO)_{12}$.

It should be noted that these reactions occur in the same manner regardless of the nature of the azole salt used as a reactant. On the whole, the picture is quite similar to the one observed when iron carbonyls are reduced electrochemically or with alkali metals [8,9,11]. A gradual consumption of the anion-radicals is observed during further reaction until their signals disappear completely. The accumulation of carbonylferrate ions $[Fe(CO)_{11}]^{2-}$, is simultaneously observed, which may be determined on the basis of IR spectral data or by isolating the corresponding salts preparatively.

Earlier, we have reported that in the reaction of iron carbonyls with azoles in ether or THF the low-yield products from the substitution of carbonyl ligands by heterocyclic ligands, $(AzH)Fe(CO)_n$, $n = 3,4$, are formed [10,12,13]. The main products of the reaction, however, are the salts of carbonylferrate anions, $[(AzH)_6Fe]^{2+}[Fe_3(CO)_{11}]^{2-}$, and coordination polymers, $[Az_2Fe]_n$, i.e., compounds where the oxidation state of the central atom differs from the initial state. Investigation of these reactions by ESR shows that even at −80°C signals from anion-radicals of iron carbonyls also appear which in this case are the same as in the reactions with azole anions. The reduction in the first stages of the reactions with azoles may also occur via formation of intermediate iron carbonyl complexes of azoles i.e., by a similar mechanism. In the reactions of iron carbonyl with azoles not only does the reduction of iron take place but also oxidation to Fe^+ and Fe^{2+}. Oxidation-reduction disproportionation of the central atom is the characteristic reaction of Mn, Fe and Co carbonyls occurring under the action of various nitrogen bases. It is quite possible that some paramagnetic species of azole-containing oxidized iron carbonyls are also formed in the early stages of the reactions.

The results obtained in the present study may shed light on the mechanisms of iron carbonyl transformations under the action of nitrogen bases [see for example 14—16].

References

1 A.D. Garnovsky, N.E. Kolobova, O.A. Osipov, K.N. Anisimov, I.B. Zlotina, G.K. Mitina and Yu.V. Kolodyazhny, Zh. Obshch. Khim. 42 (1972) 929.
2 A.N. Nesmeyanov, V.N. Babin, N.S. Kochetkova, E.I. Mysov, Yu.A. Belousov and L.A. Fedorov, Dokl. Akad. Nauk SSSR, 200 (1971) 1112.
3 R.B. King and K.-N. Chen, Inorg. Chem., 16 (1977) 3372.
4 V.N. Babin, Yu.A. Belousov, I.R. Lyatifov, R.B. Materikova and V.V. Gumenyuk, J. Organometal. Chem., 214 (1981) C11.
5 V.N. Babin, Yu.A. Belousov, V.V. Gumenyuk, R.B. Materikova, R.M. Salimov and N.S. Kochetkova J. Organometal. Chem., 214 (1981) C13.
6 V.N. Babin, V.V. Gumenyuk, S.P. Solodovnikov and Yu.A. Belousov, Z. Naturforsch., 36b (1981) 400.
7 Yu.A. Belousov, V.V. Gumenyuk, V.N. Babin, S.P. Solodovnikov and N.S. Kochetkova, Koord. Khimiya in press.
8 D. Micholova, J. Klima and A. Vlcek, Inorg. Chim. Acta, 27 (1978) 167.
9 P.J. Krusic, J. San Filippo, B. Hutchinson, R.L. Hance and L.U. Daniels, J. Amer. Chem. Soc., 103 (1981) 2129.
10 V.N. Babin, Kandidatskaya dissertatsiya, INEOS, Moscow, 1972.
11 P.A. Dawson, B.M. Peake, B.H. Robinson and J. Simpson, Inorg. Chem., 19 (1980) 465.
12 A.N. Nesmeyanov, V.N. Babin, N.S. Kochetkova and Yu.S. Nekrasov, Dokl. Akad. Nauk SSSR, 200 (1970) 601.
13 A.N. Nesmeyanov, V.N. Babin, N.S. Kochetkova, Yu.S. Nekrasov, Yu.A. Belousov and S.Yu. Silvestrova, Dokl. Akad. Nauk SSSR, 218 (1974) 1368.
14 W. Hieber, W. Beck and G. Braun, Angew. Chem., 72 (1960) 795.
15 W. Hieber, Adv. Organometal. Chem., 8 (1970) 1.
16 H. Behrens and H. Wakamatsu, Z. Anorg. Allgem. Chem., 320 (1963) 30.