



The art and science of
amateur experimentalism

[Hydroxylamine via HCL, Nitromethane, and H2O?](#)

Khemi - 20-9-2016 at 17:10

Can you arrive at (H3NO) Hydroxylamine hydrochloride by refluxing (6mol)

648g HCL
450g H2O
366g Nitromethane

and if so, how long should the reflux take at 100c? How much distillate should be removed before crystallization will take place?

What is the anticipated yield of H3NO.hcl?

I truly appreciate the help/advice.

madcedar - 20-9-2016 at 20:30

Sure, I didn't check your ratios but Axo did it here (with pictures):

<https://www.sciencemadness.org/whisper/viewthread.php?tid=58...>

nitro-genes - 21-9-2016 at 00:58

Attachment: [Action of mineral acids on primary nitroparafins.pdf](#) (433kB)

This file has been downloaded 377 times

zed - 21-9-2016 at 16:31

Ahhh. Something I hadn't suspected.

Nitromethane seems to produce Hydroxylamine PLUS Carbon Monoxide under these conditions. Gotta do something about that CO gas.

Perhaps this experiment is best performed, as an outdoor experiment.

nitro-genes - 22-9-2016 at 03:15

IIRC, only using highly concentrated sulfuric (>85%) carbon monoxide is formed in large quantities, it's still best to perform this reaction outside though. Not only due to any potential CO formed, but a layer (good stirring) of nitromethane saturated with HCl at >100 deg C. may also be potentially explosive (although I couldn't find any examples where this was the case). The reaction with concentrated sulfuric is more dangerous, as this produces some exotherm upon mixing/heating, and heating should be performed cautiously in the beginning. Also not sure if even very concentrated HCl would produce any CO at all, as Axt's

pressure bottle would have exploded if this was the case.

[Edited on 22-9-2016 by nitro-genes]

Tsjerk - 22-9-2016 at 04:34

I repeated Axo's experiment a long time ago and I can tell that the reaction works. I do advice though to recrystallize the product a couple of times as it seems that HCl "sticks" to the crystals.

nitro-genes - 22-9-2016 at 07:09

Both sulfuric drain cleaner and hardware store HCl can be contaminated with substantial amounts of transition metals, especially iron. Copper and copper salts are known to catalyse decomposition of hydroxylamine, not sure if this is the same for Fe³⁺ or still applies under very acidic conditions, though maybe something to keep in mind?

Cryolite. - 22-9-2016 at 08:46

I just looked into it. ~0.2% of either ferrous or ferric iron contamination induces extremely violent (boiling) decomposition of 50% hydroxylamine in water. See the attached paper.

However, the authors of that study performed their tests under neutral conditions. The presence of acid stabilizes hydroxylamine as hydroxylammonium, much like acid stabilizes hydrazine as hydrazinium.

In fact, this <https://infoscience.epfl.ch/record/176224/files/Billeter%20e...> says that under acidic conditions, ionic iron doesn't do much of anything to decompose hydroxylamine.

Thus, as long as you keep the solution acidic and crystallize the hydroxylamine salt out of solution, I wouldn't worry about iron contamination too much.

Attachment: [je030121p.pdf](#) (132kB)
This file has been downloaded 269 times

[Edited on 22-9-2016 by Cryolite.]

nitro-genes - 22-9-2016 at 10:49

Thanks for looking that up, wouldn't have guessed 10 ppm ionic iron would have such dramatic effects. Better recrystallize the acid hydroxylamine when planning to use the freebased hydroxylamine in a synthesis. 😊

Thanks for the input!

Khemi - 2-10-2016 at 18:49

If performed I would use a flask, fitted with a condenser, with a pressurized equalized additional funnel with a male outlet on top to direct any gas that is evolved, outside.

I do not like the idea of making this in a pressurized vessel. I do like the idea of making it in the manner I laid out, even if the yield is slightly less.

Can someone confirm if my ratios (in my original post) are on point if I intend on carrying out this synthesis in this manner?

648g of 31.45%

450g H₂O
366g Nitromethane

Im guessing 175g of Hydroxylamine.HCl would be about the yield, give or take a few grams.

Do my ratios look ok?

greenlight - 24-11-2020 at 07:26

Thought I would add to this instead of making a 200th hydroxylamine thread.

The acid-catalyzed hydrolysis of nitromethane with hydrochloric acid was attempted without sealing of mixture in a vessel or pressure application.

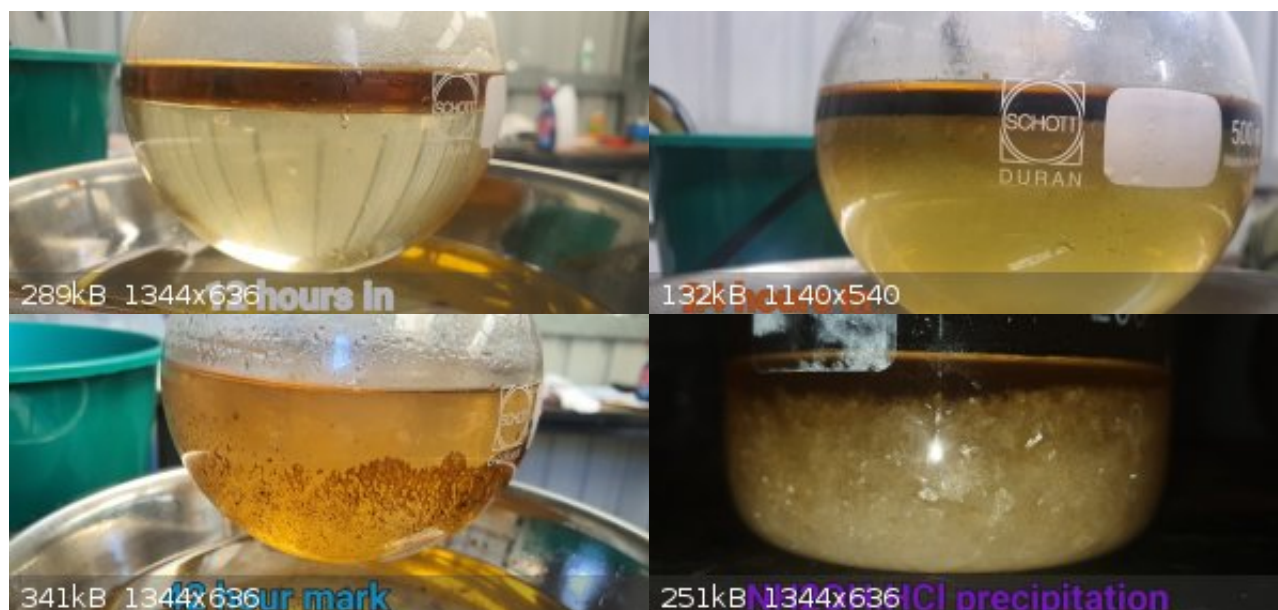
228 grams of 32% hardware store hydrochloric acid was mixed with 122 grams of remote control car fuel grade nitromethane in a round bottom flask. A condenser was attached with a loose smaller size plastic stopper placed on top and the flask placed in a 100°C oil bath. The apparatus was set up outside.

After 8 hours of heating, the had formed a dark top layer. Reflux was continued for 42 hours peridically with the apparatus being shut off at night time. Slowly, the nitromethane layer became smaller and the aqueous layer darker yellow until a homogenous mixture resulted. Small amounts of white fuming was noticed during this time

The mixture was transferred to a beaker and heating continued on a hotplate until 1/3 of the solvent was removed. At this time heating was turned off and and the dark yellow-orange liquid left to cool. After room temperature was reached, slight agitation of the beakers contents resulted in a crash precipitation of a large amount of white hydroxylamine hydrochloride flakes. The crop of crystals was filtered and dried while the solvent was returned to heat and reduced ny half volume. A second crop of hydroxylamine was recovered and after drying, final yield was 51.53g.

Theoretical yield would be 138.80g so this corresponds to a 37% yield overall with no pressure involved.

[Edited on 24-11-2020 by greenlight]





sffap - 22-12-2020 at 16:21

I've also performed this synthesis more times than I care to remember but I found the sweet spot for ~75% yields was to use 25% HCl instead so that you keep more of the HCl in the liquid phase. A highly efficient reflux condenser is very handy too to keep everything from escaping. Remember MeNO₂ boils around 100 C.

However, you don't need to perform the reaction at 100 C either. The last reaction I did was outside in winter and the ambient temp prevented my oil bath from getting the reaction mixture above 94 C but after 40 hrs constantly refluxing that MeNO₂ layer was entirely gone, and the remaining liquid only had a light straw-yellow colouration.

As others have mentioned, multiple recrystallisations from water (and a few cold methanol washes at the end) work wonders for eliminating the remaining acid which I believe is formic acid. Boiling the reaction mixture hard to reduce the volume and induce crystallisation will eliminate a fair bit of acid so watch out for those fumes too!

Stirring is also unnecessary as it doesn't seem to drive the reaction forward in any meaningful way.
