Thermal runaway prevention of high purity metals reacting with organic reagents

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Many severe chemical accidents occurred in the past while running reactions involving high purity metals reacting with organic reagents. A typical example of such reactions is the formation of alkali metal alkoxides from alkali metals reacting with pure alcohols.

Such reactions seem at the first glance very easy to run smoothly, so that they were for a long time considered as to be rather safe, the heat flow they generated seeming easy to evacuate as a consequence of their relatively low reaction rate. But despite thorough thermal reaction calorimetry studies, which all led to define apparently safe reaction conditions, a severe accident occurred 1994 in France. All investigations made at that time failed in demonstrating clearly its origins which kept a large part of misunderstanding.

More than five years later, just by serendipity, we could demonstrate that trace amounts of water in the organic reagent increased the enthalpy of the reaction of sodium with alcohols by much more than the simple reaction of the contained water reacting with sodium could yield by sodium hydroxide formation.

Further, the diffusion rate of low concentration impurities in metals becomes important as soon as the temperature reaches more than about 90% of the absolute melting temperature [1]. This will result in the formation of a fine impurity layer at the metal-organic reagent interface. Moreover, by becoming superficial atoms, these impurities will have their chemical potential enhanced as a consequence of their interfacial position. By becoming more reactive, they will be preferentially removed from the interface. The metallic phase becomes extremely pure [2] with less than a few ppm total impurity, and electrochemical interfacial charge buildup will occur. This results in thermochemical instability, with reaction rates oscillating by a factor of more than 20 over periods in the minute range. Although unexplained at that time, such oscillating reaction rates had already been observed by [3] for metals reacting with aqueous halogenacids.

The reaction enthalpy of alkali metals with alcohols could be shown as to be nearly athermic as long as the alcohols are completely water-free. But water contents by no more than about 0.4% by weight increase the exothermicity of the enthalpy of dilution of the formed alcoxide up to more than 270 kJ/mol in the not yet consumed free alcohol. At high reaction rates, the result is the formation of interfacial hot spots with local adiabatic temperature increasing higher than 200K. Such hot spots are hotter than what is required for starting runaway processes if no prevention measures have been taken.

Since most of the formation reactions of organometallic compounds from the elemental metallic phase are reversible, equilibria between simultaneously present elements will take place while the formation reaction goes on. Therefore, the presence of more than one metallic species in the organic phase will result in the contamination of the metallic interface by the equilibrium set amount of a minor species, keeping so the electrical potential of the metallic conductive phase at the mixed potential as defined by Nernst's law taking into account the relative concentrations and normal potentials of all electrochemically interchangeable species at the interface. Since this mixed potential results from fast electrochemical reactions, it remains always close to equilibrium conditions. Therefore, it stabilises the electrical potential of the metal phase and avoids the reaction rate fluctuations as resulting from the use of nearly pure metals.The reaction becomes stable and controllable provided metallic impurities are present in the organic phase.

[1] A.M. Brown, M.F. Ashby, *Acta Metallurgica* **28** (1980) 1085-1101.
[2] S. Walter, A. Hatterer, Patent ANVAR n° 844008078 (10/04/1984)
[3] E.S. Hedges, J.E. Myers, *J. Chem. Soc.* **127** (1924) 604, **127** (1925) 445, **127** (1925) 1013