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Acknowledgment. We thank the Dirección General de Investigación Cientifica y Técnica (project PB87-0690), Spain, for financial support and the Dirección Regional de Educación y Universidad, Murcia, Spain, for a grant to J.G.

Supplementary Material Available: Tables of complete bond lengths and angles (Tables S1 and S5), thermal parameters (Tables S2 and S6), coordinates for H atoms (Tables S3 and S7), and bond lengths and angles involving H atoms (Tables S4 and S8) (24 pages); tables of observed and calculated structure factors (Tables S9 and S10) (61 pages). Ordering information is given on any current masthead page.

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Contribution from the Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione del CNR, 50132 Firenze, Italy, and Dipartimento di Chimica Organica, Università di Firenze, Firenze, Italy

Chemoselective Oxidation of 3,5-Di-*tert*-butylcatechol by Molecular Oxygen. Catalysis by an Iridium(III) Catecholate through Its Dioxygen Adduct

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Received November 19, 1991

The selective oxidation of 3,5-di-*tert*-butylcatechol ($DTBCH_2$) to 3,5-di-*tert*-butyl-*o*-benzoquinone (DTBQ) by molecular oxygen is catalyzed by the Ir(III) catecholate complex $[(triphos)Ir(DTBC)]^+$ through its dioxygen adduct $[(triphos)\overline{Ir(OO)}(DTBSQ)]^+$ [triphos = $MeC(CH_2PPh_2)_3$; DTBC = 3,5-di-*tert*-butylcatecholate; DTBSQ = 3,5-di-*tert*-butylsemiquinonate]. The following overall stoichiometric equation is suggested by analysis of the oxidation products and H_2O_2: $DTBCH_2 + O_2 \rightarrow DTBQ + H_2O_2$. The rates of reaction of the substrate as well as the formation of products are shown to be first order with respect to catalyst and substrate concentrations and zero order with respect to the partial pressure of O_2 in the range 15–725 psi. The kinetic parameters for the oxidation reaction are estimated in the temperature range 38–60 °C. Kinetic and thermodynamic data are consistent with a rate-determining step involving the attack of free catechol to the O_2 adduct. For partial pressures of O_2 higher than 725 psi, the oxygenation of $DTBCH_2$ to 3,5-di-*tert*-butyl-1-oxacyclohepta-3,5-diene-2,7-dione competes with DTBQ formation.

Introduction

As part of our studies on the transport and activation of dioxygen by metal species,[1-4] we have recently communicated the preparation and characterization, including an X-ray analysis, of iridium catecholate dioxygen adducts of the formula $[(triphos)\overline{Ir(OO)}(\overline{SQ})]BPh_4$ (triphos = $MeC(CH_2PPh_2)_3$; SQ = DTBSQ = 3,5-di-*tert*-butylsemiquinonate (**2a**) or PhenSQ = 9,10-phenanthrenesemiquinonate (**4a**)) (Scheme I).[5]

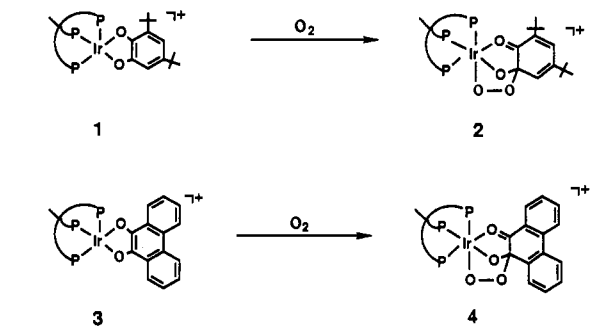
In a preceding article,[4] we reported that the related rhodium complex $[(triphos)Rh(DTBC)]BPh_4$ (**5**) (DTBC = 3,5-di-*tert*-butylcatecholate) reacts in CH_2Cl_2 solution with O_2 at low temperature to give a dioxygen adduct, $[(triphos)\overline{Rh(OO)}(DTBSQ)]BPh_4$ (**6**), which was assigned the "open" structure (a) shown in Scheme II.

In light of the iridium results, the rhodium complex, which, by the way, has never been isolated in the solid state, has carefully been re-examined by concluding that it shares the primary geometry with the iridium compounds, i.e. the "closed" one (b).[6]

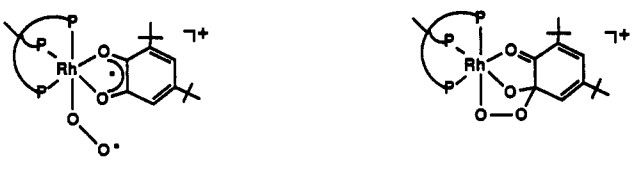
Both the rhodium and iridium dioxygen adducts catalyze the oxidation of 3,5-di-*tert*-butylcatechol ($DTBCH_2$) under a steady stream of O_2 to give 3,5-di-*tert*-butyl-*o*-benzoquinone (DTBQ) and H_2O_2.[4,5] However, while the iridium-assisted reaction is rigorously chemoselective, the rhodium complex is able also to oxygenate the catechol, producing appreciable amounts of 3,5-di-*tert*-butyl-1-oxacyclohepta-3,5-diene-2,7-dione (DTBA) (*intra*diol C–C cleavage) and of 3,5-di-*tert*-butyl-2-pyrone (DTBPyr) (*extra*diol C–C cleavage)[4] (Scheme III).

Since very few kinetic and thermodynamic data for metal-catalyzed oxidation reactions of catechols to *o*-quinones are reported in the literature,[7] we decided to study the kinetics of the chemoselective oxidation of $DTBCH_2$ to DTBQ at different dioxygen pressures and concentrations of the iridium catalyst and

Scheme I



Scheme II



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[‡] Università di Firenze.

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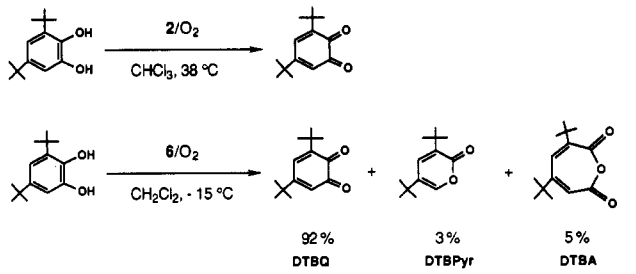
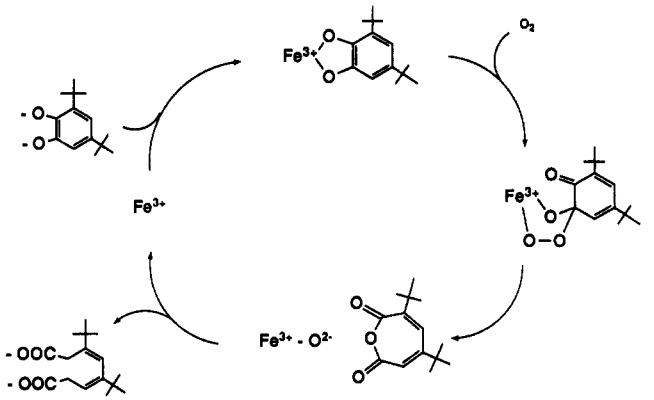
Scheme III



Scheme IV



substrate. Herein, we present the results obtained and a mechanistic interpretation of the catalysis cycle. The information provided is of particular relevance as the dioxygen adducts **2**, **4**, and **6** are considered among the most reliable synthetic models for catechol 1,2-dioxygenases.[8] Indeed, according to a recent model study,[9] an intermediate species in the 1,2-dioxygenase catalysis cycle is believed to be an iron peroxide exhibiting close structural analogies with **2**, **4**, and **6** (Scheme IV).

Experimental Section

Materials and Methods. All manipulations were performed under a pure nitrogen atmosphere unless otherwise stated. 3,5-Di-*tert*-butylcatechol ($DTBCH_2$) and 9,10-phenanthraquinone (PhenQ) were recrystallized from *n*-pentane and 1,4-dioxane, respectively. Dichloromethane, *n*-heptane, and chloroform were distilled over P_2O_5, Na, and K_2CO_3, respectively. All the other chemicals were commercial products and were used as received without further purifications. [(triphos)$IrCl(C_2H_4)$],[10] DTBA,[11] and DTBPyr[12] were prepared according to literature methods. The solid compounds were collected on sintered-glass frits and washed with *n*-pentane before being dried in a stream of nitrogen. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrometer using samples mulled in Nujol between KBr plates. Proton NMR spectra were recorded at 299.945 MHz on a Varian VXR 300 spectrometer. Chemical shifts are relative to tetramethylsilane as external reference or calibrated against the solvent as the reference signal. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian VXR 300 spectrometer operating at 121.42 MHz. Chemical shifts are relative to external 85% H_3PO_4 with downfields values reported as positive. Conductivities were measured with a Model 990101 Orion conductance cell connected to a Model 101 conductivity meter. The conductivity data were obtained at sample concentration of ca. 10^{-3} M in nitroethane solutions at room temperature. GC analyses were performed on a Shimadzu GC-14 A gas chromatograph equipped with a flame ionization detector and a 30-m (0.25-mm i.d., 0.25-μm FT) SPB-1 Supelco fused silica capillary column. GC–MS analyses were performed on a Shimadzu QP 2000 apparatus equipped with a column identical to that used for GC analyses. Reactions under controlled pressure of O_2 were performed with a Parr 4565 reactor equipped with a Parr 4842 temperature controller. UV/visible spectra were recorded on a Shimadzu UV-2100 spectrophotometer using quartz cells. The materials and the apparatus used for the electrochemical experiments have been described elsewhere.[3,4] Unless otherwise stated, the potential values are relative to an aqueous calomel electrode (SCE) and refer to a controlled temperature (±0.1 °C). Low-temperature macroelectrolysis tests were performed by using an Ag/AgCl reference electrode, the potential of which was −0.02 V vs SCE.

Synthesis of the Catecholate Complexes. [(triphos)Ir(DTBC)]Y (Y = BPh_4 (1a), PF_6 (1b)). To a solution of [(triphos)$IrCl(C_2H_4)$] (0.44 g, 0.5 mmol) and DTBQ (0.11 g, 0.5 mmol) in CH_2Cl_2 (20 mL) at room temperature was added $NaBPh_4$ (0.21 g, 0.6 mmol) in 15 mL of ethanol. As a result, the orange solution immediately turned violet. On partial evaporation of the solvent violet crystals of **1a** precipitated in 87% yield. Anal. Calcd for $C_{79}H_{79}BIrO_2P_3$: C, 69.95; H, 5.87; Ir, 14.17; P, 6.85. Found: C, 69.69; H, 5.78; Ir, 14.01; P, 6.74. Λ_M = 46 Ω^{-1} cm^2 mol^{-1}. IR: ν(C–O) 1304 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): A_3 spin system, δ −7.72. ^1H NMR (CD_2Cl_2, 298 K): 1.47 (s), 1.49 (s) ppm (*tert*-butyl hydrogens). UV/vis ($CHCl_3$) [λ_{max}, nm (ϵ, cm^{-1} mol^{-1} L)]: 246 (21 310), 279 (sh), 389 (sh), 571 (2970). The PF_6^- salt **1b** was obtained in 85% yield by using $[Bu_4N]PF_6$ instead of $NaBPh_4$. Anal. Calcd for $C_{55}H_{59}F_6IrO_2P_4$: C, 55.88; H, 5.00; Ir, 16.26; P, 10.50. Found: C, 55.70; H, 5.00; Ir, 16.31; P, 10.47.

[(triphos)Ir(PhenC)]Y (Y = BPh_4 (3a), PF_6 (3b)). Addition of $NaBPh_4$ (0.21 g, 0.6 mmol) in ethanol (10 mL) to an orange solution of [(triphos)$IrCl(C_2H_4)$] (0.44 g, 0.5 mmol) and PhenQ (0.10 g, 0.5 mmol) in CH_2Cl_2 (15 mL) at room temperature gave a deep green solution. On slow evaporation of the solvent green-blue crystals of [(triphos)Ir(PhenC)]BPh_4 precipitated in 85% yield (PhenC = phenanthrenecatecholate). Anal. Calcd for $C_{79}H_{67}BIrO_2P_3$: C, 70.58; H, 5.02; Ir, 14.29; P, 6.91. Found: C, 70.11; H, 4.98; Ir, 14.01; P, 6.77. Λ_M = 43 Ω^{-1} cm^2 mol^{-1}. IR: ν(C=C) 1596 (s), 1510 (m), ν(C–O) 1286 (vs), 1255 (vs) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): A_3 spin system, δ −8.44. ^1H NMR ($CDCl_3$, 298 K): $\delta(H_1)$ 8.38, $\delta(H_2)$ = $\delta(H_3)$ 7.52, $\delta(H_4)$ 7.98 (PhenC hydrogens). UV/vis ($CHCl_3$) [λ_{max}, nm (ϵ, cm^{-1} mol^{-1} L)]: 252 (37 590), 278 (sh), 308 (sh), 387 (sh), 656 (3070). Compound **3b** was prepared using $[Bu_4N]PF_6$ instead of $NaBPh_4$. Anal. Calcd for $C_{55}H_{47}F_6IrO_2P_4$: C, 56.45; H, 4.02; Ir, 16.44; P, 10.61. Found: C, 56.55; H, 4.00; Ir, 16.24; P, 10.48.

Synthesis of the Oxygenated Complexes. The oxygenated complexes of the formula [(triphos)$\overline{Ir(OO)(SQ)}$]Y were prepared by bubbling O_2 in a CH_2Cl_2 solution of the corresponding catecholate derivatives at room temperature. The reactions were immediate, and orange crystals were obtained by addition of *n*-butanol.

[(triphos)$\overline{Ir(OO)(DTBSQ)}$]Y (Y = BPh_4 (2a), PF_6 (2b)). Anal. Calcd for $C_{79}H_{79}BIrO_4P_3$ (**2a**): C, 68.33; H, 5.74; Ir, 13.85; P, 6.70. Found: C, 68.54; H, 5.78; Ir, 13.74; P, 6.57. Λ_M = 45 Ω^{-1} cm^2 mol^{-1}. IR: ν(C=O) 1624 (s), ν(C=C) 1557 (sh), 1538 (vs), ν(C–O) 1194 (s), 1130 (vs) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$, O_2 atmosphere, 298 K): AMQ spin system, $\delta(P_A)$ −25.11, $\delta(P_M)$ −26.80, $\delta(P_Q)$ −28.84; $J(P_AP_M)$ = 20.6 Hz, $J(P_AP_Q)$ = 26.6 Hz, $J(P_MP_Q)$ = 19.3 Hz. ^1H NMR (CD_2Cl_2, 298 K): 1.34 (s), 1.37 (s) ppm (*tert*-butyl hydrogens). UV/vis ($CHCl_3$, oxygenated solution) [λ_{max}, nm (ϵ, cm^{-1} mol^{-1} L)]: 248 (22 210), 270 (sh), 278 (sh), 378 (sh). Anal. Calcd for **2b**, $C_{55}H_{59}F_6IrO_4P_4$: C, 54.40; H, 4.86; Ir, 15.84; P, 10.22. Found: C, 54.56; H, 4.75; Ir, 15.67; P, 10.20.

[(triphos)$\overline{Ir(OO)(PhenSQ)}$]Y·0.5$CH_2Cl_2$ (Y = BPh_4 (4a), PF_6 (4b)). Anal. Calcd for $C_{79.5}H_{68}BClIrO_4P_3$ (**4a**): C, 67.30; H, 4.83; Ir, 13.55; P, 6.55. Found: C, 67.15; H, 4.78; Ir, 13.41; P, 6.37. Λ_M = 43 Ω^{-1} cm^2 mol^{-1}. IR: ν(C=O) 1608 (m), ν(C=C) 1589 (s), 1564 (vs), ν(C–O) 1154 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K): AB_2 spin system, $\delta(P_A)$ −25.65, $\delta(P_B)$ −26.99; $J(P_AP_B)$ = 19.2 Hz. ^1H NMR ($CDCl_3$, 298 K): $\delta(H_1)$ 8.10, $\delta(H_2)$ 7.74, $\delta(H_3)$ 7.52, $\delta(H_4)$ 7.98; $J(H_1H_2)$ = 7.90 Hz, $J(H_1H_3)$ = −0.04 Hz, $J(H_2H_4)$ = 0.64 Hz, $J(H_3H_4)$ = 7.36 Hz, $J(H_2H_3)$ = 7.99 Hz. UV/vis ($CHCl_3$) [λ_{max}, nm (ϵ, cm^{-1} mol^{-1} L)]: 246 (40 410), 300 (10 010), 371 (2270). Anal. Calcd for **4b**, $C_{55.5}H_{48}ClF_6IrO_4P_4$: C, 54.94; H, 3.91; Ir, 16.00; P, 10.32. Found: C, 54.66; H, 3.95; Ir, 15.89; P, 10.11.

Reactions of the Oxygenated Complexes. Oxidation of $DTBCH_2$ to DTBQ Catalyzed by [(triphos)Ir(DTBC)]PF_6 or [(triphos)$\overline{Ir(OO)(DTBSQ)}$]PF_6. Reactions between $DTBCH_2$, O_2, and a catalytic amount of either **1b** or **2b** were performed in $CHCl_3$ ($CDCl_3$ when nec-

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Table I. Kinetic Data for the Oxidation of $DTBCH_2$ to DTBQ Catalyzed by $[(triphos)Ir(DTBSQ)(O_2)]PF_6$ in $CHCl_3$ Solution

expt no.	temp, °C	$[Ir]_{in}$:$[DTBCH_2]_{in}$	$10^3[Ir]_{in}$,[a] mol L^{-1}	$10[DTBCH_2]_{in}$, mol L^{-1}	$10^2k'$, mol L^{-1} h^{-1}	R,[b] %	$k = k'/[Ir]_{in}$, h^{-1}
1	47	1:27	3.968	1.058	4.3 ± 0.6	96.33	10.8 ± 1.5
2	47	1:53	3.968	2.117	6.2 ± 0.5	98.88	15.6 ± 1.3
3	47	1:107	3.968	4.234	5.8 ± 0.1	99.95	14.6 ± 0.3
4	47	1:160	3.968	6.351	4.4 ± 0.1	99.69	11.1 ± 0.2
5	47	1.5:107	5.952	4.234	8.3 ± 0.1	99.50	13.9 ± 0.2
6	47	2:107	7.936	4.234	10.9 ± 0.6	99.31	13.7 ± 0.8
7	47	3:107	11.904	4.234	15.4 ± 0.2	99.47	12.9 ± 0.2
8	47	4:107	15.872	4.234	24.0 ± 0.4	99.92	15.1 ± 0.2
							13.4 ± 0.5[c] ($\bar{k}$)
9	38	2:103	8.204	4.234	8.4 ± 0.5	99.06	10.2 ± 0.6
10	42	2:105	8.087	4.234	9.6 ± 0.5	99.43	11.9 ± 0.6
11	53	2:110	7.710	4.234	14.5 ± 0.7	99.31	18.8 ± 0.9
12	56	2:112	7.570	4.234	15.1 ± 0.6	99.24	20.0 ± 0.7
13	60	2:115	7.388	4.234	16.7 ± 0.9	98.97	22.6 ± 1.2

[a] Corrections were made to account for the temperature dependence of catalyst concentration (oxygenated species). [b] Correlation coefficients of least-squares regressions. [c] Mean value of the kinetic constant $\bar{k}$ and its standard deviation $\sigma(\bar{k})$ were calculated as $\bar{k} = (\sum_i w_i k_i / \sum_i w_i)$ and $\sigma(\bar{k}) = [\sum_i w_i (k_i - \bar{k})^2/(n-1)\sum_i w_i]^{1/2}$, where $w_i = 1/\sigma_i^2$.

Table II. Kinetic Data for the Oxidation of $DTBCH_2$ to DTBQ Catalyzed by $[(triphos)Ir(DTBSQ)(O_2)]PF_6$ in $CHCl_3$ Solution under Controlled Dioxygen Pressure

temp, °C	p_{O_2}, psi	$[Ir]_{in}$:$[DTBCH_2]_{in}$	$10^3[Ir]_{in}$, mol L^{-1}	$10[DTBCH_2]_{in}$, mol L^{-1}	$10^2k'$, mol L^{-1} h^{-1}	R,[a] %
30	15	1:100	8.460	8.460	8.6 (2)	99.82
30	30	1:100	8.460	8.460	8.8 (4)	99.56
30	45	1:100	8.460	8.460	8.3 (2)	99.71
30	75	1:100	8.460	8.460	9.1 (6)	99.08

[a] Correlation coefficients of least-squares regressions.

essary) solutions. In a typical experiment, the catalyst was added to a thermostated solution of $DTBCH_2$ under a steady stream of dioxygen. The mixture composition was analyzed periodically (ca. every 30 min) by GC–MS, ^{31}P NMR, ^1H NMR, and UV/visible spectrometry (ca. every 15 min). The organic products were identified by comparison of their retention times and mass spectra with those of authentic specimens. Quantification was achieved with a Shimadzu C-R6A Chromatopac coupled with the chromatograph, operating with an automatic corrected area normalization method. The amount of DTBQ produced during the reaction was also determined by UV/visible spectroscopy measuring the absorbance of the reaction mixture at 572 nm (λ_{max} of a typical band of DTBQ) after dilution with $CHCl_3$ to ca. 10^{-3} M. The amount of H_2O_2 was determined by the usual method of iodometry[4,13] and was found in each case to be nearly equal to that of DTBQ. Experimental conditions are summarized in Table I. The temperature was determined with an accuracy of ±0.5 °C; the concentrations of $DTBCH_2$ and DTBQ were measured with a relative mean error of ca. ±2%. Experiments were also performed under a stationary atmosphere of O_2 by using the same general procedure, the pressure of dioxygen being determined with an accuracy of ±0.5%.

Reaction of $[(triphos)\overline{Ir(OO)}(PhenSQ)]PF_6$ with CF_3SO_3H. Reaction A. To a solution of **4b** (0.69 g, 0.5 mmol) in $CHCl_3$ (20 mL) at room temperature was added with stirring 2 equiv of neat CF_3SO_3H. The resulting light brown mixture was extracted with water, and the aqueous layer was analyzed by iodometry. The amount of H_2O_2 produced was found to be correspondent to that of initial **4b**. The $CHCl_3$ layer was evaporated at reduced pressure and the residue extracted twice with *n*-pentane. The undissolved solid was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy and shown to be a mixture of decomposition metal products. The liquid phase was concentrated to dryness, and the resulting solid was authenticated by ^1H NMR spectroscopy and GC as PhenQ.

Reaction B. Addition of 1 equiv of CF_3SO_3H, followed by working-up as described above, gave 0.5 equiv of both H_2O_2 and PhenQ. Approximately 0.5 equiv of unreacted **4b** was detected in the reaction mixture by ^{31}P NMR integration.

When reactions A and B were carried out in MeCN at room temperature, an identical course was observed, but the use of the coordinating solvent allowed us to identify the final iridium complex as $[(triphos)Ir(MeCN)_3]^+$ by $^{31}P\{^1H\}$ NMR spectroscopy (A_3 spin system, δ −32.0 ppm) (see below).

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Reaction C. To a solution of **4b** in deaerated MeCN (1.57×10^{-3} mol dm^{-3}) in a voltammetric cell thermostated at −20 °C and containing $[NEt_4]ClO_4$ as supporting electrolyte (0.2 mol dm^{-3}) was added 2 equiv of neat CF_3SO_3H. Immediately after the addition of the acid, cyclic voltammetric tests were carried out at a platinum electrode using the usual procedure.[3,4] The complex that forms by reaction of **4b** with the acid undergoes two subsequent reduction steps ($E^{0\prime}$ = +0.87 and +0.11 V, respectively), each of which displaying a directly associated response in the reverse scan. Controlled-potential coulometric tests showed that each charge transfer involves one electron/molecule. Such a redox pathway is fully consistent with the trend expected from the generation of $[(triphos)Ir(PhenQ)]^{3+}$, which can reversibly be reduced to $[(triphos)Ir(PhenSQ)]^{2+}$ and then to $[(triphos)Ir(PhenC)]^+$. As a matter of fact, a complementary voltammetric picture is exhibited by the catecholate complex **3b** under identical conditions.[6] A quite similar electrochemical behavior is exhibited at room temperature, but $[(triphos)Ir(PhenQ)]^{3+}$ rapidly decomposes to $[(triphos)Ir(MeCN)_3]^+$ and free PhenQ.

Reaction between $[(triphos)\overline{Ir(OO)}(PhenSQ)]BPh_4$ and $DTBCH_2$. An orange mixture of $[(triphos)\overline{Ir(OO)}(PhenSQ)]BPh_4$ (**4a**) (0.69 g, 0.5 mmol) and $DTBCH_2$ (1.11 g, 5.0 mmol) was allowed to react in refluxing CH_3NO_2 (8 mL) for 2 h under a pure nitrogen atmosphere. The color of the solution slowly turned violet. The solution was then cooled to room temperature and 40 mL of *n*-butanol/*n*-heptane (1/1) added causing the separation of violet crystals of $[(triphos)IrDTBC]BPh_4$ (**1a**) in 82% yield. The amounts of H_2O_2 and PhenQ (PhenQ = 9,10-phenanthrenquinone) produced in the reaction solution were determined by iodometry and by GC–MS analysis (with a Shimadzu C-R6A Chromatopac coupled with the chromatograph, operating with an internal standard method), respectively, and were found to be nearly equal to each other and to the amount of **1a** obtained.

Results

Chemoselective Oxidation of $DTBCH_2$ to DTBQ Catalyzed by 2b. The reactions between $DTBCH_2$ and O_2 (steady stream) in the presence of catalytic amounts of $[(triphos)\overline{Ir(OO)}(DTBSQ)]PF_6$ (**2b**) were performed in chloroform solutions and examined in the temperature range from 38 to 60 °C with a ratio between initial concentrations of **2b** ($[Ir]_{in}$) and substrate ($[DTBCH_2]_{in}$) variable from 1:27 to 1:160. Experimental conditions are summarized in Table I. Experiments were also carried out under a stationary atmosphere of O_2, the pressure being varied

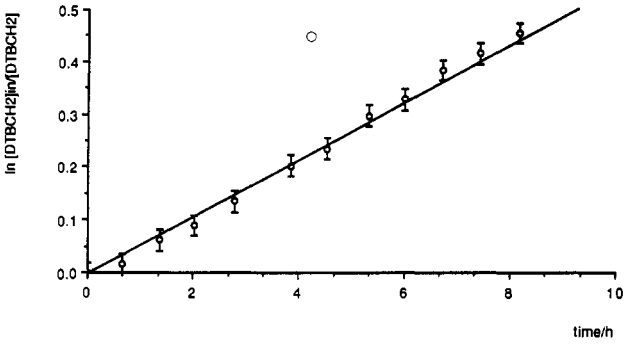


Figure 1. Plot of ln ($[DTBCH_2]_{in}/[DTBCH_2]$) versus reaction time for the oxidation of $DTBCH_2$ catalyzed by **2b**. Catalyst to substrate ratio = 1:27; temperature = 47 °C (experiment 1, Table I).

between 15 and 75 psi (Table II). There was no GC–MS evidence of the formation of any product other than DTBQ. During the reactions, hydrogen peroxide accumulated in the solutions in amounts corresponding to those of DTBQ. The only iridium species detected by $^{31}P\{^1H\}$ NMR spectroscopy during the course of the reactions was **2b**, whereas the parent deoxygenated complex **1b** was quantitatively recovered after quenching the mixture with N_2.

The substitution of **1b** for **2b** in the catalytic reactions modifies neither the rate nor the product composition, a fact that indicates the absence of any induction period. On the other hand, this finding is quite consistent with the very fast dioxygen uptake by the catecholate complex.

Kinetic Measurements. The kinetics of the oxidation reaction was followed by determining the concentration of $DTBCH_2$ in the reaction solutions as a function of time by GC sampling the reaction mixtures every 30 min.

A simple rate law for the catalytic reaction between O_2 and $DTBCH_2$ catalyzed by **2b** is

$$d[DTBQ]/dt = -d[DTBCH_2]/dt = k[Ir]^m[DTBCH_2]^n(p_{O_2})^q \quad (1)$$

In order to determine the rate dependence on the various reactants, oxidation runs were performed at different substrate (Table I, experiments 1–4) and catalyst concentrations (Table I, experiments 3, 5–8) and at different oxygen pressures (Table II).

Assuming a constant concentration of the catalyst during each reaction $[Ir] = [Ir]_{in}$ as well as a constant dioxygen pressure for experiments performed in a steady stream of O_2, one can write a simplified form of the rate law (eq 3) where k' is

$$k' = k[Ir]_{in}^m(p_{O_2})^q \quad (2)$$

$$-d[DTBCH_2]/dt = k'[DTBCH_2]^n \quad (3)$$

Plots of ln ($[DTBCH_2]_{in}/[DTBCH_2]$) versus time were linear in experiment 1–8, indicating that the reaction is first order with respect to substrate concentration. Columns k' and R in Table I report the slopes and the correlation coefficients obtained from least-squares method for these linear regressions. A typical first-order plot is shown in Figure 1 for experiment 1; the reaction remains first order for the whole time in which the experiment was observed (36% conversion, 8.17 h). The quality of these results as well as the reliability of the GC technique to determine the concentrations of $DTBCH_2$ and DTBQ was confirmed by UV/visible spectroscopy measurements. In this case the kinetics of the oxidation reaction was followed by determining the amount of DTBQ produced in the course of the reactions. The variations of the absorbance maximum for the *o*-quinone band at 572 nm are reported in Figure 2 (experiment 3; catalyst to substrate ratio 1:107, 47 °C). The plot of ln ($[DTBCH_2]_{in}/[DTBCH_2]$) vs time shown in Figure 3 gives a k' value (R = 94.00%, k = 14.4 ± 1.7 h^{-1}) which well matches the value obtained by GC determination (0.057 ± 0.008 versus 0.058 ± 0.001).

Experiments made at different dioxygen pressures (15, 30, 45, 75 psi) show that p_{O_2} does not appreciably affect the rate of the

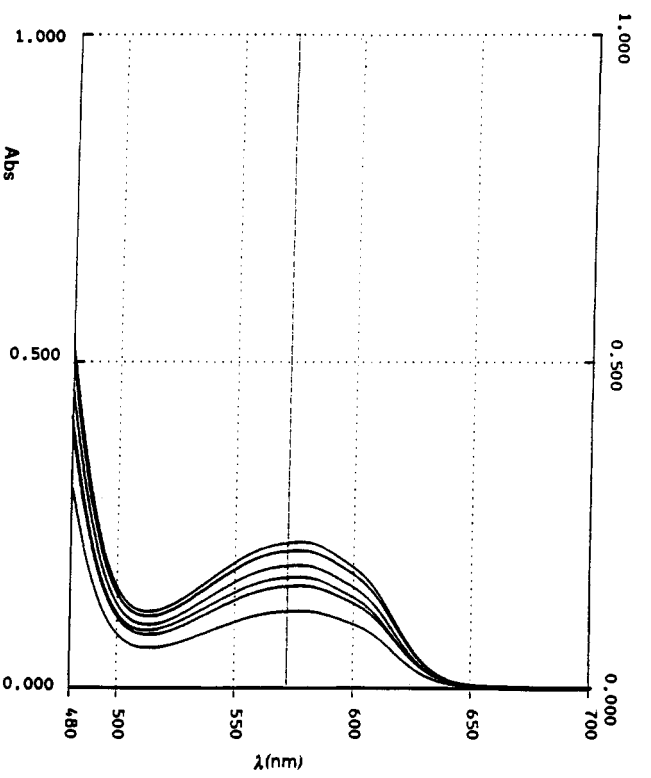


Figure 2. UV/visible spectra recorded during experiment 3. Absorbance was measured at 572 nm after diluting with $CHCl_3$ to ca. 10^{-3} M. Reaction time (hours) for each spectra in order of increasing absorbance: 0.62, 0.85, 1.22, 2.15, 2.47, 2.98. For simplicity only a few spectra are shown.

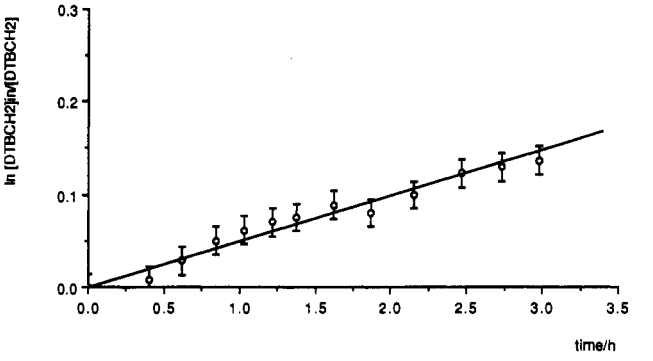


Figure 3. Plot of ln ($[DTBCH_2]_{in}/[DTBCH_2]$) versus reaction time for the oxidation of $DTBCH_2$ catalyzed by **2b** obtained by using the UV/visible spectroscopy data (experiment 3, Table I).

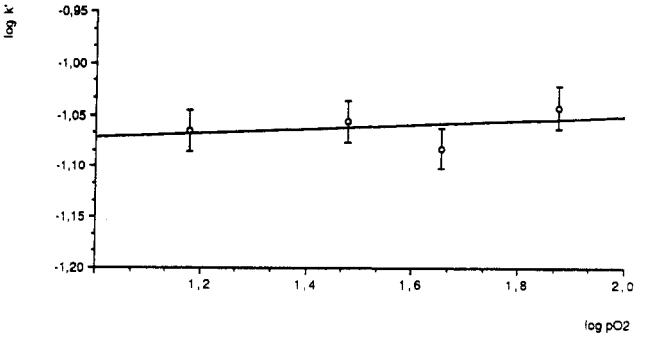


Figure 4. Plot of log k' versus log (p_{O_2}) for the experiments in Table II.

reaction (columns k' and R in Table II). This result is graphically showed in Figure 4 in which log k' versus log (p_{O_2}) is plotted. A straight line of slope 0.02 ± 0.06 was obtained. This means that $q = 0$ in eq 2, which therefore simplifies to

$$k' = k[Ir]_{in}^m \quad (4)$$

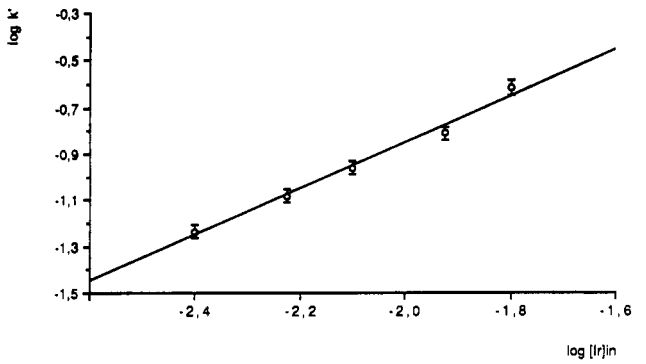


Figure 5. Plot of log k' versus log $[Ir]_{in}$ for different initial catalyst concentrations.

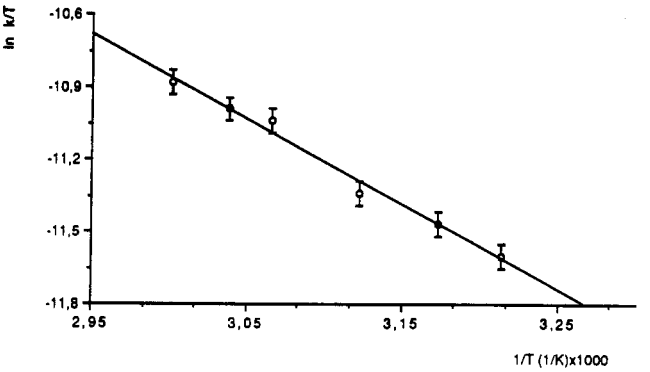


Figure 6. Plot of ln (k/T) versus $1/T$ as indicated by eq 7.

Kinetic measurements of the rate with respect to catalyst concentration (experiments 3, 5–8) indicate a first-order dependence. A plot of log k' versus log $[Ir]_{in}$ for the above five experiments gave a straight line of slope $m = 0.99 \pm 0.06$ with a correlation coefficient of 99.40% (Figure 5) showing that the reaction is also first order in the initial concentration of the catalyst.

Hence, one can conclude that the reaction follows the rate law

$$d[DTBQ]/dt = -d[DTBCH_2]/dt = k[Ir]_{in}[DTBCH_2] = k'[DTBCH_2] \quad (5)$$

with

$$k' = k[Ir]_{in} \quad (6)$$

From eq 6 a mean value of the kinetic constant k of 13.4 ± 0.5 h^{-1} at 47 °C was obtained (Table I). The activation parameters for the present oxidation reaction were determined from the temperature dependence of the kinetic constant k.

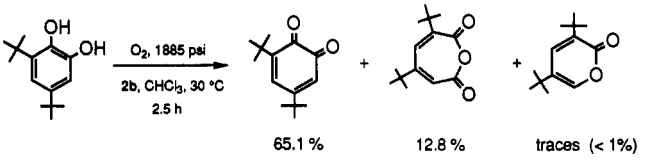
The Eyring plot ln (k/T) versus $1/T$ (Figure 6) obtained from eq 7 (k is expressed in s^{-1} and $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ are assumed

$$\ln (k/T) = 23.76 + 0.12\Delta S^{\ddagger} - 0.12\Delta H^{\ddagger}/T \quad (7)$$

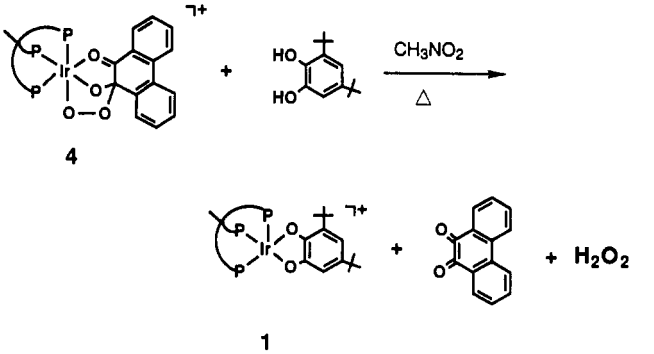
temperature-independent in the range examined) by using the k values obtained at 38, 42, 47, 53, 56, and 60 °C (experiments 6 and 9–13 in Table I) gave a straight line with a correlation coefficient of 99.37%. The slope and the ordinate intercept of this line gave $\Delta H^{\ddagger} = 7.0 \pm 0.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -48 \pm 2$ cal mol^{-1} K^{-1}, respectively, and $\Delta G^{\ddagger}(298\ K) = 21 \pm 1$ kcal mol^{-1}.

High-Pressure Experiments. Reactions between **2b**, $DTBCH_2$, and O_2 were carried out also under high dioxygen pressures. In addition to DTBQ (major product), appreciable formation of oxygenated products of $DTBCH_2$ occurs when pressures of O_2 higher than 725 psi are employed. As an example, at 1885 psi (30 °C, catalyst to substrate ratio 1:100) the product distribution after 2.5 h was 65.1% DTBQ, 22.1% $DTBCH_2$, and 12.8% DTBA plus traces of DTBPyr (less than 1%) (Scheme V). In all high-pressure reactions, hydrogen peroxide was formed in amounts corresponding to those of DTBQ. Complementary formation of H_2O was observed by ^1H NMR spectroscopy for reactions carried out in deuterated solvents.

Scheme V



Scheme VI



Reaction of [(triphos)Ir(OO)(PhenSQ)]BPh_4 with $DTBCH_2$. Under a dioxygen atmosphere, solutions of **2a,b** do not produce DTBQ unless external $DTBCH_2$ is added, a finding that confirms the *inter*molecular character of the catalytic reaction. Further evidence of the *inter*molecular path is provided by the crossover reaction of the PhenSQ complex **4a** with an excess of $DTBCH_2$ in refluxing CH_3NO_2 under nitrogen. In fact, the reaction quantitatively yields the iridium catecholate complex **1a**, PhenQ, and H_2O_2 (Scheme VI).

Reaction of [(triphos)Ir(OO)(PhenSQ)]PF_6 with CF_3SO_3H. The reaction of **4b** with 2 equiv of a strong protic acid in MeCN solution under nitrogen quantitatively gives hydrogen peroxide and the *o*-quinone complex $[(triphos)Ir(PhenQ)]^{3+}$. The latter compound is not sufficiently stable to be isolated in the solid state, but its formation can be unequivocally demonstrated by carrying out the reaction in a voltammetric cell (MeCN solution). In fact, the *o*-quinone complex is a member of the redox chain shown in eq 8 that is typical for metal catecholates, particularly for $[(triphos)M(Cat)]^+$ complexes (M = Co,[3] Rh,[4] Ir;[5] Cat = catecholate).

$$[(triphos)Ir(PhenC)]^+ \underset{}{\overset{E^{\circ\prime} = +0.11\ V}{\rightleftharpoons}} [(triphos)Ir(PhenSQ)]^{2+} \underset{}{\overset{E^{\circ\prime} = +0.87\ V}{\rightleftharpoons}} [(triphos)Ir(PhenQ)]^{3+} \quad (8)$$

The iridium(III) *o*-quinone complex can be generated by exhaustive two-electron oxidation of **3b** at +1.1 V in MeCN at −20 °C. The use of such a low temperature is necessary to slow down the decomposition of the *o*-quinone complex, a known path that proceeds according to eq 9.[3,4]

$$[(triphos)Ir(PhenQ)]^{3+} \xrightarrow{MeCN} [(triphos)Ir(MeCN)_3]^{3+} + PhenQ \quad (9)$$

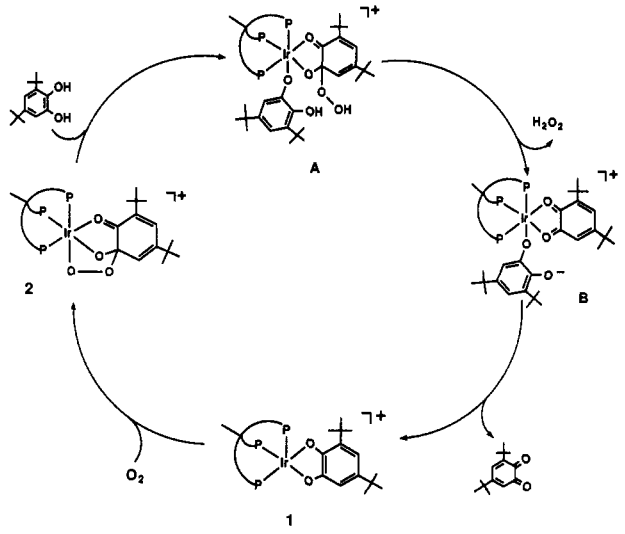
Interestingly, when **4b** is reacted with a stoichiometric amount of a protic acid, only 0.5 equiv of starting complex disappears to yield 0.5 equiv of both H_2O_2 and free PhenQ. Assuming a two-step protonation reaction of **4b**, this experiment suggests that the second protonation is faster than the first one.

The use of the PhenSQ complexes **4a,b** instead of the equally available DTBSQ derivatives in the reactions with either $DTBCH_2$ or $HOSO_3CF_3$ under nitrogen is just a consequence of their major stability under anaerobic conditions. In fact, **2a,b** reversibly lose O_2 under nitrogen converting to the parent DTBC compounds **1a,b**.[5]

Discussion

Catalytic Oxidation of $DTBCH_2$ to DTBQ. All of the experimental observables reported in the previous sections can be

Scheme VII



translated into valuable information on the mechanism of oxidation of $DTBCH_2$ to DTBQ assisted by **2b**.

A catalysis cycle that nicely fits with the chemical, spectroscopic, kinetic, and thermodynamic data is the one shown in Scheme VII. The catalyst is the catecholate complex which rapidly picks up dioxygen converting to the O_2 adduct. Such a step does not determine the reaction rate given its nondependence on the O_2 pressure. Since the dioxygen adduct is the only phosphorus-containing product detected by ^{31}P NMR spectroscopy during the catalysis cycle, reasonably this compound is a reagent in the rate-determining step as indicated also by eq 5. On the other hand, the rate equation suggests that also the catechol substrate can play a role in the rate-determining step. Indeed, according to the largely negative $\Delta S^{\ddagger}$ value (-48 ± 2 cal mol^{-1} K^{-1}) that suggests a bimolecular transition state,[9] the addition of catechol to the dioxygen adduct appears as an excellent candidate for the role of rate-determining step.

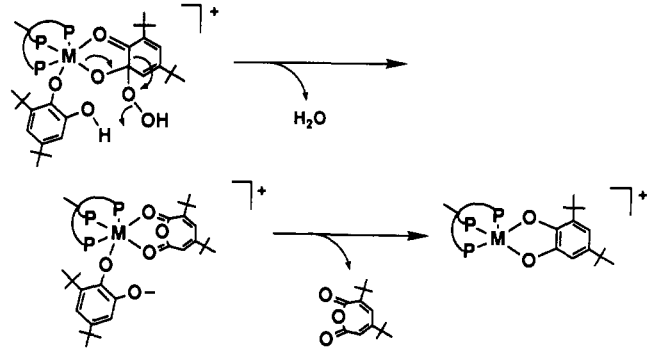
The intimate mechanism of the catechol–O_2 adduct interaction is difficult to prove. Much depends on the site of attack by the catechol at the peroxo bridge. Surveying literature data on the chemistry of alkyl peroxo complexes,[14] one learns that the α-oxygen is more nucleophilic than the β-one. Accordingly, it would be reasonable to conclude that the catechol cleaves the Ir–O(peroxo) bridge with consequent formation of a hydroperoxo group bonded to one C atom of the semiquinoid ligand as well as creation of a free coordination site at the metal. This site can be saturated by the catecholate monoanion (intermediate A). At this point, the system appears appropriately designed to allow interaction of the hydroxy hydrogen of coordinated catechol with the close hydroperoxo α-oxygen. As a result, hydrogen peroxide is evolved and the so formed *o*-quinone ligand can be easily displaced by the catecholate ligand which exhibits much better donating properties.

In light of the fact that the second protonation of the dioxygen adduct (see the reaction of **4b** with 2 equiv of protic acid) seems to be faster than the first one, it can be reasonably concluded that the rate-determining step is just the reaction between the O_2 adduct and catechol, a reaction that the largely negative $\Delta S^{\ddagger}$ suggests to proceed via an ordered transition state.

An alternative path involving initial protonation of the β-oxygen of the peroxo bridge in **2b** by catechol to give an iridium hydroperoxo complex and free catecholate would be ruled out by the $\Delta S^{\ddagger}$ value.

Comparison with Rhodium. As previously reported,[4] the catalytic reaction of the Rh–O_2 adduct **6** with $DTBCH_2$ and O_2 is less selective than that of the iridium analogue. Some muconic acid anhydride and 2-pyrone derivatives are also produced as a result of the *intra*- and *extra*diol insertion of one oxygen atom from O_2.[4,9] The formation of such products is nicely consistent with the participation of an intermediate of type A (Scheme VII) once it is taken for granted that the rhodium and iridium systems, at least in the initial stages, share the same mechanism. In fact, intermediate A may have two reaction options: protonation of the hydroperoxo α-oxygen by the close hydroxy group from bonded catechol (*o*-quinone and H_2O_2 produced) or *intra*molecular rearrangement to give oxygenation products and H_2O via a mechanism quite similar to that commonly suggested for the activity of 1,2-dioxygenases (Scheme VIII).[8] In this respect, it is worth recalling that (i) the amount of H_2O_2 produced in the Rh-assisted reaction was found to be equal to that of the *o*-quinone product[4] and (ii) both H_2O_2 and H_2O byproducts are detected in the termination mixtures of the high-pressure reactions.

Scheme VIII



Why iridium selectively favors *o*-quinone formation whereas rhodium, even though partially, promotes oxygenation paths is difficult to assess with any certainty. Actually, although belonging to the same triad, the two metals exhibit different bonding aptitudes; in particular, iridium(III) has a major tendency to coordinate alcohols via oxygen and, consequently, to promote O–H bond cleavage. As an example, iridium complexes are much better catalysts for the reduction of ketones via hydrogen transfer from alcohols than rhodium compounds.[15]

A thought-provoking result presented in this paper concerns the formation of oxygenated products of $DTBCH_2$, essentially DTBA, in the course of the iridium-assisted reactions at pressures of $O_2 > 50$ atm. This finding is really difficult to explain since in such drastic reaction conditions, alternative paths may well occur. Studies are presently under way to try to rationalize the intriguing effect of pressure on the oxidation reactions.

Comparisons with Other Kinetic Studies on Metal-Catalyzed Oxidation Reactions of Catechols to *o*-Quinones. Metal-assisted oxidation of catechols by molecular oxygen has been the subject of considerable interest in recent years.[16-31] However, very few

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kinetic and thermodynamic studies have been reported,[7,9] likely due to the low chemoselectivity of such reactions.

The oxidation reactions of catechols which selectively produce *o*-quinones conform to either of the following two equations:

$$\text{catechol} + \tfrac{1}{2}O_2 \rightarrow o\text{-quinone} + H_2O \quad (10)$$

$$\text{catechol} + O_2 \rightarrow o\text{-quinone} + H_2O_2 \quad (11)$$

To the best of our knowledge, only two kinetic and mechanistic studies have been reported in the literature. Tsuruya and coworkers[7a] have studied the kinetics of cobalt(II)–chelate catalyzed oxidation of $DTBCH_2$ to DTBQ in $CHCl_3$ showing that the rate of the reaction, conforming to eq 10, is first order with respect to the concentrations of the metal catalyst and substrate and also first order in the partial pressure of dioxygen. In a previous paper, Martell and Tyson[7b] reported a kinetic study on Mn(II)-catalyzed oxidation of $DTBCH_2$ conforming to eq 11. Despite the complexity of the system, they were able to demonstrate that the oxidation reaction follows simple first-order kinetics for dioxygen uptake. Our results on the oxidation of $DTBCH_2$ in $CHCl_3$ are, therefore, unprecedented, as the rate of the reaction has been shown to be independent on free dioxygen over a large range of partial pressures (15–725 psi).

Concluding Remarks

The present study has revealed that the catecholate complex $[(triphos)Ir(DTBC)]^+$ is an effective homogeneous catalyst for the selective oxidation of $DTBCH_2$ to DTBQ by molecular oxygen and has served to shed some light on the mechanism of the reaction in which the formation of the O_2 adduct $[(triphos)\overline{Ir(OO)}\text{-}(DTBSQ)]^+$ and its bimolecular reaction with free catechol are obligatory steps. In particular, we believe that this is the first well-documented example of a catalytic oxidation conforming to eq 11 in which the rate is first order in catalyst and substrate concentrations and zero order in free dioxygen over a large range of partial pressures.

The identification of the catalyst and the interception of the catalyst–O_2 adduct are of particular relevance. Their isolation and characterization have certainly been made possible by the use of the tripodal ligand triphos. In effect, tripodal tri- and tetradentate ligands are being largely used to study reaction mechanisms due to their ability to provide the resulting complexes with a remarkable kinetic inertness.[9,10,32]

Finally, it is worth stressing that the oxygenation of $DTBCH_2$ to DTBA (*intra*diol C–C cleavage) competes with *o*-quinone formation at high pressure of O_2. This unprecedented result will probably stimulate further studies with the prospect of using high pressures for oxygenation reactions of severe pollutants such as substituted aromatics.

Acknowledgment. Thanks are due to Prof. Piero Zanello (Università di Siena, Siena, Italy) for the electrochemical studies and to the "Progetti Finalizzati Chimica Fine e Secondaria II" CNR, Rome, Italy.

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Infrared Study on the Hydration of Mn^{2+}, Fe^{2+}, Co^{2+}, La^{3+}, Nd^{3+}, Dy^{3+}, and Yb^{3+} Ions in Dilute Aqueous Solution

Pehr-Åke Bergström and Jan Lindgren*

Received May 8, 1991

OD stretching vibration spectra of Mn^{2+}, Fe^{2+}, Co^{2+}, La^{3+}, Nd^{3+}, Dy^{3+}, and Yb^{3+} perchlorates in dilute (0.2–0.4 M) aqueous solution were obtained using infrared spectroscopy. Intensities, bandwidths, and peak positions of the hydrated cation bands are reported. The currently studied first-row transition-metal ions all have a similar effect on the coordinated water (HDO) molecules and give rise to OD stretching vibration bands at 2427 (2) cm^{-1}. Qualitatively similar spectra were obtained for the trivalent lanthanide perchlorate solutions, with a single OD band from cation-perturbed HDO molecules. This implies that the lanthanide ions only perturb the nearest-neighboring water molecules, which thus constitute the primary hydration shell, and to a similar extent as do the divalent cations. The obtained hydration numbers for the lanthanide ions are 7.8 (6) (La), 8.0 (6) (Nd), 8.7 (6) (Dy), and 8.8 (6) (Yb).

Introduction

In dilute aqueous salt solutions, the vast majority of the water molecules are hydrogen bonding to other water molecules, thus constituting the bulk. Infrared spectroscopic studies of such solutions are hindered by the intense absorption of bulk water, which conceals the information to be gained from ion-perturbed water molecules. Furthermore, the spectrum of H_2O is rather complex, with a great deal of overlap of the two fundamental OH stretching vibrations, ν_1 and ν_3, and the first overtone of the bending vibration, ν_2.[1] By addition of a small amount of D_2O, which rapidly reacts with H_2O to form HDO, and the observation of the OD stretching vibrations of the HDO molecules, the situation is greatly improved and simpler spectra can be obtained of the decoupled OD oscillator. This technique of isotopic dilution has been known for a long time.[1-3] Although the problem of the complicated H_2O spectrum can be reduced by isotopic dilution, there is still a substantial amount of HDO molecules in the bulk that contributes to the infrared spectra. By the combination of isotopic dilution and a spectral double-difference technique where the absorption from HDO molecules in the bulk is subtracted, OD vibration spectra of ion-perturbed HDO molecules can be obtained.[4]

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