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Neutralization of a Toluene Waste Stream Containing Thionyl Chloride

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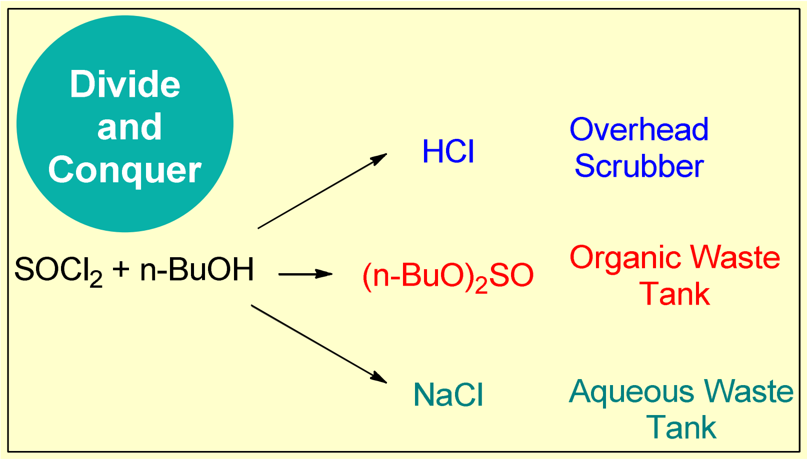
TOC graphic


Divide and Conquer
SOCl$_2$ + n-BuOH
HCl
Overhead Scrubber
(n-BuO)$_2$SO
Organic Waste Tank
NaCl
Aqueous Waste Tank

ABSTRACT:

Neutralization of thionyl chloride in was found to be ineffective with water. A solution is to use an excess of a soluble reagent to consume the thionyl chloride. Butanol was shown to convert thionyl chloride to n-butyl sulfite and hydrogen chloride. An aqueous workup removes any residual hydrogen chloride.

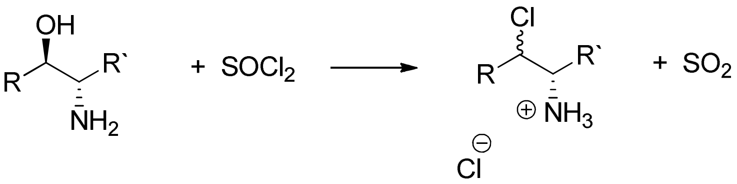
Keywords: thionyl chloride, neutralization, safety, waste

Background.

Waste is an integral part of chemical processing and multi-step complicated batch processes are often fraught with high waste to product ratios. Waste issues are typically more logistical and regulatory rather than chemical. However, there are cases where the waste presents a significant safety or disposal issue that requires a chemical resolution. Although neither glamorous nor sophisticated, solving waste issues is a necessary and sometimes challenging task.

This waste stream originated from a process that converted an α-hydroxy amine to the corresponding α-chloro amine hydrochloride with a 10-20% excess of thionyl chloride (Scheme 1). The product of interest precipitates almost quantitatively, leaving behind a dilute solution of thionyl chloride in toluene. Disposal of the flammable, reactive, and corrosive waste presented an unexpected challenge.

Scheme 1. Reaction of thionyl chloride with an α-hydroxy amine



Development.

Simply disposing of the waste into the on-site organic waste tanks was undesirable since the thionyl chloride would react vigorously with alcohols, amines and water. Besides having an uncontrolled chemical reaction taking place inside of a waste tank, this would generate hydrogen chloride that could be corrosive to the 316 stainless steel material of construction (MOC) of these tanks. It seemed prudent to neutralize the thionyl chloride before disposing of the waste.

The original notion for neutralizing the excess thionyl chloride was a simple aqueous sodium hydroxide quench, where the toluene waste stream and dilute aqueous sodium hydroxide were mixed together at ambient temperature. Bretherick's indicates there are issues with this approach.[1] The monograph points out that in one case, this led to disposal of a toluene solution with active thionyl chloride still present that reacted in an uncontrolled manner in another vessel. Bretherick's indicates the agitation in the example was inadequate and suggests "extremely good agitation" as a solution. However, when this approach was implemented in the large scale production of this product, the thionyl chloride was still unquenched.

Reagents such as thionyl chloride and its phospho-analog phosphorus oxychloride are commonly used in organic synthesis, e.g., in converting carboxylic acids to acid chlorides and alcohols to chlorides. However, their reactivities are often underappreciated. For example, when a waste stream containing thionyl chloride in ethyl acetate was drummed without neutralization a runaway reaction took place.[2] Thionyl chloride has been shown to react exothermically with DMF, THF, and MTBE.[3,4] Similarly, phosphorus oxychloride can react exothermically with acetone.[5] In one hazard study, it was shown that partially hydrolyzed phosphorus oxychloride can react unexpectedly after a period of time even in the presence of a large excess of H_2O if there is no pH control.[6] This latter investigation developed analytical methods (^{31}P NMR and Raman spectroscopy) to track the intermediates and determine when the hydrolysis was complete so the waste could be safely discarded.

After the failure to adequately neutralize the unreacted thionyl chloride in the production run, an investigation was initiated to explore the apparent lack of reactivity of thionyl chloride with water. The initial challenge was to analyze for thionyl chloride as there was no process related analytical method for thionyl chloride and developing one would have been detrimental for the project timeline. Although observation of ‘smoke’ when the solution was exposed to air was satisfactory for the production scale filtrate to indicate the presence of thionyl chloride, something more quantitative was needed for this effort. Although gas evolution is measurable, the method of choice was to measure a change in pH. Treatment of an aliquot of the thionyl chloride solution with deionized water would show a sharp drop in pH if thionyl chloride was present; monitoring the change in pH in this manner is a rapid, semi-quantitative assay. For this investigation, the pH change approach was used in nearly every case to determine the presence of thionyl chloride.

The logic behind the plan to quench the thionyl chloride was to take advantage of the products of hydrolysis. Each mole of thionyl chloride reacts with water to form one mole of sulfur dioxide and two moles of hydrogen chloride (Scheme 2); both products are gases, but the hydrogen chloride should stay in the reaction's aqueous phase. The sulfur dioxide would likely be driven overhead into the high pH scrubber system and neutralized to form a dilute solution of sodium sulfite. The scrubber waste is usually disposed by transferring directly to the on-site waste water treatment plant. One issue with this approach would be the inadvertent mixing of this stream with an acidic stream which would drop the pH and possibly release sulfur dioxide gas. This can easily occur when waste streams from multiple processes are mixed. However, this is minimized in this case as the solution is rather dilute. The hydrogen chloride left in the aqueous phase of the reaction mass would be readily handled by direct neutralization with sodium hydroxide.

Scheme 2. Hydrolysis and neutralization of thionyl chloride

$$SOCl_2 + H_2O \longrightarrow SO_2 + 2HCl$$

$$SO_2 + 2HCl + 4NaOH \longrightarrow Na_2SO_3 + 2NaCl + 3H_2O$$

With the pH change analytical tool in hand, the laboratory investigation began and the first effort to neutralize the thionyl chloride focused on reacting the thionyl chloride/toluene stream with water at an elevated temperature to accelerate the reaction. Even after heating to 90 °C for 1½ hours and extraction with dilute sodium hydroxide, addition of deionized water demonstrated a sharp drop in pH, indicating unreacted thionyl chloride was present.

To evaluate the effect of a surfactant, an acid stable surfactant CIP 200® was added to water to treat the thionyl chloride in toluene.[7] This too was heated to 90 °C and stirred for 24 hours, but the next day, the reaction mass was visibly off-gassing, a positive indication of thionyl chloride.

It would seem the problem with water as the quenching reagent for thionyl chloride is the mutual lack of solubility of both compounds in the other solvent. Water has very low solubility in toluene (0.03% at 20 °C) while thionyl chloride apparently has no affinity for water.[8] This latter point was surprising, given the rapid reaction neat thionyl chloride has when added directly to water. Thionyl chloride is evidently quite lipophilic.

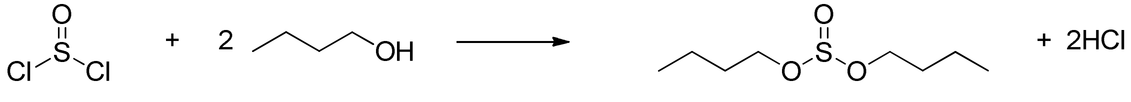
The key to quenching thionyl chloride then would be to use a toluene soluble reactant. Thionyl chloride reacts with many substrates, but an alcohol is a very convenient reactant and produces an organic product completely soluble in the toluene system. The choice was made for n-butanol (bp 116 – 118 ºC) as it was already available on-site and should react with thionyl chloride to form the requisite gases sulfur dioxide and hydrogen chloride, and relatively nonvolatile 1-chlorobutane (bp 77 – 78 ºC). 1-Chlorobutane was compatible as a component of the resultant waste stream for off-site disposal and the two gases can be readily neutralized with an aqueous workup.

To pursue this, an excess of n-butanol was added to a solution of thionyl chloride in toluene, heated to reflux to drive out the sulfur dioxide and hydrogen chloride, cooled and extracted with aqueous sodium hydroxide, and finally water. This time, the pH of the final water wash was stable, indicating no active thionyl chloride. This process was further demonstrated on a combined sample of filtrate and wash from laboratory scale processing experiments. The best process for neutralizing the thionyl chloride waste stream incorporated an excess of n-butanol relative to a full charge of thionyl chloride.

To further investigate this improved analytical methods were utilized to fully characterize the neutralization reaction. Gas chromatography was initially evaluated to quantify the 1-chlorobutane and n-butanol in a quenched toluene/thionyl chloride reaction mass that used 90% excess of butanol relative to thionyl chloride. The results were surprising, as the levels of both 1-chlorobutane and n-butanol were estimated to be less than 0.1% w/w, when they should have been in the 3% w/w range.[9] Further, the relative peak areas on the chromatogram were expected to be about the same but they were not. Rather, the 1-chlorobutane peak was less than 5% of the area of the n-butanol peak; based on the stoichiometry of the proposed chemistry they should have been nearly the same area.

^{1}H NMR was then used to analyze the thionyl chloride neutralization reaction mass and it confirmed the gas chromatography findings; n-butanol was estimated at 0.04% and there was no detectable butyl chloride.[10] It also identified the actual product of the neutralization to be n-butyl sulfite, not 1-chlorobutane; see Scheme 3. The literature precedent on this is well established; an excess of alcohol will lead to the formation of a sulfite ester and not the alkyl chloride.[11]

Scheme 3. Reaction of Thionyl Chloride with an excess of n-Butanol



^{1}H NMR estimated the concentration of n-butyl sulfite to be 7.6%; the expected concentration is 7.85%, indicating very good agreement.[10] The discovery of n-butyl sulfite was an unexpected finding based on the original notion of using an alcohol to convert the unreacted thionyl chloride to sulfur dioxide, hydrogen chloride and an alkyl halide. The large excess of alcohol charged to the quench drove the reaction toward the formation of the alkyl sulfite and hydrogen chloride. However, the end result is the same since the thionyl chloride is consumed and the aqueous workup removes any corrosive hydrogen chloride left in the quenched reaction mass, which is now safe to dispose.

It should be emphasized that none of the products from the neutralization of thionyl chloride are harmless. The corrosive hydrogen chloride is easily handled as a dilute aqueous solution and neutralized with sodium hydroxide, a very common procedure in manufacturing. Any sulfur dioxide would be handled similarly. The organic products, n-butyl sulfite as well as the low level n-butyl chloride, are potential alkylating agents. In this case, they are dilute and do not impact the disposal by combustion of the toluene waste stream. Any personnel exposure to this waste stream would be very unlikely due to the infrastructure and procedures for handling of waste streams.

The data indicates that an even larger excess of alcohol should be used to cleanly convert the thionyl chloride to the corresponding sulfite. In the last case described with enhanced analytical scrutiny, a 90% excess was adequate to convert the thionyl chloride to sulfite. There was some 1-chlorobutane formed but it was practically at trace levels. Although the quench reaction should drive off hydrogen chloride overhead to the scrubber system in this approach, the laboratory data indicated significant acid was still present necessitating an aqueous workup.

Although this was demonstrated successfully in the laboratory, timing requirements in production dictated the corrosive waste had to be disposed at a higher than normal cost before this work was completed.

Conclusion.

Often too little effort is put forth on issues like this proactively. As documented here, this particular waste issue was not fully investigated prior to full scale production. This effort highlighted two key points required to solve the issue of residual reactive compounds like thionyl chloride in lipophilic organic waste streams. First, there has to be a method to detect the reactive compound that is adequate to determine the absence or presence of significant amounts of it. The second is the choice of the chemistry reaction to consume the residual reactive compound. The important point here is to react it with a convenient lipophilic soluble reagent that does not create additional problems for the waste stream disposal. The approach of using n-butanol was shown to be more controllable, reliable, and safer than trying to quench thionyl chloride with water alone.

Experimental.

All materials were used as received from qualified vendors. Gas chromatography was performed on an Agilent 7890A with an Agilent J&W, DB-1701, 30M X 0.32mm, 1.00 µm df, column. Inlet Temperature: 270 °C, Split injection, with a 100:1 split ratio and a septum purge flow of 3.0 mL/min. Separations were performed at a constant flow of 1.80 mL/min. Gradient was 40 °C for 1.0 minute, 15 °/min. to 150 °C, no hold time, 20 °/min. to 250 °C, no hold time for a total run time: 13.33 minutes. FID detector was set at 270 °C. Make-up gas: He with constant total flow at 25.0 mL/min. Injection Volume: 1.0 μL. ^{1}H NMR spectra were obtained on a Bruker 300 MHz spectrometer in $CDCl_3$.

Aqueous Quench of Thionyl Chloride at Elevated Temperature. Toluene (114.38g) and thionyl chloride (7.5 mL, 12 g, 100 mmole) was charged to a jacketed reactor and the temperature adjusted to 20 °C. Water (13 mL, 722 mmole) was added slowly over 20 minutes; off gassing was noted during the addition. The reaction was warmed to 82-91°C for 1.5 hours and then cooled to 23.8 °C. During the high temperature hold, no visible off-gassing was noted.

Sodium hydroxide (50%, 20.31 g, 250 mmole) and water (80 mL) was charged to the addition funnel; the solution was added to the reaction over 10 minutes with no apparent exotherm. Agitation was ceased and the lower aqueous layer was removed; pH was 13.12. Water (100 mL) was added back to the toluene solution and agitated for 5 minutes. The lower aqueous layer was removed; pH was 1.70.

Aqueous Quench of Thionyl Chloride with Surfactant. Toluene (116.24 g) and thionyl chloride (7.6 mL, 12.4 g, 104 mmole) was charged into a 500 mL round bottom flask. A solution of water (47.35g) and CIP 200® (2.70 g) was charged to an addition funnel and added slowly to the toluene solution. Cooling was necessary to keep the solution at ambient temperature. The reaction was stirred at 20-30 °C for an hour and then heated to reflux (90 °C) for 24 hours. After the hold time, off-gassing was discernible.

Initial Thionyl Chloride Quench with n-Butanol. Toluene (242 mL) and thionyl chloride (13.5 mL, 22.0 g, 185 mmole) was added to a jacketed reactor. n-Butanol (22.00 g, 297 mmole) was added rapidly at 22.7 °C; there was significant off-gassing and an exotherm to nearly 27 °C. The reaction was heated to reflux (110-112 °C) for an hour and then cooled. Water (100 mL) was charged and the reaction temperature increased from 25.5 to 27.5 °C with some visible smoke formation. Sodium hydroxide (50%, 19.0g, 238 mmole) was added to adjust the pH to 11.78. Agitation was ceased and the lower aqueous layer was removed. The organic layer was washed twice with 50 mL aliquots of water; pH of the second aqueous layer was 10.15.

Quench of Thionyl Chloride Containing Reaction Mass with n-Butanol. A chlorination reaction with a 330 mmole input of α-hydroxy amine was completed and the combined filtrate of mother liquor and washes was set aside for neutralization. The total mass of combined filtrate was 960 g. Toluene is the reaction solvent and wash. The initial charge of thionyl chloride was 413 mmole.

A 475 g aliquot of the combined filtrate was transferred to a 1 L round bottom glass reactor; this corresponds to an initial charge of 204 mmoles of thionyl chloride. To an addition funnel was charged n-butanol (28.8 g, 35.5 mL, 388 mmoles). The n-butanol was added over 15 minutes with no discernible off-gassing or self-heating. The reaction was heated to reflux (105 °C) and held for 80 minutes. The heat was removed and the reaction mass was cooled to 15.6 °C. An aqueous solution of NaOH (15.23 g 50% NaOH and 83.40 g water) was added with stirring over 5 minutes. The contents were transferred to a separatory funnel and the lower aqueous phase was removed. The pH of the aqueous cut was 13.36.

The organic layer was removed and the funnel was thoroughly rinsed out with deionized water. The organic layer was recharged and washed with 100 mL deionized water. The pH of the water layer was 6.11.

Quench of Thionyl Chloride with n-Butanol; GC/NMR Analysis. Thionyl chloride (24.3 g, 204 mmoles) and toluene (450.8 g) were charged to a 1 L jacketed reactor equipped with thermocouple, mechanical agitation and reflux capabilities. Temperature was adjusted to 19.8 °C and n-butanol (28.8 g, 388 mmoles) was charged in a single portion; temperature increased to about 24 °C. The reaction temperature was increased to reflux at 111.4 °C and maintained for 110 minutes, followed by cooling to 24.2 °C. An aliquot was removed for analysis.

Deionized water (85 mL) was charged to the reactor and agitated for 45 minutes. Agitation was ceased and the pH was measured at 1.45. 50% NaOH (15.22 g, 190 mmoles) was charged and agitation was resumed. After 20 minutes, agitation was ceased and the pH was measured at 12.9.

Both lower and upper layers were separately removed and the reactor flushed with deionized water. The upper organic layer was returned to the reactor with deionized water (100 mL) and thoroughly agitated. The pH of the lower aqueous was measured at 6.81 against a fresh deionized water blank at 6.72.

Gas chromatographic analysis of the reaction mass prior to the aqueous workup indicated low levels of 1-chlorobutane and n-butanol. The n-butanol concentration was estimated to be 0.09% w/w and 1-chlorobutane was no more than 0.005% w/w. The expected concentrations were 2.9% for n-butanol and 3.3% for 1-chlorobutane.

^{1}H NMR was used to profile the reaction mass. The n-butanol low level was confirmed by comparison of n-butanol peaks to toluene; 1-chlorobutane was not detectable. However, there were distinct set of peaks that did not correspond to either analyte. These were determined to be n-butyl sulfite by comparison to a reference spectrum. The concentration for this compound was estimated to be 7.6% w/w.

Associated Content.

Gas chromatography chromatograms and NMR spectra for the final butanol quench reaction.

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[7] CIP 100® is a product of Steris Corporation; it is a formulated alkaline cleaner. CIP 200® is a formulated acidic cleaner from Steris.

[8] *High Purity Solvent Guide*, Burdick and Jackson Laboratories, Inc., 1980.

[9] GC quantitation was estimated by comparing analyte peak area responses to the peak areas of a corresponding external standard and correcting for injection volume, dilution and concentration of the standard.

[10] Concentrations of NMR samples were determined by comparing integrated resonances of the analyte relative to integrated resonances of toluene and assuming the sum of all components integrated in the NMR was 100%. All integrated areas were corrected for number of protons.

[11] Blatt, A.H., Ed., *Organic Syntheses, Collective Volume II*, 112-113, 1943.