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CATALYTIC OXIDATION OF 2,6-DI-t-BUTYLPHENOL BY SALCOMINE-TYPE COMPLEXES IN THE PRESENCE OF WATER

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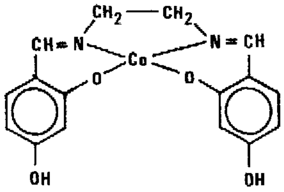
We wish to report the first example of a cobalt-Schiff's base, salcomine-type complex acting as a homogeneous catalyst for the oxidation of a substituted phenol in solutions of an organic solvent and water, under both neutral and basic conditions. This is in contrast to all previous reports of salcomine catalysis performed under anhydrous conditions [1,2,3,4] and is of particular importance to our studies on the development of catalysts for the oxygen-alkali pulping of wood.

It was in relation to these studies that we initially decided to investigate the possibility of using a salcomine-type complex as a pulping catalyst, as a number of these complexes are known to reversibly bind oxygen[5] and also to catalyse the oxidation of phenols[1].

A major disadvantage in using salcomine itself for such a purpose is that it is not water-soluble and for this reason attempts were made to prepare a more polar derivative which was water-soluble and yet retained the catalytic properties of the parent salcomine.

Of the complexes investigated the hydroxylated derivative, N,N'-ethylenebis (4-hydroxysalicylideneiminato) cobalt (1) or more simply 4-hydroxysalcomine, was the most suitable,



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being slightly soluble in water and readily soluble in 1N sodium carbonate or sodium hydroxide solution. This compound which has been reported previously as a brown solid^{6}, inactive toward oxygen, was obtained as an orange solid by the reaction of cobaltous acetate with the Schiff's base of 2,4-dihydroxybenzaldehyde and ethylenediamine.

To determine whether 1 was capable of catalysing the oxidation of phenols, its effect on the rate of oxidation of 2,6-di-*t*-butylphenol was examined, as this oxidation is known to be catalysed by unsubstituted salcomine ^{1,4}, giving the benzoquinone (80%) and the diphenoquinone (13%) as shown in Fig. 1.

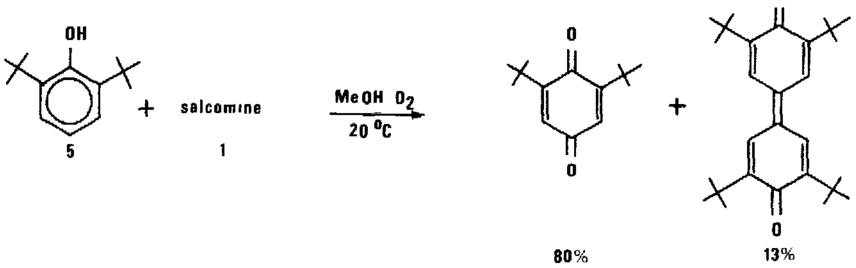

Fig. 1
Salcomine Catalysed Oxidation of 2,6-Di-*t*-butylphenol^{4}

By bubbling oxygen through a methanolic solution of the phenol and 4-hydroxysalcomine (present in a mole ratio of ten to one), for 2 hours at 20°C, it was found that considerable oxidation occurred.

The rate of the above reaction was then compared with that of the unsubstituted salcomine, prepared by the method of Diehl and Hach^{7}.

After each oxidation a quantitative determination of the amount of residual starting material, diphenoquinone, and benzoquinone was obtained by measuring the intergral ratio of the tertiary butyl groups of the three compounds in the n.m.r. spectrum of the crude product in deuterochloroform, since they each occur at a different frequency (δ 1.41, 1.33, and 1.23, respectively). This method was found to be more convenient than the isolation techniques previously described^{4}.

It was found that 4-hydroxysalcomine was a more effective catalyst for the oxidation of 2,6-di-*t*-butylphenol (57% oxidation) than the unsubstituted salcomine (43% oxidation).

To determine whether these complexes retained their catalytic activity in the presence of water the above two oxidations were repeated using methanol:water (9:1) as solvent. The use of this solvent system was necessary as neither 2,6-di-*t*-butylphenol nor its sodium salt are soluble in water alone at 20°C.

TABLE 1

Oxidation of 2,6-Di-*t*-butylphenol for 2 hours at 20°C

SOLVENT	BASE	*CATALYST	[+]SM	[+]DPQ	[+]BQ
MeOH	-	-	100	0	0
MeOH:H_2O(9:1)	-	$CoCl_2$	100	0	0
MeOH:H_2O(9:1)	Na_2CO_3	-	92	2	6
MeOH:H_2O(9:1)	Na_2CO_3	$CoCl_2$	93	7	0
MeOH:H_2O(9:1)	NaOH	-	94	6	0
MeOH:H_2O(9:1)	NaOH	$CoCl_2$	79	11	10
MeOH	-	salcomine	57	11	32
MeOH:H(9:1)	-	salcomine	61	10	29
MeOH:H_2O(9:1)	Na_2CO_3	salcomine	0	38	62
MeOH:H_2O(9:1)	NaOH	salcomine	0	50	50
MeOH	-	4-hydroxysalcomine	43	6	51
MeOH:H_2O(9:1)	-	4-hydroxysalcomine	40	10	50
MeOH:H_2O(9:1)	Na_2CO_3	4-hydroxysalcomine	0	47	53
MeOH:H_2O(9:1)	NaOH	4-hydroxysalcomine	0	56	44

[*] phenol:catalyst (10:1)

[+] SM = starting material

DPQ = 3,3',5,5'-tetra-t-butyldiphenoquinone

BQ = 2,6-di-t-butylbenzoquinone.

The presence of water was found to have no detrimental effect on the catalysis and the oxidations proceeded as before, 4-hydroxysalcomine again being the more efficient catalyst (Table 1).

As the envisaged use of a pulping catalyst of the type under investigation would be in a process involving treatment of the fibres with oxygen and alkali under elevated temperatures and pressures, the effect of base on the activity of the catalysts was then studied using methanol:water (9:1) as the solvent.

Oxidation of 2,6-di-t-butylphenol in the presence of one mole equivalent of sodium carbonate or sodium hydroxide with either salcomine or 4-hydroxysalcomine as the catalyst caused a dramatic enhancement in the rate of reaction, with no starting material detectable by n.m.r. after 2 hours. The effect was far greater than with base alone, which has been reported previously[8], and also significantly faster than with base and cobaltous chloride.

The results of the oxidations are summarised in Table 1.

A study of the general applicability of the two complexes as catalysts for phenol oxidation and oxygen-alkali pulping is currently in progress. Although 4-hydroxysalcomine would appear to be the more promising, the usefulness of the unsubstituted salcomine may be greater than originally expected as it was found that this complex could be dissolved in aqueous alkali by warming the mixture, without impairing its catalytic activity.

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