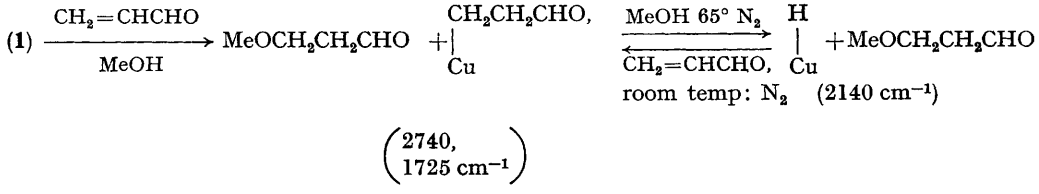
Reversible Uptake of Molecular Oxygen and Carbon Monoxide by a New Polyoxime–Copper Complex

By SUNG JHO KIM* and TAKEO TAKIZAWA

(*Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Bunkyo-ku, Tokyo*, 113, *Japan*)

Summary The copper complex of a polyoxime, $\{[CH_2]_{1\cdot6}[C(=NOH)C(=NOH)]_{0\cdot8}[C(=O)]_{0\cdot2}\}$ catalyzes the 'Michael' type addition reaction of acrolein and an alcohol yielding exclusively β-alkoxypropionaldehyde, polymerizes acrylonitrile under H_2 at 40—90 atm and reversibly takes up molecular oxygen and carbon monoxide even in methanol or water after being treated with hydrazine hydrate.

A NEW copper complex prepared from a polyoxime,[1] derived from an alternating copolymer of ethylene and carbon monoxide[2] $\{[CH_2CH_2]_{1\cdot2}[C(=O)]\}$ (molar mass 4000) by means of *C*-nitrosation of the active methylene groups and oximation of the carbonyl groups, and consisting mainly of 1,2-bis(hydroxyimino)trimethylene units, exhibited some interesting chemical behaviour never observed in its monomeric analogues. The complex was prepared by adding a large excess of cupric acetate [3·5 g $Cu(CH_3CO_2)_2$-H_2O] to a solution of the polymer (2·0 g) in 400 ml (5×10^{-3} g ml^{-1}) 1:1 dioxan–isopropanol under N_2. The complex (**1**) had Cu:OX *ca.* 1:4 (where Cu and OX are numbers of copper atoms and oxine groups in the complex). The complex (**1**) is an insoluble green powder which did not show an e.s.r. signal. It catalyses the 'Michael' type addition reaction of acrolein and an alcohol yielding exclusively β-alkoxypropionaldehyde. Methanol was the most reactive alcohol used, and n- and t-butyl alcohols were almost unreactive. I.r. spectra on the recovered complex (**2**) (KBr disc) suggest the probable formation of a Cu–C and Cu–H bond. Complex (**1**) can initiate the polymerization of acrylonitrile under H_2 at 40—70 atm. The resulting polyacrylonitrile was a grey powder, soluble in DMF but insoluble in acetone. Its molar mass could not be determined owing to the low viscosity of the solution of the polymer in DMF. The i.r. spectrum of the polymer (KBr disc) was in good agreement with that reported by Anand and Deshpaude,[3] a strong absorption was observed at 1665 cm^{-1} and no absorption at 900—1000 cm^{-1}. This suggests stereoregularity in the structure of the polymer. It is well known that hemocyanine, a metalloenzyme containing copper, can reversibly take up molecular oxygen[4] and carbon monoxide.[5] (**1**) can take them up reversibly by first treating it with hydrazine hydrate in suspension in methanol at room temp. under N_2 for 2 h followed by agitating with refluxing methanol for 0·5 h. The i.r. spectrum and elemental analysis of the resulting complex (**3**) were almost the same as those of (**1**) except for the appearance of a band at 2140 cm^{-1}. Most of the copper atoms in (**3**) are probably monovalent, as shown by the colorimetric determination[6] of the copper released in the decomposition of (**3**) by aq. HCl under N_2. Manometric measurement showed that (**3**) took up about 3·2 l of O_2 (in water) and 0·8 l of CO(in methanol) per gram atom copper at 20° for 6 h. The rates of uptake decreased with time and the rate for CO was



greater than for O_2. The product of the reaction of (**3**) with O_2 was heated at 70° for 4 h *in vacuo*, then it became capable of taking up 3·0l of O_2 (in water) or 0·8l of CO (in methanol). The product of (**3**) with CO took up 1·2l of O_2 (in water) or 0·8l of CO (in water). The uptake of CO was confirmed in the i.r. spectrum by a band at 2100 cm^{-1} probably due to CO co-ordinated to the copper. The activities decreased with a decrease in copper content and complexes with less than 15·84% of copper were almost inactive. The properties described were not observed in normal copper(II) complexes of *vic*-dioximes such as dimethylglyoxime.

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[1] S. J. Kim and T. Takizawa, *Makromol. Chem.*, in press.
[2] M. M. Brubaker, D. D. Coffman, and H. H. Hoehn, *J. Amer. Chem. Soc.*, 1952, **74**, 1509.
[3] L. C. Anand and A. B. Deshpaude, *Chem. Ind.*, 1966, **20**, 1457.
[4] For example, W. A. Rawlinson, *Austral. J. Exptl. Biol. Med. Sci.*, 1940, **18**, 131.
[5] R. W. Root, *J. Biol. Chem.*, 1934, **104**, 239.
[6] J. Hoste, *Analyt. Chim. Acta*, 1953, **9**, 263.