

Re: copper etching

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From: Wilco Oelen (*photo_at_woelen.nl*)

Date: 12/28/04

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farooq_w@hotmail.com wrote:

> *Wilco Oelen wrote:*

> > *farooq_w@hotmail.com wrote:*

> > > *Wilco,*

> > > *The chance of chlorine evolving from a iron-HCl-H2O2 mixture is*

> > *almost*

> > > *zero because of the instant reaction, similar to*

> > *hypochlorite-peroxide*

> > > *reaction, between gaseous Cl2 and H2O2. The noxious vapors are*

> *oxygen*

> > > *from peroxide decomposition loaded with HCl vapors from the heat of*

> > *the*

> > > *reaction.*

> > *With this I have to disagree. I have experience with mixing 30% H2O2*

> > *and 30% HCl. If you do this, then a strong smell of Cl2 can be noticed.*

> > *Not so much, that the liquid starts bubbling, but sufficient to be*

> > *choking. The smell of Cl2 is quite different from the smell of HCl.*

> *Cl2*

> > *especially is formed, when the liquid is heated somewhat. This is why*

> > *the fumes are so corrosive, much more than plain HCl-fumes.*

>

> *Wilco,*

> *Somehow I didn't feel convinced that the HCl-H2O2 mixture could evolve*

> *chlorine gas so I checked a very comprehensive monograph on hydrogen peroxide; it did not mention the reaction of HCl with H2O2*

> *(conductivity measurements of HCl in hydrogen peroxide were given*

> *though), instead it was written that elemental chlorine is reduced to*

> *chloride by hydrogen peroxide. If you remember the experiments with*

> *copper where I used concentrated (~12M) HCl, copper turnings with pure*

> *35% H2O2. No odor at all, except vigorous bubbling due to oxygen was*

> *noticed.*

- > Lets take the electrode potentials of two half cells:
- > $\text{Cl}_2 + 2e \text{ ----> } 2\text{Cl}(-) + 1.36 \text{ V}$
- > $\text{H}_2\text{O}_2 + 2\text{H}(+) + 2e \text{ ----> } 2\text{H}_2\text{O} + 1.77 \text{ V}$
- >
- > Then theoretically the oxidation of chloride to chlorine is possible as
- > E for the overall reaction $(1.77 - 1.36)\text{V}$ is positive though the
- > difference is quite small. But remember that H_2O_2 has quite weird
- > reactions.
- >
- > Why didn't I notice chlorine from $\text{HCl}-\text{Cu}-\text{H}_2\text{O}_2$ mixture, using much more
- > concentrated reagents? You mixed concentrated HCl and 30% H_2O_2 , and
- > immediately noticed chlorine odor or did it take some time for the odor
- > to be noticeable?

I did the following:

Mix up H_2O_2 (30%) with HCl (somewhere between 30% and 35%). The ratio is something like 2 volumes of conc. HCl to 1 volume of 30% H_2O_2 , total volume was somewhere between 30 and 50 ml. I don't remember exactly anymore, but much less volume of H_2O_2 than volume of HCl . Immediately after mixing, there was no odour of Cl_2 . I added copper wire, which quickly dissolved. There was a lot of bubbling of oxygen and the liquid became quite hot. After some time, I smelled Cl_2 .

So, what I think is that H_2O_2 and HCl do react to form Cl_2 , but only small amounts, as I already mentioned in the earlier posts and slowly. But it is sufficient to be a problem when storing the mixture of H_2O_2 and HCl .

I know that with hypochlorite the reaction is the other way around (hypochlorite and H_2O_2 give O_2 and water, very nice red light effect!). In acid environments, the situation is quite different.

But, in order to settle the problem for once and for all, I'll do a little (and careful) experiment with 30% H_2O_2 and 37% HCl . I'll let you know the result in a follow up post. It might also be that the presence of certain metal ions influence the reaction.

Wilco