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# ROLE OF PYRIDINE IN THE CATALYTIC ACTIVATION OF SODIUM HYPOCHLORITE IN THE PRESENCE OF MANGANESE PORPHYRIN

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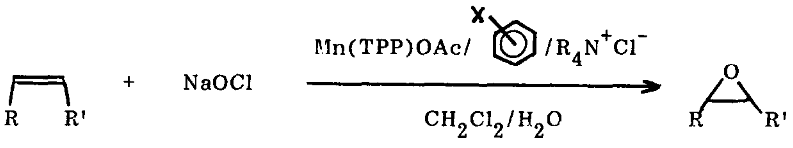
Summary : Steric and electronic influences of various substituted pyridines support the hypothesis of the coordination of pyridine in the manganese porphyrin-catalysed epoxidation of olefins with sodium hypochlorite solution.

Sodium hypochlorite can be considered as a cheap and readily available representative of the family of "single-oxygen-donors" in catalytic oxygenations. Whereas many publications have been devoted to other single-oxygen-donor molecules such as hydrogen peroxide or alkylhydroperoxides, until recently no catalytic epoxidation has been reported with sodium hypochlorite [1].

In the presence of small amounts of pyridine (0.15 equivalent / olefin) the catalytic system is able to epoxidise a large variety of olefins in good yield (60-90 %) [2].

Here we wish to report the results concerning the influence of various substituted pyridines supporting the hypothesis of the coordination of pyridine on the manganese porphyrin during the catalytic reaction. The metalloporphyrin used in these epoxidations is Mn(TPP)OAc (TPP = meso-tetraphenylporphyrin) and it has to be noted that the corresponding chloride derivative, Mn(TPP)Cl, has been recently described as an efficient catalyst in oxidation reactions with $O_2$/reducing agent or PhIO [3].



Two olefins have been considered in this study : styrene (see table 1) and cyclohexene (see table 2).

In the case of styrene, the rate is highly modified by the addition of small quantities of pyridine (run 2 compared to 1). The catalytic reaction is complete within 30 mn instead of 5 hours for the same reaction without amine.

Such an influence may be *a priori* interpreted in two ways : (i) the oxidation *in situ* of

Table 1. Epoxidation of styrene in the presence of various substituted pyridines.

| Run | | Conversion in % | Epoxide yield in % | Reaction time* |
|---|---|---|---|---|
| 1 | No amine [8] | 95 | 74 | 5 hrs |
| 2 | Pyridine | 100 | 80 | 30 mn |
| 3 | 2,6-dimethylpyridine | 100 | 75 | 2 hrs |
| 4 | 2,6-diterbutylpyridine | 96 | 77 | 5 hrs |
| 5 | 3,5-dimethylpyridine | 100 | 80 | 30 mn |
| 6 | 4-methylpyridine | 100 | 80 | 20 mn |
| 7 | 4-cyanopyridine | 95 | 75 | 2 hrs |
| 8 | Triethylamine | 55 | 43 | 5 hrs |

* time for which the olefin conversion is stopped. Reaction conditions : styrene (4 mmoles) deperoxidized on alumina, Mn(TPP)OAc (0.025 mmole), benzyldimethyltetradecylammonium chloride (0.05 mmole), amine (0.62 mmole) in 10 mL of $CH_2Cl_2$ with 20 mL of 0.35 M NaOCl. All reactions are run under nitrogen at room temperature and monitored by g.l.c.

pyridine into N-oxide which could be used as a second stage oxidant or (ii) the effect of coordination of pyridine on the manganese porphyrin during the catalytic reaction. The first assumption can be rejected for the following reason : no conversion is observed when a pyridine N-oxide solution is used instead of hypochlorite. The same inertness has also been observed in the ruthenium-catalysed oxidation of alcohol [4], whereas the second hypothesis is supported by the results shown in figure 1 and table 1 (runs 3 to 7). The rate of epoxide formation is slowed down when large substituents are in position 2 and 6 of the pyridine ring (with 2,6-diterbutylpyridine the same reaction rate as without amine is observed). When the steric groups are moved away from the nitrogen, in position 3-5, the reaction is accelerated again (run 5 compared to 3).

The reaction is also influenced by electronic effects on the pyridine ring.

An electron-donating group like methyl in the para position increases the rate (run 6) and the opposite effect is obtained with the electron-withdrawing cyano group (run 7).

Thus, the behaviour of substituted pyridines in this catalytic reaction seems to be in agreement with the literature data related to the coordination of tertiary amines on metalloporphyrins (for electronic and steric effects, see reference 5 ; for the stabilization of a ferryl porphyrin complex with nitrogen bases, reference 6 ; and the known six-coordinated pyridine complex Mn(TPP)(py)Cl is described in reference 7).

In the same reaction conditions, alkyltertiary amines behave differently from pyridines :

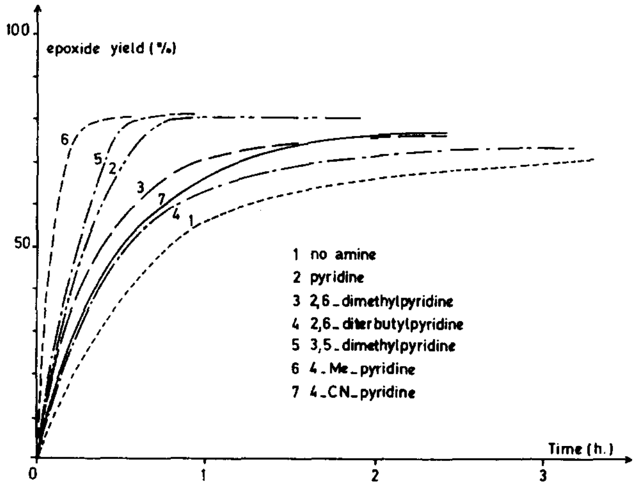


Fig. 1 : Formation of styrene oxide in the presence of various pyridines. The curves numbering refers to the entries of table 1.

e.g. in the case of $Et_3N$, the conversion is stopped to 55 % after 4 hours (run 8). Oxidation on the alkyl chains or nitrogen may probably occur with this tertiary aliphatic amine and studies are in progress to elucidate this phenomenon.

We wish also to report the electronic influence of 4-substituted pyridines on the course of cyclohexene epoxidation. Table 2 illustrates the improvements on selectivity and rate when the 4-substituent is changed from -CN to -Me. With such a cyclic olefin sensitive to allylic oxidation, the selectivity is largely influenced by the addition of pyridine (from 37 % without

Table 2. Epoxidation of cyclohexene with different 4-substituted pyridines after a reaction time of 4 hours at room temperature *

| 4-X-pyridines | Conversion in % | Epoxide yield in % | Selectivity in % |
|---|---|---|---|
| X = -Me | 95 | 80 | 85 |
| X = -H | 85 | 72 | 85 |
| X = -CN | 64 | 41 | 64 |
| no pyridine | 59 | 22 | 37 |

* Experimental conditions as described in Table 1. Selectivity is defined in reference 7.

amine up to 85 % with 4-Me-pyridine leading in this case to a comfortable yield of 80 % in cyclohexene oxide).

As a conclusion, all the indications described in this paper (absence of reaction with pyridine N-oxide, rate-decrease with 2,6-disubstituted pyridines, electronic effects...) are strongly consistent with the coordination of pyridine on the manganese-porphyrin during the reaction.

Other studies are in progress to define the exact rôle of coordinated pyridine in the different complexes involved in the catalytic cycles.

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8. One should note the large influence of the styrene concentration on the selectivity in the catalytic reaction run without amine, e.g. the selectivity is 45 % for a 0.1M solution in styrene and rises up to 78 % with a 0.4M solution. The selectivity is defined as the ratio of epoxide with respect to the converted olefin.

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