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LETTER

Spin trapping of radicals formed by sonolysis of some organometallic compounds

Detlef Rehorek
Department of Chemistry, Karl-Marx University of Leipzig, Leipzig O-7010 (F.R.G.)

Silvana Di Martino, Silvana Sostero, Orazio Traverso*
Department of Chemistry and Photochemistry Center of C.N.R., University of Ferrara, 44100 Ferrara (Italy)

and **Terence J. Kemp**
Department of Chemistry, University of Warwick, Coventry CV4 7AL (U.K.)

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It is well established that ultrasound has a profound influence on the reactivity of many organometallic compounds [1, 2]. In some cases products of remarkable catalytic activity are generated [3]. However, little is known about the mechanisms underlying these reactions. Based on product analyses, Suslick *et al.* [3–5] have concluded that metal carbonyls undergo non-radical cleavage of metal–CO bonds upon sonolysis. It was shown by Riesz and co-workers [6] that spin trapping provides a suitable method for detecting free radicals formed in ultrasound-induced chemical reactions. The usefulness of this method for the detection of free radicals in sonochemical reactions of organometallics was demonstrated for a variety of organotin compounds [7]. So far, however, spin trapping of sonolytically generated metal-centred radicals has failed. Here we wish to report spin trapping studies on some organometallic carbonyl compounds where, at least in one case, spin adducts of metal-centred radicals were obtained upon irradiation with ultrasound.

Experimental

All experiments were carried out at ambient temperature. Solutions containing 0.1 M organometallic compound and 0.01–0.05 M spin trap were purged with purified argon for at least 30 min prior to sonication. Standard EPR quartz flat cells attached to an H-shaped mixing cell [8] were used. An ordinary ultrasonic laboratory cleaning bath (Bransonic 220, 125 W) operating at 55 kHz served as the source of ultrasonic radiation. A sonication time of 3 min was chosen. Particular care was taken in order to avoid inadvertent photolysis of the samples. The time interval between sonication and recording the EPR spectrum was about 3–5 min. All spectra were recorded in the X-band using a Bruker model ER 200 tt EPR spectrometer.

Nitrosodurene and 2-methyl-2-nitrosopropane (MNP) were used as spin traps. All compounds were either commercially available or synthesized according to literature procedures.

Results and discussion

Three types of sonochemical reaction were observed. No radicals were detected when benzene solutions of $[Mn(CO)_5]_2$ and $[Re(CO)_5]_2$, respectively, were sonication in the presence of nitrosodurene. This result is in agreement with previous findings by Suslick and Schubert [4] who revealed that Mn–CO cleavage rather than homolytic scission of the Mn–Mn bond occurs. Since spin adducts of both $^{\cdot}Mn(CO)_5$ and $^{\cdot}Re(CO)_5$ radicals are sufficiently persistent to be detected under our experimental conditions, the lack of EPR signals of spin adducts cannot be attributed to the decay of spin adducts. The spin trapping results rather suggest that, unlike photolysis, there is no formation of transient paramagnetic species upon sonolysis of these two dimers. When dichloromethane was used as a solvent, weak EPR signals ($a_N = 1.376 \pm 0.008$ mT, $a_H = 0.858 \pm 0.008$ mT (2H); Fig. 1) assigned to the spin adducts of chloromethyl radicals [9] were recorded. Although blank experiments (neat CH_2Cl_2 without metal carbonyl) did not yield any spin adduct signals under the same conditions, these findings cannot be considered as strong evidence for chlorine abstraction by intermediate free $^{\cdot}Mn(CO)_5$ and $^{\cdot}Re(CO)_5$ radicals, respectively, especially since addition of ethyl iodide

Fig. 1. EPR spectrum of the chloromethyl spin adduct to nitrosodurene recorded 3 min after sonication of dichloromethane solution of 0.1 M $[Re_2(CO)_{10}]$ and 0.05 M nitrosodurene (sonication time: 3 min).

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*Author to whom correspondence should be addressed.

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(*c.* 2 M) did not result in an increase of ethyl spin adducts as compared with blank experiments, i.e. when no metal complex was present. However, interaction of dichloromethane with short-lived $^{\bullet}M(CO)_5$ radical pairs (M = Re, Mn) may lead to cleavage of the C–Cl bond.

When $[(CH_3)_5C_5Rh(CO)_2]$ is sonicated in the presence of nitrosodurene in CH_2Cl_2 solution, an EPR spectrum almost identical to that observed during photolysis [10] is recorded (Fig. 2). As discussed previously [10], the spin adducts may be assigned to those of the $^{\bullet}Rh(CO)_2$ ($a_N = 1.600 \pm 0.005$ mT, a_{Rh} not resolved, $g = 2.012 \pm 0.001$) and ($^{\bullet}CH_2C_5H_4^-$) radicals, respectively.

When MNP was used as spin trap, only spin adducts of radicals derived from $(CH_3)_5C_5^-$ ($a_N = 1.594 \pm 0.008$ mT, $a_H = 1.264 \pm 0.008$ mT (2H)) together with di-tert-butyl aminoxyl radicals ($a_N = 1.562 \pm 0.005$ mT, $a_{13\text{-}C} = 0.424 \pm 0.008$ mT) were detected (Fig. 3).

Apparently, sonolysis has the same effect on the rhodium complex as photolysis [10]. Due to the lower molecular mass of $[(CH_3)_5C_5Rh(CO)_2]$ as compared with $[Re(CO)_5]_2$, the rhodium complex may diffuse into the vapour phase of the ultrasonically generated cavities where it undergoes $Rh\text{–}C_5(CH_3)_5$ bond cleavage.

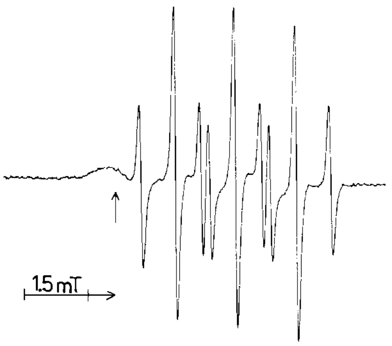

Fig. 2. EPR spectrum recorded after sonication of 0.1 M $[(CH_3)_5C_5Rh(CO)_2]$ in the presence of 0.01 M nitrosodurene (solvent: dichloromethane; sonication time: 2 min). The low-field line of the spin adduct of the Rh-centred radical is indicated by an arrow (for a computer simulation of this spectrum, see ref. 10).

Fig. 3. EPR spectrum of spin adducts formed during the sonication of 0.1 M $[(CH_3)_5C_5Rh(CO)_2]$ in the presence of 0.01 M MNP (solvent: dichloromethane; sonication time: 3 min).

A third type of reaction is observed during the sonolysis of some dimeric mixed-ligand complexes such as $[CH_3C_5H_4Mo(CO)_3]_2$, $[(CH_3)_5C_5Mo(CO)_2]_2$ and $[(CH_3)_5C_5Fe(CO)_2]_2$. Nitrosodurene anion radical is the major paramagnetic product in these reactions. In addition, small amounts (about 10%) of spin adducts of a carbon-centred radical are detected for $[CH_3C_5H_4Mo(CO)_3]_2$ ($a_N = 1.379 \pm 0.008$ mT, $a_H = 0.688 \pm 0.008$ mT (2H), in CH_2Cl_2; Fig. 4).

This spin adduct does not originate from radicals formed from either the solvent or the spin trap itself [9, 10]. Therefore, it is tentatively assigned to a spin adduct of the cyclopentadienylmethyl radical ($^{\bullet}CH_2C_5H_4^-$) formed by homolytic scission of the $Mo\text{–}C_5H_4CH_3$ bond and subsequent deprotonation as discussed for the pentamethylcyclopentadienyl analogue [10]. When MNP is used as spin trap, only di-tert-butyl aminoxyl radicals were observed. The EPR signal intensity was considerably higher than in the blank experiments (i.e. with no metal complex present). At present, the mechanism for its formation remains obscure. No evidence for spin adducts of metal-centred radicals was found in the case of the dimeric iron and molybdenum complexes. On the other hand, it is known that both iron- and molybdenum-centred radicals form persistent spin adducts with nitrosodurene and 2-methyl-2-nitrosopropane

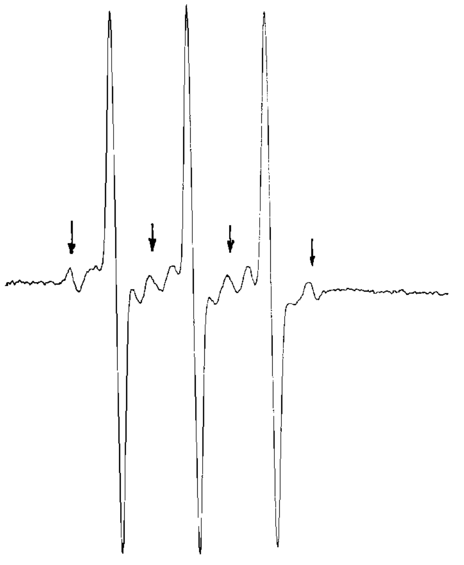

Fig. 4. EPR signals of paramagnetic species generated by sonolysis of 0.1 M $[CH_3C_5H_4Mo(CO)_3]_2$ in the presence of 0.01 M nitrosodurene (solvent: toluene; sonication time: 3 min), signals due to a spin adduct of a C-centred radical are indicated by arrows.

[11–13]. Therefore, metal–metal bond cleavage may be ruled out as a possible route for these complexes. It is assumed that nitrosodurene anion radicals are formed by electron transfer between coordinatively unsaturated metal–metal bonded dimers and nitrosodurene. Since only traces, if at all, of radicals derived from the non-CO ligand were trapped, cleavage of metal–CO bonds appears to be the most likely route for generating coordinatively saturated complexes.

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