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The Formation of Adducts of some *o*- and *p*-Quinones with Copper(I) Chloride and Bromide

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The reaction of CuX (X = Cl, Br) with some o- and p-quinones in pyridine gives the diamagnetic adducts [CuX(py)]$_2$·quinone (2) (X = Cl) and (3) (X = Br). IR data suggest that 2 and 3 are olefin complexes.

Introduction

The CuX–O$_2$–amine system, which is responsible for several catalytic oxidations, has been the subject of numerous studies in order to clarify the species involved in the catalytic reactions [1–6]. It has been shown recently that 9,10-phenantrenequinones are transformed by the CuX–O$_2$–L system (L = pyridine, 2,2′-dipyridine, *o*-phenanthroline) to diphenato copper(II) complexes [7]. Copper(I) quinone adducts or catecholato complexes are possible intermediates in these reactions. Furthermore, it has been reported recently that [CuX(py)]$_2$·*p*-benzoquinone complexes are formed from CuX and *p*-benzoquinone in the presence of pyridine and their olefinic nature was stated [8]. The same complex could be isolated earlier by Hashimoto *et al.* [9] starting from [CuCl(OMe)py]$_2$ and hydroquinone. In order to verify the possibility of *o*-quinone copper(I) complexes being intermediates and to get more insight into the mechanism of oxygenolysis of *o*-quinones by the CuX–O$_2$–amine system, we decided to extend this study to the reaction of a series of *p*- and *o*-quinones with CuX (X = Cl, Br).

Experimental

The quinones *p*-benzoquinone (*1a*), 1,4-naphthoquinone (*1b*), anthraquinone (*1c*), 1,2-naphthoquinone (*1d*), and 9,10-phenanthrenequinone (*1e*) (Aldrich, Europe) were used without further purification and 4,5-dimethoxy-*o*-benzoquinone (*1f*) was prepared according to the literature [10].

Pyridine was purified by distillation over potassium hydroxide and calcium hydride and dichloromethane distilled over P$_2$O$_5$. All reactions were carried out under argon.

Magnetic susceptibilities were measured with a Bruker B-E 10B8 instrument.

General Procedure for the Preparation of [CuX(py)]$_2$·quinone Adducts

Copper(I) chloride or bromide and the quinone were separately dissolved or suspended in the solvents indicated in Table I (molar ratio Cu:quinone = 2:1) and the quinone solutions were added slowly to the Cu(I)X solutions. In cases when the reactants did not dissolve totally in the solvent, the mixture was heated up quickly and subsequently cooled to room temperature. In some instances crystals separated instantaneously after adding the quinone solutions. The coloured microcrystals were filtered off, washed with a small amount of pyridine, acetonitrile or dichloromethane, and dried in vacuum. Yields (not optimized) are listed in Table II.

TABLE I. Preparation of [CuX(py)]$_2$·quinone Adducts.

Complex	CuX (mmol)	Solvent (ml)	Quinone (mmol)	Solvent (ml)
2a	20	py (20)	10	py (5)
3a[a]	20	py (20)	10	py (5)
2b[a]	20	py (20)	10	py (20)
3b[a,b]	20	CH$_2$Cl$_2$ (50)	10	py (60)
2c[a]	20	py (20)	10	py (15)
2f[a]	10	py (10)	5	py (5)
3d[a,b]	10	py (10)	5	CH$_3$CN (10)
2e	20	py (20)	10	py (10)
3e	20	C$_6$H$_6$ (15)	10	py (10)

[a] The mixture was heated up shortly under argon. [b] Half of the solvent was pumped off, and the compound precipitated on adding ether to the solution.

Results and Discussion

Extending the work of Calderazzo *et al.* [8] we used the following *p*-quinones: *p*-benzoquinone (*1a*),

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TABLE II. Analytical, Physical and Infrared Data for $[CuXpy]_2 \cdot$Quinone Adducts.

Complex		M.p (°C)	Colour	Yield (%)	Analysis (%)[a] C	H	N	Cu	X	ν(CO) (cm^{-1})[b]
$[CuCl(py)]_2 \cdot p\text{-}C_6H_4O_2$	(*2a*)	240(dec.)	red	90	41.25 (41.38)	2.91 (3.04)	6.10 (6.06)	27.90 (27.37)	15.15 (15.27)	1644 (1647)
$[CuBr(py)]_2 \cdot p\text{-}C_6H_4O_2$	(*3a*)	145–147	red	43	34.61 (34.74)	2.31 (2.55)	5.04 (5.06)	23.05 (22.97)	29.20 (28.80)	1637 (1647)
$[CuCl(py)]_2 \cdot 1{,}4\text{-}C_{10}H_6O_2$	(*2b*)	118–120	yellow	62	46.17 (46.70)	3.10 (3.13)	5.42 (5.44)	23.57 (24.71)	12.67 (13.78)	1650 (1650)
$[CuBr(py)]_2 \cdot 1{,}4\text{-}C_{10}H_6O_2$	(*3b*)	120–124	brick red	51	39.28 (39.82)	2.70 (2.67)	4.80 (4.64)	20.56 (21.07)	26.11 (26.50)	1648 (1650)
$[CuCl(py)]_2 \cdot C_{14}H_8O_2$	(*2c*)	256–259	pale yellow	65	51.80 (51.07)	3.26 (3.21)	4.67 (4.96)	21.93 (22.51)	12.40 (12.56)	1680 (1672)
$[CuBr(py)]_2 \cdot 1{,}2\text{-}C_{10}H_6O_2$	(*3d*)	68–70	green	47	39.27 (39.81)	2.56 (2.67)	4.80 (4.64)	20.95 (21.06)	26.01 (26.49)	1646 (1663)
$[CuCl(py)]_2 \cdot 9{,}10\text{-}C_{14}H_8O_2$	(*2e*)	65–68	yellow	63	49.53 (51.14)	3.11 (3.21)	4.50 (4.97)	21.97 (22.55)	12.52 (12.43)	1680 (1679)
$[CuBr(py)]_2 \cdot 9{,}10\text{-}C_{14}H_8O_2$	(*3e*)	91–94	yellow	83	43.30 (44.12)	2.40 (2.77)	4.40 (4.29)	19.35 (19.45)	23.19 (24.46)	1670 (1679)
$[CuCl(py)]_2 \cdot 4{,}5\text{-}(CH_3O)_2C_6H_2O_2$	(*2f*)	117(dec.)	brown	71	40.90 (41.22)	3.42 (3.46)	5.30 (5.34)	24.30 (24.24)	13.33 (13.52)	1644 (1647)

[a] Calculated values in parenthesis. [b] Taken in Nujol, ν(CO) values of the free ligands in parenthesis.

1,4-naphthoquinone (*1b*), anthraquinone (*1c*) and *o*-quinones: 4,5-dimethyl-*o*-benzoquinone (*1f*), 1,2-naphthoquinone (*1d*) and 9,10-phenanthrenequinone (*1e*) to react with copper(I) chloride and bromide in the presence of pyridine or mixtures of pyridine and other solvents such as dichloromethane, acetonitrile and benzene. Upon mixing the solutions of the quinone and the copper(I) halide intensively coloured solutions were obtained, from which the coloured complexes precipitated on standing, on cooling down and/or evaporating part of the solvent. The complexes were formed according to eqn. (1).

$$\begin{array}{lcl} 2CuX + \text{quinone} & \xrightarrow{py} & [CuX(py)]_2 \cdot \text{quinone} \qquad (1) \\ \quad\quad 1 & & 2\ X = Cl \\ & & 3\ X = Br \end{array}$$

No adducts could be isolated of anthraquinone and 4,5-dimethoxy-*o*-benzoquinone with copper(I) bromide and of 1,2-naphthoquinone with copper(I) chloride.

Molecular weight determination could not be carried out because of low solubility of the complexes in common organic solvents, suggesting a rather high molecular complexity. All complexes are very sensitive to air and take up dioxygen in solution. The oxygenation of the *o*-quinone adducts resulted mostly in mixtures of different carboxylato copper(II) complexes as supported by their IR-spectra in the $\nu(CO_2)$ frequency region. In the case of 9,10-phenanthrenequinone, well-defined diphenato copper(II) complexes could be isolated as reported earlier [7].

The most important information about the structure of these complexes comes from their IR spectra. The spectra of the chloro derivatives are generally identical to those of the bromo analogues. All complexes exhibit a very intense absorption in Nujol between 1637 and 1680 cm^{-1}, which can be assigned to the C=O stretching vibration of the co-ordinated ligand. The changes in the ν(CO) frequencies of the complexes as compared to those of the free ligands show only a very small (0–17 cm^{-1}) decrease of the C=O stretching vibrations upon complexation, which suggests that no significant electron transfer to the quinones has taken place and the carbonyl groups are not directly involved in the co-ordination to copper(I). Examination of the C=C stretching vibrations of the co-ordinated quinones showed that only slight changes could be observed compared to that of the free ligands. $[CuCl(py)]_2 \cdot p\text{-}C_6H_4O_2$ (*2a*) and $[CuBr(py)]_2 \cdot p\text{-}C_6H_4O_2$ (*3a*) have ν(C=C) absorptions at 1603, 1284 and 1598, 1280 cm^{-1} respectively (the ν(C=C) of the *p*-benzoquinone are at 1588 and 1306 cm^{-1}). $[CuBr(py)]_2 \cdot 1{,}2\text{-}C_{10}H_6O_2$ (*3d*) shows

C=C stretching vibrations at 1595 and 1290 cm^{-1} (ν(C=C) in the free quinone are at 1584 and 1284 cm^{-1}). At the complexes of 1,4-naphthoquinone (*1b*) (ν(C=C) 1575 and 1292 cm^{-1}) the higher wavenumber band disappears and the lower one does not show significant change (*2b* gives ν(C=C) at 1291 cm^{-1} and *3b* shows ν(C=C) at 1280 cm^{-1}). 4,5-Dimethoxy-*o*-benzoquinone (*1f*) (ν(C=C) = 1576 and 1244 cm^{-1}) also did not show significant changes in the C=C stretching vibrations upon complexation in $[\mathrm{CuCl(py)}]_2\cdot 4,5\text{-}(\mathrm{CH_3O})_2\mathrm{C_6H_2O_2}$ (*2f*) (ν(C=C) = 1580 and 1247 cm^{-1}). The spectra are interpretable as arising from the formation of a relatively stable complex with some charge transfer leading to the lowering of bond order in the quinones, as in many charge-transfer complexes of quinones with organic donor molecules found earlier [11, 12]. Therefore the quinone adducts should be regarded as olefin complexes. Labile, similar complexes of copper(I) chloride and dimethyl fumarate were characterized and isolated with diethylenetriamine as ligand [13].

The thermogravimetric analyses under argon showed that in general the pyridine ligands are released first, in the temperature range of 200–250 °C, followed by the volatile quinone ligands. The melting points of CuX (X = Cl, Br) were in all cases well recognisable in the curves.

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