ACTIVATION OF MOLECULAR OXYGEN BY COPPER SALTS IN ACETIC ACID AND APPLICATION TO OXIDATION OF 1,4-DIPHENYLBUTADIENE AND OF 2,6-DI-t-BUTYLPHENOL: A 2,4-DIPHENYLFURAN SYNTHESIS

I. MAMALIS, A. F. NOELS, G. TIHANGE, R. WARIN, P. TEYSSIÉ

Laboratoire de Chimie Macromoléculaire et de Catalyse Organique, Université de Liège, Institut de Chimie, B 6, Sart Tilman 4000 Liège (Belgium)

and A. J. HUBERT

Laboratoire de Synthèse Organique et de Catalyse, Université de Liège, Institut de Chimie, B 6, Sart Tilman 4000 Liège (Belgium)

Summary

The stoichiometry and the kinetics of molecular oxygen absorption by the Cu(OAc)$_2$–LiBr system in solution in acetic acid–acetic anhydride (1:1) mixture has been investigated in the presence respectively of 1,4-diphenyl-1,3-butadiene (3) and of phenols as substrates.

The former affords 2,5-diphenylfuran (5), whereas 2,6-di-t-butylphenol (10) leads to the formation of quinoid derivatives (12).

The results are discussed on the basis of a duality of mechanism: the copper–LiBr catalyst used acts both as a dioxygen activation catalyst and as a halogenation system, this last aspect receiving further support from the copper halide-catalyzed oxidation of indene.

Introduction

Copper-based catalysts are widely used in oxidation processes of organic substrates on both industrial and laboratory scales. For example, oxychlorination of alkanes or the acetic anhydride synthesis from acetaldehyde are typical copper-based oxidation processes [1]. In contrast, the oxidative coupling of acetylenes are particularly useful as bench-scale reactions, whereas the oxidation of 2,6-dimethylphenol is the basis of the development of important commercial thermoplastics with outstanding chemical and mechanical properties [3a]. Other more particular oxidation reactions based on copper catalysis have been reported, such as the oxidative decarbonylation of aldehydes [4], the oxidation of enamines [5, 6] and the acetoxylation reactions of butadiene [7].

The oxidation of phenols has also been extensively investigated in relation to important enzymatic systems such as tyrosinases [8]: in this context various biomimetic copper-catalyzed oxidations, such as that of muconic esters [8, 9] or the formation of quinones from phenols [9], have been abundantly discussed in the literature.

Recently, an investigation of copper-catalyzed oxycyanation of conjugated dienes has received much attention as a straightforward access to dehydroadiponitrile [10]. From a mechanistic point of view, the kinetics of the Cu(I)/LiCl–O$_2$ reactions in acetic acid by Henry [11] is particularly informative.

Results and discussion

We have previously reported on the oxygen absorption promoted by the acetoxylation copper-based catalyst [Cu(OAc)$_2$–LiBr] [12]. Significant information relative to the role of LiBr as an efficient promoter of copper catalysts in hydrocyanation [13, 14] and acetoxylation processes [7] has been obtained both from spectral (EPR and particularly ^{7}Li NMR) measurements [12] and also from the rates of oxygen uptake by the catalyst in the HOAc–Ac$_2$O medium: the role of additives such as acetic anhydride and water has thus been established.

We wish now to complete the previous publications by reporting on the particular behaviour of two typical substrates: 1,4-diphenyl-1,3-butadiene (3) and 2,6-di-t-butylphenol (10).

In contrast to butadiene and isoprene, diphenylbutadiene does not afford the corresponding diacetoxyalkenes [7] (1,4- and 1,2-addition products) despite the fact that the kinetics of oxygen absorption are very similar (Fig. 1 curves a and b): instead, 2,5-diphenylfuran (5) is obtained in moderate yield (30%) with this substrate.

The di-t-butylphenol case leads also to particularly significant observations: fast oxygen absorption is observed when the phenol is added to the copper catalyst in the HOAc–Ac$_2$O system (Fig. 2) and the quinoid derivative (12) is formed in 60% yield. The curves of Fig. 2 are very similar to those reported by Capdevielle and Maumy [15] when using Cu–O$_2$ complexes such as Cu$_4$Cl$_4$O$_2$ as catalysts (see also [15] for copper-catalyzed oxidation of phenols).

One single quinoid product (12) was isolated from the reaction mixture in 60% yield, in contrast to the 2,6-di-t-butyl-4-methylphenol case which led to the formation of a complex mixture of products. On the other hand, pyrocatechol afforded mainly small amounts of brominated products, together with the diacetate resulting from acetylation of the phenolic groups (it is noteworthy that this last reaction appears to be significantly catalyzed by this copper catalyst system: a result to be related to the recently described cobalt acetate-catalyzed esterification of phenols [16]). However, both components of the catalyst (Cu and Li salts) present the same slight catalytic effect which may be related to a Lewis acid catalytic activity.
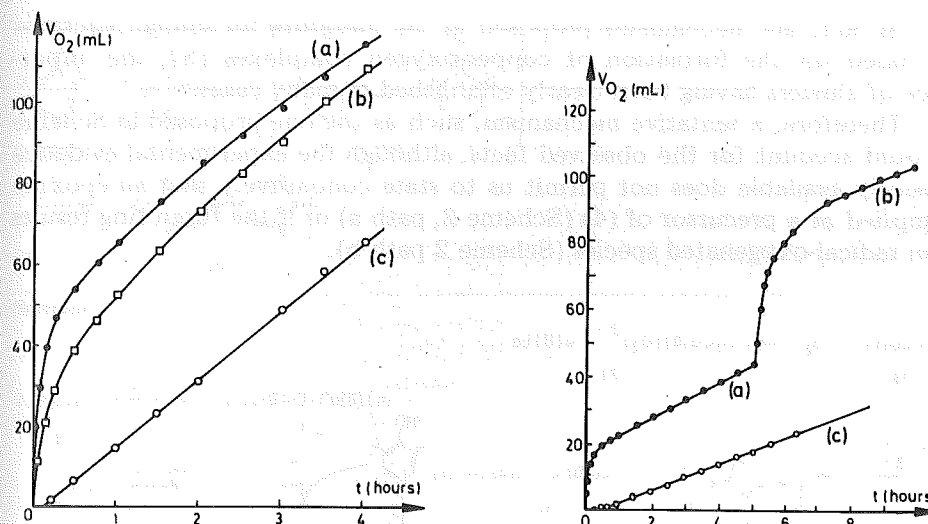
Fig. 1. Kinetics of absorption of dioxygen by isoprene (a) and 1,4-diphenyl-1,3-butadiene (b) in HOAc–Ac$_2$O; (c) absorption of dioxygen in the absence of substrate [12]. Conditions: Cu(OAc)$_2$ 2.5 mmol, LiBr 10 mmol, substrate 50 mmol; Ac$_2$O 4 ml, HOAc 8 ml; T = 69.5 °C, P_{O_2} = 1 atm.

Fig. 2. Oxidation of 2,6-di-t-butylphenol (10) by Cu(OAc)$_2$–LiBr in HOAc–Ac$_2$O. Conditions: see Fig. 1. 2,6-Di-t-butylphenol: (a) 0.5 mmol, (b) 1.0 mmol added to (a) after 5 h, (c) absorption of dioxygen in the absence of substrate; T = 63 °C.

The mechanisms postulated for the oxidation of phenolic substrates under these conditions stress the key role of dioxygen as an oxidizing agent to regenerate copper(II) and complete the catalytic cycle [3].

In fact, we have already reported that the behaviour of potential intermediates (the dibromides *versus* the epoxides) under diacetoxylation reaction conditions afforded some support to the participation of vinyl-epoxides such as (9) as potential intermediates in the copper-catalyzed oxidations of dienes by molecular dioxygen.

Similarly, the formation of the furan moiety (5), together with the similarity between the oxidation of the phenol (10) under our conditions and the results reported in the literature [3, 8a], also add support to the hypothesis of oxygen transfer from a copper–oxygen complex to the substrate: the same quinoid compound (12) was isolated under our conditions. However, the kinetic features of the oxygen uptake in our work were essentially different from those reported in [8a], due probably to markedly different reaction conditions (solvent, copper complex): the reaction was run with Cu$_2$[(OH)$_2$(ClO$_4$)·H$_2$O] in the aprotic solvent DMF in [8a], whereas the kinetics were performed in acetic acid–acetic anhydride 1:1 in our case (Fig. 2). The main difference between the results reported in Fig. 2 and the curves published in [8a] corresponds essentially to the existence of an oxygen absorption by our system even in the absence of substrate.

In fact, the mechanisms proposed in the literature for similar reactions are based on the formation of copper-oxygen complexes [8], the importance of clusters having been clearly established in many cases.

Therefore, a tentative mechanism, such as the one proposed in Scheme 1, could account for the observed facts, although the experimental evidence presently available does not permit us to state conclusively that an epoxide is implied as a precursor of (4) (Scheme 2, path a) or if the furan ring results from radical-oxygenated species (Scheme 2 path b).

$$2 \, Ln \, Cu(I) + O_2 \longrightarrow LnCu(II)(O_2)^{2-} Cu(II) Ln$$
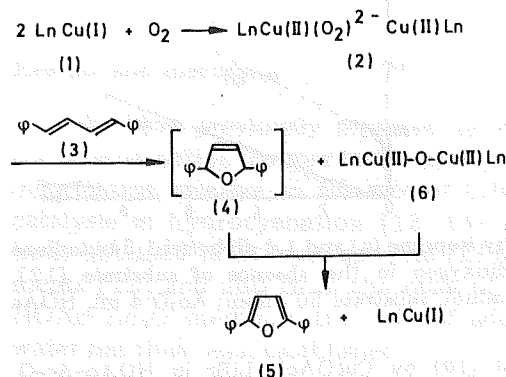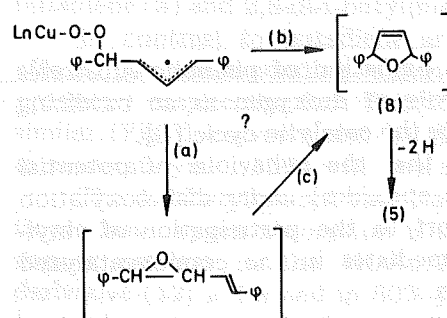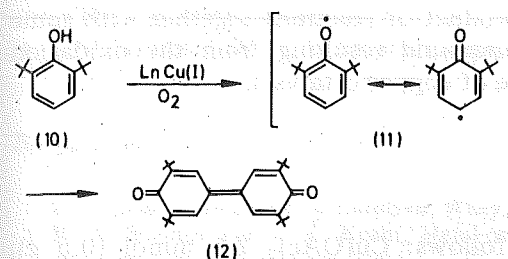

Scheme 1.

(c) = Cu catalyzed epoxide rearrangement

Scheme 2.

The quinoid compound (12) would obviously result from dimerization pathways involving phenoxyl radical species (Scheme 3).

The formation of the quinoid compound (12) has been reported to occur quantitatively during the oxidation of 2,6-di-t-butylphenol (10) by molecular oxygen under basic conditions. Copper catalysis affords therefore the same product in acceptable yield (60%) even under acidic conditions (HOAc–Ac$_2$O). It is noteworthy that oxidation of (10) in acetonitrile in the presence of Cu$_4$Cl$_4$O$_2$ affords the dihydrogenated precursor of (12) [15] (Scheme 4). The present results confirm therefore that the oxidation of

Scheme 3.
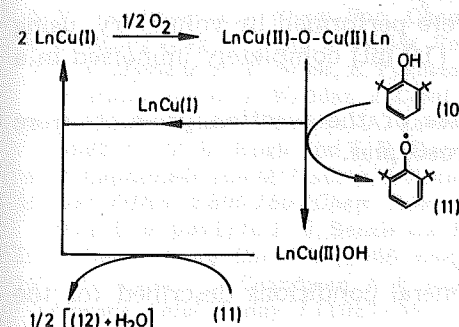
Scheme 4.

phenols can be effectively controlled by adjusting the proper experimental conditions (solvent, catalyst, pH together with the key role of polymetallic species).

It is also noteworthy, as far as the copper-mediated direct oxygen transfer hypothesis is concerned, that hydroxyacetates are formed from butadiene under acetoxylation conditions in the absence of acetic anhydride. Such products could result from the ring opening reaction of vinyloxirane (9) intermediate [12]. However, the halogenating properties of the catalyst are clearly established in the pyrocatechol case, which affords small amounts of brominated substitution products.

Moreover, the participation of halogenated intermediates in related copper-catalyzed oxidations is further supported by the occurrence of iodo derivatives as intermediates in benzoquinone formation during the copper(II) acetate–iodine-catalyzed oxidation of cyclohexanedione derivatives to benzoquinones [20].

Note that the halogenating properties of CuCl$_2$·2H$_2$O–LiCl systems are well established, as shown by classical oxychlorination processes [1]. We have also investigated such reactions with indene in acetic acid [17]: trans-1,2-dichloroindenes are formed as the main product (60%), together with 1-acetoxyindene and a hydrocarbon resulting from the cationic dimerisation in indene owing to the acidity of the medium. In contrast, the CuCl$_2$·2H$_2$O–LiOAc·2H$_2$O system affords a 1:1 mixture of dichloroindanes

and of a chlorhydrin (30% of the product of reaction) together with some indenyl monoacetate (the final compound resulting from the oxidation of indene in acetic acid in the absence of copper catalyst).

Experimental

Standard conditions were as follows: $Cu(OAc)_2$ 2.5 mmol (0.5 g); LiBr 10 mmol (0.85 g); substrate 50 mmol; HOAc 8 ml; Ac_2O 4 ml. P_{O_2} = 1 bar, T = 25 °C. In fact, these conditions correspond to those reported for acetoxylation reactions of butadiene [7, 12].

Measurements of oxygen uptake were performed by volumetry, using a glass reactor fitted with a gas burette (10 ml) completely immersed in a thermostat.

Analytical techniques: the structures of the reaction products were established using IR, UV and NMR spectroscopies.

Isolation of products
Preparation of 1,4-diphenylfuran (5)

The reaction was run under the general conditions described for the diacetoxylation of butadiene [7].

The solvent (HOAc–Ac_2O) was evaporated and the residue was taken up in ether. The ether solution was washed with sodium bicarbonate and water. The organic layer was dried on Sikkon (Fluka) and evaporated.

The residue was recrystallised from ethanol–water, affording white crystals in 60% yield. M.p. = 88 - 89 °C (reported: 91 °C).

The IR spectrum (KBr) shows typical bands at 3050(s) (arom. CH stretching), 1600, 1585, 1500, 1450 (arom. ring), 1210(s) (C—O—C), 750(s) (olefinic CH), 740 and 710(m) (arom. CH) cm^{-1}.

The ^1H NMR spectrum is identical to that reported in the literature [20].

Preparation of 3,5,3',5'-tetra-t-butyl-4,4'-diphenoquinone (12)

The quinone (12) was oxidized for one hour under the conditions reported for the diacetoxylation reaction of butadiene [7, 12] using 2,6-di-t-butylphenol as substrate. The solvent was evaporated *in vacuo*, the residue was taken up in ether and washed with a solution of $NaHCO_3$. The organic layer was dried on Sikkon and the solvent evaporated. The residue was recrystallized from ethanol–dichloromethane (m.p. 244 - 245 °C, reported 246 °C [18]).

The UV and IR spectral data correspond to those reported in the literature [18] but the NMR spectra were not published.

The ^{13}C NMR spectrum in $CDCl_3$ shows peaks at δ (from TMS) = 186.48 (C=O quinone), 150.46 (C=C quat.), 136.14 (O=C—C (t-butyl)), 126.02 (=CH), 36.03 (t-butyl), 29.6 (CH_3) ppm.

The ^1H NMR spectrum in $CDCl_3$ shows peaks at δ (from TMS) = 7.68 (s, 1, =CH) and 1.34 (s, 9, t-butyl) ppm.

References

1 G. Parshall, *Homogeneous Catalysis*, Wiley, New York, 1980, pp. 216 - 221.
2 R. A. Sheldon and J. K. Koshi, *Metal-catalyzed Oxidation of Organic Compounds*, Academic Press, New York, 1981.
3 (a) G. Davies and M. A. El-Shazly, *Inorg. Chem.*, 22 (1983) 1257 and ref. therein; (b) G. Davies, M. F. El-Shazly and M. W. Rupich, *Inorg. Chem.*, 20 (1981) 3757.
4 V. Van Rheenen, *Tetrahedron Lett.*, (1969) 985.
5 V. Van Rheenen, *J. Chem. Soc., Chem. Commun.*, (1969) 314.
6 E. Ballog-Hergovich and G. Speier, *Reaction Kinet. Catal. Lett.*, 22 (1975) 139.
7 I. N. Mamalis, A. F. Noels, E. Puentes, R. Warin, P. Teyssié, A. J. Hubert. J. Grandjean, R. Hubin and D. Y. Waddan, *J. Catal.*, 102 (1986) 357.
8 (a) S. M. Nelson, F. Esho, A. Lavery and M. Dew, *J. Am. Chem. Soc.*, 105 (1983) 5693; (b) M. M. Rogic and T. R. Demmin, *J. Am. Chem. Soc.*, 100 (1978) 5472.
9 P. Capdevielle and M. Maumy, *L'Actualité Chimique*, (1985) 5.
10 *Ger. Offen.* 2 805 760 (*Chem. Abstr.*, 89 (1978) 214, 924); 2 812 151 (*Chem. Abstr.*, 90 (1979) 5941) to R. J. Benzie and D. Y. Waddan.
11 P. Henry, *Inorg. Chem.*, 5 (1966) 688.
12 I. N. Mamalis, J. Grandjean, A. F. Noels, E. Puentes, D. Waddan, A. J. Hubert and Ph. Teyssié, *Catal. Today*, 1 (1987) 59.
13 E. Puentes, I. Mamalis, A. F. Noels and A. J. Hubert, P. Teyssié and D. Y. Waddan, *J. Catal.*, 82 (1983) 365.
14 E. Puentes, A. F. Noels, R. Warin, A. J. Hubert, P. Teyssié and D. Y. Waddan, *J. Mol. Catal.*, 31 (1985) 183.
15 P. Capdevielle and M. Maumy, *Tetrahedron Lett.*, 24 (1983) 5611.
16 S. Ahmad and J. Iqbal, *J. Chem. Soc., Chem. Commun.*, (1987) 114.
17 N. Govers, *Thesis*, Liège, 1975.
18 M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, 22 (1957) 1439.
19 *Proton NMR collection*, Sadtler Research Laboratories, 1980. Spectra no. 12.030M.
20 C. A. Horiuchi, Y. Suzuki, M. Takahashi and J. Y. Satoh, *Chem. Lett.*, (1987) 393.