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AN ESR STUDY OF THE PHOTOCHEMICAL REACTIONS OF GROUP VIB METAL CARBONYLS WITH PHENANTHROQUINONE AND THE RADICAL LIGAND EXCHANGE WITH GROUP VA ORGANOMETALS

DOUGLAS WEIR and JEFFREY K.S. WAN

Department of Chemistry, Queen's University, Kingston, Ontario, K7L 3N6 (Canada)

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Summary

Photolyses of Group VIB metal hexacarbonyls with phenanthroquinone in toluene solution led to the formation of some stable metal carbonyl-quinone radical complexes. These parent radical complexes underwent further ligand exchange reactions between the carbonyl and Group VA organometals. The ESR observations provide some insights into the reaction mechanisms as well as the dynamics and the probable exchange sites in the thermal substitution reactions.

Introduction

In recent years the synthetic chemistry of metal quinone complexes has been of great interest. These complexes are interesting generally because both the metal centre and the quinone ligands can be redox active [1]. For example, quinones can bond to the metal of various oxidation states via one of the three forms: quinone, semiquinone, and catechol. Since the first major study was carried out by Eaton [2], who oxidized catechols in the presence of diamagnetic metal ions, many other complexes have been synthesized directly by the reactions of metal carbonyls with quinones [3—6]. However, few of these complexes have been studied by ESR and only the Co, Ir, Pd, and Ni complexes have been systematically examined [7].

The ability of quinones to form paramagnetic radical complexes with various organometals has recently attached much attention [8,9]. The successful application of the powerful combined technique of ESR/HPLC (high performance liquid chromatography) to organometallic radical reactions [10] provides further opportunity to isolate some of these stable metal quinone radical complexes for detailed spectroscopic and chemical studies. Thus, we have presented a different approach to the "spin trapping" chemistry of unstable

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organometallic radicals by generating initially a stable quinone-metal carbonyl radical complex which is then allowed to undergo thermal exchange between the carbonyl and the Group VA organometal ligands [11]. In this report we examined the photochemical reactions between Group VIB metal carbonyl and phenanthroquinone (PQ) which led to ESR characterization of the relatively stable metal carbonyl-PQ radical complexes. The diamagnetic Group VIB metal-PQ complexes in the form of $M(PQ)_3$ are well known [3] and the data from electrochemical redox reactions of the diamagnetic neutral quinone complexes of Group VIB metals are available in literature [12,13]. The photochemical generation of metal carbonyl-PQ radical complexes involves only one quinone ligand and thermal ligand exchange reactions between these radical complexes and Group VA organometals yield a series of heterobinuclear and trinuclear metal-organic radical complexes containing the Group VIB metal carbonyl and Group VA organometals. ESR observations provide some insights into the reaction mechanisms as well as the dynamics and the possible exchange sites of the thermal substitutions.

Experimental

9,10-Phenanthroquinone was available from Aldrich and was vacuum sublimed before use. Toluene solvent was refluxed over molecular sieves and distilled. Metal hexacarbonyls supplied by Pressure Chemicals were used as received.

In a typical experiment a sample containing 1 cm^3 of solvent and a few mg each of metal carbonyl and PQ was outgassed by nitrogen and sealed off. The sample, contained in a pyrex tube, was irradiated in situ in the ESR cavity by a 200 W super pressure mercury lamp equipped with a remote controlled shutter. The normal irradiation period was less than 60 s which was sufficient to generate the stable paramagnetic metal carbonyl-PQ complexes. After the reaction was completed as monitored by ESR, Group VA organometal, (triphenylphosphine, triphenylarsine, and triethylamine) was then added to the sample containing the metal-carbonyl-PQ radical complex. The ligand substitution normally proceeded thermally, but in a few cases a short pulse of light was introduced to increase the radical concentration and therefore the resolution.

ESR spectra were recorded on a Bruker 420 X-band spectrometer with 100 kHz field modulation and temperature accessory. To enhance spectral resolution, the second-derivative mode of presentation was obtained in the usual way with the first phase-sensitive detector operating at 100 kHz and a second one operating at 50 kHz. *g*-Factors were measured using the Bruker NMR oscillator to monitor the field and the Hewlett Packard 5342 frequency counter to measure the microwave frequency.

Results and discussion

1. ESR observations on the photolysis of Group VIB metal hexacarbonyls with phenanthroquinone

a) $W(CO)_6$. Degassed toluene solutions containing $W(CO)_6$ and a series of *ortho*-quinones, including PQ, 1,2-napthoquinone, 3,5-di-t-butyl-*o*-benzoquinone (DTBQ), and acenaphthenequinone, were photolyzed within the ESR cavity. In all cases ESR spectra exhibiting similar patterns but different g-factors and proton coupling constants to those of the parent semiquinone radical anions, were observed. A typical spectrum in the $W(CO)_6/PQ$ system is shown in Fig. 1 and the corresponding spectral parameters are given in Table 1. No hyperfine interaction with ^{183}W (14.28%, $I = 1/2$) was observed in all the spectra. Nevertheless, the paramagnetic species is undoubtedly a complex involving the semiquinone and the metal carbonyl as supported by the substantial redistribution of the spin densities within the semiquinone moiety. The fact that the proton hyperfine pattern is similar to the uncomplexed parent semiquinone strongly indicates that only one semiquinone is involved in the complex. These observations are consistent with the other heavy metal-PQ radical complexes such as $(UO_2\dot{-}PQ)^+$ [8,14] which also failed to show any hyperfine splitting with ^{235}U, even when samples with 5% enriched ^{235}U isotope were used. Furthermore, the involvement of the tungsten carbonyl in the radical complex is clearly evidenced by the efficient ligand exchange between the carbonyl and other Group VA organometals introduced after the initial radical complex was formed. The thermal ligand substitution reactions will be reported in section 2.

The necessity of irradiation suggests that the thermal reaction between $W(CO)_6$ and quinone at room temperature is insignificant. The photochemical generation of the quinone-tungsten carbonyl radical complex can be accounted for by the following mechanism:

$$W(CO)_6 + h\nu \xrightarrow{\text{toluene}} W(CO)_5 + CO \tag{1}$$

$$W(CO)_5 + PQ \rightarrow PQ \dot{-} W(CO)_4 + CO \tag{2}$$

In order to establish that reaction 1 is the primary photochemical reaction, separate experiments were carried out by photolyzing a solution containing only $W(CO)_6$ until a slightly yellow color appeared. PQ was then immediately introduced into the yellow solution and the resulting $PQ\dot{-}W(CO)_4$ radical com-

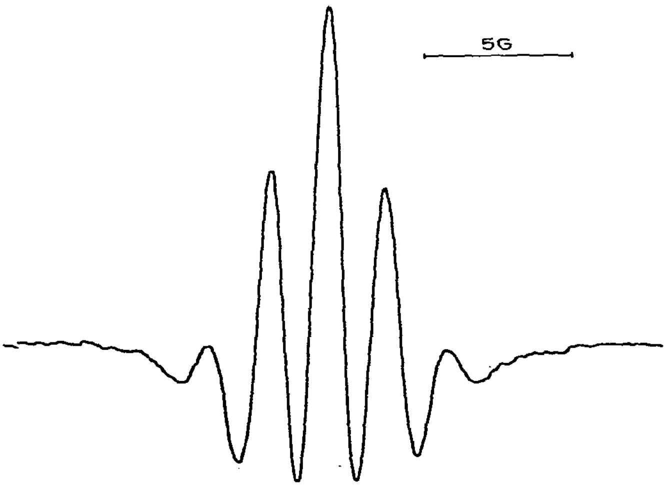


Fig. 1. The second-derivative ESR spectrum of $W(CO)_4\dot{-}PQ$ in toluene at 25° C.

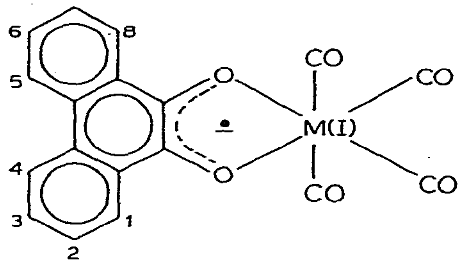
TABLE 1

ESR PARAMETERS OF GROUP VIB METAL CARBONYL-PHENANTHROQUINONE RADICAL COMPLEXES IN TOLUENE SOLUTION AT 25°C

Radical complex	g-factor	Coupling constants [a] (gauss)	
		a(H)	a(Metal)
$PQ^{\dot{-}}$ (uncomplexed)	2.0048 ± 0.00005	H(1,8) = 1.34, H(3,6) = 1.67 H(2.7) = 0.21, H(4,5) = 0.42	
$W(CO)_4^{\dot{-}}PQ$	2.0056	H(1,8,3,6) = 1.99 H(2,7,4,5): unresolved	
$Mo(CO)_4^{\dot{-}}$	2.0045	H(1,8,3,6) = 2.00 H(2,7,4,5) = 0.76	
$Cr(CO)_2^{\dot{-}}(PQ)_2$	1.9692	H: unresolved	a(Cr) = 26.9
$Cr(PQ)_3^{\dot{+}}$ [b]	1.9686	H: unresolved	a(Cr) = 28.2

[a] The proton numbering system is shown in Structure I. [b] Data are taken from ref. 13.

plex was observed by ESR. Photo-dissociation of metal hexacarbonyls to give the square pyramidal $M(CO)_5$ intermediate species has been established [15] along with the indication that $M(CO)_5$ could exist in solution for a period of up to a few minutes. The addition of PQ to a yellow solution containing $W(CO)_5$ led to instant formation of the radical complex as the reactive $W(CO)_5$ with a square pyramidal structure is conveniently suited for the approaching bulky quinone. Upon coordination the metal lost another carbonyl ligand and an electron is transferred from the metal to the quinone π^* orbital. The *trans* effect of the semiquinone ligand is expected to "labilize" the two carbonyl ligands *trans* to the semiquinone. This is indeed the result as observed in subsequent thermal exchanges between these two carbonyls and Group VA organometals. Based upon the ESR evidence, we propose the following structure for the Group VIB metal carbonyl-*ortho*-quinone radical complexes:



(I)

b) Mo(CO)₆. The reaction of $Mo(CO)_6$ with PQ in toluene solution was found to proceed under room light and without high intensity UV irradiation. Similar to $W(CO)_6$ the reaction produced the $Mo(CO)_4^{\dot{-}}PQ$ radical complex with the ESR parameters given in Table 1. Again no Mo splitting was observed (^{95}Mo: 15.78%, $I = 5/2$).

c) Cr(CO)₆. While $W(CO)_6$ and $Mo(CO)_6$ appear to behave in similar manner towards the coordination with quinones to yield the radical complex I, the reaction of $Cr(CO)_6$ with PQ showed a very different set of ESR observations. Irradiation of a toluene solution containing $Cr(CO)_6$ and PQ at room temperature led to the observation of a single line ESR spectrum which was not present when the two reactants were separately photolyzed. The single line spectrum has a very low *g*-factor of 1.9692 (Table 1) but the isotope hyperfine lines of ^{53}Cr were clearly identified (Fig. 2). The ^{53}Cr splittings are in the order of 26.9 gauss (^{53}Cr: 9.54%, $I = 3/2$). Two chromium paramagnetic complexes with similar ESR parameters are known in the literature. The first one is the $Cr(CO)_6^+$ paramagnetic species with a *g*-factor of 1.945 but no Cr splittings as proposed by Pickett and Pletcher [12]. The second one is the $Cr(PQ)_3^+$ radical complex with a *g*-factor of 1.9686 and $A(^{53}Cr)$ of 28.2 gauss, reported by Pierpont and coworkers [13]. The paramagnetic species observed in our system is not expected to be the $Cr(CO)_6^+$ since the present radical was found to be stable for at least several hours. The possibility of the species being $Cr(PQ)_3^+$ was also ruled out because of the evidence of subsequent ligand exchange between CO and organometals. We have, therefore, concluded that the radical is probably a complex involving either one or two quinones coordinated to some form of a chromium carbonyl. Further elucidation of the structure of this interesting radical complex will follow from ligand exchange studies which we shall now deal with.

2. *Thermal ligand substitution of Group VA organometals in the PQ-metal carbonyl paramagnetic complexes*

When triphenylphosphine was added to a toluene solution containing the $W(CO)_4\dot{-}PQ$ radical complex at room temperature, the ESR observation showed the formation of a "new" species with different spectral parameters (Fig. 3). The radical is assigned to $W(CO)_3PPh_3\dot{-}PQ$ which is formed by thermal

Fig. 2. The second-derivative ESR spectrum of $Cr(CO)_2\dot{-}(PQ)_2$ in toluene at 25° C. The upper insert shows the hyperfine lines of Cr isotope (^{53}Cr: 9.54%, $I = 3/2$).

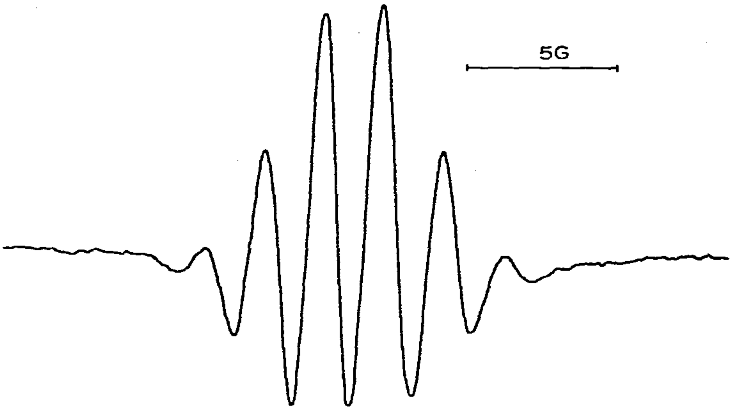


Fig. 3. The second-derivative ESR spectrum of the substituted $W(CO)_3PPh_3\dot{-}PQ$ radical complex in toluene at 25°C.

exchange reaction between the carbonyl and the phosphine:

$$W(CO)_4\dot{-}PQ + PPh_3 \rightarrow W(CO)_3PPh_3\dot{-}PQ + CO \quad (3)$$

The fact that only one carbonyl in the parent radical complex was replaced by a phosphine is indicated by the ESR hyperfine structure which showed only one phosphorus nucleus (Table 2). To confirm that the reaction is not due to some secondary processes involving $W(PQ)_3$, which is likely to be one of the stable products, a sample of $W(PQ)_3$ was synthesized by the method of Pierpont [3]. Irradiation of a toluene solution of $W(PQ)_3$ alone did not yield any observable paramagnetic species. Addition of triphenylphosphine to the

TABLE 2

ESR PARAMETERS OF GROUP VA ORGANOMETALS-SUBSTITUTED $M(CO)_x(PQ)_y$ RADICAL COMPLEXES IN TOLUENE SOLUTION AT 25°C

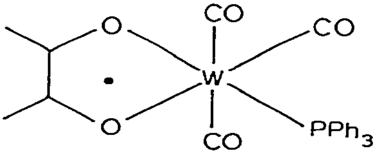
Radical complex	g-factor	Coupling constants [a] (gauss)		
		s(H)	a(Metal)	a(other)
$PQ^{\dot{-}}$ (uncomplexed)	2.0048 ± 0.00005	H(1,8) = 1.34, H(3,6) = 1.67 H(2,7) = 0.21, H(4,5) = 0.42		
$W(CO)_3PPh_3\dot{-}PQ$	2.0055	H(1,8,3,6) = 2.04		a(P) = 2.04
$W(CO)_3AsPh_3\dot{-}PQ$	2.0057	H(1,8,3,6) = 2.03		a(As) = 3.62
$W(CO)_x(NEt_3)_y\dot{-}PQ$	2.0047	H(1,8,3,6) = 1.59 H(2,7,4,5) = 0.40		
$Mo(CO)_2(PPh_3)_2\dot{-}PQ$	2.0050	H(1,8,3,6) = 1.87 H(2,7,4,5) = 0.44		a(P) = 7.15 (2P)
$Mo(CO)_3AsPh_3\dot{-}PQ$	2.0047	H(1,8,3,6) = 2.03 H(2,7,4,5) = 0.43		a(As) = 4.07
$Mo(CO)_x(NEt_3)_y\dot{-}PQ$	2.0051	H(1,8,3,6) = 1.61 H(2,7,4,5) = 0.43		
$Cr(CO)PPh_3\dot{-}(PQ)_2$	1.9736		a(Cr) = 25.8	a(P) = 39.25

[a] The proton numbering system is shown in structure I.

$W(PQ)_3$ solution also failed to produce any radical complexes either thermally or photochemically.

Similar exchange reaction also occurred with triphenylarsine. The ESR parameters of the substituted radical complex, $W(CO)_3AsPh_3^{\dot{-}}PQ$, are given in Table 2. With triethylamine, the substituted radical complex $W(CO)_3N(C_2H_5)_3^{\dot{-}}PQ$ has a substantial shift in the *g*-factor and a reduced hyperfine proton coupling constants in the PQ moiety. The nitrogen splitting, however, was not resolved.

Although lability of the carbonyl ligands is characteristic of the 17-electron metal carbonyl species [16] and the ligand exchanges between carbonyl and organometals have been observed in the manganese carbonyl-PQ [9] and rhenium carbonyl-quinone radical complexes [11], the ease of ligand substitution with tungsten carbonyl appears to be due to the *trans* effect of the semiquinone radical ligand which greatly enhanced the lability of the equatorial carbonyls. The small ^{31}P hyperfine splitting is also consistent with the structure in which the phosphine is *trans* to the radical semiquinone [17]:



(II)

Thermal substitution reaction between the $Mo(CO)_4^{\dot{-}}PQ$ and triphenylphosphine led to the replacement of both the carbonyl ligands *trans* to the radical semiquinone. The ESR spectrum of the substituted radical complex $Mo(CO)_2(PPh_3)_2^{\dot{-}}PQ$ exhibits additional splittings due to two equivalent phosphorus nuclei. The small phosphorous hyperfine coupling constant (Table 2) again suggests a structure similar to II but with an additional phosphine replacing the equatorial CO. Substitution with triphenylarsine was much slower thermally and both heat and excess arsine were required to ensure complete reaction. With arsine only one of the two equatorial carbonyl ligands was replaced and the resulting radical complex $Mo(CO)_3AsPh_3^{\dot{-}}PQ$ showed a very small splitting due to one As nucleus (Table 2). With triethyl amine, substitution proceeded thermally but it can not be ascertained whether one or two carbonyl ligands were replaced since the nitrogen splittings were not resolved.

Substitution reactions involving the chromium carbonyl-quinone radical complex were much more difficult. With triphenylphosphine, the reaction took a few hours to complete and only one carbonyl was replaced by the phosphine. Attempts to replace the carbonyl ligand with triphenylarsine was not successful.

Both the parent radical complex and the phosphine-substituted complex in the chromium carbonyl-PQ system have a low *g*-factor, a significant Cr splitting and in the case of the substituted radical a relatively large phosphorus splitting (Table 2). Based upon all the chemical as well as ESR observations, we propose that the parent complex is $Cr(CO)_2^{\dot{-}}(PQ)_2$ and that the substituted radical complex is $Cr(CO)PPh_3^{\dot{-}}(PQ)_2$. The parent complex is likely to have a structure

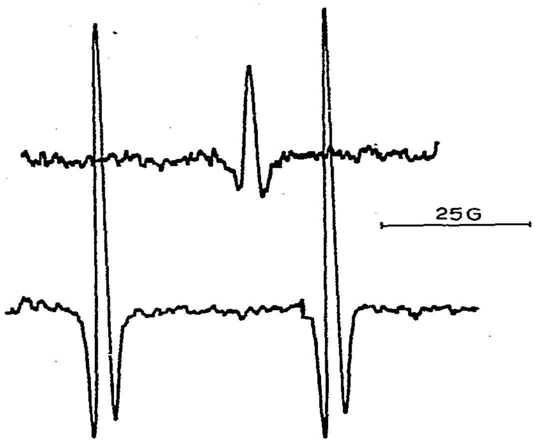
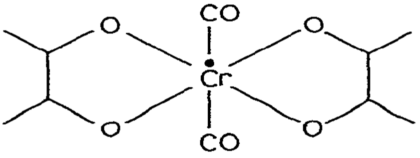


Fig. 4. The second-derivative ESR spectra of (a) $Cr(CO)_2^{\cdot-}(PQ)_2$ and (b) $Cr(CO)PPh_3^{\cdot-}(PQ)_2$ in toluene at 25° C. Note the significant *g*-shift between the two radical complexes.

similar to III in which both phenanthroquinones are expected to be in the same



(III)

plane. The substantial reduction in proton coupling constants and the larger numbers of protons in the two equivalent quinone ligands can account for the appearance of a "single line" spectrum (Fig. 2) without any proton resolution. In the substitution reaction the phosphine now must replace one of the two axial CO ligands which are not as labile as those in the other W and Mo complexes, since the *trans* effect by the semiquinone ligands is inoperative here. The relatively much larger P splitting in the substituted radical (Fig. 4) is consistent with the axial substitution [17]. With triphenylarsine the axial CO ligands are not labile enough to undergo exchange reactions.

The results reported here should also be of interest to the synthetic organometallic chemists who may wish to utilize the radical complex as an intermediate to enhance ligand substitutions in the overall synthesis of metal-quinone complexes. Furthermore, the radical complex and the substitution reactions are not limited to quinone ligands only and they have been extended to a wide range of 1,2-dicarbonyl compounds [10].

Acknowledgement

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