

Reexamination of the photochemical oxidative decarbonylation of $\text{Cr}(\text{CO})_6$ by *ortho*-quinones: Low-temperature photolysis of $\text{Cr}(\text{CO})_6$ with *ortho*- and *para*-quinone isomers

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Abstract

In order to stabilize and identify intermediates in the photochemical formation of $\text{Cr}^{\text{III}}(\text{SQ})_3$ (SQ = *ortho*-semiquinone radical-anion) out of $\text{Cr}^0(\text{CO})_6$ and *ortho*-quinones (*o*-Q), this reaction has been studied at lower temperatures ($T < 230$ K). For comparison, the same reaction was performed for the corresponding *para*-quinone (*p*-Q) ligands. Both quinone isomers gave $\text{Cr}^0(\text{CO})_5\text{L}$ (L = quinone) complexes, which were characterized by IR and UV/Vis spectroscopy.

Warming the solution of $\text{Cr}^0(\text{CO})_5(\text{o-Q})$ in the absence of CO afforded $\text{Cr}^{\text{III}}(\text{SQ})_3$, with no evidence for any carbonyl-containing intermediate. This is explained in terms of a concerted mechanism involving chelate ring formation accompanied by electron transfer to the *o*-Q ligand.

Introduction

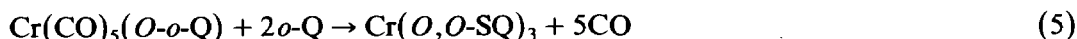
It was recently shown [1,2] that $\text{Cr}^0(\text{CO})_6$ undergoes a rapid photochemical oxidative decarbonylation by *o*-quinones (*o*-Q) to produce Cr^{III} complexes containing *o*-semiquinone radical-anions (SQ) according to reaction 1. Such a rapid substitution of



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all six carbonyl ligands accompanied by the change of Cr-oxidation state is unprecedented in metal carbonyl photochemistry. Usually, only one or two CO ligands are substituted photochemically by Lewis bases, the Cr-oxidation state remaining at zero [3].

Based on the results of a quantum yield and flash-photolytic study, the following mechanism was formulated for reaction 1 [2] in which S denotes a solvent molecule, *O-o-Q* and *O,O-SQ* denote an *o*-quinone molecule and its *o*-semiquinone radical-anion, bound to the metal via one and two oxygen atoms, respectively:



Whereas eqs. 2–4 represent normal steps in a photochemical substitution reaction of $\text{Cr}(\text{CO})_6$, step 5, which comprises the electron transfer steps, is specific for these *o*-quinones. Originally [2], reaction 4 was suggested to involve an oxidative addition to give $\text{Cr}^1(\text{CO})_5(O\text{-SQ})$.

The above mechanism was formulated purely on kinetic grounds, since no reaction intermediates could be detected by conventional flash-photolysis [2]. In order to establish the nature of the intermediates and redox steps involved in reaction 1, and to ascertain the reason for the high labilization of Cr–CO bonds, this reaction has been studied at lower temperatures with the objective of stabilizing and identifying reactive intermediates. The results of this study are described below. For comparison, and to permit more detailed characterization of reaction 4, the photochemical reaction of $\text{Cr}(\text{CO})_6$ with *para*-quinones was also studied. Since the unsubstituted *p*-benzoquinone (*p*-Q) readily polymerizes, the substituted *ortho*- and *para*-quinones 3,5-di-butyl-1,2-benzoquinone (*o*-DBQ) and 2,6-di-butyl-1,4-benzoquinone (*p*-DBQ) were used instead.

Experimental

Materials

$\text{Cr}(\text{CO})_6$ (Fluka) was used without further purification. 2,6-di-butyl-1,4-benzoquinone (Aldrich) and 1,4-benzoquinone (Fluka) were sublimed under vacuum, 3,5-di-butyl-1,2-benzoquinone (Aldrich) was used as obtained. CH_2Cl_2 and n-hexane were distilled from Na wire. Toluene was purified by shaking with H_2SO_4 , and after subsequent washing and drying it was distilled from LiAlH_4 . The solvents were stored under pure nitrogen and the reactions were performed under nitrogen or argon. During the reactions at room temperature the stirred solutions were irradiated with argon bubbling through in order to remove evolved CO.

Equipment

UV/Vis spectra were recorded on a Perkin–Elmer Lambda-5 Spectrophotometer provided with a PE 3600 Data Station and a Carl Zeiss (Jena) M-40 Spectrophotometer. Infrared spectra were measured on a Nicolet FTIR 7199 B interferometer provided with a liquid-nitrogen cooled Hg–Cd–Te detector (32 scans, resolution 1

cm^{-1}) and on a Perkin–Elmer 257 grating Spectrophotometer.

The photochemical reactions were performed by irradiating solutions of $\text{Cr}(\text{CO})_6$ and at least a five-fold molar excess of ligand contained in a Pyrex vessel, with light from a medium- or high-pressure Hg lamp. Filtering of the light did not change the course of the reaction. Reactions at low temperature were performed in Oxford Instruments cryostats and the home-made cryogenic cell used for the reaction in LXe has been described elsewhere [4].

To determine the extinction coefficients of the thermally labile photoproduct $\text{Cr}(\text{CO})_5(p\text{-DBQ})$, its concentration was assessed spectrophotometrically after its quantitative conversion to $\text{Cr}(\text{CO})_4\text{bipy}$ (bipy = 2,2'-bipyridine): Part of the green solution obtained by irradiation of $\text{Cr}(\text{CO})_6$ with $p\text{-DBQ}$ in CH_2Cl_2 was transferred to the UV-cell immediately after the irradiation and at the same time an excess of solid bipy was added to the remaining solution. The absorption spectrum of the solution in the UV-cell was then measured as a function of time, and the absorbance values were extrapolated to the time of interruption of the irradiation. Meanwhile, the reaction with bipy was completed and the concentration of the $\text{Cr}(\text{CO})_4\text{bipy}$ complex formed was determined. This concentration had to be equal to the original concentration of the photoproduct.

Results

Reaction of $p\text{-DBQ}$

Irradiation of $\text{Cr}(\text{CO})_6$ with $p\text{-Q}$ in toluene at room temperature afforded a green solution with an absorption band at 704 nm and another between 400 and 450 nm. The position of the latter band was rather uncertain owing to its coincidence with a free ligand band. After a few minutes of irradiation a brown precipitate was formed; its IR spectrum showed that this material did not contain a CO ligand, and it was therefore assumed to be a polymer with bridging quinone molecules.

In order to prevent this reaction, the sterically hindered $p\text{-DBQ}$ molecule was used instead and reactions were performed in various solvents at room temperature and at 223 K. The reactions were monitored by UV/Vis and IR spectroscopy.

Irradiation at room temperature of a toluene solution of $\text{Cr}(\text{CO})_6$ and $p\text{-DBQ}$ again produced a green air-sensitive photoproduct, which decomposed thermally with liberation of free $p\text{-DBQ}$. The photoproduct absorbed at 692 and 435 nm. A similar photoproduct was obtained in CH_2Cl_2 , and had absorption maxima at 641 ($\epsilon \approx 3200 \text{ M}^{-1} \text{ cm}^{-1}$) and 435 nm ($\epsilon \approx 2800 \text{ M}^{-1} \text{ cm}^{-1}$).

The IR spectra of the irradiated solutions exhibited two new bands at 2065 and 1952 cm^{-1} . When an excess of pyridine was added to the green CH_2Cl_2 solution, the colour immediately changed to yellow owing to the formation of $\text{Cr}(\text{CO})_5\text{py}$ (py = pyridine), which gave a single absorption band at 407 nm and an IR band at 1937 cm^{-1} . Identical spectral features were obtained after irradiation of a mixture of $\text{Cr}(\text{CO})_6$ and pyridine in CH_2Cl_2 for a short time. Addition of bipy converted the green photoproduct initially into $\text{Cr}(\text{CO})_5(N\text{-bipy})$, which was characterized by its known [5] absorption spectrum, and finally into $\text{Cr}(\text{CO})_4\text{bipy}$.

Apparently, the $p\text{-DBQ}$ ligand is only weakly bonded to the metal in this photoproduct, probably via its C_4 -oxygen atom: $\text{Cr}(\text{CO})_5(O\text{-}p\text{-DBQ})$ (I). This structural formula is confirmed by the close similarity between the IR frequencies

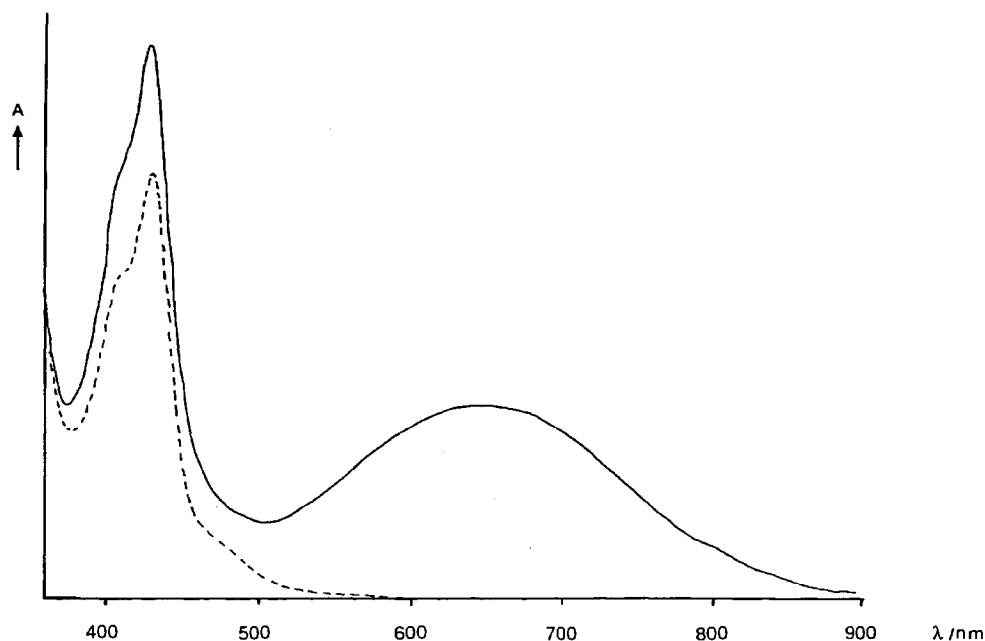


Fig. 1. Electronic absorption spectra of $\text{Cr}(\text{CO})_6$ and $p\text{-DBQ}$ (1/10) in CH_2Cl_2 at 223 K, before (— —) and after (—) irradiation.

for this product and those for other $\text{Cr}(\text{CO})_5(O\text{-donor})$ complexes (see Table 1). It is evident that no electron transfer has taken place during this reaction.

In order to stabilize complex I and to compare its spectroscopic properties with those of the corresponding $o\text{-DBQ}$ complex, which is not stable at room temperature, the above reaction was also performed in various solvents at about 220 K. Figure 1 shows the absorption spectra of a solution of $\text{Cr}(\text{CO})_6$ and $p\text{-DBQ}$ (ca. ten-fold excess) in CH_2Cl_2 at 223 K, before and after photolysis. The structured band between 400 and 440 nm belongs to the $p\text{-DBQ}$ ligand. The intensity of this band increased, however, upon irradiation and subtraction of the spectra afforded a new band at about 430 nm.

A second band showed up at about 650 nm. When the reaction was performed in *n*-hexane at 223 K, the latter absorption band was found at still lower energy as a composite band with maxima at ca. 680 and 750 nm, respectively. A similar solvent dependence was observed during the room temperature experiments (*vide supra*).

These reactions were also monitored by IR spectroscopy not only in CH_2Cl_2 and *n*-hexane but also in liquid xenon (LXe), which has several important advantages over all other solvents. First of all, vibrational frequencies measured in LXe are very close to those obtained for the free molecule in the gas phase because of the very weak solvent-solute interactions. This weakness of interactions ratio means that reactive intermediates of photochemical reactions, such as $\text{Cr}(\text{CO})_5(\text{H}_2)$ [6], can be more easily stabilized and identified.

A second important property of this solvent is its complete transparency in the IR (and UV/Vis), which makes it possible to measure IR bands in frequency regions where normal solvents absorb. Moreover, because of this transparency, long optical pathways, and so very low solute concentrations, can be used. This is of

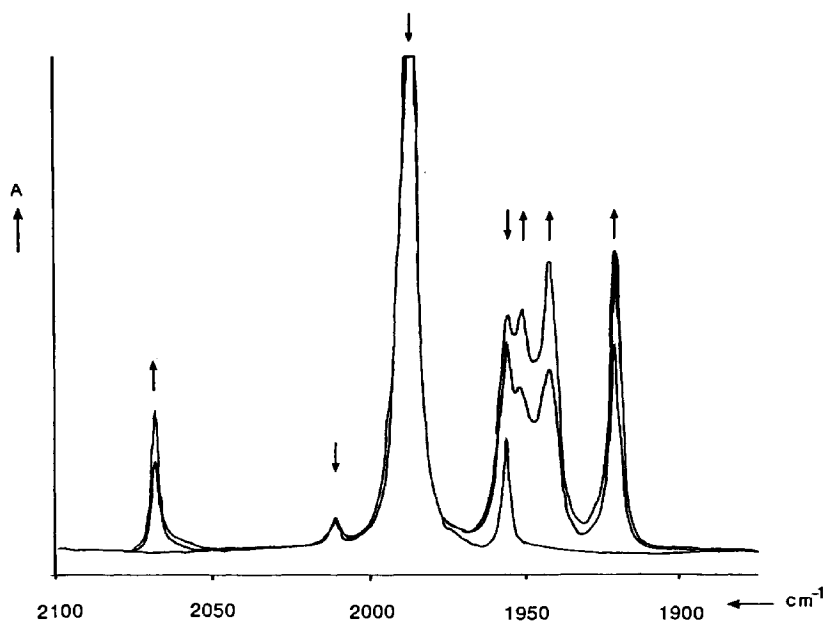


Fig. 2. IR spectral changes in the CO-stretching region during the photochemical reaction of $\text{Cr}(\text{CO})_6$ with *p*-DBQ (1/10) in liquid xenon (P 13 bar, T 223 K).

importance in view of the low solubility of most organometallic compounds in LXe. For the experiment in LXe, use was made of a home-made high-pressure cryostat [4] in which LXe was kept at a pressure of 13 bar and a temperature of 223 K. The sample cell had an optical pathway of 30 mm.

Figure 2 shows the IR spectral changes in the CO-stretching region for the reaction of $\text{Cr}(\text{CO})_6$ with *p*-DBQ in LXe. Irradiation of the reaction mixture causes the disappearance of the $\text{Cr}(\text{CO})_6$ bands at 2012, 1979 and 1957 cm^{-1} , and the growth of five new bands at 2068, 1994, 1952, 1943 and 1922 cm^{-1} . These data and those obtained in CH_2Cl_2 and *n*-hexane, are collected in Table 1. For comparison, this table also contains the corresponding frequencies for $\text{Cr}(\text{CO})_5(\text{THF})$ and $\text{Cr}(\text{CO})_5(2\text{-MeTHF})$, obtained by irradiation of solutions of $\text{Cr}(\text{CO})_6$ and an excess of THF or 2-MeTHF in CH_2Cl_2 and *n*-hexane, respectively.

The close correspondence between these frequencies and those obtained for complex I, again confirms the correctness of the molecular formula $\text{Cr}(\text{CO})_5(O\text{-}p\text{-DBQ})$ for this complex. The CO-stretching frequencies are assigned on the assumption of C_{4v} symmetry (but see the Discussion). The frequency of the axial CO vibration, $\nu(\text{CO})(A_1^1)$ is most sensitive to the polarity of the solvent. Upon going from CH_2Cl_2 to LXe, this frequency increases from 1895 to 1922 cm^{-1} .

Since LXe is transparent between 1500 and 1700 cm^{-1} , the shifts of $\nu_s(\text{CO})$, $\nu_{as}(\text{CO})$ and $\nu(\text{CC})$ of the *p*-DBQ ligand upon coordination could also be observed. The free ligand has three IR bands in the CO-stretching region (1667, 1661 and 1648 cm^{-1}) instead of two because of Fermi resonance with a ligand combination mode [7]. $\nu(\text{CC})$ of the free ligand has its frequency at 1601 cm^{-1} . The Fermi resonance disappears when the ligand coordinates to the metal and the IR spectrum of complex I only shows two CO-stretching modes of the *p*-DBQ ligand (1632 and 1551 cm^{-1}) and one $\nu(\text{CC})$ at 1589 cm^{-1} . Such a relatively large decrease in the

Table 1
Spectroscopic (IR, UV/Vis) data of the photoproducts $\text{Cr}(\text{CO})_5\text{L}$ (L = quinone, THF, 2-MeTHF) in different solvents

Compound	Solvent (temp.)	CO-stretching frequencies (cm^{-1}) ^a				$\lambda_{\text{max}}^{\text{MLCT}}$ (nm) (ϵ , $\text{mol}^{-1} \text{cm}^{-1}$)
		A_1'	E	B_1	A_2'	
$\text{Cr}(\text{CO})_5(\text{O-}p\text{-Q})$	Toluene (RT)					704
	LXe (223 K)	1930 m	1952/1956 vs		2067 w	
$\text{Cr}(\text{CO})_5(\text{O-}p\text{-DBQ})$ (I)	Toluene (RT)		1952 vs		2065 w	692
	CH_2Cl_2 (RT)		1952 vs		2065 w	641 (3200)
	CH_2Cl_2 (223 K)	1895 m	1944 vs		2070 w	650
	n-Hexane (223 K)	1919 m	1942/1950 vs	1993 vw	2067 w	680, 750
	LXe (223 K)	1922 m	1943/1952 vs	1994 vw	2068 w	
$\text{Cr}(\text{CO})_5(\text{O-}o\text{-DBQ})$ (II)	CH_2Cl_2 (223 K)	1892 m	1940 vs		2062 w	680, 760
	n-Hexane (223 K)	1924 m (1919 w)	1963 m (1955 w)		2057 w (2066 vw)	860
$\text{Cr}(\text{CO})_5(\text{THF})$	CH_2Cl_2 (RT)	1889 m	1937 vs		2074 w	
	n-Hexane (RT)	1913 m	1941 vs		2074 w	
$\text{Cr}(\text{CO})_5(2\text{-MeTHF})$	CH_2Cl_2 (RT)	1890 m	1936 vs		2074 w	
	n-Hexane (RT)	1913 m	1939/1942 vs		2073 w	

^a vs = very strong, m = medium, w = weak, vw = very weak; assignments in C_{4v} symmetry.

p-DBQ- $\nu(\text{CO})$ frequencies is further evidence for the coordination of the *p*-DBQ ligand via its oxygen donor atom.

Prolonged irradiation of the reaction mixture did not cause the photochemical transformation of I into $\text{Cr}(\text{CO})_4(\text{O-}i\text{p-DBQ})_2$, probably because of bulk of the tertiary-butyl groups. The influence of these substituents becomes evident when the unsubstituted *p*-quinone (*p*-Q) ligand is used for the reaction in LXe. In this case prolonged irradiation leads to the formation of $\text{Cr}(\text{CO})_4(\text{O-}i\text{p-Q})_2$ with IR bands at 1933 and 2031 cm^{-1} . This reaction with *p*-Q could not be performed in *n*-hexane or CH_2Cl_2 because much higher quinone concentrations had to be used during the IR measurements in these solvents and this led to polymerization of the quinone.

Reactions of *ortho*-DBQ

Since irradiation of a room temperature solution of $\text{Cr}(\text{CO})_6$ and *o*-DBQ directly produces $\text{Cr}(\text{DBSQ})_3$, reactive intermediates of reaction 1 had to be studied at lower temperatures.

Irradiation of a CH_2Cl_2 solution of $\text{Cr}(\text{CO})_6$ and *o*-DBQ (ca. ten-fold excess) at 223 K afforded a photoproduct with a broad, structured absorption band with maxima at 680 and 760 nm. Higher energy bands could not be observed due to interference from bands from the *o*-DBQ. Just as in the case of the reaction with *p*-DBQ, the absorption band shifted to longer wavelength when the reaction was performed in *n*-hexane. Unfortunately, only one of the absorption maxima (860 nm) could be observed in this latter solvent owing to the restricted wavelength region of the UV/Vis. spectrophotometer ($\lambda < 900$ nm). This reaction was also followed by IR spectroscopy in both solvents. The data are presented in Table 1, and the IR spectrum in the CO-stretching region of the photoproduct, obtained in CH_2Cl_2 at 223 K, is shown in Fig. 3.

The close correspondence between the IR and UV/Vis spectra of this photoproduct and those of complex I is clear evidence that in this case again a pentacarbonyl complex $\text{Cr}(\text{CO})_5(\text{O-}i\text{o-DBQ})$ (II) is formed. The $\nu(\text{CO})$ frequencies are again similar to those of other $\text{Cr}(\text{CO})_5(\text{O-donor})$ complexes, showing that no electron transfer takes place during the formation of II.

Unfortunately, this reaction could not be performed in LXe because of the low solubility of *o*-DBQ in this solvent. Even in *n*-hexane, the IR bands of the photoproduct are rather weak owing to the low solubility of *o*-DBQ in this solvent at lower temperatures. There is, however, clear evidence from this spectrum that the photoproduct consists of two isomers in *n*-hexane since all the IR bands are doublets. The frequencies of the less abundant isomer are given in brackets in Table 1.

Prolonged irradiation did not result in the photosubstitution of a second CO group. Apparently, formation of $\text{Cr}(\text{CO})_4(\text{O-}i\text{o-DBQ})_2$ is prevented by steric hindrance by the *t*-butyl groups.

Complex II is thermally stable at 220 K and is not converted into the final photoproduct $\text{Cr}(\text{DBSQ})_3$ of reaction 1 at this temperature. In order to accomplish this conversion, the solution was slowly warmed up to room temperature after the reaction. However, this did not lead to formation of $\text{Cr}(\text{DBSQ})_3$, but instead to a back-reaction of the photoproduct with the CO still present in the solution. This back-reaction, which occurred between 250 and 270 K, was also observed when a solution of $\text{Cr}(\text{CO})_6$ and *o*-DBQ was irradiated in this temperature range. In this

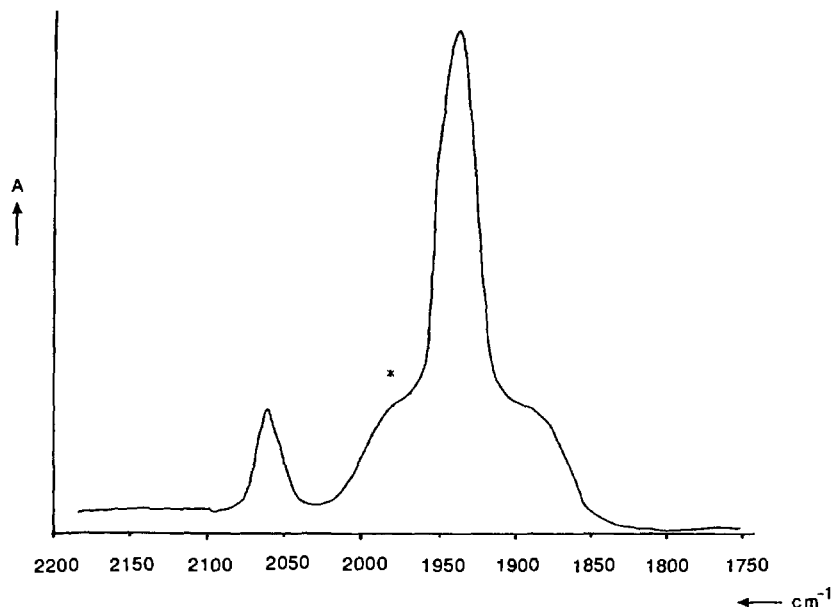


Fig. 3. IR spectrum in the CO-stretching region of the photoproduct obtained by irradiation of $\text{Cr}(\text{CO})_6$ with DBQ (1/10) in CH_2Cl_2 at 223 K.

case no photochemical event due to this back-reaction was observed. At temperatures above 270 K, the photochemical conversion into $\text{Cr}(\text{DBSQ})_3$ began to dominate, since the irradiated solution then showed the red colour of this complex with no evidence of a carbonyl-containing photoproduct or intermediate.

In order to prevent the back-reaction with CO, a cold solution of complex II in toluene, obtained by irradiation outside the IR cell at low temperature, was evacuated several times. This solution was then injected into the cell at about 235 K and allowed to warm up to room temperature in the dark. Complete conversion of II into $\text{Cr}(\text{DBSQ})_3$ then occurred above 273 K, and there was no evidence for any side-product or intermediate.

Discussion

The results clearly show that the *para*- and *ortho*-quinone isomers both react photochemically with $\text{Cr}(\text{CO})_6$ to give $\text{Cr}(\text{CO})_5\text{L}$ (L = quinone) complexes that are stable at temperatures below 270 K. According to the IR data, all the quinones are coordinated to the metal as simple O-donor ligands, like THF and 2-MeTHF. There can only be a weak metal to quinone π -back-bonding, since the $\nu(\text{CO})(A_1')$ frequency, which is most sensitive to such an interaction, is only slightly higher for these complexes than for the corresponding THF/2-MeTHF compounds.

Before discussing the consequences of these findings for the mechanism (eqs. 2–5) of reaction 1, we consider some spectroscopic properties of complexes I and II. Both compounds show an intense absorption band in the visible region, which shifts to higher energy upon going to a more polar solvent. This behaviour is characteristic of a metal to ligand L charge transfer (MLCT) transition in $\text{M}(\text{CO})_5\text{L}$ (M = Cr, Mo, W) complexes (see e.g. ref. 8). The low energy of these transitions is consistent with the low energy of the lowest π^* orbitals of the quinone ligands. The

difference in energy between the π^* orbitals of the *ortho*- and *para*-quinones is reflected in the different positions of the MLCT bands of complexes I and II: complex II, containing the stronger oxidant *o*-DBQ ($E_{1/2} - 0.49$ V vs. SCE [9]), absorbs at 680 and 750 nm, whereas the less oxidizing *p*-DBQ ($E_{1/2} - 0.64$ V vs. SCE [9]) forms complex I absorbing at 650 nm. In accord with the above assignment, the absorption band is shifted to higher energy when the unsubstituted *p*-quinone is replaced by its di-butyl derivative.

In addition to these MLCT bands and ligand bands at higher energy, a LF band was observed at 435 nm in the case of complex I. Such a LF band is typical of $\text{Cr}(\text{CO})_5\text{L}$ complexes [3].

The MLCT band of I, studied in *n*-hexane, consists of two sub-bands. These bands do not belong to different isomers since no such isomers are observed in the corresponding IR spectrum of this complex. The two sub-bands are therefore assigned to MLCT transitions from different metal-*d* orbitals, and their coincidence in the CH_2Cl_2 spectrum is attributed to a difference in solvatochromic behaviour for these transitions. Such non-coincident MLCT transitions have been observed for example for several α -diimine complexes [10], and characterized by resonance Raman excitation profiles in the case of $\text{W}(\text{CO})_4(\alpha\text{-diimine})$ [10a] and $\text{Fe}(\text{CO})_3(\alpha\text{-diimine})$ [10b].

The IR spectra of I in *n*-hexane and in LXe at low temperatures show a splitting of $\nu(\text{CO})(\text{E})$, which means that its degeneracy is lifted and that the complex has no C_{4v} symmetry. Such a lowering of symmetry normally occurs when free rotation of the ligand L in $\text{Cr}(\text{CO})_5\text{L}$ is inhibited by steric or electronic effects. Electronic effects, normally caused by metal to ligand L π -backbonding [11], are not important here since the CO-stretching frequencies of I closely resemble those of the complexes of THF and 2-MeTHF, which are pure σ -donors (Table 1). Probably, free rotation of the *p*-DBQ ligand is inhibited by the interaction of its H-atoms with the equatorial carbonyls of the $\text{Cr}(\text{CO})_5$ moiety. This splitting of $\nu(\text{CO})(\text{E})$ was observed only in the *n*-hexane spectra, since the bands were too broad in the CH_2Cl_2 spectra.

In the $\text{Cr}(\text{CO})_5(\text{THF})$ complex the ligand rotates freely, since there is no splitting of the E-mode. $\text{Cr}(\text{CO})_5(2\text{-MeTHF})$ shows only a small splitting of this vibration, caused by steric effects of the 2-Me group.

The MLCT band of complex II shows two sub-bands even in the CH_2Cl_2 spectrum. As in the case of complex I, these sub-bands probably belong to MLCT transitions from different metal d_π -orbitals. However, without further evidence, e.g. from resonance Raman spectra, we cannot rule out the possibility that the sub-bands belong to the different isomers of II observed in the IR spectra. The presence of two isomers is understandable in view of the inequivalence of the two-oxygen-atoms of the *o*-DBQ ligands, which can both bind to the metal. However, their bonding properties seem to be too similar to account for such a large spectral shift (680 vs. 750 nm).

The formation of complex II as an intermediate in reaction 1 is consistent with the mechanism described in eqs. 2–5. Apparently, the addition of *o*-quinone to $\text{Cr}(\text{CO})_5$ is a simple Lewis acid-base interaction, since no change of oxidation states takes place during reaction 4, the product from which still contains the unreduced ligand.

The charge transfer to the *o*-DBQ must thus occur during the reaction represented in eq. 5. It is conceivable that the step immediately after the coordination of

o-DBQ (i.e. the initial process in reaction 5) is the intramolecular closure of the Cr(*O,O*-*o*-DBQ) chelate ring *. This process must have a rather high energy barrier, since it only occurs at temperatures above 270 K.

However, this chelate ring formation does not lead to a stable Cr⁰(CO)₄(*O,O*-*o*-DBQ) species, as it does in the case of comparable ligands with conjugated double bonds, e.g. α -diimines [5,12]. Apparently, chelation of the oxidizing *o*-DBQ ligand is accompanied by an electron transfer to the *o*-DBQ ligand to give Cr^I(CO)₄(*O,O*-DBSQ). This complex is highly reactive, owing to a combination of two effects: (i) the metal to CO π -backbonding is weakened, and a CO ligand can therefore be more easily released, (ii) this complex is a 17-electron carbonyl species for which very fast associative substitution reactions are expected [14]. The Cr^I(CO)₄(*O,O*-DBSQ) complex will therefore undergo further very rapid oxidative substitution by another *o*-quinone molecule to give an even more reactive Cr^{II}(CO)₂(*O,O*-DBSQ)₂ intermediate, which in turn will react with one more *o*-quinone molecule to give the final product, Cr^{III}(*O,O*-DBSQ)₃.

The very high reactivity of Cr^I(CO)₄(*O,O*-DBSQ) and of other intermediates keeps their concentration at very low but kinetically significant levels, and precludes their direct observation.

The crucial step in the formation of the Cr^{III}(DBSQ)₃ complex is the Cr^I(*O,O*-DBSQ) chelate ring formation from Cr⁰(*O*-*o*-DBQ). Such a chelation concerted with the metal-to-quinone electron transfer has been observed also for the oxidative addition of *o*-quinones to square-planar cobalt(II) complexes [15]. It seems that this process is typical of the oxidative addition of *o*-quinones to Lewis acidic oxidizable metal complexes. The overlap between the *d* _{π} -orbital and the low-lying π^* -quinone orbital increases strongly during the chelation, opening the pathway for the metal-to-quinone electron transfer.

Conclusion

Both *ortho*- and *para*-quinones react photochemically with Cr(CO)₆ to give Cr⁰(CO)₅(quinone). This means that the first electron transfer reaction in the formation of Cr^{III}(SQ)₃, formed from Cr(CO)₆ and *o*-quinones, takes place at a later stage, probably during the chelate ring formation of the *o*-quinone ligand. This electron transfer produces highly labile Cr^I(CO)₄(SQ) species, and initiates a series of very fast reactions, ultimately giving the Cr^{III}(SQ)₃ complexes.

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* Such chelate ring formation also takes place for complexes of α -diimines monodentately bound to Cr(CO)₅ by only one N-atom, producing stable Cr(CO)₄(*N,N*) species [5,12].

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