EPR Study of the Precursors of Chelate Paramagnetic Complexes Formed in Photochemical Reactions of $[Mo(cp)(CO)_3]_2$ ($cp=\eta^5$-C_5H_5) with *o*-Quinones

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Synopsis. Experimental evidence has been obtained by EPR spectroscopy for the paramagnetic precursors expected in the photochemical reactions of $[Mo(cp)(CO)_3]_2$ with *o*-quinones to produce paramagnetic chelate complexes.

There have been extensive studies on the photochemical reactions of metal carbonyl complexes containing a metal–metal bond, because the molecules display fascinating and diverse photochemical properties. By photo-irradiation of the complexes the homolytic cleavage of the metal–metal bond commonly occurs in solutions and the resulting paramagnetic species undergo various reactions.1–4)

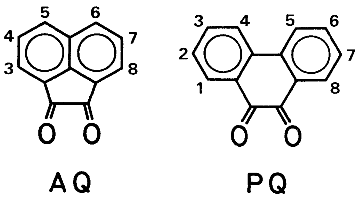
In the previous paper, we reported that the photochemical reaction of $[Mo(cp)(CO)_3]_2$ with a series of *o*-quinones and 1,2-diketones yields paramagnetic chelate complexes of $Mo(cp)(CO)_2$ and *o*-quinones (or 1,2-diketones) in which the *o*-quinones coordinate bidentately to the Mo of $Mo(cp)(CO)_2$ by the two carbonyl oxygens.5) In order to know the mechanism of the formation of the chelate paramagnetic complexes, we have examined the photochemical reactions of $[Mo(cp)(CO)_3]_2$ with *o*-quinones at lower temperatures by EPR and observed paramagnetic precursors of the chelate complexes. In this paper we report the observation of the precursors, their structures and the formation mechanism of the chelate paramagnetic complexes estimated from these results.

Experimental

$[Mo(cp)(CO)_3]_2$ was commercially obtained from Strem Chemicals and used as received. Toluene was used as a solvent; it was dried by distillation over molecular sieves in a vacuum line. 1,2-Acenaphthenequinone (AQ) and 9,10-phenanthrenequinone (PQ) (Fig. 1) were vacuum sublimed before use.

$[Mo(cp)(^{13}CO)_3]_2$ was synthesized from $[Mo(cp)(CO)_3]_2$ by the photosubstitution of CO with ^{13}CO under ^{13}CO atmosphere6–8) in toluene. Almost complete substitution by ^{13}CO's was confirmed by mass spectra.

Typical sample solutions contain 1 mg of $[Mo(cp)(CO)_3]_2$ and 1 mg of either of the *o*-quinones in 1 cm^3 of toluene, and they were prepared in a vessel connected to a 5-mm o.d. quartz tube. The solutions were degassed on the vacuum line and kept at liquid-nitrogen temperature until just before photolysis. The solution in the quartz tube was cooled to an appropriate temperature and irradiated in situ in an EPR cavity with a 100-W high-pressure mercury lamp equipped with a UV-cut filter (<310 nm) and a remote-controlled shutter.



AQ PQ

Fig. 1. *o*-Quinones.

EPR spectra were recorded on the JEOL JES-FE2XG X-band spectrometer using 100-kHz field modulation. The temperature was controlled by standard accessories. The microwave frequency was monitored with a Takedariken TR-5501 frequency counter equipped with a TR-5023 frequency converter. The magnetic field was measured with an Echo electronics EFM-2000 NMR oscillator, and the magnetic field difference between the NMR probe and the sample positions was calibrated by DPPH.

Results and Discussion

As reported in the previous paper, the degassed toluene solution containing $[Mo(cp)(CO)_3]_2$ and AQ exhibits an EPR spectrum showing formation of the paramagnetic chelate complex, $[Mo(cp)(CO)_2(aq)]$, after photo-irradiation at room temperature.5) However, we observed that the EPR spectra apparently show formation of two kinds of paramagnetic species **a** and **b** when the photo-irradiation is made at temperatures lower than −60 °C (Fig. 2). The EPR parameters of the paramagnetic species **b** are identical to those of the paramagnetic complex observed at higher temperatures and, therefore, **b** is identified as the chelate paramagnetic complex. As shown in Fig. 2, the signal intensity of **a** decreased after stopping photo-irradiation, but the signal intensity of **b** increased. The time-dependent changes of EPR signal intensities are shown in Fig. 3. This clearly indicates that the decrease of the signal intensity of **a** well corresponds to the increase of the

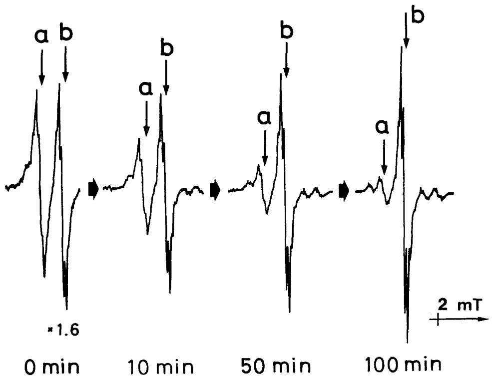


Fig. 2. Changes of EPR spectra observed after stopping photoirradiation of a toluene solution containing $[Mo(cp)(CO)_3]_2$ and AQ at −60 °C.

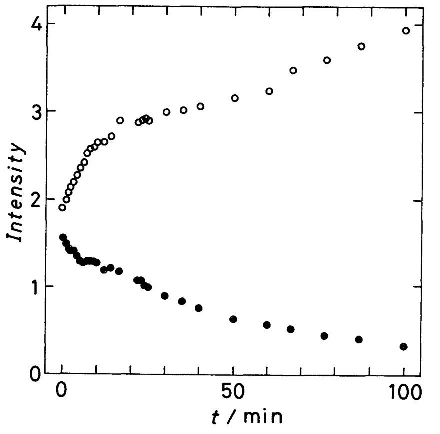


Fig. 3. Time-dependent changes of EPR signal intensities of paramagnetic species, **a** (●) and **b** (○).

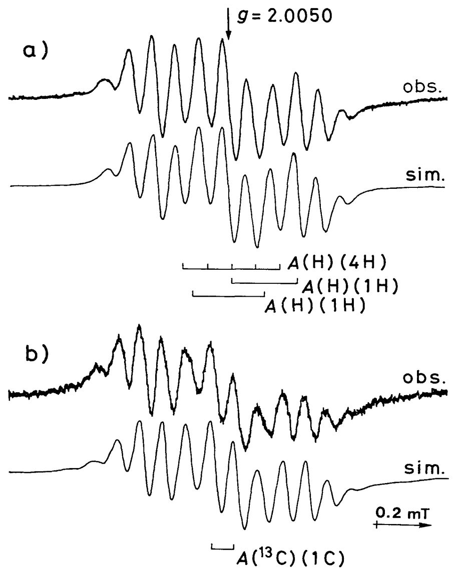


Fig. 4. ESR spectra of the precursor observed during photoirradiation of toluene solutions containing $[Mo(cp)(CO)_3]_2$ and PQ at −70 °C and the simulated spectra; a) $[Mo(cp)(CO)_3]_2$, b) $[Mo(cp)(^{13}CO)_3]_2$.

signal intensity of **b**. From these facts, the paramagnetic species **a** seems to turn to **b**, i.e., **a** is considered to be a precursor of the chelate paramagnetic complex **b**. The EPR spectrum of the paramagnetic species **a** exhibited the hyperfine (hf) splittings due to the protons of AQ, and when the ^{13}C enriched complex, $[Mo(cp)(^{13}CO)_3]_2$, was used the spectrum exhibited the line-width broadening probably due to the hf interactions with ^{13}C's ($I=1/2$) in ^{13}CO's.

In the reaction with PQ formation of a precursor of the chelate paramagnetic complex was also observed. The hf structure in the EPR spectrum for the precursor is well explained by the hf interactions with the protons of PQ as evidenced by the simulation calculation of the spectrum (Fig. 4a). When $[Mo(cp)(^{13}CO)_3]_2$ was used, the EPR spectrum exhibited an additional doublet hf splitting which can be apparently attributed to the hf interaction with ^{13}C in ^{13}CO (Fig. 4b).

As mentioned above, the EPR spectra of the precursors in cases of both AQ and PQ exhibit the hf splittings due to the *o*-quinone protons and the ^{13}C's in CO's. It is reasonable to consider, therefore, that in the precursors the *o*-quinones and the CO's are coordinating to Mo. However, the two carbonyl groups of PQ are not equivalent in the precursor as seen from the proton hf splittings, i.e., the precursors do not have the chelate form. We have recently reported that $Mo(cp)(CO)_3$ produced by the photocleavage of the Mo–Mo bond of $[Mo(cp)(CO)_3]_2$ is trapped by a series of *p*-benzoquinones yielding a paramagnetic complex, $[Mo(cp)(CO)_3(p\text{-benzoquinone})]$, where the *p*-benzoquinone ligands are coordinating to Mo by one of their carbonyl oxygens.[9] The precursors observed in this study are, therefore, considered to be complexes in which the *o*-quinones coordinate to Mo of $Mo(cp)(CO)_3$ by one of their two carbonyl oxygens.

The EPR parameters of the precursors are listed in Table 1 together with the data for the chelate complexes taken from the previous paper.[5] The hf couplings of the *o*-quinone protons were assigned in reference to the spin distribution calculated for the *o*-quinone ligands in the complexed form by the Hückel-McLachlan MO method. Though the calculations predict different hf couplings for the 3,4,5,7 protons in the AQ complex, these couplings were not

Table 1. EPR Parameters for the Paramagnetic Complexes

o-Quinone	Metal	*g* value	$a_{Mo}/10^{-4}$ T	$a_H/10^{-4}$ T$^{a)}$
AQ	$Mo(cp)(CO)_3$$^{b)}$	2.0055	—	$a_H3,4,5,7=1.1$ (4H)
	$Mo(cp)(CO)_2$$^{c)}$	2.0003	5.0	$a_H3,5,6,8=1.0$ (4H), $a_{^{13}C}=0.5$ (2C)$^{d)}$
PQ	$Mo(cp)(CO)_3$$^{e)}$	2.0050	—	$a_H1=2.63$ (1H), $a_H3=2.37$ (1H), $a_H2,4,6,8=0.80$ (4H), $a_{^{13}C}=0.75$ (1C)$^{d)}$
	$Mo(cp)(CO)_2$$^{c)}$	1.9957	11.2	$a_H1,3,6,8=1.0$ (4H), $a_{^{13}C}=1.9$ (2C)$^{d)}$

a) The number of equivalent protons is indicated in parentheses. b) The data for the precursor in which AQ coordinates to Mo by the C_2-oxygen. c) The data for the chelate complex. Ref. 5. d) The hf coupling constant of ^{13}C's in carbon monoxides. The number of equivalent ^{13}C's is indicated in parentheses. e) The data for the precursor in which PQ coordinates to Mo by the C_{10}-oxygen.

resolved in the observed EPR spectra. The ^{95,97}Mo (I=5/2) hf couplings were observed as satellite signals, but reliable coupling constants could not be determined because of the mutual overlaps between the satellite signals and the overlaps with the intense center signal. However, the hf coupling constants were estimated to be much smaller than those of the complexes of the chelate form. One can also see that the g values of the precursors are much closer to those of the free anion radicals of the corresponding o-quinones ($g \approx 2.005$) than the case of the chelate complexes. These facts suggest that the unpaired electron is mostly transfered from Mo(cp)(CO)$_3$ to the o-quinones to form complexes of Mo(cp)(CO)$_3^+$ ligated by the o-quinone anion radicals, as in the case of the p-benzoquinone complexes. It is notable that the unpaired electron populates more on the o-quinone ligand in the precursors than in the final products having chelate structure. It is seen also from the table that the ^{13}C hf couplings of the CO groups in the precursors are smaller than those in the final products. This may be also a support for the above estimation.

These results suggest a stepwise reaction mechanism for the formation of the chelate paramagnetic complexes. In the first step, Mo(cp)(CO)$_3$ produced by photocleavage of the Mo–Mo bond of [Mo(cp)(CO)$_3$]$_2$ is trapped by the o-quinones yielding the precursors in which the o-quinones coordinate to Mo of Mo(cp)(CO)$_3$ by one of their two carbonyl oxygens. In the second step, the chelate paramagnetic complexes are formed by elimination of one CO group from the precursors. The same reaction mechanism has been assumed by Sarbasov et al. in the photochemical reaction of [Mo(cp)(CO)$_3$]$_2$ with 3,6-di-t-butyl-1,2-benzoquinone.[10] They postulated the mechanism according to only the hf splittings due to the ligand quinone protons. In this paper, we clearly observed the conversion of the precursors to the chelate complexes by EPR intensity changes and also obtained clear experimental information on the structures of the precursors by using [Mo(cp)(^{13}CO)$_3$]$_2$. It is reasonable to consider that the chelate paramagnetic complexes of other o-quinones or 1,2-diketones are also formed via the precursors of the same type.

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