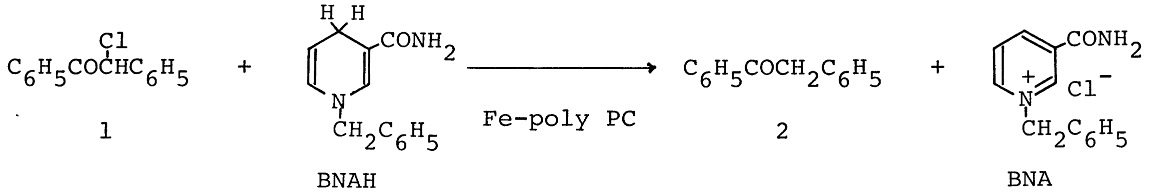
CHEMISTRY LETTERS, pp. 1157-1160, 1974. Published by the Chemical Society of Japan

CATALYSIS BY IRON-POLYPHTHALOCYANINE. REDUCTIVE DEHALOGENATION OF α-CHLORODEOXYBENZOIN WITH 1-BENZYL-1,4-DIHYDRONICOTINAMIDE

Hiroo INOUE, Ryuji AOKI, and Eiji IMOTO
Department of Applied Chemistry, College of Engineering, University
of Osaka Prefecture, Sakai-shi, Osaka 591

Iron-polyphthalocyanine catalyzed the reductive dehalogenation of α-chlorodeoxybenzoin with 1-benzyl-1,4-dihydronicotinamide in benzene or 80 vol% aqueous methanol. The accelerating activity of the iron-polyphthalocyanine became larger as compared with those of various iron complexes under the similar condition.

Iron-polyphthalocyanine (Fe-poly PC) is an electroconductive conjugated polymer$^{1)}$ which has a catalytic ability for the oxidation of hydrocarbons with oxygen.$^{2)}$ We now report a new catalytic function of the Fe-poly PC upon the reduction of α-chlorodeoxybenzoin (1) with 1-benzyl-1,4-dihydronicotinamide (BNAH) to deoxybenzoin (2). In this reaction Fe-poly PC was employed as an electron-transfer carrier intervening between (1) and BNAH.



A solution of a mixture of (1) (0.084 mmol) and BNAH (0.336 mmol) in dry benzene (6 ml) in the absence of Fe-poly PC was heated at 80°C for 48 hr in a sealed tube. (2) was produced in 15% yield with a 75% recovery of (1). The amounts of (1) and (2) were determined by glc analysis. The reduction of the carbonyl group of (1) did not occur at all. The amount of (2) produced increased almost linearly with the passage of time, although the reaction proceeded very slowly. In a large scale reaction, 1-benzylnicotinamide chloride (BNA) was isolated in amounts corresponding approximately to those of (2). When 80 vol% aqueous methanol was used as the solvent, the rate of the reaction became twice faster than that in the case of benzene.

The reaction of (1) and BNAH has been examined in the presence of Fe-poly PC (C, 53.16; H, 2.72; N, 17.71; Fe, 6.6%: λ_{max} (KBr method); 725 nm: ρ_{20}, $2x10^6$ ohm-cm) which was prepared by the method described in our previous paper.[2)] Fe-poly PC (n = 1.4, where n represents the molar ratio of (1)/Fe(II) ion) was suspended in dry benzene containing (1) and BNAH in amounts described above and the solution was heated at 80°C. The initial rate of the reaction became 10-15 times faster than that in the absence of Fe-poly PC. The reaction time ($t_{1/2}$) required for 50% formation of (2) was 11 hr. The values of $t_{1/2}$ at n = 3 and 4.5 were 23 and 34 hr, respectively. In the reaction BNAH was converted to BNA. The formation of BNA caused the lowering of the activity of Fe-poly PC. In order to minimize the effects of BNA on the reaction, the reaction of (1) and BNAH in the presence of Fe-poly PC has been carried out in 80 vol% aqueous methanol under the conditions similar to the case of benzene. The reaction proceeded much more rapidly than in benzene (Fig. 1); the values of $t_{1/2}$ at n = 1.4 and 14 were 0.4 and 2 hr, respectively. The initial rate at n = 1.4 was faster than that in the absence of Fe-poly PC by a factor of about

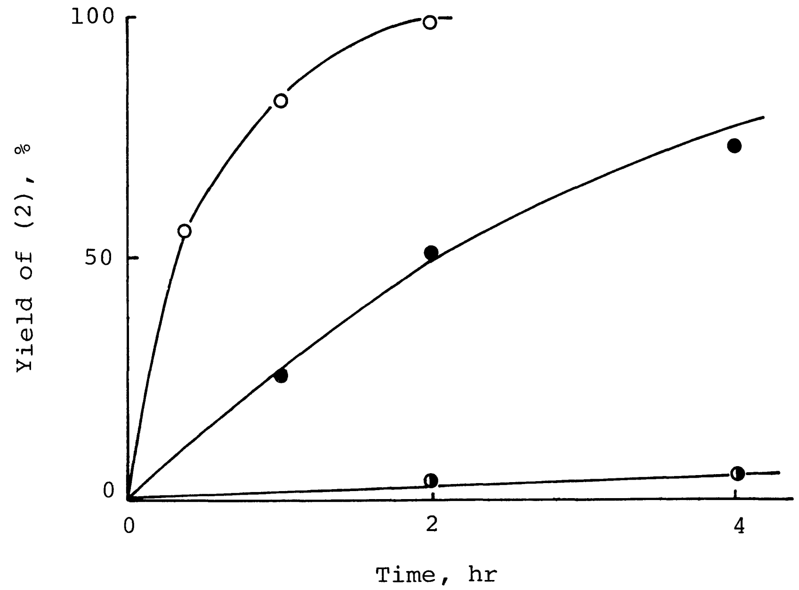


Fig. 1. Plot of the yields of (2) against time in the reaction of (1) and BNAH in 80 vol% aqueous methanol at 80°C: in the presence of Fe-poly PC at n = 1.4 (○) and 14 (●) and the absence of Fe-poly PC (◑).

10^2. The dramatic acceleration presents obvious evidence supporting the catalytic function of Fe-poly PC.

The accelerating ability of Fe-poly PC on the reduction of (1) with BNAH was compared with that of various metal complexes. Employing dry benzene as the solvent with the metal complex at n = 0.5-1.5, the following order of the catalytic activity was observed: Fe(II)-poly PC > Fe(II)-PC, Cu(II)-PC, Co(II)-PC, Fe(III)$(acac)_3$ > $FeCl_3py_2$, $FeCl_3$ > Na_2-PC, K_2-PC and no metal complex (Table 1). Comparison of the activity led to the conclusions that 1) the enhancement of the rate becomes larger when the complex contains the transition metal ion undergoing a redox reaction and the bond between metal ion and ligand has the covalent character, and 2) both Fe(II) and Fe(III) complexes show the accelerating activity for the reduction of (1) with BNAH. These conclusions indicate obviously that Fe-poly PC performs its function by undergoing a change in oxidation state of iron ion and acts as an electron-transfer carrier which intervens between (1) and BNAH, although the role of the conjugated system of Fe-poly PC remains obscure. In addition, it has been reported previously

Table 1. The reaction of (1) and BNAH in dry benzene in the presence of various metal complexes at 80°C[a)]

Metal Complex	n	Time, hr	Yield of (2), %
Fe-poly PC	1	9	73
Fe-poly PC	1.5	48	95
Fe-PC	1	24	72
$Fe(acac)_3$[b)]	1	9	59
$Fe(acac)_3$[b)]	1	48	95
$FeCl_3py_2$	1	24	28
$FeCl_3$	1	24	23
Cu-PC	1	9	63
Co-PC	1	48	90
Na_2-PC	0.5	48	25
K_2-PC	0.5	48	12
H_2-PC	0.5	48	15
None	–	48	15

a) The concentration of (1); 1.4×10^{-2} mol/l and the molar ratio of BNAH to (1); 4 : 1. acac = acetylacetone; PC = phthalocyanine; py = pyridine

b) $Fe(acac)_3$ is soluble in benzene.

that organic halogen compounds are reduced by iron-porphyrins3) and dihydropyridines are oxidized by potassium ferricyanide quantitatively.4)

On the basis of the evidences now available, the mechanism of the catalytic reaction occurring on Fe-poly PC would be explained to proceed by the following three steps; the reduction of (1) by Fe(II)-poly PC giving α-keto radical (3) (step a) and the oxidation of BNAH by Fe(III)-poly PC giving a cation radical (4) (step b), followed by the reaction of (3) and (4) to produce (2) and BNA (step c). In the case of the Fe(III) complexes, the reaction would be initiated by the step b.

$$1 + \mathrm{Fe(II)\text{-}poly\ PC} \longrightarrow \underset{3}{\mathrm{C_6H_5CO\dot{C}HC_6H_5}} + \mathrm{Fe(III)\text{-}poly\ PC\ Cl^-} \qquad \text{(a)}$$

$$\mathrm{BNAH} + \mathrm{Fe(III)\text{-}poly\ PC\ Cl^-} \longrightarrow \underset{4}{\mathrm{BNAH^{\dot{+}}\ Cl^-}} + \mathrm{Fe(II)\text{-}poly\ PC} \qquad \text{(b)}$$

$$3 + 4 \longrightarrow 2 + \mathrm{BNA} \qquad \text{(c)}$$

References

1) J. E. Katon, "Organic Semiconducting Polymer", Marcel Dekker INC., New York, N. Y. (1970), Chapter 3.

2) H. Inoue, Y. Kida, and E. Imoto, Bull. Chem. Soc. Japan, 38, 2214 (1965); ibid., 40, 184 (1967); ibid., 41, 684, 692 (1968); T. Hara, Chem. Ind. 23, 490 (1972).

3) C. E. Castro, J. Amer. Chem. Soc., 86, 2310 (1964).

4) K. Wallenfels and M. Gellrich, Chem. Ber., 92, 1406 (1959).

(Received August 5, 1974)