Cooperative effects in free radical release at the solid-solid interface: the case of hard metal lung disease

Laura Prandi, Ivana Fenoglio, Ingrid Corazzari, Bice Fubini

Department of Chemistry IFM and Interdepartmental Center G. Scansetti for Studies on Asbestos and other Toxic Particulates, University of Torino, Via P.Giuria 7, 10125 Torino, Italy

Pure metal cobalt and WC dusts do not generate much free radicals and are not particularly toxic to cells or humans [1]. When in intimate mixture, they constitute a pathogenic entity and cause the occupational disease known as hard metal lung disease. The implication of Reactive Oxygen Species (ROS) in some phases of the development of the hard metal lung disease has been previously hypothesized. When tested, the mixed dust had acquired, by simple mixing, a remarkable potential to generate free radicals, measurable as homolytic rupture of the C-H bond. The source of radicals would be the oxidation of metallic cobalt-to-cobalt ions in solution, leaving an electron-rich surface tungsten carbide. At the carbide surface atmospheric oxygen would be activated in a Reactive Oxygen Species (ROS) form, which would generate radicals at the carbide water interface [2, 3]. The intermediates of these reactions are still unknown.

The present work reports measurements carried out in oxygen deprived and enriched aqueous solutions, which indicate that oxygen plays a crucial role in the reaction taking place. The spin trapping technique using two different spin trapping agents, 5,5-dimethyl-pyrroline *N*-oxide (DMPO) and the 5-diethoxyphosphoryl-5-methyl-1-pyrroline *N*-oxide (DEPMPO) demonstrated the involvement of the superoxide anion as intermediate. Measurements carried out in the presence of both superoxide dismutase (SOD) and catalase confirmed this hypothesis. SOD and catalase did not suppress completely the homolytic cleavage of the C-H bond, suggesting that hydrogen abstraction and consequent release of carboxylate radical from formate occurs both at the surface and in solution. All results are consistent with the existence of two mechanisms, which occur at the same time, one involving the superoxide anion in solution and the other at the surface. The results confirm that the reactivity of the surface of hard metal dusts is modulated by the nature of the WC support.

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[3] D. Lison, P. Carbonelle, L. Mollo, R. Lauwerys, B. Fubini (1995) Chemical Research in Toxicology, 8, 600-606.