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SPECIFIC CATALYSIS BY Co(II)PHTHALOCYANINE-TETRASULFONATE IN THE SELECTIVE REDUCTION OF ACETYLENE WITH SODIUM BORONHYDRIDE

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Co(II)phthalocyanine-tetrasulfonate sodium exhibits a specific catalysis for the selective reduction of acetylene with $NaBH_4$ and the electric reduction with a cathodic voltage at above -1.0 v *vs* "sce".

It has recently been demonstrated that Mo(V)thiol complexes$^{1)}$ and Co(III)-tetraphenylporphin-tetrasulfonate$^{2)}$ act as a non-protein model for nitrogenase in the reduction of N_2-ase substrates. In this communication we wish to report that Co(II)phthalocyanine-tetrasulfonate sodium (CoPcTS) exhibits a specific catalysis for the selective ethylene formation in the reduction of acetylene with $NaBH_4$ and the electric reduction with a cathodic voltage at above -1.0 v *vs* "sce" (standard calomel electrode).

When acetylene (0.1-0.7 atm) was admitted into an alkaline (pH= 8-12, borate buffer) solution of CoPcTS (0.1-1.0 mmol) and $NaBH_4$(1-10 mmol) at 27°C, ethylene was formed at a considerable rate with a small amount of ethane and hydrogen. It was found that the introduction of CO or O_2 (0.1 atm) in the reaction system inhibited the catalysis completely, but the activity was slowly regenerated by consumption of the inhibitor gases with excess $NaBH_4$. The maximum activity for ethylene formation was observed by CoPcTS at the pH of 9 to 10, and the apparent activation energy was determined to be *ca* 8 kcal/mol at temperatures from 0° to 40°C. The catalytic behavior of CoPcTS could be repeated several times without loss of activity by fresh addition of $NaBH_4$. Sodium dithionate, in place of $NaBH_4$ as a reductant, gave only a very slow formation of ethylene in the presence of CoPcTS. When the reaction was carried out in D_2O, cis-$C_2H_2D_2$(64%), C_2D_4(22%)$^{3)}$, C_2HD_3 (8%) and trace of C_2H_3D were observed without the formation of trans- and ansym-$C_2H_2D_2$. The analysis was carried out by mass- and IR-spectrometry.$^{4)}$
The catalytic ethylene formation took place in a solution of FePcTS or NiPcTS at

such low rates as one-twentieth of the rates with CoPcTS, but hardly in a solution of CuPcTS and H_2PcTS with excess of $NaBH_4$ under similar reaction conditions.

Visible absorption spectroscopy showed that CoPcTS (670 nm) was readily reduced in an alkaline solution with $NaBH_4$ to a "leuco-species" (ν_{max} 470 and 700 nm)[5] which was rapidly oxidized with acetylene (0.1-0.7 atm) at 27°C and CoPcTS (670 nm) was regenerated. In contrast to this observation, no appreciable change could be observed when acetylene was introduced into a solution of mono-negative CoPcTS($CoPcTS^-$), which was independently prepared from CoPcTS with $Na_2S_2O_4$ at room temperature.[6] The"leuco-species" having a smilar visible spectra could be obtained by the reaction of $CoPcTS^{2-}2Na^+$ and $CoPc^{2-}2Na^+$ (520 nm)[7] in dry THF(tetrahydrofuran) with ethanol, C_2H_2 or water as a protic substance. It was confirmed by the IR-spectrometry that the "leuco-species" gave a characteristic IR-absorption peak at 3000 cm^{-1}(or 2180 cm^{-1})[8] for the sample obtained from $CoPcTS^{2-}2Na^+$ and H_2O (or D_2O) in THF. The similar IR-absorption peaks were also observed for the "leuco-species" from $CoPcTS^{2-}2Na^+$ and C_2H_2 (or C_2D_2). These results suggested that a proton combines with a peripheral N-atom of phthalocyanine in an aqueous solution under the reduction process.

From the polarographic study of CoPcTS in an alkaline solution, the two reduction waves were observed at the cathodic voltages of E_1= -0.7 v and E_2= -1.3 v vs "sce". The second-reduction wave could be attributed to the formation of a proton-adduct of $CoPcTS^{2-}$ in an alkaline solution.

When acetylene (0.5 atm) was introduced into an alkaline solution (pH=9.6, Na_2CO_3-$NaHCO_3$ buffer) of CoPcTS (0.45 mmol/70 cm^3) and the cathodic voltages from 0 to -1.6 v vs "sce" were applied at an inert graphite-electrode (surface area: ca 3 cm^2), ethylene was selectively formed with the cathodic voltages above -1.0 v vs "sce", as shown in Figure 1. It is interesting to note from Figure 1 that the activity and selectivity for ethylene formation by CoPcTS were much better than those by Mo(V)-cysteine complex ($Na_2Mo_2O_4(cysteine)_2 5H_2O$) under similar reaction conditions. At above -1.5 v a small amount of ethane was formed in the presence of CoPcTS, probably owing to a direct reduction of acetylene with reactive hydrogen which was generated at the graphite-electrode.

Accordingly, a possible mechanism is concluded that the specific catalysis by CoPcTS for the selective formation of ethylene in the acetylene reduction takes place through hydrogen-transfer from a proton-adduct of $CoPcTS^{2-}$ which has been formed with $NaBH_4$ as a strong reductant in an alkaline solution as shown in the following scheme:

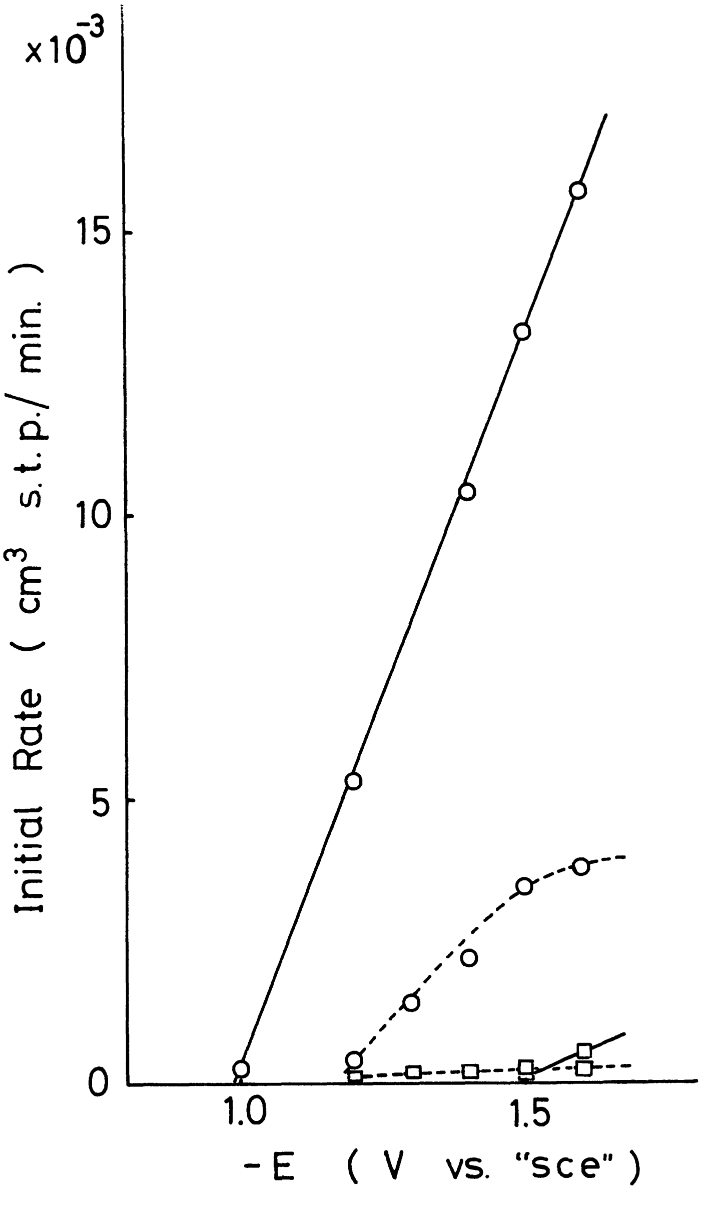
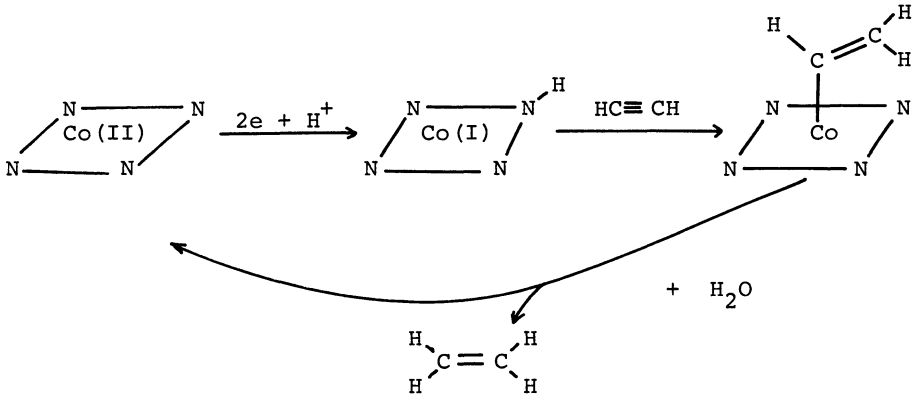


Figure 1.

Electric reduction of acetylene on an inert graphite-electrode in an alkaline (pH=9.6, Na_2CO_3-$NaHCO_3$ buffer) solution of CoPcTS ($CoPc4SO_3Na$, 0.45 mmol/70 cm^3) (——) and of Mo(V)-cysteine complex ($Na_2Mo_2(cysteine)_25H_2O$, 0.66 mmol/50 cm^3) (----) by applying various cathodic voltages from 0 to -1.6 v vs "sce" at 27°C.
The initial rates of ethylene (-○-) and ethane (-□-) formations are plotted against the cathodic voltages applied at the graphite-electrode.



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1) G.N. Schrauzer and P.A. Doemeny, J. Am. Chem. Soc., 93, 1608 (1971).

2) E.B. Fleisher and M. Krishmamurtly, ibid., 94, 1382 (1972).

3) C_2HD_3 and C_2D_4 may have resulted from the reduction of C_2D_2 with $NaBH_4$ in D_2O. C_2D_2 was formed by rapid hydrogen exchange reaction of C_2H_2 with D_2O in the reaction system. (C_2HD was hardly detected throughout the reaction.)

4) R.L. Arnett and B.L. Crawford, J. Chem. Phys., 18, 118 (1950).

5) The "leuco-species" was different from mono-negative CoPcTS because the characteristic absorption peaks at 470 and 700 nm had different intensity ratios.

6) Y. Bansho, T. Shimura, O. Ueda, H. Tanzaki and K. Takeda, Kogyo-Kagaku Zashi (Japan), 74, 1870 (1971).

7) The electron configuration of di-negative CoPc ($CoPc^{2-}$) has been elucidated as $Co(I)Pc^{2-}(d^8 + \pi^1)$ cf. R. Taube, Z. Chem. 6, 8 (1966).

8) A proton adduct of CoPc "$CoPcH^+$" gives an IR-peak at 2900-3000 cm^{-1}, which could be assigned to a stretching vibration of NH at a peripheral N-atom of phthalocyanine. ND of $CoPcD^+$ at 2180 cm^{-1}, cf. A.N. Sidorov and A.N. Terenin, Optics and Spectroscopy, 11, 175 (1961).

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