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ELECTROCHEMICAL REACTIONS OF *o*-ANISYLCOPPER AND *p*-TOLYLCOPPER. INFLUENCE OF PYRIDINE AND $LiClO_4$ *

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Summary

Oxidation potentials of *o*-anisylcopper and *p*-tolylcopper are measured in dimethylformamide and pyridine. The oxidation process refers to species in solutions which change with solvent and supporting electrolyte. Differences in donor power of the solvent shift the oxidation potential more than the difference in the nature of the aryl group. Increasing nucleophilicity of the organocopper complex due to coordination of pyridine leads to formation of a pyridinatocopper-lithium complex with partial reduction of copper to Cu^0.

Introduction

Knowledge of organocopper chemistry is still largely empirical, despite the continued interest in the use of organocopper reagents in organic syntheses [1]. The composition and aggregation state of organocopper compounds changes with the method of preparation and is influenced by a variety of coordination phenomena [2]. The organocopper compounds are nearly always characterized by polymeric or cluster structures in the solid state and can exist also as aggregates in solution [3]. The structure and stoichiometry of the species in solution as well as the coordination of the metal atom with the solvent are obviously relevant to the mechanism of reaction brought about by organocopper reagents. The influence of the counterion X on the stability and reactivity of $R_nCu_{n+m}X_m$ (R = aryl) was also demonstrated [4].

Correlations of physico-chemical properties with reactivity or reaction mechanisms are almost completely lacking, but recently House proposed a correlation of the tendency of the electron transfer as the first step in the addition of $[Me_2CuLi]_2$ to unsaturated carbonyl compounds, with the difference ($E_{red} - E_{ox}$) between the reduction potential of the acceptor species (E_{red}) and the oxidation potential of the organocopper derivative (E_{ox}) [5]. (E_{ox} were not determined.)

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* Dedicated to Professor Ernst Otto Fischer on the occasion of his 60th birthday on November 10, 1978.

However quantitative information on the redox properties of organocopper compounds and derivatives has been missing. In the present paper we report the first evidence for a well defined electrode process involving arylcopper compounds, which allows measurement of the polarographic half-wave potential ($E_{1/2}$) of the species in solution. We report also the influence of pyridine as coordinating solvent on $E_{1/2}$ and its effect on the electrochemical behaviour of a reaction of $(CuR)_n$ and $LiClO_4$. The organocopper complexes examined were *o*-anisylcopper (*o*-AnCu) and *p*-tolylcopper (*p*-TolCu) [6].

Results

The octameric orange solid $(o\text{-AnCu})_8$ [7] and the tetrameric yellow $(p\text{-TolCu})_4$ [4a] are both readily soluble in dimethylformamide (DMF) and pyridine (Py). With rigorous exclusion of oxygen and moisture the DMF solutions are apparently stable (UV spectra) for several hours at 0°C, as well as in the presence of $(NEt_4)ClO_4$ or $LiClO_4$ in 0.1 *M* concentration used as supporting electrolytes for the electrochemical measurements. However, when $LiClO_4$ is added to pyridine solutions a noticeable discolouration occurs. In ethereal suspensions of the above organocopper the addition of pyridine in a 4/1 molar ratio causes their rapid dissolution, followed by immediate precipitation of light yellow solids by addition of $LiClO_4$ in equimolecular amount *. These new compounds are very sensitive to oxygen and moisture but thermally stable up to 130°C. Gas chromatography and atomic absorption spectroscopy give the stoichiometric ratios Py/Cu = 4, R/Cu = 1, Li/Cu = 1.4, ClO_4/Cu = 1, consistent with the formula $R_3(Py)_{12}Cu_3Li_4(ClO_4)_3$ (R = *o*-An (I) and *p*-Tol (II)). Attempts to recrystallize I and II from pyridine led to $[CuPy_4]ClO_4$. On heating the aryl groups in I and II decompose to the corresponding arenes. The IR spectra show, besides weak absorption bands of the aryl group R, the bands characteristic of $[CuPy_4]ClO_4$ [8]. New broad absorption bands are present in the 300—500 cm^{-1} region.

o-AnCu, *p*-TolCu and I and II give well defined anodic waves at the dropping mercury electrode (DME), corresponding to oxidation processes at about —0.065 V vs. saturated calomel electrode (SCE) in DMF—$(NEt_4)ClO_4$ and DMF—$LiClO_4$ and at about —0.69 V in Py—$(NEt_4)ClO_4$ solutions. The limiting anodic currents of *o*-AnCu and of the compound I increase with time becoming constant only after about 30 minutes (Fig. 1). The characteristics of the wave are consistent with a monoelectronic, reversible electrode oxidation process (Table 1 and Fig. 2).

When $LiClO_4$ is added to the orange Py$(NEt_4)ClO_4$ solution of *o*-AnCu the colour turns immediately to lemon-yellow and a mixed anodic—cathodic wave can be observed at —0.69 V vs. SCE. In a few minutes it becomes a wholly cathodic wave, with $E_{1/2}$ at the same potential. Freshly prepared solutions of *o*-AnCu in Py—$LiClO_4$ give only the cathodic wave at the same potential. The limiting current increases with time, as for the DMF solutions. The wave shows the characteristics of a monoelectronic reversible electrode reduction process. A very similar behaviour, except for the increase of the limiting current with time, is shown also by *p*-TolCu (II) and $[CuPy_4]ClO_4$ under the same experimental

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* No reaction is apparent if the lithium salt is substituted by $(NEt_4)ClO_4$ and the latter can be quantitatively recovered after two days of reaction at 0° C.

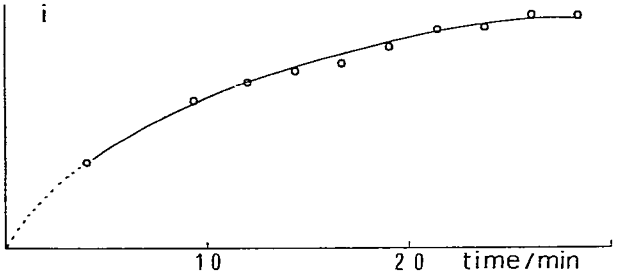

Fig. 1. Increase of limiting current (arbitrary units) with time after dissolution of *o*-AnCu in DMF—$LiClO_4$ (0.1 *M*) solutions.

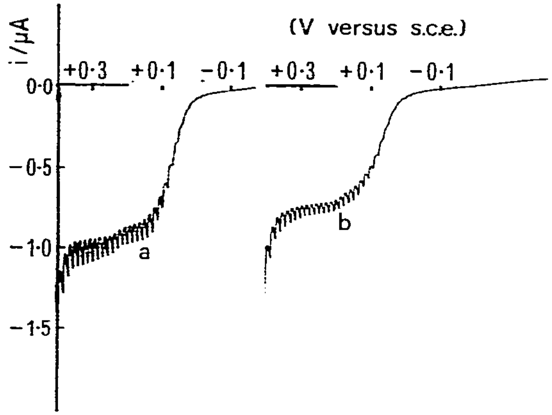

Fig. 2. Anodic waves of *o*-AnCu (a) and *p*-TolCu (b) in DMF—$LiClO_4$ (0.1 *M*) at 0°C.

TABLE 1

CHARACTERISTICS OF THE ANODIC WAVE IN VARIOUS MEDIA AT 0°C

Compound	Medium	c (mg l^{-1})	i (μA)	$E_{1/2}$ (V vs. SCE)	$\Delta E/\Delta \log[id - i/i]$ (mV)
o-AnCu	DMF—$LiClO_4$	73.0	0.38	+0.063	55
o-AnCu	DMF—$(NEt_4)ClO_4$	170.0	0.46	+0.062	39
o-AnCu	Py—$(NEt_4)ClO_4$	95.0	0.38	—0.68(max)	
p-TolCu	DMF—$LiClO_4$			+0.070	56
I	DMF—$LiClO_4$	180.0	0.23	+0.050	62
II	DMF—$LiClO_4$	270.0	0.78	+0.10	

TABLE 2

CHARACTERISTICS OF THE CATHODIC WAVE IN Py—$LiClO_4$ 0.1 *M* at 0°C

Compound	c (mg l^{-1})	i (μA)	$E_{1/2}$ (V vs. SCE)	$\Delta E/\Delta \log[i/id - i]$ (mV)
o-AnCu	459.1	2.96	—0.693	52
p-TolCu			—0.695	54
I	1365.0	3.20	—0.695	57
II	321.0	0.80	—0.694	50
$[CuPy_4]ClO_4$	417.0	1.44	—0.689	49

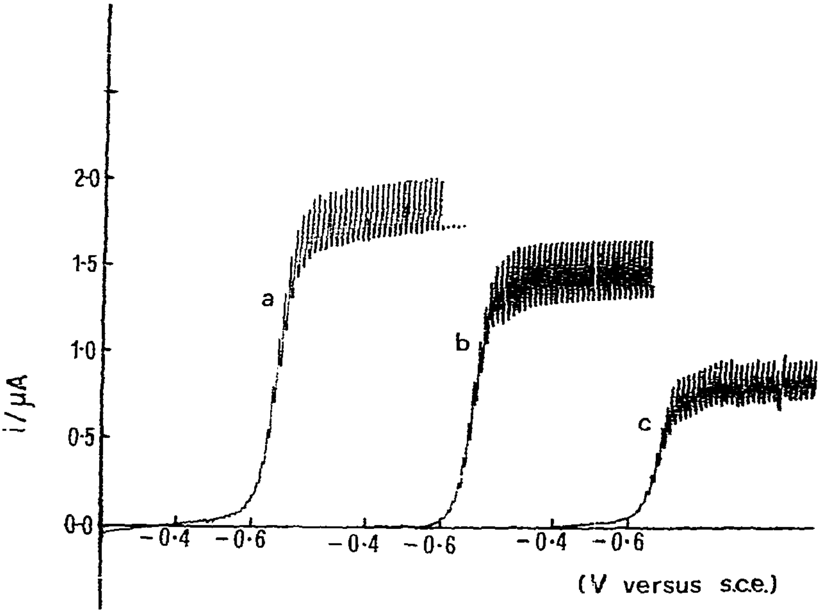

Fig. 3. Cathodic waves of *o*-AnCu (a), *p*-TolCu (b), *p*-TolCuPy$_4$LiClO$_4$ (c) in Py—LiClO$_4$ (0.1 *M*) at 0°C.

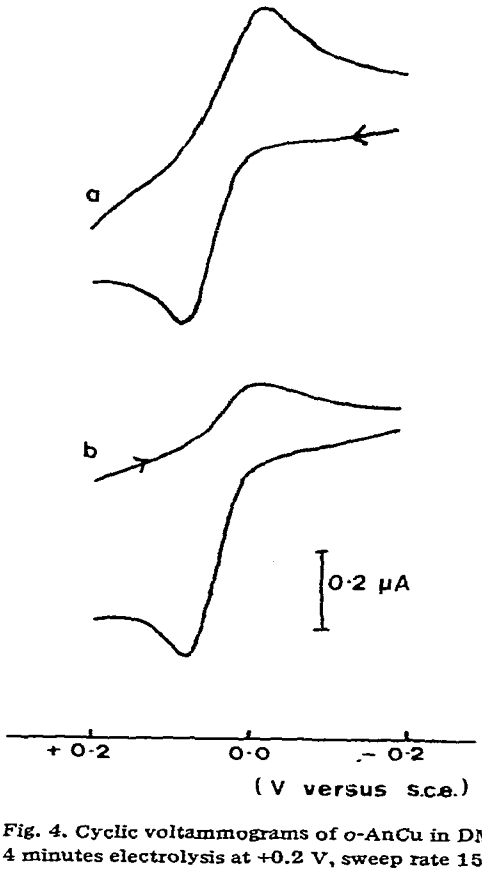

Fig. 4. Cyclic voltammograms of *o*-AnCu in DMF—LiClO$_4$ (0.1 *M*), 0°C, sweep rates 150 mV/sec (a); after 4 minutes electrolysis at +0.2 V, sweep rate 150 mV/sec (b).

conditions. The cathodic wave occurs at about the same potentials (Table 2, Fig. 3).

The oxidation products formed by the electron transfer process from *o*-AnCu at the DME appear to be stable on the time scale of cyclic voltammetry down to a sweep rate of about 150 mV/sec. For lower sweep rates the decomposition of the primary oxidation product becomes apparent from the decrease of the cathodic peak (Fig. 3).

Controlled potential oxidation of *o*-AnCu in DMF—$\mathrm{LiClO_4}$ in the region of the anodic wave at +0.3 V vs. SCE gives a pale yellow solution with formation of a dark coloured precipitate on the anodic mercury pool. The total number of electrons involved is $n = 1$. After oxidation the solution shows a cathodic wave ($E_{1/2}$ — 0.03 V) and can be reduced at —0.4 V vs. SCE giving copper with $n = 0.7$ (calculated from the amount of starting organocopper compound). Controlled potential reduction of *o*-AnCu in Py—$\mathrm{LiClO_4}$ at —0.8 V vs. SCE yields a clear and colourless solution. The number of F/mole consumed increases from $n = 0.5$ to 0.75 with decreasing concentration of the starting solution.

Discussion

The increase of the polarographic current with time when the solid $(o\text{-AnCu})_8$ and I are dissolved in pyridine, points out the dissociation of clusters into smaller aggregates in solution. In DMF—$\mathrm{(NEt_4)ClO_4}$ and DMF—$\mathrm{LiClO_4}$ the examined compounds are oxidized at potentials between +0.06 and —0.10 V vs SCE showing relatively little influence of the nature of the aryl group or supporting electrolyte. Electro-oxidation of $(\mathrm{CuR})_n$ in DMF gives a transient $[\mathrm{RCu}]^+$ species, which undergoes decomposition to solvated cuprous ion and products of reaction of aryl radicals. The cuprous ion can be electroreduced to copper amalgam. In Py—$\mathrm{(NEt_4)ClO_4}$ the same pattern is found at more negative potentials.

$$\mathrm{RCuL}_n \xrightarrow{-e} [\mathrm{RCuL}_n]^+ \rightarrow [\mathrm{CuL}_m]^+ + \text{unidentified decomposition products} \qquad (1)$$

$$[\mathrm{CuL}_m]^+ \xrightarrow{e} \mathrm{Cu(Hg)} + m\mathrm{L} \qquad (2)$$

(L = DMF or Py)

In Py—$\mathrm{LiClO_4}$ all the compounds examined undergo electroreduction at about the same potentials at which oxidation occurs in Py—$\mathrm{(NEt_4)ClO_4}$. The strong shift of the redox potentials towards more negative values relative to DMF solutions points out the increase in nucleophilicity of the copper atom by coordination of pyridine. In the presence of $\mathrm{LiClO_4}$ this leads to formation of complex cations, which are assumed to be of $[\mathrm{RCuPy}_x\mathrm{Li}]^+$ type. The overall electrode process would be:

$$[\mathrm{RCuPy}_x\mathrm{Li}]^+ + e \rightarrow [\mathrm{RCuPy}_x\mathrm{Li}]^0 \qquad (3)$$

$$[\mathrm{RCuPy}_x\mathrm{Li}]^0 \rightarrow \mathrm{Li}^+ + \mathrm{Cu}^0 + \text{decomposition products of } \mathrm{R}^- \qquad (4)$$

Complexes I and II very likely give in pyridine solutions the same electroactive species as $(\mathrm{RCu})_n$.

Formation of complexes I and II from ethereal suspensions by addition of pyridine and $LiClO_4$ involve exchange of one Cu^I with one Li^I atom and reduction of an other Cu^I to Cu^0, as is shown by the following equation, which of course does not represent the actual reaction sequence. The pyridine ligand is omitted for simplicity.

$$4\ Cu^IR + 4\ LiClO_4 \rightarrow R_3Cu^0Cu_2^ILi_4(ClO_4)_3 + R + Cu^IClO_4$$

I and II as formulated represent a novel type of ate complexes, which deviate from the usual $R/Cu + Li = 1$ ratio found in all known examples [9]. The investigations on the chemistry of I and II are being carried out to collect evidence for the actual structure. Compounds of these kind of stoichiometries have been isolated or postulated in the organocopper series [4a,10].

Interaggregate exchange reactions between organocopper ate complexes and organolithium compounds were previously reported. The new species exhibit higher reactivity or selectivity as compared with the starting compounds [11—13].

The partial reduction of Cu^I by a non-electrochemical reaction path is consistent with the number of electrons consumed per molecule $n < 1$, from relatively concentrated pyridine solutions of $(CuR)_n$.

Conclusion

Oxidation potentials of arylcopper compounds can be measured in suitable solvents by polarography and cyclic voltammetry. These potentials do not refer necessarily to the structures existing in the solid state but to the aggregates which can be formed in solution by dissociation of the parent clusters and coordination of solvent and ions of the supporting electrolyte.

Differences in donor power of the solvent appear to be more effective in displacing the redox potential than the difference in nature of the aryl group between *o*-anisyl and *p*-tolyl.

Increase of nucleophilicity of the organocopper complex due to the pyridine in the presence of $LiClO_4$ leads to formation of a complex pyridinato cation of copper and partial reduction to Cu^0.

Experimental

Chemicals

All reactions and measurements were carried out in a dry oxygen-free atmosphere. Solvents were accurately deaerated by bubbling dry nitrogen before use. DMF and pyridine were carefully dried on type 4A molecular sieves. $(NEt_4)ClO_4$ and $LiClO_4$ were recrystallized and dried under vacuum at 40 and 150°C respectively. *o*-AnCu and *p*-TolCu were prepared after Camus et al. [6], $[Cu(Py)_4]ClO_4$ after Chen et al. [8].

Preparation of compounds I and II

A slight excess of Py over the molar ratio 4/1 was added to a suspension of about 0.5 g of the organocopper complex in ether (20 ml), giving a clear orange-red solution. This turned immediately to yellow by addition of an equimolecular amount of $LiClO_4$, with formation of a yellow precipitate. The solid was filtered off and washed repeatedly with ether. I: Found: Cu, 10.57; Li, 1.61; Py, 52;

o-An, 18.1. $An_3Py_{12}Cu_3Li_4(ClO_4)_3$ calcd.: Cu, 10.67; Li, 1.55; Py, 53.11; *o*-An, 18.15%. II: Found: Cu, 11.11; Li, 1.70; Py, 57; Tol, 16.1. $Tol_3Py_{12}Cu_3Li_4(ClO_4)_3$ calcd.: Cu, 10.96; Li, 1.60; Py, 54.57; Tol, 15.89%. The arene and pyridine were determined gas-chromatographically after decomposition of the complexes with methylene chloride (Py value rather approximate, owing to tailing of the corresponding peak). Thermal decomposition of I in boiling xylene afforded about 80% of the theoretical amount of anisole.

Apparatus

Polarographic measurements were made on an AMEL model 471 multipolarograph with model 260 Stand and X-Y recorder. Cyclic voltammetry was investigated on an AMEL model 448 polarograph with 448/YA and 448/XB attachments. A model 694 universal cell was used. The characteristics of the DME (DMF—0.1 $(NEt_4)ClO_4$ at 25°C) were flow rate m = 1.297 mg^{-1}; drop time = 3 sec; height of mercury level = 64 cm.

A Metroohm saturated calomel electrode with a saturated aqueous solution of NaCl was used as a reference electrode. This was separated by means of a liquid bridge containing the same supporting electrolyte as the investigated solution. A platinum ring was used as the counter electrode in the three-electrode arrangement. Cyclic voltammetry was carried out in the same apparatus. Controlled potential electrolysis was carried out with an AMEL model 557/SU potentiostat equipped with a recorder and a model 563 multipurpose unit. Experiments were made in a model 693 universal cell; a mercury pool of ca. 6 cm^2 was used as the working electrode in the three-electrode arrangement.

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