Oxidation with a Higher Valency Oxide of Nickel prepared by Ozonisation

By J. S. BELEW* and CHWANG TEK-LING
(*Department of Chemistry, Baylor University, Waco, Texas* 76703)

NAKAGAWA[1] has shown that a higher valency oxide of nickel (which he termed nickel peroxide) prepared from nickel(II) sulphate and sodium hypochlorite is an effective oxidising agent for many functional groups, including the selective oxidation of allyl alcohols to αβ-unsaturated aldehydes and ketones. Others[3] have shown that this reagent prepared by Nakagawa's procedure causes oxidative polymerizations. The preparation of nickel oxide from nickel(II) salt solution by ozonisation has been previously attempted.[4] Tubant and Riedel[5] treated a concentrated sodium hydrogen carbonate solution of a bivalent nickel oxide salt with ozonised air at 0° and obtained a deep red solution which they thought was a colloidal suspension of NiO_2.

Table

Reactant	Product	Yield (%)
Benzyl alcohol[a]	Benzaldehyde	Quantitative[b]
Cinnamyl alcohol[c]	Cinnamaldehyde	45[d]
Triphenylphosphine[e]	Triphenylphosphine oxide	86
Tri-n-butylphosphine[e]	Tri-n-butylphosphine oxide	92
Benzyl alcohol[f]	Benzoic acid	84
Cinnamyl alcohol[g]	Cinnamic acid	71

[a] A solution of 20 mmoles of benzyl alcohol in 26 ml. of benzene and 6·5 g. of higher valency nickel of oxide were refluxed for 1 hr. in nitrogen.

[b] The unchanged alcohol in the reaction mixture could not be detected by vapour-phase chromatography.

[c] A solution of 22·6 mmoles of cinnamyl alcohol in 30 ml. of benzene and 6 g. of higher valency oxide of nickel were stirred at 50° for 1 hr.

[d] Yield was calculated as cinnamaldehyde 2,4-dinitrophenylhydrazone.

[e] A solution of 10 mmoles of the phosphine in 50 ml. of light petroleum and 6 g. of higher valency oxide of nickel were refluxed in an atmosphere of nitrogen for 5 hr.

[f] A solution of 20 mmoles of benzyl alcohol in 50 ml. of 1 M-sodium hydroxide solution and 8 g. of higher valency oxide of nickel were stirred in an atmosphere of nitrogen for 3 hr. at 30°

[g] A solution of 20 mmoles of cinnamyl alcohol in 50 ml. of 1 M-sodium hydroxide solution and 11·7 g. of higher valency oxide of nickel were stirred at 50° for 6 hr. under an atmosphere of nitrogen.

We have found that when ozone is passed into an alkaline solution of nickel(II) sulphate, a black precipitate is obtained which has oxidizing properties equal if not superior to the reagent prepared from nickel(II) sulphate and sodium hypochlorite. It has the advantage of being effective in smaller quantities although our yields in some instances are lower. Results of the reactions are summarized in the Table.

The oxidising agent was made by adding 7N-NaOH (300 ml.) dropwise during 2 hr. to a vigorously stirred solution of nickel(II) sulphate hexahydrate (1 mole) in water (1·71 l.) while an ozone–oxygen mixture was introduced into the reaction mixture at the rate of 0·6 l./min. (67 mg. ozone/l.) for 24 hr. at room temperature. The precipitated higher valency oxide of nickel was washed well with water, dried over anhydrous calcium chloride under reduced pressure, ground and stored over anhydrous calcium chloride. Drying the product at 80° caused a decrease in its activity as an oxidizing agent. Iodometric analysis[1] of our product gave a value of about $3\cdot9 \times 10^{-3}$ gram-atom of available oxygen per gram (if it is assumed that the available oxygen is solely responsible for liberating iodine); Nakagawa reported for his oxide a value of about $3\cdot5 \times 10^{-3}$ gram-atom of available oxygen per gram.

In each of the reactions, the residue obtained after filtration was extracted in a Soxhlet apparatus under nitrogen atmosphere and products were determined as indicated in the Table.

(*Received, September 8th,* 1967; *Com.* 964.)

[1] K. Nakagawa, R. Konaka, and T. Nakata, *J. Org. Chem.*, 1962, **27**, 1597.

[2] K. Nakagawa, H. Onoue, and K. Minami, *Chem. Comm.*, 1966, 730, and the references cited therein.

[3] J. Sugita, *J. Chem. Soc.* (*Japan*), 1966, **87**, 603, 607 (*Chem. Abs.*, 1966, **65**, 15522e); A. Ujhidy, L. Marko, and B. Babos, *Tetrahedron Letters*, 1963, 881; A. Ujhidy, B. Babos, L. Marko, and A. Mueller, *Chem. Ber.*, 1965, **98**, 2197.

[4] A. Mailfert, *Compt. Rend.*, 1882, **94**, 860.

[5] C. Tubant, and W. Riedel, *Z. anorg. Chem.*, 1911, **72**, 219 (*Chem. Abs.*, 1912, **6**, 45).