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EPR studies of the paramagnetic complexes formed in the photochemical reactions of $Mo(CO)_6$ with *o*-semiquinones

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Abstract

The photochemical reactions of $Mo(CO)_6$ with 9,10-phenanthrene and 1,2-acenaphthene semiquinone radicals (PSQ, ASQ) were investigated by EPR. The photoirradiation produces the paramagnetic complexes in which the semiquinones coordinate to $Mo(CO)_4$ in the chelate form. Most unpaired electron densities populate the quinone ligands, but the spin densities delocalize onto the metal moiety more so in the PSQ complex than in the ASQ complex. This difference in the spin distribution with ligands is interpreted in terms of the MO theory. To confirm the reaction scheme proposed for the above reactions, the reactions between the semiquinone radicals and $Mo(CO)_5(s)$ (s = solvent molecule), which were prepared by photoirradiation to $Mo(CO)_6$ in tetrahydrofuran or in 1,2-dimethoxyethane, were also examined.

Introduction

The photochemical reactions of metal carbonyl compounds with quinones have been widely studied. These photochemical reactions usually yield metal quinone complexes, which is of interest because the metal center and quinone ligands can be redox active. For example, the quinones can be bound to the metals in various oxidation states via one of their three forms, i.e., quinone, semiquinone, and catechol [1]. Wan et al. have reported that the photochemical reactions of $M(CO)_6$ (M = Mo, W) with 9,10-phenanthrenequinone yield paramagnetic products, and have postulated the structure in which the metal is coordinated by 9,10-phenanthrenequinone [2]. On the other hand, we have reported that the photochemical reactions of $[Mo(cp)(CO)_3]_2$ (cp = η^5-C_5H_5 or η^5-$CH_3C_5H_4$) with quionones yield paramagnetic complexes of the type of $Mo(cp)(CO)_2$(quinone) [3-5]. The complexes show such interesting properties as the spin distribution between the quinone and the metal moiety $Mo(cp)(CO)_2{}^+$ changes appreciably with the quinone ligands. It

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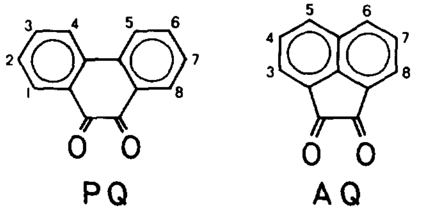


Fig. 1. *o*-quinones.

seems interesting to investigate the formation and the properties of the complexes having no cyclopentadienyl group for comparison and also interesting to investigate the reactions with quinones in the diffrent oxidation state.

In the present work, we studied the photochemical reactions of $Mo(CO)_6$ with phenanthrene- and acenaphthene-semiquinone anion radicals. We show that the reactions yield paramagnetic products and discuss the structure of the product based on their EPR spectra.

Experimental

$Mo(CO)_6$ was commercially obtained from Strem Chemicals and used as received. 9,10-Phenanthrenequinone (PQ) and 1,2-acenaphthenequinone (AQ) (Fig. 1) were vacuum sublimed before use. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) used as solvents were purified by distillation from $LiAlH_4$ under nitrogen and stored in vessels with the sodium-perylene anion in vacuo. For the sample preparation for EPR measurements, one of these solvents was disstilled through a vacuum line to an EPR tube containing the reagents.

Typical sample solutions were obtained according to the following procedure: The THF solution (~ 1 ml) of the *o*-quinone (~ 1 mg) was contacted with potassium metal to produce the semiquinone anion radical. To the formed radical solution, excess 18-crown-6 was added, and then the solution was mixed with $Mo(CO)_6$ (~ 5 mg). All the sample preparation were performed in a closed system in vacuo. The photochemical reactions were accomplished by photoirradition with a 100 W high-pressure mercury lamp or by exposure to the sunlight at room temperature.

EPR spectra were recorded on a JEOL JESFE2XG X-band spectrometer using 100 KHz field modulation at room temperature. The microwave frequency was monitored with a Takedariken TR5501 frequency counter equipped with a TR5023 frequency converter. The magnetic fields were measured with an Echo electronics EFM2000 NMR oscillator.

Results and discussion

The THF solution containing $Mo(CO)_6$ and phenanthrene semiquinone anion radical (PSQ) showed the EPR spectrum as shown in Fig. 2a. This spectrum is identical with that of the PSQ solution containing no $Mo(CO)_6$ and attributed to PSQ itself. By photoirradiation, the spectrum changed to the one shown in Fig. 2b. It exhibits hyperfine (hf) splittings due to the magnetic isotopes, ^{95}Mo (15.8%

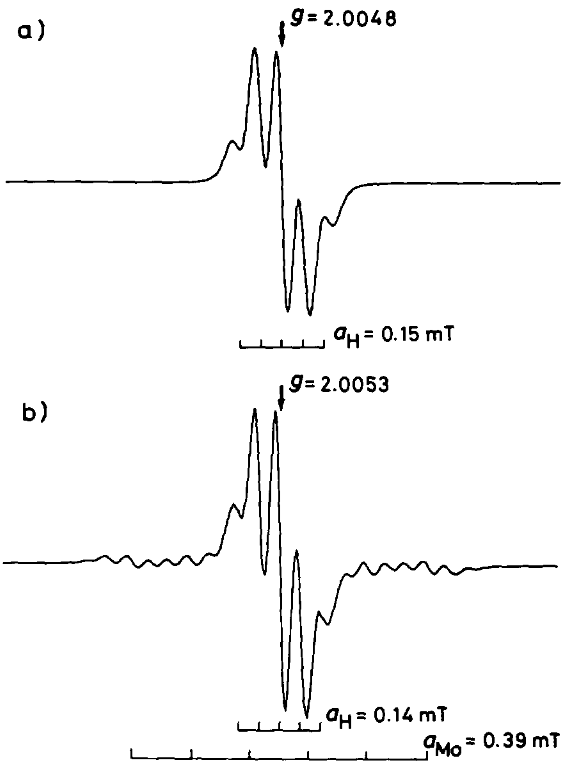
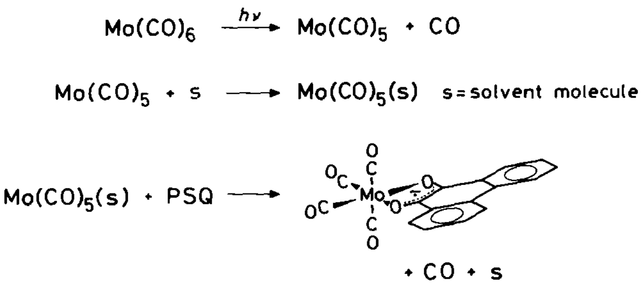


Fig. 2. First-derivative X-band EPR spectra in the THF solution of $Mo(CO)_6$ and PSQ at room temperature (a) before photoirradiation, (b) after photoirradiation.

$I = 5/2$, $\mu = -0.9099\ \mu_N$) and ^{97}Mo(9.6%, $I = 5/2$, $\mu = -0.9290\ \mu_N$), beside the hf splittings due to the the PSQ ligand protons, indicating that the photoirradiation produces a paramagnetic complex in which PSQ coordinates to the molybdenum carbonyl compound.

It has been reported that one of the CO's is eliminated from $Mo(CO)_6$ by photoirradiation and the formed $Mo(CO)_5$ is substantially coordinated by a solvent molecule to yield $Mo(CO)_5(s)$ (s = solvent molecule), in which the solvent molecule is labile for substitution [6,7]. In the photochemical reaction of $Mo(CO)_6$ with PSQ, the solvated complex, $Mo(CO)_5(s)$, may be formed at the first stage and then it may be converted to the paramagnetic complex by the reaction with PSQ. In order to confirm this reaction mechanism, we examined the reaction of PSQ and $Mo(CO)_5(s)$ which was prepared by photoirradiation to the THF solution of $Mo(CO)_6$, and confirmed the formation of the paramagnetic complex, which was the same as that obtained in the above experiments, by observation of the EPR spectrum. The formation of the paramagnetic complex was also observed when DME was used instead of THF in the above reactions, and its EPR parameters were almost identical to those obtained in the THF solution. Therefore, the produced paramagnetic complex is not coordinated by the solvent molecule.

On the other hand, no paramagnetic complex formation was observed when the solution did not contain the crown ether. This result indicates that the counter



Scheme 1.

cation of PSQ, K^+, is tightly bound to the carbonyl oxygens of PSQ and disturbs the formation of the paramagnetic complex, i.e., the PSQ ligand coordinates to Mo by its carbonyl oxygens in the paramagnetic complex. In the complex, the hf splitting constants due to the PSQ protons were symmetric about its two carbonyl oxygens, clearly indicating that the produced paramagnetic complex has a chelate structure coordinated by the two carbonyl oxygens of PSQ to Mo.

From these results, the formation mechanism and the structure of the paramagnetic complex are estimated as the Scheme 1.

In the photochemical reaction of $Mo(CO)_6$ with acenaphthene semiquinone (AS) too, the formation of the paramagnetic chelate complex was observed as in the case of the reaction with PSQ. The EPR parameters of the paramagnetic complexes are listed in Table 1 with those of related compounds for comparison.

In a previous paper, we reported that the chelate paramagnetic complexes, $Mo(cp)(CO)_2$(quinone), formed by the photochemical reaction of $[Mo(cp)(CO)_3]_2$ with *o*-quinones show large changes of the *g* value and Mo hf coupling constant with the quinone ligands. These changes were ascribed to the changes of the spin distribution between the metal moiety $Mo(cp)(CO)_2{}^+$ and the quinone ligands [3,5]. The complexes observed here also show changes of the *g* value and Mo hf coupling constant with the quinone ligands, but they are much smaller than those observed in the $Mo(cp)(CO)_2$(quinone) system. It is also seen that the Mo hf coupling constants are smaller than those in the $Mo(cp)(CO)_2$(quinone) system and the quinone proton hf coupling constants are nearly the same as those in the respective free anion radicals. These facts indicate that most of the unpaired electron in the complexes of

Table 1

EPR parameters for the paramagnetic complexes and related compounds

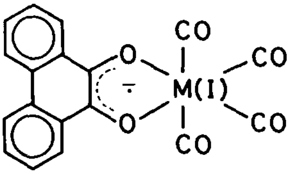
o-Quinone	Metal	Solvent	*g* value	a_{Mo}/mT	a_H/mT
PSQ	K^+/18-crown-6	THF	2.0048	–	$a_H^{1,3,6,8} = 0.15$
	$Mo(CO)_4$	THF	2.0053	0.39	$a_H^{1,3,6,8} = 0.14$
		DME	2.0053	0.37	$a_H^{1,3,6,8} = 0.14$
	$Mo(cp)(CO)_2{}^{+\,a}$	toluene	1.9957	1.12	$a_H^{1,3,6,8} = 0.10$
ASQ	K^+/18-crown-6	THF	2.0048	–	$a_H^{3,5,6,8} = 0.12$
	$Mo(CO)_4$	THF	2.0048	0.20	$a_H^{3,5,6,8} = 0.11$
	$Mo(cp)(CO)_4{}^{+\,a}$	toluene	2.0003	0.50	$a_H^{3,5,6,8} = 0.10$

[a] $cp = \eta^5\text{-}C_5H_5$. Ref. 3.

$Mo(CO)_4$(quinone) populate the *o*-quinone ligands; *o*-quinone coordinates to Mo as a near radical anion. The EPR parameters, however, show some differences in the spin distribution between the PSQ and the ASQ complexes. The following facts suggest that unpaired electron delocalizes more so onto the metal moiety, $MoCO_4$, in the PSQ complex than in the ASQ complex; the PSQ complex has a g value deviating more from the free anion value and has a larger Mo hf coupling constant than those in the ASQ complex.

As was shown in the previous paper [3], the unpaired electron orbital in the complexes having quinone ligand is considered to be an antibonding orbital formed between the π type orbital of the metal moiety and the π LUMO of the quinones, and hence decrease of the quinone LUMO causes an increase in the contribution of the π-type orbital of the metal moiety to the unpaired electron orbital, leading to larger spin density on the metal moiety. Since the level of the LUMO of PQ is lower than that of AQ [3], the observed results which indicate that the spin delocalization onto the metal moiety is larger in the PSQ complex than in the ASQ complex can be well understood by such a model of the unpaired electron orbital.

Recently Wan et al. observed by EPR spectroscopy that the photoirradiation of $M(CO)_6$ (M = Mo, W) and PQ in solution generates paramagnetic complexes [2]. They postulated the following structure for the produced complexes. The complexes



are one stage more oxidized compared to the complexes reported here. According to their structure, the complexes contain even number of electrons, and hence it seems curious that they are paramagnetic. The results obtained in this work imply that the paramagnetic complexes formed from $M(CO)_6$ (M = Mo, W) and PQ may have a different structure or a different electron configuration from that postulated by Wan et al.

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