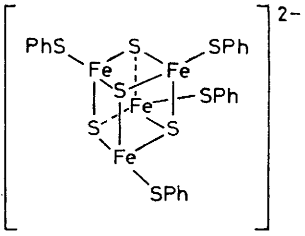
Electron-transfer Reduction of Protons to Hydrogen mediated by a Phenyl-lithium-activated Fe_4S_4 Cluster

Hiroo Inoue* and Makoto Sato

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591, Japan

A synthetic Fe_4S_4 cluster mediates the transfer of electrons from phenyl-lithium to protons from benzenethiol, in a homogeneous system, resulting in the generation of hydrogen.

The design of hydrogen-generating systems which incorporate a synthetic iron–sulphur cluster is of importance in connection with hydrogenase reactions. Recent studies have disclosed the reduction of acetylene to ethylene by the $Fe_4S_4(SPh)_4{}^{3-}$–acetic acid–acetic anhydride system in *N*-methylpyrrolidin-2-one[1] and by electrochemically reduced $Fe_4S_4(SPh)_4{}^{2-}$ in methanol/tetrahydrofuran, accompanied by the evolution of hydrogen,[2] and the reduction of protons from benzenethiol to hydrogen with $Fe_4S_4(SPh)_4{}^{3-}$ in *N*,*N*-dimethylacetamide (though in low yield).[3] We now report a novel hydrogen-generating system using a phenyl-lithium-activated cluster, $Fe_4S_4(SPh)_4(Bu^n{}_4N)_2$ (**1**), which transfers electrons from



(1)

Table 1. Catalytic generation of H_2 using an iron–sulphur cluster.[a]

		mol/Fe_4S_4[b]		
PhLi:(**1**)	Solvent	H_2	9,9′-Bi-acridan	PhPh
4:1	Et_2O	0.4	0.4	0.9
8:1	Et_2O	1.0	0.8	1.9
8:1	Et_2O–HMPT	1.6	0.8	2.4
10:1	Et_2O	1.5	0.7	2.4
10:1	Et_2O–HMPT	2.2	0.8	2.9
12:1	Et_2O	1.8	0.7	2.6
16:1	Et_2O	1.1	0.7	1.9

[a] (**1**), 0.2 mmol in Et_2O (8.8—11.2 ml) or Et_2O (7 ml)–HMPT (5 ml), PhSH:PhLi = 10:1; 0 °C, Ar. Time = 1 h (Et_2O) and 3 h (Et_2O–HMPT). [b] *I.e.* mol of product per Fe_4S_4 unit.

phenyl-lithium to protons to give *ca.* equimolar amounts of biphenyl and hydrogen [equation (1)].

$$2\mathrm{PhLi} + 2\mathrm{PhSH} \xrightarrow{\mathrm{PhLi}/(\mathbf{1})} \mathrm{PhPh} + \mathrm{H_2} + 2\mathrm{PhSLi} \qquad (1)$$

The reactions were carried out as follows, using similar procedures to those used previously.[4] The cluster (**1**) was added to a frozen solution of phenyl-lithium in degassed diethyl ether. The mixture, after melting, was stirred under argon at 0 °C for 30 min. To the resulting solution, a solution containing an excess of benzenethiol in degassed diethyl ether or hexamethylphosphoric triamide (HMPT) was added with stirring at 0 °C. Spontaneous hydrogen evolution was observed after the addition of the benzenethiol and the reaction went nearly to completion after 1 h (Et_2O) or 3 h (Et_2O–HMPT). In the former solvent the iron-sulphur cluster precipitated during the reaction; in the latter solvent the reaction system was homogeneous. As Table 1 shows, the amount of hydrogen, measured by a volumetric technique, increased with increasing amounts of phenyl-lithium up to a molar ratio, PhLi:(**1**), of 12:1 and decreased above this molar ratio. The use of HMPT raised the efficiency of the hydrogen generation. The use of acetic acid and methanol instead of benzenethiol [AcOH or MeOH: PhLi:(**1**) = 20 or 30:10:1 in ether] also resulted in the generation of hydrogen (1.7 or 1.1 mol per Fe_4S_4 unit, respectively).

To investigate the oxidation state of the iron–sulphur cluster after the reaction, acridine was added to the mixture after 1 h (Et_2O) or 3 h (Et_2O–HMPT) and the amount of 9,9′-biacridan produced was determined [acridine is not reduced by (**1**)]. Acridan was not produced in this reaction. The cluster (**1**) was regenerated by treatment with acridine. As Table 1 shows, the iron–sulphur cluster is reduced after the generation of hydrogen and can supply 1 or 2 electrons to acridine. Furthermore, after the acridine was added, the amount of biphenyl produced was measured by g.l.c. As Table 1 shows, the amount of biphenyl produced coincides reasonably with the total amount of hydrogen and 9,9′-biacridan produced, indicating that the reduced cluster mediates the transfer of electrons between phenyl-lithium and protons to give biphenyl and hydrogen. In addition, we found that the hydrogen-generating system consisting of phenyl-lithium, (**1**), and benzenethiol (12:1:24 molar ratio) in diethyl ether reduces diphenylacetylene to *cis*- and *trans*-stilbenes (0.08 and 0.15 mol/Fe_4S_4, respectively) with concomitant generation of hydrogen (1.4 mol/Fe_4S_4).

The above results provide evidence that a phenyl-lithium-activated iron–sulphur cluster exhibits catalytic activity for the generation of hydrogen by transferring electrons from phenyl-lithium to protons.

This work was supported by a Grant-in-Aid for Special Project Research from the Ministry of Education, Science and Culture.

Received, 25th June 1982; Com. 740

References

1 R. S. McMillan, J. Renaud, J. G. Reynolds, and R. H. Holm, *J. Inorg. Biochem.*, 1979, **11**, 213.
2 K. Tanaka, M. Tanaka, and T. Tanaka, *Chem. Lett.*, 1981, 895.
3 G. Christou, R. V. Hageman, and R. H. Holm, *J. Am. Chem. Soc.*, 1980, **102**, 7600.
4 H. Inoue, N. Fujimoto, and E. Imoto, *J. Chem. Soc., Chem. Commun.*, 1977, 412; H. Inoue, M. Suzuki, and N. Fujimoto, *J. Org. Chem.*, 1979, **44**, 1722; H. Inoue and M. Suzuki, *J. Chem. Soc., Chem. Commun.*, 1980, 817.