

RADICAL INITIATION: SINGLE ELECTRON TRANSFER

We saw in the section on redox reactions that single electrons can be transferred from one species to another. Because one electron is transferred at a time, radicals can be initiated this way.

Metals that are high in the activity series, such as lithium or sodium, can easily donate their valence electrons to organic compounds. As a result, those organic compounds become radicals.

The possibility for this reaction is most easily understood in terms of carbonyl chemistry. Carbonyls are electrophiles. The electrophilic carbon normally accepts a pair of electrons from a nucleophilic donor. However, a single electron could be thought of as a nucleophile, too.

For example, if benzophenone is dissolved in an unreactive solvent, such as ether, over a few pieces of sodium, the sodium can transfer an electron to the carbonyl.

The interesting thing about this reaction is that, although benzophenone is a white (or colourless) compound and ether is a colourless liquid, the ether solution turns deep blue after a couple of hours. Benzophenone radical anion is a deep blue colour.

Benzophenone radical has long played an important role in research labs. For many years, sodium has been used as a drying agent for organic solvents. Because of the well-known propensity of sodium to react with water, any traces of water in a flask of ether are destroyed. They are converted to

sodium hydroxide and hydrogen gas. However, in the absence of water -- that is, if the sodium has already done its job -- the sodium can transfer electrons to benzophenone in solution, producing a blue colour.

Benzophenone thus works as an indicator to let researchers know that the solvent is dry.

After a few more hours, the colour changes once more to a deep purple. That's because a second electron gets transferred to the benzophenone radical, forming benzophenone dianion. That's when you know the solvent is really, really dry. However, all of this has to be done under a nitrogen atmosphere, or else the benzophenone radical anion undergoes additional reaction with oxygen, producing yellow schmutz all over the flask instead of the beautiful purple colour. This drying method also works with benzene or toluene, or with a little modification, saturated hydrocarbons such as pentane. It doesn't work with many other solvents, which might instead react directly with the sodium.

But what would happen if, at this point, we carefully introduced some protons? Maybe it is in the form of an acid, either strong (HCl) or very weak (NH₄Cl). The benzophenone dianion would surely get protonated, and since it is a dianion it would get protonated twice.

The overall result is a reduction of the benzophenone to the corresponding alcohol, 1,1-diphenylmethanol. It would be just like we had added sodium borohydride, a source of nucleophilic hydride (that's a proton plus two electrons) and then did an acid workup (adding a second proton. In this case, we have just adding the components (two electrons, two protons) in a different order.

Furthermore, this method of reducing things isn't really limited to carbonyls. Alkynes and aromatics are also susceptible to reduction to the radical anion or dianion, although a more active metal than sodium is required. These reductions require lithium.

Interestingly, these latter reactions are very regiospecific and stereospecific. The sites of the anions (and subsequent protonations) are as far apart as possible. That means that the anions are found at the 1,4-positions in the case of the benzene ring. That can be understood in terms of a simple electron repulsion factor.

Furthermore, the remaining double bonds are in the more substituted positions; that's understandable in terms of the trend of alkene stability, in which more substituted double bonds are more stable.

In the case of alkynes, the trans alkene always results from lithium reduction. This reaction is complementary to hydrogenation with Lindlar's catalyst, which always results in cis alkenes.

It may be surprising that the dianion is not required in order to get this keep-the-negative-charges-far-apart selectivity. Normally, these reductions are conducted in liquid ammonia. Under those conditions, the initial radical anion is protonated before the second electron donation. The dianion never actually forms, yet the selectivity is still the same.

These reactions are sometimes called "dissolving metal reductions" because the lithium metal dissolves in the liquid ammonia. The metal actually undergoes ionization to produce Li^+ and e^- . This "salt" is called "lithium electride" and it produces a bright blue colour in the liquid ammonia. If you

keep adding more and more lithium to the ammonia, at some point the solution turns gold in colour.

Source: <http://employees.csbsju.edu/cschaller/Reactivity/radical/radicalSET.htm>