Kurze Mitteilungen

Maximalumfang: 6 Schreibmaschinenseiten (alles inbegriffen). Bis zum 10. des Monats bei der Redaktion eingehende Manuskripte können günstigenfalls am 15. des folgenden Monats veröffentlicht werden.

$C_{12}B_2Cu_2F_8H_{32}S_4O_7$: A Versatile Redox Catalyst Isolated from Autoxidized $Cu(CH_3CN)_4BF_4$ in Dimethylsulfoxide *

Harald Gampp and Andreas D. Zuberbühler **
Institute of Inorganic Chemistry, University of Basel

Abstract

The autoxidation product of $Cu(CH_3CN)_4BF_4$ in dimethylsulfoxide (DMSO) could be isolated as solid $Cu_2(O)(DMSO)_4(dioxane)(BF_4)_2$, $C_{12}B_2Cu_2F_8H_{32}S_4O_7$. The catalytic activity of this product on the oxidation of 2,6-dimethylphenol (**1**), benzoin (**2**), and 3,5-di-t-butylcatechol (**3**) by molecular oxygen was studied. As oxidation products poly(2,6-dimethyl-1,4-phenylene ether) (**1a**), benzil (**2a**), and 3,5-di-t-butyl-o-benzoquinone (**3a**) were isolated in good yields.

* Received November 17, 1977
** PD. Dr. A. D. Zuberbühler, Institut für Anorganische Chemie, Spitalstrasse 51, CH-4056 Basel

The oxidation of organic substrates catalysed by cuprous chloride in pyridine not only has been claimed as a model system for various oxygenases but also has received interest as a synthetic method in organic chemistry [1–4]. However, attempts to isolate the catalytic species have failed so far and yielded inactive cupric oxide only [3].

In the course of our studies on the autoxidation of Cu(I) in DMSO [5] it turned out that this reaction results in the formation of a versatile redox catalyst. Here we report on the isolation of the active species as a solid and its catalytic action on the oxidation of 2,6-dimethylphenol (**1**), benzoin (**2**), and 3,5-di-t-butylcatechol (**3**) with dioxygen to give poly(2,6-dimethyl-1,4-phenylene ether) (**1a**), benzil (**2a**), and 3,5-di-t-butyl-o-benzoquinone (**3a**), respectively.

The solid catalyst can be precipitated from freshly autoxidized solutions of $Cu(CH_3CN)_4BF_4$ [6] in DMSO by a 5–10 fold excess of benzene, chloroform, diethylether, or dioxane. It is filtered off and dried under vacuum.

The catalytic oxidation is achieved by adding Cu(I) (a) or the solid catalyst (b) to a solution of the substrate in DMSO. Alternatively, substrate may be added to solutions of autoxidized Cu(I) (c). In every run 1 mmol substrate and 0.2 mmol copper in 10 ml purified DMSO [5] are reacted. The course of the reaction is measured in a gas volumeter under pure O_2 at 25 °C and atmospheric pressure. The two components are mixed as soon as thermal equilibrium is obtained in the reaction vessel. When no more O_2 is consumed, the catalyst is deactivated with 1 ml concentrated HCl and 150 ml H_2O. The products of the reaction were isolated either by extraction with chloroform or by directly filtering off the precipitate. The yields of all the products are near 70% after recrystallization. They were identified by comparison with authentic samples (**1a**, **2a**) or by IR, NMR, and melting point (**3a** [7]).

Simple cupric salts like the sulfate, chloride, or the nitrate showed no activity. Adding an excess of imidazole as an additional ligand to the reaction mixture also completely inhibits the oxidation.

The kinetics of the O_2 consumption depend on the method and substrate used. In every case equimolar amounts of dioxygen and substrate are needed, however (see Table 1).

Table 1: Molar ratio of dioxygen consumed to substrate initially present.

substrate	method (a)	(b)	(c)
2,6-dimethylphenol	0.92 (21)[1]	0.53 (19)[2]	0.92 (30)
	0.20 (2)	0.05 (2)	0.21 (2)
benzoin	0.96 (20)	0.97 (12)	0.98 (5)
	0.91 (1)	0.57 (1)	0.89 (1)
di-t-butylcatechol	0.99 (20)	0.94 (22)	0.95 (24)
	0.45 (1)	0.55 (3)	0.42 (3)

[1] Reaction time in hours.
[2] Interrupted before end of reaction.

In method (a) after a rapid initial reaction the rate of oxygen uptake decreases monotonously. With methods (b) or (c) an induction period, the length of which increases among others with the age of the oxidized copper species, is observed for the substrates **1** and **2** (see Fig. 1). At the same time the maximum rate of gas uptake decreases. As shown in Fig. 2 with substrate **3** no induction period is obtained. Actually, after an initial rapid reaction, the extent of which depends on the method chosen, an almost constant rate of O_2 uptake follows for several hours.

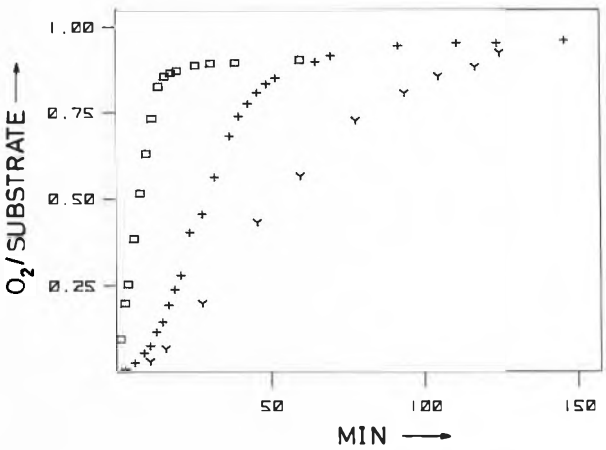

Fig. 1: Copper catalysed oxidation of benzoin with molecular oxygen. □: method (a), Y: method (b), +: method (c) (freshly autoxidized copper solution).

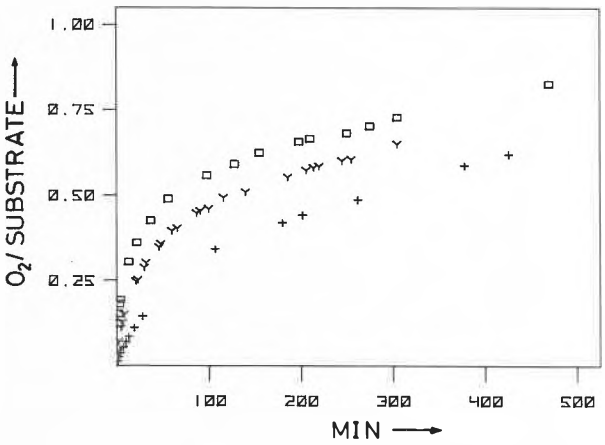

Fig. 2: Copper catalysed oxidation of 3,5-di-t-butylcatechol with molecular oxygen. □: method (a), Y: method (b), +: method (c) (autoxidized copper solution 5 days old).

The differences between **3** and the other substrates is further made evident by another phenomenon. Each substrate molecule looses two electrons upon the oxidation. Together with the fact that one molecule of substrate requires one molecule of O_2 this means that dioxygen is reduced to the state of peroxide. Hydrogen peroxide is formed during the autoxidation of Cu(I) in DMSO but is not stable in these solutions and reacts further with the solvent to give dimethylsulfone [8]. In the case of **1** and **2** 70–80% of the expected amount of sulfone are actually found by gas chromatography. With **3** neither sulfone nor peroxide could be identified in the reaction mixture (the presence of H_2O_2 was tested with catalase, DMSO: $H_2O = 0.05$, in aqueous borate at *p*H 8).

The colour of the solid catalyst changes slowly from brown to green upon standing, concomitantly the catalytic activity is lost. Stability, composition and activity of the solid depend on the apolar solvent used for precipitation. The catalyst obtained with chloroform decomposes after several hours, with dioxane the product is stable for several days. The catalyst obtained from a 0.8 M Cu(I) solution was isolated and identified by several methods.

IR (KBr): 1060 cm^{-1} (vst., br., ν_{SO} and ν_{BF})

^{1}H-NMR (D_2O, Cu(II) was reduced with NaCN): 3.8 ppm (s, dioxane), 2.75 ppm (s, DMSO) (standard: sodium 3-trimethylsilyl-propanesulfonate). Integral corresponds to dioxane: DMSO = 1:3.3.

Analysis: $C_{12}B_2Cu_2F_8H_{32}S_4O_7$ [10]

Calc.	C 20.1	H 4.5	S 17.9	N 0.0	Cu 17.7%
Found	C 19.9	H 4.6	S 18.1	N 0.0	Cu 17.7%

The elemental analysis corresponds to $Cu_2O(DMSO)_4(dioxane)(BF_4)_2$.

The solid catalyst is active not only in DMSO but also in pyridine it promotes the oxidative coupling of **1** to yield the polymer **1a**. In pyridine, too, an induction period is observed, in contrast to results with the catalyst obtained directly from cuprous chloride in pyridine [4].

Our results show the autoxidation product of Cu(I) in DMSO to be a versatile redox catalyst. In spite of many similarities its properties are significantly different from those of the CuCl-pyridine-system. One main point is the possibility to isolate the active species [3, 4]. The analysis suggests a dimeric, probably oxo bridged cupric complex in accordance with the strongly reduced EPR activity of autoxidized Cu(I) solutions [5]. Aprotic solvents seem to be the only requirement for catalytic activity whereas additional strongly basic ligands like pyridine are no must. For substrates **1** and **2** the redox stoichiometry is described by:

$$\underset{(\mathbf{1},\mathbf{2})}{SH_2} + O_2 + (CH_3)_2SO \rightarrow \underset{(\mathbf{1a},\mathbf{2a})}{S} + H_2O + (CH_3)_2SO_2$$

according to that of mixed function oxidases.

The significance of the system described here as a synthetic tool in organic chemistry and as model for enzymatic reactions is studied further.

This work was supported by the Swiss National Science Foundation (Project No. 2.477-0.75).

References

1 *T. Kametani, Y. Satoh, M. Takemura, Y. Ohta, M. Ihara* and *K. Fukumoto:* Heterocycles *5* (1976) 175.
2 *J. Tsuji* and *H. Takayanagi:* Tetrahedron Lett. (1976) 1365.
3 *C. E. Kramer, R. Davies, R. B. Davis* and *R. W. Slaven:* JCS Chem. Comm. (1975) 606.
4 *H. Finkbeiner, A. S. Hay, H. S. Blanchard* and *G. F. Endres:* J. Org. Chem. *31* (1966) 549.
5 *G. Rainoni* and *A. D. Zuberbühler:* Chimia *28* (1974) 67.
6 Ger. Pat. No. 1230025 cited from Chem. Abstracts *66* (1967) 46487e.
7 *A. Rieker, W. Rundel* and *H. Kessler:* Z. Naturforschg. *24b* (1969) 547.
8 *H. Gampp* and *A. D. Zuberbühler:* to be published.
9 *I. C. Gunsalus, H. E. Conrad* and *P. W. Trudgil* in *T. E. King, H. S. Mason* and *M. Morrison* (Eds.): Oxidases and Related Redox Systems. Wiley, New York 1965, 417.
10 Presence of copper prevents determination of O. Copper was determined complexometrically.