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A FOURIER TRANSFORM ^{13}C NMR STUDY OF η-(2,3,5,6-TETRAMETHYL-1,4-BENZOQUINONE) COMPLEXES OF NICKEL, COBALT, RHODIUM AND IRIDIUM

GEORGE M. BODNER* and THEODORE R. ENGLEMANN

William A. Noyes Laboratory, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801 (U.S.A.)

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Summary

^{13}C NMR spectra are obtained for a series of quinones, hydroquinones and quinonoid complexes of Ni, Co, Rh and Ir in $CDCl_3$, $EtOH/D_2O$ and D_2SO_4 solutions. Evidence is presented which suggests that neutral η^4-duroquinone complexes of the type $(C_{10}H_{12}O_2)M(C_5H_5)$ are protonated in strongly acidic media to produce dications, $[(C_{10}H_{14}O_2)M(C_5H_5)]^{2+}$, in which the quinone functions as a η^6-hydroduroquinone ligand.

Introduction

Quinonoid derivatives undergo reaction to produce transition metal complexes of an unusually diverse nature. 2,3,5,6-Tetramethyl-1,4-benzoquinone (duroquinone) has been found to function as either a two electron η-ene ligand in $[L_2Ni]_2Dq$ [1] and $[L_2Pt]_2Dq$ [2], or as a four electron η-diene ligand in η-$(C_5H_5)M(Dq)$ complexes of Co, Rh and Ir [3]. Quinones with low reduction potentials [4] such as 1,4-benzoquinone (E^0 = —0.51, —1.14 V) react with $Ni(CO)_4$ to form Ni^{II} salts of the hydroquinone dianion analogous to quinhydrone complexes [5,6]. 2,3,5-Trimethyl-1,4-benzoquinone (E^0 = —0.75, —1.35 V) reacts with $Ni(CO)_4$ in the absence of a cyclic diene to form a paramagnetic Ni^{II} complex $(TMQ)_2Ni$ in which the quinone is formally a five electron η-donor while in the presence of COD it reacts with $Ni(CO)_4$ to form a paramagnetic (COD)Ni(TMQ) complex in which the quinone is formally a η-arene hydroquinone dianion ligand [5]. 2,3,5,6-Tetramethyl-1,4-benzoquinone (E^0 = —0.84, —1.45 V) reacts with $Ni(CO)_4$ in the presence of COD to form a tetrahedral [7], diamagnetic Ni^0 complex in which the quinone is formally a four electron η-diene ligand [5,8,9]. 1,2-Benzoquinone derivatives have been found to undergo reaction to produce bidentate *O*-bound 1,2-hydroquinone

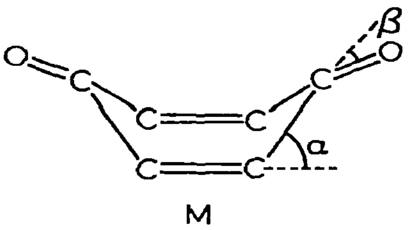

Fig. 1. Proposed structure for 2,3,5,6-tetramethyl-1,4-benzoquinone complexes of Ni, Co and Rh from X-ray crystallographic studies. (Dq)Ni(COD), $\alpha = 7.5°$; (Dq)Co(C_5H_5), $\alpha = 21°$, $\beta = 9°$; (Dq)Rh(C_5H_5) $\alpha = 23°$, $\beta = 9°$; (Dq), $\alpha = \beta = 0°$.

dianion ligand [2,10] while 1,4-benzoquinone reacts with $Co(CN)_5^{3-}$ to form *O*-bound bridged species [11,12]. 2,3,5,6-Tetrachloro-1,4-benzoquinone reacts with L_2Pt derivatives via a vinylic chlorine abstraction to form complexes containing Pt—C σ bonds [2].

Crystallographic studies of η-cyclopentadienyl-η-(2,3,5,6-tetramethyl-1,4-benzoquinone) complexes of cobalt [13] and rhodium [14] have shown a marked deviation from the D_{2h} symmetry of the free ligand [15] indicative of η-diene complexation (see Fig. 1), while η-cyclooctadiene-η-(2,3,5,6-tetramethyl-1,4-benzoquinone)nickel [7] exhibits only a slight deviation from planarity. Schrauzer and Dewhirst [3] have suggested that this distortion arises from a repulsive interaction of the metal *d* orbitals with the C=O portion of the filled $2b_{1u}$ and empty $2b_{2g}$ orbitals of the duroquinone ligand. Struchkov et al. [14,16] have argued that the magnitude of this distortion is not dependent upon either steric effects or electronic effects of other ligands, but rather upon the nature of the transition metal.

Schrauzer and Thyret [3,17] have suggested that the carbonyl groups in (Dq)Co(C_5H_5) are protonated in strongly acidic medium. We report herein a study of the ^{13}C NMR spectra of 2,3,5,6-tetramethyl-1,4-benzoquinone complexes of Ni, Co, Rh and Ir in $CDCl_3$ and D_2SO_4 solution to test the hypothesis that protonation of the quinone carbonyls in sulfuric acid medium would decrease the reduction potential of the quinone ligand [4] and thereby lead to the conversion of the η-diene duroquinone complexes to their η-arene hydroduroquinone dication analogs.

Experimental

η-Cyclopentadienyl-η-(2,3,5,6-tetramethyl-1,4-benzoquinone) complexes of rhodium and iridium were prepared from the reaction of 2.0 g of the metal trichloride trihydrate with 4.0 g of duroquinone in refluxing ethanol followed by chromatography on silica gel eluted with 80/20 benzene/methanol and treatment of the resultant metal duroquinone chloride with cyclopentadienylthallium in tetrahydrofuran solution [3,18]. η-Cyclopentadienyl-η-(2,3,5,6-tetramethyl-1,4-benzoquinone)cobalt was prepared from the reaction of η-(C_5H_5)Co$(CO)_2$ with excess duroquinone in refluxing xylene followed by chromatography on silica gel eluted with benzene/methanol [17]. η-1,5-Cyclooctadiene-η-(2,3,5,6-tetramethyl-1,4-benzoquinone)nickel was prepared from the reaction of 3.5 ml of $Ni(CO)_4$ with 2.6 g of duroquinone and 20 ml of COD in refluxing methylene chloride under argon. After 6 h the volatile material was distilled into a dry-ice-cooled vessel, the dark red-brown residue was dissolved in 20 ml of methylene chloride, filtered, concentrated, and the resultant complex precipitated by the addition of 100 ml of light petroleum ether [5,8,9]. Complexes were characterized by microanalysis and infrared spectroscopy.

^{13}C NMR spectra were obtained in $CDCl_3$, D_2SO_4 and 95% EtOH/5% D_2O solutions on a Varian Associates XL-100-FT spectrometer operating at 25.16 MHz equipped with an internal deuterium lock. The ^{13}C NMR chemical shifts in $CDCl_3$ and EtOH/D_2O solutions were measured relative to the internal solvent resonances and are reported in ppm downfield from TMS using the following conversions:

$$\delta(\text{TMS}) = \delta(CDCl_3) - 76.9_8 \text{ ppm, and } \delta(\text{TMS}) = \delta(CH_3CH_2OH) - 18.3_1 \text{ ppm.}$$

The D_2SO_4 spectra were calibrated with an external $CHCl_3$ capillary and the chemical shifts are reported in ppm downfield from TMS using the conversion: $\delta(\text{TMS}) = \delta(CHCl_3) - 77.1_8$ ppm. All data are the result of at least two independent measurements with a precision of ±0.06 ppm.

Results

^{13}C NMR chemical shift data for a series of quinones, hydroquinones and quinonoid complexes are given in Table 1 and presented graphically in Fig. 2. Berger and Ricker [19] have reported ^{13}C NMR data for 1,4-benzoquinone and 2,3,5,6-tetramethyl-1,4-benzoquinone in complete agreement with our results. Attempts to obtain spectra for 2,3,5,6-tetramethyl-1,4-hydroquinone have failed due to the marginal solubility of this derivative, and we will therefore use 1,4-benzoquinone and 1,4-hydroquinone as model systems for this study. The reduction of 1,4-benzoquinone to 1,4-hydroquinone leads to a shielding of the C(1,4) and C(2,3,5,6) resonances of 36.3_5 and 19.2_5 ppm respectively. The

TABLE 1

^{13}C NMR CHEMICAL SHIFTS FOR QUINONES AND QUINONE COMPLEXES OF Ni, Co, Rh AND Ir

Compound	Solvent	C(1,4)	C(2,3,5,6)	CH_3	C_5H_5
2,3,5,6-tetramethyl-1,4-benzoquinone	$CDCl_3$	-187.3_7[a]	-140.2_9	-12.1_6	
	D_2SO_4	-191.9_3	-146.4_5	-12.8_2	
1,4-benzoquinone	$CDCl_3$	-186.9_5	-136.2_2		
1,4-hydroquinone	EtOH/D_2O	-150.6_0	-116.9_7		
(Dq)Ni(COD)[b]	$CDCl_3$	-153.6_9	-112.1_8	-12.0_9	
(Dq)Co(C_5H_5)	$CDCl_3$	-157.2_4	-91.2_7	-14.4_9	-85.4_1
	D_2SO_4	-131.8_3	-97.9_5	-9.8_3	-89.6_7
(Dq)Rh(C_5H_5)	$CDCl_3$	-161.6_5	-93.5_1(9)[c]	-14.7_7	-88.2_4(1)
	D_2SO_4	-133.6_0(4)	-100.9_6(6)	-9.2_2	-90.8_8(2)
(Dq)Ir(C_5H_5)	$CDCl_3$	-164.8_1	-82.9_7	-14.8_6	-81.8_3
	EtOH/D_2O	-161.8_8	-85.8_4	-14.8_3	-83.8_4
	D_2SO_4	-130.0_8	-92.5_0	-8.6_9	-83.4_0

[a] Chemical shifts in ppm downfield from TMS with a precision of ±0.06 ppm. [b] Dq = 2,3,5,6-tetramethyl-1,4-benzoquinone. COD = 1,5-cyclooctadiene. [c] $^1J(^{103}Rh^{13}C)$ coupling constants in Hz, ±1 Hz.

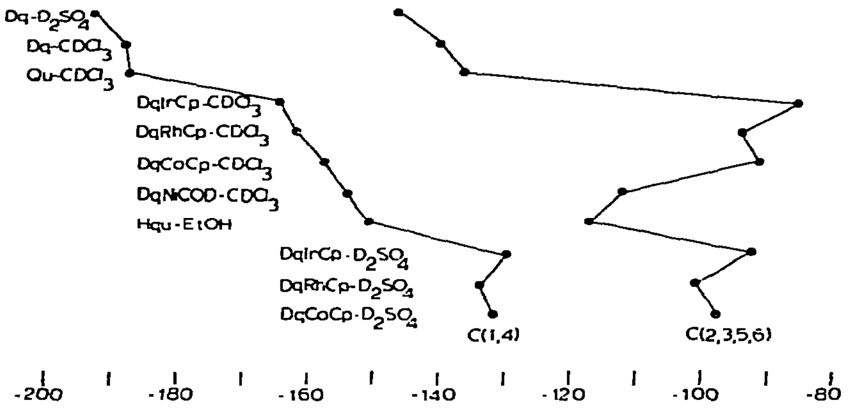

Fig. 2. ^{13}C NMR chemical shifts for quinones, hydroquinones and quinonoid complexes in ppm downfield from TMS. Dq = 2,3,5,6-tetramethyl-1,4-benzoquinone, Qu = 1,4-benzoquinone, Hqu = 1,4-hydroquinone.

C(1,4) and C(2,3,5,6) carbon environments in hydroquinone can be thought to be the sum of the {C(1) + C(4)} and {C(2,6) + C(3,5)} carbon environments in phenol. Using substituent parameters for phenol [20] we would predict a deshielding of the C(1,4) and C(2,3,5,6) resonances in hydroquinone of —19.0 and 10.8 ppm relative to benzene, in accord with experimental values of —21.9 and 11.7 ppm.

Maciel and co-workers have studied solvent effects on the C=O resonance in organic carbonyls [21-23]. They have observed only slight changes in the carbonyl chemical shift in aprotic solvents whereas the carbonyl chemical shift is directly proportional to the acidity of protic solvents. Maciel argues that the deshielding of the carbonyl resonance with increasing solvent acidity arises from an increase in the C=O dipole upon protonation [21]. Chloroform and sulfuric acid deshield the carbonyl resonance in acetone, relative to neat acetone, by —2.3 and —39.2 ppm respectively, while the carbonyl resonance in hexachloroacetone exhibits only a slight susceptibility to solvent effects. Maciel suggests that this is a result of the decreased basicity of the carbonyl in hexachloroacetone due to the electron withdrawing character of the CCl_3 substituents. In sulfuric acid solution we note that both the C(1,4) and C(2,3,5,6) resonances in 2,3,5,6-tetramethyl-1,4-benzoquinone are deshielded relative to chloroform solution. The magnitude of this effect would suggest a marginal basicity for the carbonyl groups in the free ligand.

It is therefore of interest to note a marked *shielding* of the C(1,4) resonance in (Dq)Ir(C_5H_5) with increasing solvent acidity in the order $CDCl_3$ < EtOH < D_2SO_4, coupled with a concomitant deshielding of the C(2,3,5,6) resonance. If we define δ' such that: $\delta' = \delta[C(2,3,5,6)] - \delta[C(1,4)]$, then for (Dq)Ir($C_5H_5$), δ' decreases from 81.8_4 ppm in $CDCl_3$ to 76.0_4 ppm in EtOH and 37.5_8 ppm in D_2SO_4, while δ' is 50.7_3 ppm for 1,4-benzoquinone and 33.6_3 ppm for 1,4-hydroquinone. These data are consistent with the conversion of the neutral η-diene 2,3,5,6-tetramethyl-1,4-benzoquinone complex to a η-arene 2,3,5,6-tetramethyl-1,4-hydroquinone dication in acidic medium. The C(2,3,5,6) resonance in (Dq)Rh(C_5H_5) in $CDCl_3$ solution exhibits nuclear spin—spin coupling with the

^{103}Rh nucleus while the C(1,4) resonance does not, in accord with the crystallographic data. In D_2SO_4 solution coupling is observed to both the C(1,4) and C(2,3,5,6) resonances, suggestive of direct overlap of rhodium atomic orbitals with the carbonyl carbon atoms. A slight deshielding (—0.7 ppm)* of the CH_3 resonance in 2,3,5,6-tetramethyl-1,4-benzoquinone is observed in sulfuric acid solution consistent with, if not indicative of, the removal of electron density from the duroquinone ring upon protonation, whereas the CH_3 resonances for the (Dq)M(C_5H_5) complexes are shielded by approximately 5 ppm in sulfuric acid solution as expected from the proposed reduction of the duroquinone ring. Attempts to obtain spectra of (COD)Ni(Dq) in D_2SO_4 solution have failed, possibly due to the formation of a paramagnetic material. This would be consistent with the known paramagnetic character of η-arene hydroquinone derivatives of Ni^{II} [5].

We have observed a shielding of arene resonances upon complexation in η-(arene)M$(CO)_3$ complexes of Cr, Mo and W, and in η-$(C_5H_5)_2$M complexes of Fe, Ru and Os [24,25]. If we define the complexation chemical shift to be the difference between the chemical shift of the free arene and the chemical shift of the complexed arene, then the complexation chemical shift increases in the order Mo < Cr < W and Ru < Fe < Os. An analogous order is observed for the C(1,4), C(2,3,5,6) and C_5H_5 resonances in (Dq)M(C_5H_5) complexes in D_2SO_4 solution, Rh < Co < Ir, suggestive of a η-arene complex. In $CDCl_3$ solution this order is observed for the C(2,3,5,6) and C_5H_5 resonances only. The order of increasing C(1,4) resonance chemical shifts for duroquinone complexes in $CDCl_3$ solution, Ni < Co < Rh < Ir, is in agreement with the order of increasing overlap of transition metal *d* orbitals with the $2b_{1u}$, b_{3g} and $2b_{2g}$ orbitals of the duroquinone ring [3] suggesting a deshielding of the C(1,4) resonance with increasing distortion from planarity.

Gubin and Khandkarova [26] have studied the electrochemical reduction of (Dq)M(C_5H_5) complexes of Rh and Ir in aprotic solvents and they conclude that complexation leads to a shift of the reduction potentials for duroquinone to more negative values. This is in accord with the calculations of Schrauzer and Dewhirst [3] which indicate a marked increase in the energy of the $2b_{2g}$ orbital upon complexation. Our studies differ in that, first, we used a strongly protic medium and it has been observed that the reduction potentials of quinones are substantially less negative in aqueous solutions even at pH > pK_2, while the reduction potential becomes positive at very low pH [4]. Second, the process observed by Gubin and Khandkarova involves the reduction of a formally 18 electron system with an external source of electrons, rather than the reduction of the quinone via the transfer of electron density from the transition metal to the ligand invoked herein.

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* It has been suggested that in the absence of bulk magnetic susceptibility corrections, chemical shift differences of less than one ppm be ignored.

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