# OXIDATION OF SEVERAL SUBSTITUTED OLEFINS BY ATMOSPHERIC OXYGEN IN THE PRESENCE OF THE TPPMnC1 - NaBH<sub>4</sub> CATALYTIC SYSTEM

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Methoxytetraphenylporphin- $Mn^{III}Cl$  (TPPMnCl) in the presence of NaBH<sub>4</sub> catalyzes the oxidation of olefins with the formation of ketones and secondary or tertiary alcohols depending on the extent of substitution at the olefin double bond [1, 2].

In the present work, we studied the oxidation of 2,3-dimethyl-2-butene, 2-methyl-2-pentene, and isobutylene by the action of the TPPMnCl-NaBH<sub>4</sub> catalytic system.

## EXPERIMENTAL

The olefin samples were purified to remove impurities over sodium. A sample of TPPMnCl was prepared as described by Boucher [3]. A sample of chemically pure grade  $NaBH_4$  was used without further purification. A sample of N,N-dimethylformamide (DMF) was purified by the standard method [4] and used as the solvent.

The olefins were oxidized by the air at  $23 \pm 2^{\circ}$ C in glass vessels equipped with a magnetic stirrer for 0.7-2 moles/liter olefin,  $8 \cdot 10^{-3}$  mole/liter TPPMnCl, and  $1.7 \cdot 10^{-1}$  mole/liter NaBH<sub>4</sub>.

A sample of TPPMnCl was stirred in DMF until completely dissolved. The olefin sample was added to this solution and then  $NaBH_4$  was added. The introduction of  $NaBH_4$  was considered the reaction onset.

The consumption of the hydrocarbon and accumulation of the oxidation products in the reaction mixture was determined by gas-liquid chromatography on a Perkin-Elmer chromatograph using a column packed with PÉG-6000 at 110°C column temperature.

| Olefin                | Olefin<br>concentra-<br>tion, mole/<br>liter | Reaction<br>products | Time, h | Yield of reaction<br>products, %   |  |
|-----------------------|--|----------------------|---------|------------------------------------|--|
|                       |  |                      |         | relative<br>to starting<br>olefin* | relative to<br>the catalyst<br>(• 10 <sup>-3</sup> ) |
| 2,3-Dimethy1-2-butene | 1,7  | Dimethy1-2-butano1   | 1<br>24 | 10<br>30                           | 0.9  |
| Isobutylene           | 0,7  | tert-Butyl alcohol   | 1<br>24 | 15<br>40                           | 1.2  |
| 2-Methyl-2-pentene    | 2  | 2-Methyl-2-pentanol  | 1<br>24 | 20<br>50                           | 2  |

TABLE 1. Oxidation of Substituted Olefins by Atmospheric Oxygen in the Presence of  $TPPMnCl-NaBH_4$ 

\*The amount of alcohols formed was found relative to the consumption of the starting olefins and directly using calibration curves for the corresponding tertiary alcohols.

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#### **RESULTS AND DISCUSSION**

The experimental results are given in Table 1.

The oxidation of all the olefins studied virtually stopped at 24 h. The existence of a conversion limit of the starting hydrocarbons is the result of destruction of the catalyst [2].

The data in Table 1 confirm our previous finding of oxidation of the olefin at the most substituted carbon atom and an increase in the reaction rate with increasing substitution at the double bond (in the series consisting of isobutylene and 2-methyl-2-pentene) [1, 2].

## CONCLUSIONS

The oxidation of olefins in the presence of methoxytetraphenylporphin manganese (III) chloride complex proceeds regioselectively to give the products of oxidation at the most substituted carbon atom.

#### LITERATURE CITED

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### SOLVATION OF PYROCATECHOL BY SULFOXIDES

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Highly solvated complexes are formed in the extraction of polyfunctional organic compounds by solvating extraction agents [1]. These effects may be expected for strongly basic extraction agents such as sulfoxides [2] in the distribution of pyrocatechol (PC) since the energy of the intermolecular interactions is significantly greater than the energy of the intramolecular hydrogen bonding of the hydroxyl groups.

On the other hand, there have been reports of the possibility of interaction of several ketones [3] and phosphine oxides [4] concurrently with two proton-donor groups. Thus, elucidation of the composition of the solvates formed in the extraction of PC by sulfoxides holds considerable interest.

The experimental method was the same as in our previous work [5]. Extraction methods were used to determine the composition of the solvates formed [6]. The saturation method (Fig. 1) indicated monosolvates in the extraction of PC. On the other hand, the saturation method gives the composition of a solvate with a minimum solvate number [7]. The composition of the solvates was also determined by the dilution and isomolar methods (Figs. 2 and 3). These results showed that only monosolvates are formed in the entire range of reagent concentrations in the sulfoxide-diluent-water-PC system, while the formation of highly solvated complexes does not occur.

The distribution of PC between the aqueous phase and sulfoxides (S) may be represented by two alternative equilibrium schemes with the corresponding constants:

$$P_{C-aq} + S_{org} \underset{P_{a}^{\vee}}{\overset{ke}{\longrightarrow}} [P_{C} \cdot S]_{org}$$

$$P_{C,aq} \underset{P_{a}^{\vee}}{\overset{P_{c}}{\longrightarrow}} P_{C,org}$$
(1)

$$P_{C \text{-}org} + S_{org} \xleftarrow{kfor} [PC \cdot S]_{org}$$
(2)

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