Tetrahedron Letters No. 14, pp. 881-883, 1963. Pergamon Press Ltd.
Printed in Great Britain.

THE ROLE OF NICKEL CATALYST IN THE OXIDATION OF DIACETONE-1-SORBOSE BY SODIUM HYPOCHLORITE

A.Ujhidy, L.Markó and B.Babos
University of Chemical Industries, Institute of Organic Chemistry, Veszprém, Hungary.

(Received 8 March 1963)

The oxidation of diacetone-l-sorbose, I,to 2-keto-l-gulonic acid,II/which is an intermediate in the synthesis of vitamin C / is effected usually with alkaline sodium hypochlorite solutions in the presence of nickel salts /1,2/. Although the process is of considerable practical value, nothing is known about the mechanism of this oxidation.

Sodium hypochlorite and nickel salt solutions produce a finely divided, black precipitate, designated usually as nickelic hydroxide. The following observations strongly suggest that this substance is the true catalyst in the above oxidation of I:

1./ The nickel salt proved to be essential for a practical rate of reaction, as in the absence of nickel no II could be isolated from the reaction mixture in experiments /70°C, 1 hour reaction time, NaOCl: I molar ratio 3,6:1/ which on addition of a nickel salt /0,56 %, based on I and calculated as metallic nickel/ produced yields of II usually in the range of 90 %.

2./ Nickelous hydroxide proved to be ineffective as catalyst of the oxidation. With black nickelic hydroxide preformed from a nickel salt and sodium hypochlorite, oxidation rapidly sets in on the addition of I and the reaction mixture has to be cooled intensely. Changing however, the order of the additions of the components to nickel salt, NaOH, I and, at last NaOCl, the oxidation of nickelous to nickelic hydroxide appears to be rather inhibited by I, the color of the precipitate changing only very

> slowly from green over gray to black, the oxidation requiring accordingly an induction period that is considerably prolonged. The same will be the case when the addition of NaOCl does not follow the rate of the oxidation. In this case the initially black nickelic hydroxide precipitate changes to gray, oxidation will stop and can be re-initiated only with a large surplus of sodium hypochlorite.

Nakagawa and co-workers /3/ oxidized alcohols to carboxylic acids with stoichiometric amounts of nickelic hydroxide, designated by them as "nickel peroxide". In view of the results presented above, the conclusion seemed to be justified, that in the transfer of oxygen from sodium hypochlorite to I nickelic hydroxide is an intermediate. Actually, a stoichiometric amount of separately prepared nickelic hydroxide readily oxidized I, as shown by separate experiments, to II.

Nickelic hydroxide was prepared as described by Nakagawa /3/ It contained after washing and drying at room temperature 3.5 mg-atom active oxygen and 6.5 mg-atom nickel per gram, thus corresponding to an approximate composition $Ni/OH/_3.2H_2O$. Its quantity used in stoichiometric oxidation was calculated on the basis of the active oxygen content. Oxidation of I was carried out as follows.

The calculated amount of nickelic hydroxide, necessary to secure the intended oxygen: I ratio, was suspended in water by stirring. To this suspension was gradually added a solution prepared from 46 g /0,175 g mole/ I and 10 g/ 0,25 g mole/ NaOH in 140 ml of water. Temperature rose spontaneously to about 50°C. Then the reaction was completed by heating the mixture to 70°C for 90 minutes. After left cooling the mixture was filtered by suction and the nickel containing precipitate was washed several times with water. The combined filtrates were then concentrated in vacuo below 30°C to 360 ml, and cooled to 0°C. II was precipitated from the solution with ice-cold hydrochloric acid. The product was characterised by its acid number and specific rotation.

The yield of II was found to vary with the active oxygen: I ratio. Using a theoretical amount of nickelic hydroxide, /oxygen:I = 2:1/, a 49.0 % yield of II was secured. At the ratio of oxygen:I = 3,6:1, the yield obtained was 73,6 %. This beneficial effect of excess oxidizing agent was observed in catalytic oxidation experiments too and indicated, that some side reactionsusing oxygen took place.

The results thus furnish evidence that in the oxidation of I by sodium hypochlorite in the presence of nickel salts, nickelic hydroxide is the active agent of the oxygen transfer.

Acknowledgment. The authors wish to thank Prof. Dr.A.Müller for his interest in the work and for helpful discussions.

REFERENCES

/1/ Weijlard,J., J.Am.Chem.Soc. 1954. 67, 1031
/2/ Rubtsov, I.A., Balyakina, M.V., Gryzlova, L.G., Zhdanovich, E.S. Preobrazhenskii, N.A., Trudy Vsesoyuz. Nauch. Issledovatel. Vitamin. Inst. 1954, 5, 17; C.A. 1957, 51 7307
/3/ Nakagawa, K., Konaka, R., Nakata, T., J.Org.Chem. 1962. 27, 1957