OPTIMIZATION OF ALKYLATION OF AMMONIA AND AMINES REACTION TO SELECTIVELY FORM AMMONIUM SALTS

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BACKGROUND

Amines and alkyl halides can react in nucleophilic substitution reactions. When amines are reacted with alkyl halides in equivalent amounts, the products include primary amines (57%), secondary amines (24%), tertiary amines (3%), and trace amounts of quaternary ammonium salts. However, when significantly less than one equivalent of the amine is reacted with excess alkyl halide, the product will be much more selective, and will only result in the quaternary ammonium salt. The experimental goal is to find the ratio of reactants that optimizes this reaction, so that the ammonium product is maximally formed, with little formation of side products.

The >>1 equivalent amine to excess alkyl halide ratio has previously been determined, but a major goal is to specify a numerical ratio that maximizes the ammonium product. Other potential optimizations are the alkyl halide reactant, reaction temperature, and amine substitutions.

This result could be potentially useful, given that ammonium is an essential nutrient in soil for plants growing in hypoxic conditions. It is also used regularly in combination with other molecules in many important chemical compounds.

EXPERIMENTAL PLAN

Part 1: 5mL of THF (solvent) is added to a beaker over a hot plate at ___°C, then __ drops of amine is added, then __ drops of alkyl halide is added. Reaction observed and recorded. (The values left blank will be determined in each trial based on Table 1, and varied based on results).
Part 2: The solution is vacuum filtered, then product set aside to dry.
Part 3: Melting point and NMR are taken and compared to possible products. Melting point is used to observe purity and composition, NMR confirms composition.

Table 1: Potential experimental reactants and amounts

Trial	Temperature	Amine used	Amount (drops)	Alkyl Halide used	Amount (drops)
1	200°C	NH3	5	Iodomethane	30
2	200°C	NH3	4	Iodomethane	30
3	250°C	NH3	3	Iodomethane	25
4	250°C	NH3	2	Iodomethane	25
5	250°C	NH3	1	Iodomethane	25
6	200°C	NH3	4	Bromomethane	30
7	250°C	NH3	3	Bromomethane	25
8	250°C	NH3	2	Bromomethane	25

*All temperatures, reactants, and amounts are subject to change based on hypotheses developed during experiment

REACTION MECHANISM

FEASIBILITY

The experiment is somewhat feasible, given that the iodomethane and THF are already available, and the chemicals can be reasonably handled with appropriate protective wear (lab goggles, gloves, appropriate clothing) and hoods to prevent excessive exposure to fumes. However, the ammonia and bromomethane are not in stock. The iodomethane is very toxic and would have to be handled with extreme care. The ammonia costs $101.00 for every 100mL (100mL should be sufficient for the entire experiment, given that only a few drops are used per trial). The bromomethane is more expensive, but is not completely necessary to run the experiment. If used, small amounts could be ordered, and only a few trials with bromomethane could be run.

Table 2: Feasibility of chemicals

Chemicals	Cost	In Stock?	Hazards
NH3 (ammonia) 0.4M in THF	$101.00, 100mL	No	Flammable; oral, inhalation, and dermal toxicity; can cause severe damage to eyes (3)
Iodomethane	$210.00, 100mL	Yes (Rm 327)	Flammable; oral, inhalation, and dermal toxicity; eye

Bromomethane	$24.10, 1 mL	No	and skin irritant; carcinogenic (4) Flammable; oral, inhalation, and dermal toxicity; eye toxicity (5)

REFERENCES

(1) Karty, J. Organic Chemistry: Principles and Mechanisms, Second.

(2) National Center for Biotechnology Information. PubChem Database. Ammonium ion, CID=223, https://pubchem.ncbi.nlm.nih.gov/compound/Ammonium-ion (accessed on Feb. 24, 2020)

(3) Ammonia solution 718939. https://www.sigmaaldrich.com/catalog/product/aldrich/718939?lang=en®ion (accessed Feb 24, 2020).

(4) Safety Data Sheet for Iodomethane Solution. https://www.emdmillipore.com/US/en/product/msds/EMD_CHEM-IX0185?Origin=PDP (accessed Feb 23, 2020).

(5) Safety Data Sheet for Bromomethane Solution https://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=US&language=en&productNumber=48624&brand=SUPELCO&PageToGoToURL=https://www.sigmaaldrich.com/catalog/search?term=Bromomethane&interface=All&N=0&mode=match%20partialmax&lang=en®ion=US&focus=product (accessed Feb 23, 2020).

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