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HYDRAZINE SULFATE SYNTHESIS

OPTIMIZED OTC PROCEDURE

The hydrazine sulfate synthesis which I have done successfully many times is a slightly modified procedure based on the method described by GB392845. Everything is OTC ingredient optimized and the yields are high, the hydrazine is freebased into methanol by a modified procedure similar to GB876038. This results in hydrazine hydrate in methanol. However, if the methanol contains sufficient sodium methoxide or potassium methoxide, by methods such as US2278550 or US4267396, then anhydrous hydrazine in methanol is the result :-). Good yields of alkali azides may be obtained by reaction of the methanolic hydrazine with isopropyl nitrite. See US1628380, US5098597, US5208002. Small scale syntheses for alkali azides are favored by anhydrous methods in my experience.

There is no problem using OTC materials if you compensate the approach and adjust for total water, and keep to the molar proportions. I could write up the details for Hydrazine Sulfate OTC optimized quick and easy. The reaction is a bit complicated by foaming at a point, so a lot of empty space in the reaction vessel is required, as headroom for preventing overflows. This constraint places the yield limit to about 140 grams of hydrazine sulfate for a "pickle jar" sized reaction vessel. Actually I do the reaction in a 4 liter erlenmeyer equipped with a 4 liter foam overflow return reservoir. A 6 liter flat bottomed florence flask would be better. The oxidation of urea proceeds just fine in the cold and I prechill the basified hypochlorite to 10 below 0 degrees centigrade. Get it stirring with a large stirbar, and pour the warm urea/gelatine solution into the vortex of the mixture. I let the reaction proceed on its own gentle exotherm for about 1 and one half hours, and through to a point of 75 per cent subsiding of foaming, before applying any supplemental heating to finish the oxidation. The foaming can get wild when the heat is applied if the reaction has not proceeded far enough towards completion before the heating is applied. This synthesis goes through some interesting color changes which help to track the progress of the reaction towards completion.

About two minutes after pouring in the warm urea/gelatine solution the mixture changes from light yellowish green to white and the mixture foams to double its volume. After ten minutes the stiff foam begins to break free under the influence of the stirbar and slowly subsides while becoming more mobile and stirrable. After one hour the foam has subsided to about two thirds its initial highpoint. A slight orange color is noted. The foam continues to fall and then heat is applied very gradually, because just a small heating will kick the reaction back into a vigorous foaming, and this is when the overflow may occur. The idea is to just nudge the reaction rate a bit, and then let it proceed to run on its own energy again. The orange color will become very pronounced and darker at this stage of the reaction, as the foaming subsides nearly completely. At this point it is safe to increase the temperature rapidly up about 85 or 90 degrees centigrade to drive the reaction to completion. At the endpoint of the reaction the dark orange color will dissipate almost completely, and the solution color will suddenly fade to a very pale slight yellow tint, almost clear. When you see that color change, the reaction is complete. Peak the temperature, and then discontinue heating. Immediately remove the flask to a cool water bath.

EXPERIMENTAL:

1500 ml of 10 per cent sodium hypochlorite is placed into a 2 liter glass jar, lightly sealed with a lid, and placed into the freezer overnight to chill to 15 below 0 degrees centigrade. Into the prechilled 1500 ml of "liquid pool chlorinator" is dropped a stirbar and while stirring, 194 grams of fine prilled NaOH is added into the vortex at a rate as fast as it will dissolve and not accumulate on the bottom. Because of the exotherm, the addition must be done in two portions in order to prevent excessive warming and thermal decomposition of the hypochlorite. The first portion of the NaOH should be about 110 grams, and then the solution should be rechilled in the freezer to about 0 degrees centigrade before adding in the same manner the remaining 84 grams of NaOH. The basified hypochlorite is then returned to the freezer for keeping, and to rechill to 15 below 0 degrees centigrade for its use later in the hydrazine synthesis.

In a separate half liter jar having a lid, 132 grams of urea is dissolved in 70 ml of hot distilled water.

In yet another half liter jar having a lid, 1.8 (one and eight tenths gram) grams of gelatine is dissolved in

70 ml of hot distilled water.

Shaking of these containers will facilitate the solution, and supplemental warming of the containers in a hot water bath will also be required. After these warm solutions are prepared, and all solids are dissolved, the two solutions are combined just before use, and the combined solutions are kept standing in a bowl of warm water to maintain everything in solution and prevent the mixture from congealing, which will occur if the mixture is allowed to cool.

A 4 liter Erlenmeyer flask is placed upon a stirrer hotplate and a three inch stirbar is placed in the flask. The heat remains off. Into the neck of the flask is placed a wide mouth plastic funnel of one gallon capacity, the neck of the funnel is enlarged with a bushing cut from a two inch length of one and five eighths OD, one and one quarter ID, tygon vinyl tubing, for a snug fit in the neck of the flask. The plastic funnel serves as an overflow reservoir and return path for any foaming which may exceed the capacity of the flask during the reaction.

The previously prepared, cold basified hypochlorite solution is poured into the flask and the stirrer started without any heating. The previously prepared, warm combined solution of urea and gelatine is poured through the funnel into the well stirred hypochlorite.

After a couple of minutes the reaction will initiate, and after fifteen minutes the foaming mixture will occupy twice the original volume, and the foam will temporarily be very rigid and motionless, but this will not persist for more than a few minutes. The foam will begin to very slowly disintegrate and stir down. The foam is viscous enough to cause uncoupling of the stirbar on the stirplate, at speed settings above 40 per cent, so it is better to have it stir successfully at a conservative setting.

About one hour after the reaction is begun, supplemental heat is applied, cautiously at first, because about ten minutes later a renewed episode of foaming will occur. This is a very transient and less viscous foaming which dissipates quickly. The onset of this foaming will be indicated by a dark orange color about the reaction mixture. When this episode of foaming occurs the reaction is nearing completion, and with increasing heating of the mixture to about 90 degrees centigrade, the reaction is complete at about one and one half hours from the beginning.

I do not even measure the temperature endpoint, but establish the endpoint by observing the color shift from orange to a very pale yellow, almost clear.....very light tint to the solution. When the mixture has become hot enough, and all the foaming has subsided, the moisture will begin to reflux on the walls of the flask above the liquid and in the neck area of the flask. This happens when a mixture is nearing the boiling point, which is plenty hot enough for this reaction. So when the refluxing moisture and color change have occured, the heating is stopped and the flask is removed to a cooling bath. After the mixture has cooled down, it is acidified by the dropwise addition of dilute sulfuric acid, with stirring, and using the same overflow funnel setup as before. 1100 ml of density 1.260 new battery electrolyte, which is 35 per cent sulfuric acid, is added at a rate of 3 or 4 drips per second to the stirred solution, and an exotherm is evident during the neutralization / acidification. The acidified mixture is cooled to about 10 to 15 degrees centigrade for precipitation of the hydrazine sulfate, and allowed to stand for several hours to complete the precipitation. Do not chill the mixture very cold or huge amounts of Glaubers Salt (hydrated sodium sulfate) will settle out along with the hydrazine sulfate.

The hydrazine sulfate is filtered and dried, yield is 159 grams.

In the previous communication about the usefulness of urea, I failed to mention a patent which shows the usefulness of urea in synthesis of methylamine. EP 0037862 discloses a high yield synthesis for methylamine nitrate. Also see GB1548827 for a closely related synthesis. It is my guess that paraformaldehyde would react with a diluted urea/ammonium nitrate eutectic. There was a mention of the nitrate process at the Hive, but no details or followup information was posted in the methylamine FAQ. Also see GB168333.