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MECHANISM OF ORGANOMETALLIC RADICAL TRAPPING. THE OXIDATIVE ADDITION OF QUINONES TO PHOTOGENERATED $CpTiCl_2^{\cdot}$

A. VLČEK, JR.

J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Vlašská 9, 118 40 Prague 1 (Czechoslovakia)

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Summary

The $CpTiCl_2^{\cdot}$ radical photogenerated from Cp_2TiCl_2 has been found to add oxidatively to various *ortho*- and *para*-quinones to give titanium(IV) complexes of semiquinone radical-anionic ligands, which have been characterized by ESR spectroscopy. Detailed investigation of the reaction with 3,5-di-t-butyl-1,2-benzoquinone reveals that *o*-quinones add to the titanium(III) atom primarily through one oxygen atom only, the chelate ring being formed in a subsequent intramolecular displacement of a weakly bound solvent molecule (toluene, tetrahydrofuran, pyridine). Information was obtained on the redox and coordination properties of $CpTiCl_2^{\cdot}$ and its oxidation product. The reactant orbital matching leading to the oxidative addition is briefly discussed.

Introduction

Both *ortho*- and *para*-quinones are well known to add oxidatively to various coordinatively unsaturated organometallic and coordination compounds [1]. We have recently shown [2–8] that the reaction mechanism and the nature of the products of these reactions are directly related to the structure of the metal-containing compound entering into the reaction with the quinone. Both *ortho*- and *para*-quinone isomers may thus be employed as useful traps for photogenerated reducing metal-centered radical species. More detailed investigation of these radical-trapping reactions may reveal information about the solution structure and properties of unstable intermediates involved in organometallic photochemistry.

It has been clearly demonstrated that Cp_2TiCl_2 ($Cp = \eta^5\text{-}C_5H_5^-$) undergoes photochemical dissociation of one Cp ligand to give the $CpTiCl_2^{\cdot}$ radical containing a titanium(III) atom [9–12]. Reaction of this radical species with a series of *ortho*-

and *para*-quinones * has been studied in order to demonstrate the radical-trapping ability of the quinones and to obtain information on the solution properties of $CpTiCl_2^{\cdot}$, which are far from simple and not fully understood [12]. Moreover, this complex is a suitable model compound for mechanistic studies since the d^1 electron configuration of the titanium(III) central atom makes the orbital correlation of the reactants and products quite simple.

Experimental

Cp_2TiCl_2 and quinones were obtained from Fluka, except for *o*-DBQ and *p*-DBQ (EGA-Chemie and Aldrich, respectively). Toluene (Lachema, Brno) was purified by repeated vigorous stirring with H_2SO_4 followed by stirring with water and by distillation from P_2O_5 and then from $LiAlH_4$. Pyridine (Merck) was purified by distillation from KOH. Solutions of Cp_2TiCl_2 in toluene (8×10^{-3} *M*) and in toluene/pyridine mixtures (10^{-2} *M*) containing the appropriate quinone were deoxygenated by flushing with pure argon. Solutions in tetrahydrofuran (THF) were prepared by dissolving Cp_2TiCl_2 (10^{-2} *M*) and quinones in oxygen- and moisture-free THF inside a Schlenk tube. Pure THF was obtained by distillation of Merck-Uvasol THF from the benzophenone/sodium metal under argon directly into the closed burette which was used to transfer the solvent into the Schlenk apparatus. The concentration of CQ and *o*-DBQ was 2×10^{-3} *M* in all experiments, but a 4×10^{-3} *M* concentration was used for the quinones which do not significantly absorb visible light (*p*-DBQ, PQ).

The ESR cells were filled with the reactant solutions by use of syringes under argon. These solutions were irradiated inside the cavity of the Varian E-4 X-band ESR spectrometer by the focused light of the high-pressure 200 W mercury-arc lamp. The 546 nm spectral line was selected by use of an appropriate glass filter (Carl Zeiss, Jena).

The ESR spectra of $SQ^{\cdot-}$ radicals were measured in 2×10^{-3} *M* solutions of Q in toluene partially reduced by sodium amalgam (producing $Na^+ SQ^{\cdot-}$ ion-pairs) or in THF solutions containing 2×10^{-3} *M* quinones and 10^{-1} *M* Bu_4NPF_6 which were electrochemically reduced at the mercury electrode inside the ESR cell.

Results

Irradiation of the solutions of Cp_2TiCl_2 with both *ortho*- and *para*-quinones in toluene, THF or 2×10^{-2} *M* pyridine/toluene produces radicals which can be readily detected by ESR. Identical radicals are formed under irradiation by polychromatic light and that by 546 nm-monochromatic light, which is absorbed solely by Cp_2TiCl_2, which is thus shown to be the only photoactive species involved. Photolyzed solutions of Cp_2TiCl_2 without quinones exhibit broad singlet ESR signals at high fields ($1.9 < g < 2.0$), which are attributed to solvated $CpTiCl_2$ radicals

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* Following abbreviations stand for the quinones used: *o*-DBQ = 3,5-di-t-butyl-1,2-benzoquinone; PQ = 9,10-phenanthrenequinone; CQ = *o*-chloranil (3,4,5,6-tetrachloro-1,2-benzoquinone), *p*-DBQ = 2,6-di-t-butyl-1,4-benzoquinone. One-electron reduced forms, i.e. semiquinone radical anions are denoted SQ, e.g. DBSQ, CSQ, PSQ.

TABLE 1

ESR PARAMETERS OF SEMIQUINONE ANION RADICALS AND THEIR COMPLEXES WITH $CpTiCl_2$

(a_H values in mT, estimated accuracy ±0.05 mT, g values determined with accuracy ±0.0001).

Compound	Toluene		THF		Tol. + Py [b]	
	g	a_H	g	a_H	g	a_H
o-DBSQ	2.0046 [d]	0.27 [d]	2.0051	0.32	–	–
$[CpTiCl_2(O\text{-DBSQ})]$ (I)	2.0047	0.35	2.0050	0.35	2.0050	0.35
$[CpTiCl_2(O,O\text{-DBSQ})]$ (II)	2.0038	0.37	2.0035	0.38	2.0038	0.36
PSQ	2.0045 [d]	–	2.0050	–	–	–
$[CpTiCl_2(PSQ)]$	2.0040	–	2.0042	–	2.0040	–
CSQ	2.0063 [d]	–	2.0062	–	–	–
$[CpTiCl_2(CSQ)]$	2.0055	–	2.0058 [a]	–	–	–
p-DBSQ	–	–	2.0051	0.20	–	–
$[CpTiCl_2(p\text{-DBSQ})]$	2.0035	0.14	2.0036	0.14	2.0040 [c]	0.10 [c]

[a] Estimated accuracy ±0.0003. [b] 2×10^{-2} M pyridine in toluene. [c] 2×10^{-1} M pyridine in toluene. [d] Refers to Na^+ $SQ^{\overline{\cdot}}$ ion pairs.

[11,12]. These signals were never present in the ESR spectra of the solutions of Cp_2TiCl_2 with *ortho*- or *para*-quinones irradiated under identical experimental conditions. All radicals produced by the irradiation of the solutions of Cp_2TiCl_2 with both *ortho*- and *para*-quinones may thus be regarded as products of the reaction between the primary product of the Cp_2TiCl_2 photolysis, i.e. the $CpTiCl_2$ radical [9–12], and the particular quinone.

The ESR spectra of these species (Table 1) exhibit signals at g values in the range typical for complexes containing a single semiquinone radical-anionic ligand [1–3]. The g values and the proton splitting constants (a_H) differ significantly from the values for the corresponding free semiquinones (Table 1).

The evidence indicates that all the studied reactions between photogenerated $CpTiCl_2$ and quinones may be best described as oxidative additions producing titanium(IV) complexes with ligated semiquinone radical-anions (SQ).

Although the reactions of photogenerated $CpTiCl_2$ with both *ortho*- and *para*-quinone isomers are mechanistically similar, the photo- and thermal-stability of the products are quite different.

Reactions with *ortho*-quinones produce radicals which are thermally stable but decompose upon prolonged irradiation. Their ESR spectra were thus measured after short-time polychromatic (10 s) or 546 nm monochromatic (15 s) irradiation. Only very weak signals were observed under continuous irradiation of the solutions of Cp_2TiCl_2 with *ortho*-quinones due to the secondary photolysis leading to ESR-inactive species. On the other hand, the products of the photochemical reaction of Cp_2TiCl_2 with *para*-quinones quickly decompose thermally. Corresponding weak ESR signals may thus be observed only under continuous polychromatic or 546 nm monochromatic irradiation, and disappear immediately when the irradiation is interrupted.

Specific features of the reactions with individual quinones

3,5-Di-t-butyl-1,2-benzoquinone, o-DBQ. Short photolysis of Cp_2TiCl_2 with *o*-

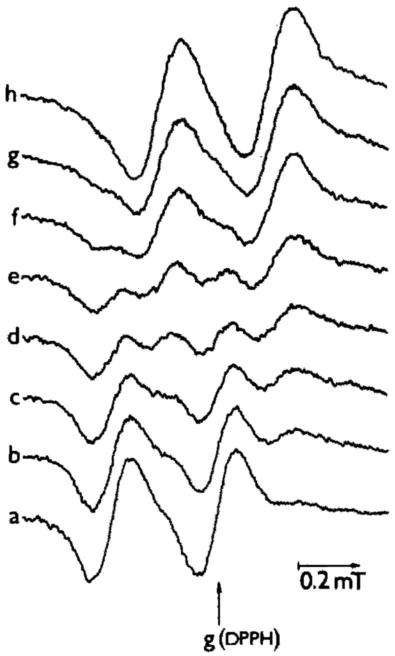

Fig. 1. ESR spectra of the radicals formed by the photochemical reaction of Cp_2TiCl_2 with *o*-DBQ in toluene irradiated for 14 s with 546 nm light, (a) immediately after interruption of the irradiation, (b) 80 s, curves c–h measured at *t* 2,3,4,6,8 and 12 min, respectively.

DBQ produces radical I, whose ESR spectrum (Fig. 1) consists of a doublet at a *g* value very close to that of free *o*-DBSQ (Table 1). This radical is converted in the dark into another radical species II, which is thermally stable but decomposes rapidly when irradiated. The radical II is characterized by another doublet ESR signal centered at a *g* value significantly lower than that for either free *o*-DBSQ or of that corresponding to radical I (Fig. 1). The decrease in the *g* value is accompanied by a slight increase in a_H *. This behaviour parallels that observed in oxidative addition of *o*-quinones to d^7-metal-centered radicals, e.g. $Co(CN)_5^{3-}$ [2,3] or $Mn(CO)_5$ [13,14]. By analogy with these systems, radical I is regarded as a titanium(IV) complex containing a monodentate *o*-DBSQ radical-anionic ligand (denoted by *O*-DBSQ) whereas the radical II can be regarded as a species containing chelated *o*-DBSQ ligand (*O*,*O*-DBSQ) bound to the titanium(IV) central atom by both oxygen donor atoms. The rate of the conversion I → II, decreases significantly when other potential ligands are present: the conversion is complete in about 10 min in pure toluene, in 15–20 min in THF, and in approx. 30 min in 2×10^{-2} *M* pyridine/toluene. The chelate-ring formation seems thus to involve intramolecular displacement of a solvent molecule from the titanium(IV) central atom by the free oxygen-donor atom of the *o*-DBSQ monodentate ligand. The overall mechanism may thus be depicted as shown in eq. 1–3 (solvent molecules are omitted).

$$Cp_2Ti^{IV}Cl_2 \xrightarrow{h\nu} CpTi^{III}Cl_2^{\cdot} + Cp^{\cdot} \qquad (1)$$

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* The hyperfine splitting is due to the hydrogen atom at the C(4)-position of the *o*-DBQ ring [3].

$$CpTi^{III}Cl_2^{\cdot} + o\text{-DBSQ} \xrightarrow[\text{very fast}]{} [CpTi^{IV}Cl_2(O\text{-DBSQ})] \qquad (2)\,*$$

$$[CpTi^{IV}Cl_2(o\text{-DBSQ})] \xrightarrow[\text{slow}]{} [CpTi^{IV}Cl_2(O,O\text{-DBSQ})] \qquad (3)$$

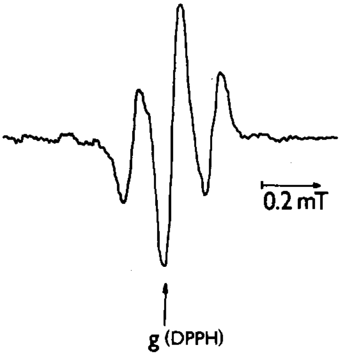

Fig. 2. ESR spectrum of the radical formed in the THF solution of Cp_2TiCl_2 and p-DBQ under continuous irradiation by 546 nm light.

9,10-Phenanthrenequinone (PQ). The reaction with PQ in toluene produces small amounts of a thermally stable radical characterized by a weak broad signal with unresolved hyperfine splitting (hfs). The g value of this signal is somewhat lower than that of free PSQ. In THF or 2×10^{-2} M pyridine/toluene, similar but more intense signals with apparent hfs are observed. The ESR signals show no change with time in any of these solvents. Formation of the [$CpTiCl_2$(PSQ)] adduct may thus be assumed, but the available experimental data are not sufficient to indicate unambiguously the mode of the bonding of the PSQ ligand to the titanium(IV) central atom, but chelate coordination by both oxygen donor atoms seems most probable.

ortho-Chloranil (CQ). Only one weak broad singlet ESR signal was observed after short polychromatic irradiation of solutions containing Cp_2TiCl_2 and CQ in toluene. The corresponding signal obtained in THF solutions at the begining of continuous 546 nm-monochromatic irradiation is extremely weak, and disappears upon prolonged irradiation with concomitant formation of other very weak unidentified signals. The initial singlet ESR signals with g values slightly lower than that of free CSQ were attributed to the [$CpTiCl_2$(CSQ)] adduct; the mode of CSQ coordination cannot be specified. It is evident that formation of this radical adduct is not the main reaction in the Cp_2TiCl_2/CQ system. Alternatively, splitting of the C–Cl bonds [10] in the CQ molecule by photogenerated $CpTiCl_2$ radicals could be assumed.

2,6-Di-t-butyl-1,4-benzoquinone (p-DBQ). The radical adduct formed by the continuous irradiation of solutions containing Cp_2TiCl_2 and p-DBQ is characterized by a triplet (1/2/1) ESR signal (Fig. 2) typical for a p-DBSQ radical-anion and its complexes [2,3]. The hyperfine splitting is due to two symmetrically equivalent hydrogen atoms on the C(3) and C(5) positions of the quinone ring [2]. The a_H and

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* Two Cl^- ligands are supposed to be present in the product of reaction 2 in analogy with the well-characterized radical adduct of $CpTiCl_2$ with Bu^tNO_2, i.e. [$CpTiCl_2(Bu^tNO_2^{\cdot})$] [12].

g values, which are significantly lower than those for free p-DBSQ together with the concomitant absence of the $CpTiCl_2$ radical (vide supra), show that the observed radical species is an adduct of p-DBSQ with $CpTiCl_2$.

Pure triplet ESR signals were found in THF and 2×10^{-2} M or 2×10^{-1} M pyridine/toluene, whereas overlap with another unidentified signal was observed in pure toluene under continuous irradiation by 546 nm light. The interfering signal in toluene corresponds to some photolabile radical whose concentration is lowered by continuous polychromatic irradiation. The ESR signals observed in 2×10^{-2} M and 2×10^{-1} M pyridine are much weaker than those in THF or toluene, and are characterized by different a_H and g values (Table 1). The evidence is thus consistent with the formation of $[CpTiCl_2(p\text{-DBSQ})]$ species in toluene and THF, whereas formation of the $[CpTiCl_2(py)(p\text{-DBSQ})]$ complex must be assumed in 2×10^{-2}–2×10^{-1} M pyridine/toluene.

The ESR data show that the symmetry equivalence of the hydrogen atoms on C(3) and C(5) is retained in the coordinated p-DBSQ ligand. The p-DBSQ is thus most probably linked to the titanium(IV) central atom by its C(4)–oxygen atom, as in its other transition or non-transition metal adducts [2,3,14,15]. This interpretation is supported by the typical decrease of the a_H value [2,14,15]. However, the unusually low g value [2] as well as the chemical behaviour, high thermal lability, which are quite different from those for the analogous $[CpTiCl_2(O\text{-DBSQ})]$ species, show that other interpretations of the observed ESR spectrum cannot be excluded. η^4-Coordination by both C=C bonds or the Ti–C(4) bonding might be possible, but no other complexes of p-semiquinones coordinated through either η^4- or M–C(4) bonding are known.

The mass spectrum of the residue obtained by the evaporation of the THF solution of Cp_2TiCl_2 and p-DBQ after irradiation for 2 h with 546 nm light shows the presence of a small amount of the CpH–DBQ adduct and of $[CpTiCl_2(DBQH)]$. No evidence was observed for any decomposition of the quinone moiety during the photolysis.

Photolysis of Cp_2TiCl_2 and 1,4-benzoquinone or 2,3,5,6-tetramethyl-1,4-benzoquinone in THF solutions gave extremely weak ESR signals, which were not further studied.

Discussion

ortho-Quinones, like their *para*-isomers, add oxidatively to photogenerated $CpTiCl_2$ radicals, and the reaction may be used to trap these unstable species. As usual [3], the o-DBQ is the most useful quinone, producing the most stable adducts. The $CpTiCl_2$ is known to be a Lewis-acidic metal-centered radical, which is able to coordinate various ligands such as phosphines [12], THF [11,12,16], and probably also other ethers and amines, as indicated by complicated ESR spectra obtained after the irradiation of Cp_2TiCl_2 in these solvents [11,12]. The unpaired electron has been found to be located in the $d_{x^2-y^2}$ orbital in the $CpTiCl_3^-$ complex, whereas the weakly solvated $CpTiCl_2$ radical (e.g. in THF) has the $d_{z^2}^1$ configuration [17]. In the pseudo-tetrahedral symmetry of $CpTiCl_2L^{\cdot}$ radical complexes [16,17], both $d_{x^2-y^2}$ and d_{z^2} are of π-symmetry with respect to the Ti–L bond. The one-electron oxidative addition of quinones to $CpTiCl_2$ may thus be viewed as a coordination of one quinone oxygen atom via its lone-electron pair to the titanium(III) central atom.

This Lewis acid–base interaction is concerted with the overlapping of the empty π^* LUMO orbital of the quinone (via its substantial oxygen p_z component) with the singly occupied titanium $d\pi$ orbital (either d_{z^2} or $d_{x^2-y^2}$). This π-overlap provides the route for the $\pi_d \rightarrow \pi^*$ one-electron transfer, which is concerted with the Ti–O σ-bond formation, resulting in the complex of titanium(IV) with ligated semiquinone radical-anion. Such a mechanism for oxidative addition of quinone to the Lewis acidic coordinatively unsaturated complexes was previously invoked to explain the reaction of photogenerated $Cr(CO)_5$ with quinones [7,8].

Moreover, the course of the reaction with *o*-DBQ clearly shows that in the primary product of the oxidative addition there is one more free coordination place left, permitting closure of a thermally stable Ti^{IV}–(*O*,*O*-DBSQ) chelate ring or coordination of another ligand, e.g. pyridine.

It is thus evident, that the oxidative additions of quinones may be used not only to trap unstable organometallic radicals but also to examine their chemical properties. In the particular case described above, there seems to be potential in exploiting the redox and Lewis acid–base properties of the $CpTiCl_2$ radical in photocatalysis by Cp_2TiCl_2 or by related cyclopentadienyl titanium complexes.

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