Reactions of 1,2-Dicarbonyls with Metallic Copper under Argon and Dioxygen. Oxidative C–C Bond Scission by Metallic Copper†

Gábor Speier* **and Zoltán Tyeklár**
Institute of Organic Chemistry, Veszprém University of Chemical Engineering, 8201 Veszprém, Hungary

1,2-Diketones such as benzil, 2,2′-furil, and di(2-pyridyl) diketone react with metallic copper in pyridine under argon by electron transfer from the copper to the 1,2-diketones, giving semidionato copper(I) and μ-enediolato-dicopper(I) complexes in low equilibrium concentrations as detected by e.s.r. and visible absorption spectra. Under dioxygen with a 1 : 1 stoicheiometry of copper to 1,2-diketones, a facile oxidative C–C bond cleavage occurs to give well defined carboxylate copper(II) complexes with ligands such as pyridine, 2,2′-bipyridine, and *NNN′N′*-tetramethylethylenediamine.

The oxidative cleavage of catechols to muconic acids is catalysed by the iron-containing catechol 1,2-dioxygenase[1–4] or by a similar enzyme containing copper[5] in its active site. In these enzymatic reactions *o*-quinones have been assumed to be formed.[6] The modelling of these reactions with relevance to catechol 1,2-dioxygenase is of current interest. In these studies mainly iron[7] and copper[8] as well as vanadium,[9] ruthenium,[10] and cobalt[11] complexes have been used with substrates such as catechols and *o*-quinones. It has been shown that 1,2-dicarbonyl compounds,[12,13] *o*-quinones,[14] and enedioles[13] or catechols[15] are oxidatively cleaved to the corresponding carboxylic acids by dioxygen in the presence of copper(I) halides in pyridine and subsequent hydrolysis.

In these model reactions the formation of copper–oxygen complexes is assumed, but knowledge of their true structure is limited.[16–19] Probably an oxygenated copper(II) species formed under the conditions is capable of inducing the ring scission, eventually yielding copper(II) carboxylates. In the case of strongly oxidizing quinones, semiquinonato and catecholato copper complexes may be formed first and their oxygenolysis then lead to the same results.[14,20,21] Considering the potentials of the Cu^{II}–Cu^{I} (−0.153 V[22]) and Cu^{I}–Cu^{0} (−0.521 V[22]) redox couples, it seems apparent that the more electronegative copper(0) complexes would be more suitable for providing electrons either to the dioxygen molecule or to the 1,2-dicarbonyl substrates. Since no well defined copper(0) complexes have been reported,[23,24] we considered the utility of metallic copper in heterogeneous systems. It has been shown that metallic copper transfers electrons to strong π acids in isocyanide as the solvent to give radical anions detected by e.s.r. spectroscopy.[25] On the other hand it has been observed that benzoin can be oxidized to benzoic acid by dioxygen in pyridine (py) in the presence of metallic copper.[26] In this paper we present our results on the reactions of metallic copper with some 1,2-dicarbonyl compounds as rather good electron acceptors, in pyridine under argon and also in a dioxygen atmosphere to elucidate the chemistry of the oxidative C–C bond scission.

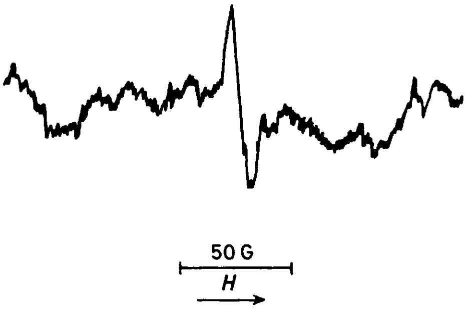
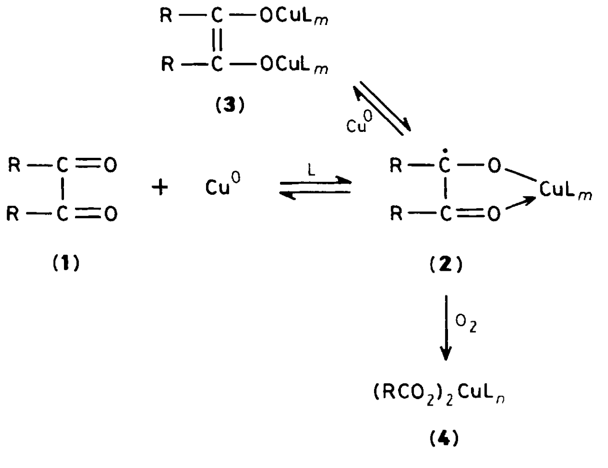


Figure 1. E.s.r. spectrum of complex (2a) in pyridine, $g = 2.0016$



	R	L	n
(a)	Ph	py	2
(b)	Ph	bipy	1
(c)	Ph	tmen	1
(d)	C_4H_3O	py	2
(e)	C_5H_4N	py	0

Scheme.

Results and Discussion

In the reaction of benzil with copper powder in pyridine under argon a slight darkening of the yellow solution has been observed. The e.s.r. spectrum of this brownish solution indicates the presence of paramagnetic species (Figure 1). A poorly resolved absorption of low intensity at $g = 2.0016$ reveals the presence of a semidione radical anion (2a)[27] (Scheme). The quality of the signal is due to its low concentration and transient nature under the conditions. Even at lower temperature the quality could not be improved. The solution soon becomes e.s.r.-silent without apparent change of its colour. No e.s.r. signal related to the formation of copper(II) species is observed. The

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† *Non-S.I. unit employed:* G = 10^{-4} T.

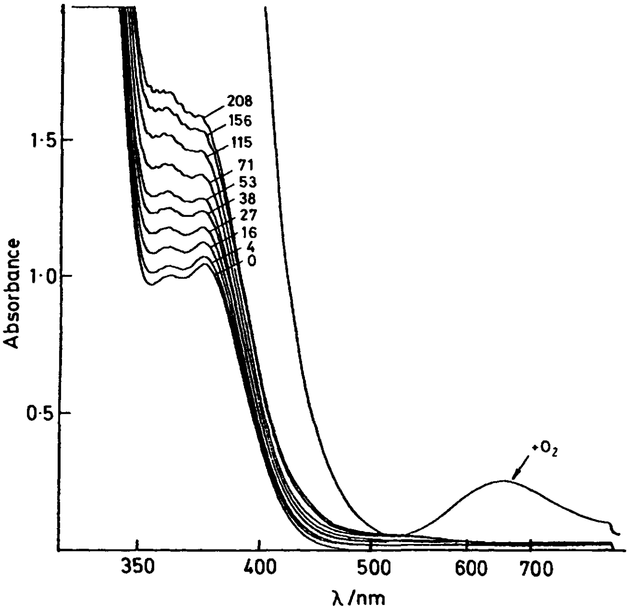

Figure 2. Visible spectrum of the reaction products from benzil with Cu^0 in pyridine as a function of time (min); [PhCOCOPh] = 2.7 × 10^{-2} mol dm^{-3}

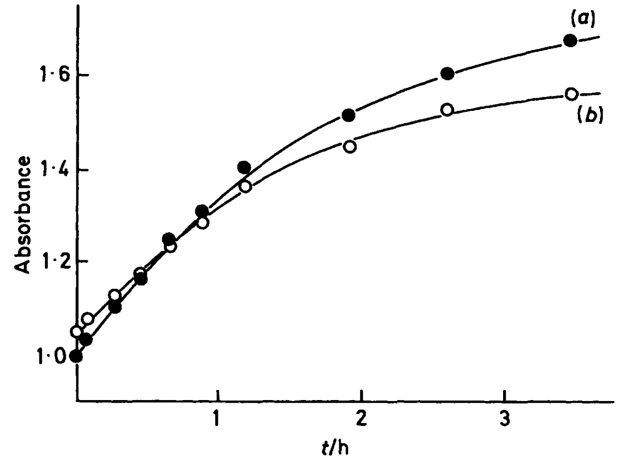

Figure 3. The change in the maxima of m.l.c.t. bands in the visible spectrum of complex (**3a**) in the reaction of benzil with Cu^0 in pyridine as a function of time. [PhCOCOPh] = 2.7 × 10^{-2} mol dm^{-3}

visible spectrum of the solution (Figure 2) lacks the presence of absorptions characteristic of *d–d* transitions of copper(II) species but absorptions at 366 and 383 nm can be regarded as metal-to-ligand charge-transfer (m.l.c.t.) bands of a μ-enediolato-dicopper(I) pyridine complex (**3a**). On exposure to air a new band at 650 nm develops, which may be assigned to a *d–d* transition of a copper(II) species. For many copper(I) complexes with π-donor ligands, absorption bands in the visible region have been assigned to m.l.c.t.[28] The concentration of the μ-enediolato-dicopper(I) pyridine complex (**3a**) increases with time and approaches the equilibrium concentration as shown in Figure 3, where the absorbances of the two c.t. bands are plotted against time. These facts support the assumption that under the conditions no e.s.r.-active species, *i.e.* copper(II) or semidione, is present and the equilibria in the Scheme are shifted largely to the side of (**1**) and partly in favour of (**3**) as shown in Figure 3.

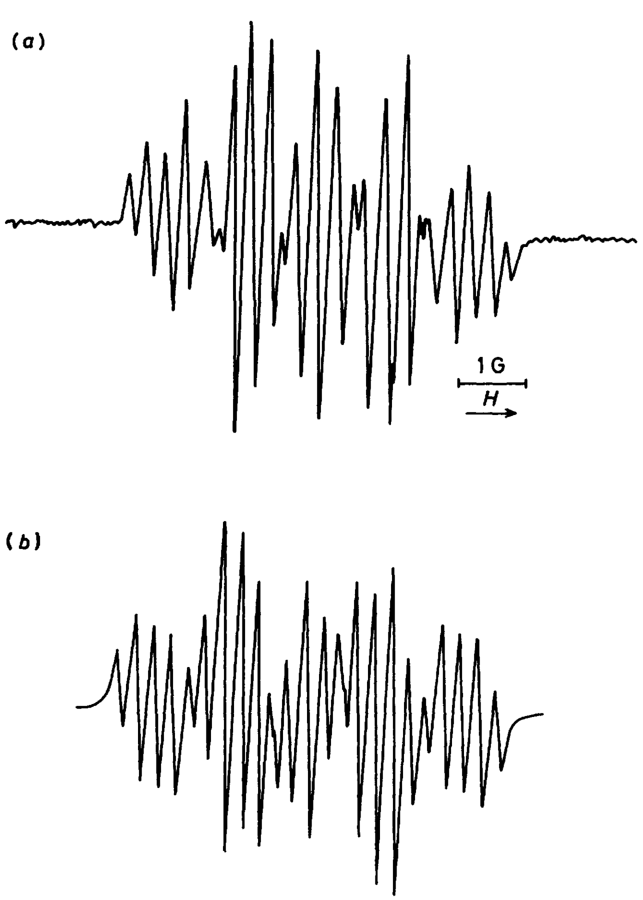

Figure 4. E.s.r. spectrum (*a*) of complex (**2d**) in pyridine (g = 2.0016) and its simulation (*b*) (simulated coupling parameters: a_{Cu} = 0.26, a_{H} = 0.26, a_{H} = 1.98, and $a_{2\mathrm{H}}$ = 1.26 G)

In the reaction of 2,2′-furil (**1d**) with copper powder in pyridine under argon a permanent signal with hyperfine structure appears in the e.s.r. spectrum[29] [Figure 4(*a*)] indicating a considerable higher stability of the semidione copper complex (**2d**) from 2,2′-furil compared to that from benzil. Adding 2,2′-bipyridine (bipy) to the solution containing (**2d**) gave no change in the e.s.r. spectrum. On addition of *NNN′N′*-tetramethylethylenediamine (tmen) the original feature of the spectrum collapsed to a poorly resolved signal. Simulation of the e.s.r. hyperfine structure of compound (**2d**) [Figure 4(*b*)] supported the assumption that the di(2-furil) semidionato ligand is co-ordinated to the copper(I) centre. The spin population on the copper(I) is low compared to that of the radical anion (**2d**). The semidione anions prepared by reduction from 1,2-diketones form a mixture of *cis* and *trans* isomers. The two isomers give rise to differences in the e.s.r. spectra since in the case of the *cis* forms larger coupling constants with respect to atoms in the R groups have been found.[30,31] The better planarity in the *trans* isomers compared to the *cis* ones may be responsible for the different delocalisation of the unpaired electron. The simulated coupling parameters (see Figure 4) indicate that in the di(2-furil) semidionato copper(I) complex (**2d**) the two 2-furyl rings are non-equivalent, probably due to deviation of planarity in the semidionate ligand.

In the case of the copper(I) semidionate complex (**2d**) the signals are stable and could also be recorded after several days. The solution showed absorptions at around 420 nm in the visible spectrum. These may arise from (**2d**) but also form the μ-enediolate complex (**3d**) so that its assignment remains dubious. Considering the equilibria in the Scheme with 2,2′-furil the

Table 1. Characterization of carboxylato copper(II) complexes

Complex	Colour	Yield (%)	M.p. (°C)	Reaction time (h)	Analysis* (%)			
					C	H	N	Cu
(**4a**) $[Cu(C_6H_5CO_2)_2(py)_2]$	Blue	92	315	6	61.9 (62.1)	4.4 (4.4)	6.0 (6.0)	13.5 (13.7)
(**4b**) $[Cu(C_6H_5CO_2)_2(bipy)]$	Blue	95	234	7	62.0 (62.4)	3.9 (3.9)	6.1 (6.1)	13.8 (13.8)
(**4c**) $[Cu(C_6H_5CO_2)_2(tmen)]$	Blue	93	195	5.5	56.0 (56.9)	6.2 (6.3)	6.6 (6.6)	15.3 (15.1)
(**4d**) $[Cu(C_4H_3CO_2)_2(py)_2]$	Violet	97	104	4	54.3 (54.1)	3.8 (3.6)	6.3 (6.3)	14.1 (14.3)
(**4e**) $[Cu(C_5H_4NCO_2)_2]$	Violet	100	183	3.5	46.8 (46.8)	2.6 (2.9)	9.1 (9.2)	20.9 (20.7)

* Theoretical values in parentheses.

Table 2. Infrared (cm^{-1})^a and electronic^b spectra of carboxylato copper(II) complexes

Complex	$\nu(CO_2)_{asym.}$	$\nu(CO_2)_{sym.}$	$\lambda_{max.}$/nm (log ε)
(**4a**)	1 601	1 379	263 (3.49), 266 (3.49), 269 (3.46), 274 (3.37), 299 (sh) (2.77), 408 (1.45), 720 (1.26)
(**4b**)	1 554	1 397	302 (4.29), 313 (4.25), 427 (2.20)
(**4c**)	1 551	1 379	263 (4.42), 298 (sh) (4.15), 311 (sh) (4.04), 463 (2.66), 658 (2.38)
(**4d**)	1 600	1 352	253 (4.5), 292 (sh) (3.8), 758 (2.2)
(**4e**)	1 628	1 340	259 (sh) (4.59), 261 (sh) (4.58), 263 (4.58), 266 (4.58), 269 (sh) (4.57), 273 (sh) (4.56), 291 (sh) (4.54), 305 (sh) (4.52), 429 (4.37), 614 (4.21)

^{a} Nujol mulls. ^{b} In CH_2Cl_2.

Table 3. E.s.r. parameters* and magnetic moments at room temperature

Complex	$g_{\perp}$	$g_{\parallel}$	$\mu_{eff.}$
(**4a**)	2.07	2.45 (weak)	1.79
(**4b**)	2.09	—	1.87
(**4c**)	2.10	2.28	1.83
(**4d**)	2.06	2.29	1.69
(**4e**)	2.09	2.18	1.84

* From solid samples.

situation is somewhat different from that with benzil in yielding a higher concentration of (**2d**).

The reaction product of di(2-pyridyl) diketone with metallic copper is e.s.r.-silent even at low temperature, showing the absence of any paramagnetic species. The visible absorption bands at 349 and 372 nm provide evidence for the formation of the μ-enediolato-dicopper(I) pyridine complex (**3e**). These bands can be attributed to m.l.c.t. transitions.

In that case the concentration of the semidione copper(I) complex is the lowest and the μ-enediolato-dicopper(I) complex can be ascertained only on the basis of the visible spectrum.

From these results it can be concluded that the 1,2-dicarbonyl compounds (**1a**)—(**1e**) in pyridine solvent react with metallic copper in heterogeneous systems by electron transfer from copper(0) to the 1,2-diketones, resulting in semidionato-copper(I) (**2**) and μ-enediolato-dicopper(I) complexes (**3**) with py, bipy, and tmen as auxiliary ligands (Scheme). There is an equilibrium among the species (**1**)—(**3**) resulting in only small concentrations of (**2**) and (**3**). Furthermore, depending on the 1,2-diketone, in the case of 2,2′-furil the semidione complex (**2d**) and with benzil and di(2-pyridyl) diketone the μ-enediolato complexes (**3a, e**) show slightly enhanced stability.

Benzil, 2,2′-furil, and di(2-pyridyl) diketone react with metallic copper (ratio 1:1) under an atmosphere of dioxygen in pyridine. In all cases an induction period was observed. With 2,2′-furil in certain instances days were required even when irradiating with u.v. light. Heating usually shortened the induction period. In the reaction of benzil with metallic copper the addition of copper(I) benzoate reduced the induction period. At room temperature the dioxygen uptake was complete within 8—10 h. For 1 mol of the diketone, 1 mol dioxygen was consumed. After acidic hydrolysis of the oxygenated mixture using benzil as the diketone, benzoic acid was isolated as the only organic product. This shows unambiguously that the C(1)–C(2) bond in benzil is oxidatively cleaved in the presence of metallic copper and hints at the formation of carboxylato copper complexes. Indeed, it was shown that benzil, 2,2′-furil, and di(2-pyridyl) diketone in the presence of metallic copper and amine ligands such as py, bipy, and tmen are easily oxygenated and as a result of oxidative C(1)–C(2) bond cleavage the analytically pure carboxylato copper(II) complexes (**4**) (Scheme) are formed. The yields, physical and analytical data are collected in Table 1.

The number of nitrogen-containing ligands in complexes (**4**) varies comprising two unidentate py [(**a**) and (**d**)], one bidentate bipy or and tmen [(**b**) or (**c**)], and none in the case of the bidentate pyridine-2-carboxylate ligand. Complexes (**4**) show characteristic $\nu(CO_2)$ frequencies and electronic spectra (Table 2). The carboxylate co-ordination seems to be unidentate according to the $\nu(CO_2)_{asym} - \nu(CO_2)_{sym}$ values.[32] The room-temperature magnetic moments suggest that the complexes are mononuclear or in the case of association they exhibit slight or no antiferromagnetic coupling.[33] These assumptions are also supported by the powder e.s.r. spectra (Table 3). Compound (**4b**) exhibits an isotropic spectrum suggesting grossly misaligned 'tetragonal' axes.[34] All other carboxylato copper(II) complexes show axial spectra with lowest $g < 2.03$. Complex (**4e**) has a planar structure.[35]

The mechanism of the oxygenolysis of the 1,2-dicarbonyl compounds by metallic copper to carboxylato copper(II) complexes (**4**) is uncertain. In complexes (**2**) and (**3**) both the organic ligands and copper(I) are redox-active. It is reasonable to assume that either (**2**) or (**3**) reacts with dioxygen in the former case *via* radical pairing or oxidative addition leading to peroxidic species or a trioxametallocycle, which decompose after C–C bond scission to complexes (**4**). In the latter case the reaction of (**3**) with dioxygen may give, *via* electron transfer from the μ-enediolate ligand to dioxygen, a semidione complex (**2**) and oxygenated copper species. Then either a pathway mentioned previously or that involving oxygenated copper species leads to complexes (**4**). The elucidation of the mechanism of oxygenolysis needs further experimental work.

Experimental

All reactions (except those with dioxygen) were carried out in an atmosphere of pure, dry argon using standard Schlenk-type glassware and techniques. Infrared spectra were recorded on a Specord 75 IR (Carl Zeiss, Jena) spectrometer, visible spectra on a Specord M 40 (Carl Zeiss) spectrophotometer, e.s.r. spectra on a JEOL JES-FE3X spectrometer between 20 and −180 °C. The magnetic susceptibilities were determined on a Bruker B-E 10B8 system. Melting points were measured on an Electrothermal Apparatus. Elemental analyses were carried out in the Microanalytical Laboratory of this University.

Copper powder (Reanal) and 2,2′-bipyridine (Reanal) were used as supplied. *NNN′N′*-Tetramethylethylenediamine (Reanal) was distilled before use and stored on activated molecular sieve (A-4) under argon. Benzil,[36] 2,2′-furil,[37] and di(2-pyridyl) diketone[38] were prepared according to literature methods. Pyridine was purified by standing over KOH and then distilled over CaH_2 under argon.

E.S.R. Experiments.—In a Schlenk tube, the 1,2-diketone (10^{-2} mmol), copper powder (6.4 mg, 0.1 g-atom), and pyridine (10 cm^3) were stirred at room temperature under argon for 2 h. A slight darkening of the yellow solution was observed. The supernatant was then transferred to an e.s.r. tube under argon and sealed. The spectra were run at room temperature. The simulation for the semidione copper(I) complex (**2d**) was carried out on a EMU-11 (KFKI) computer, spectra being generated by superposition of the Lorentz curves so derived. The amplitude was calculated at 0.1-G intervals.

Oxygenation of 1,2-*Diketones* (**1a**)—(**1c**) *in the Presence of Metallic Copper: General Procedure.*—The 1,2-diketone (10 mmol), copper powder (0.64 g, 10 g-atom), the chelating ligand tmen or bipy (10 mmol) or none of it, and pyridine (30 cm^3) were stirred under an atmosphere of dioxygen at room temperature until dioxygen uptake ceased (250 cm^3). The pyridine was then evaporated under reduced pressure and the residue triturated with diethyl ether (40 cm^3), filtered off, washed with ether, and dried *in vacuo* to give the carboxylato copper(II) complexes (**4**). Their characterization and yields are given in Table 1.

Acidic Hydrolysis of Dibenzoatobis(pyridine)copper(II) (**4a**).—Compound (**4a**) (1.36 g, 3 mmol) was treated with 10% hydrochloric acid (10 cm^3) and the colourless material precipitated was extracted with ether (3×10 cm^3). The joint organic layers were dried over $MgSO_4$ and the ether evaporated *in vacuo* to give benzoic acid (0.36 g, 98%), m.p. 121—122 °C (lit.,[39] 122.4 °C).

Acknowledgements

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