CLEANING UP WITH ATOM ECONOMY

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Introduction

Cleaning up the environment and, more importantly, preventing pollution are important issues in today's world. The theme for the 2002 National Chemistry Week is "Chemistry Keeps Us Clean." While the chemical industry is traditionally viewed more as a cause than a solution to pollution, chemistry does offer unique solutions in the area of waste prevention. One of the most fundamental of these solutions is the application of the green chemistry principle of atom economy to chemical reactions.

Atom economy moves the practice of minimizing waste to the molecular level. Traditionally, chemists have focused on maximizing yield, minimizing the number of steps or synthesizing a completely unique chemical. Green chemistry and atom economy introduce a new goal into reaction chemistry: designing reactions so that the atoms present in the starting materials end up in the product rather than in the wastestream. This concept provides a framework for evaluating different chemistries, and an ideal to strive for in new reaction chemistry (1,2,3).

Green Chemistry Principle: Atom Economy

Atom economy means maximizing the incorporation of material from the starting materials or reagents into the final product. It is essentially pollution prevention at the molecular level. For example, a chemist practicing atom economy would choose to synthesize a needed product by putting together basic building blocks, rather than by breaking down a much larger starting material and discarding most of it as waste.

Atom economy is an important development beyond the traditionally taught concept of percent yield. Barry Trost, from Stanford University, published the concept of atom economy in *Science* in 1991 (4). In 1998 he received the Presidential Green Chemistry Challenge Award (5) for his work. At the award ceremony, Paul Anderson (1997 ACS President) commented, "By introducing the concept of 'atom economy,' Dr. Trost has begun to change the way in which chemists measure the efficiency of the reactions they design." Atom economy answers the basic question, "How much of what you put into your pot ends up in your product?" (6). To meet the challenge of atom economy, Trost has developed a number of palladium and ruthenium catalysts. These catalysts enable chemical synthesis to proceed by simple addition reactions (7).

Associated Chemistry Topics

- law of conservation of matter
- chemical reactions
- stoichiometry
- percent yield

Vocabulary

Atom Economy –

1) The mass of desired product divided by the total mass of all reagents, times 100

$$\text{Percent Atom Economy} = \frac{\text{Mass of Desired Product}}{\text{Total Mass of all Reagents}} \times 100$$

2) The mass of desired product divided by the total mass of all products and byproducts produced, times 100
3) A measure of the efficiency of a reaction (8)

Green Chemistry –

1) Designing chemical products and processes to reduce or eliminate the use or generation of hazardous materials
2) Using chemistry for pollution prevention
3) Benign by design, sustainable chemistry

Molecular Weight – mass of one mole of a compound (units of grams per mole)

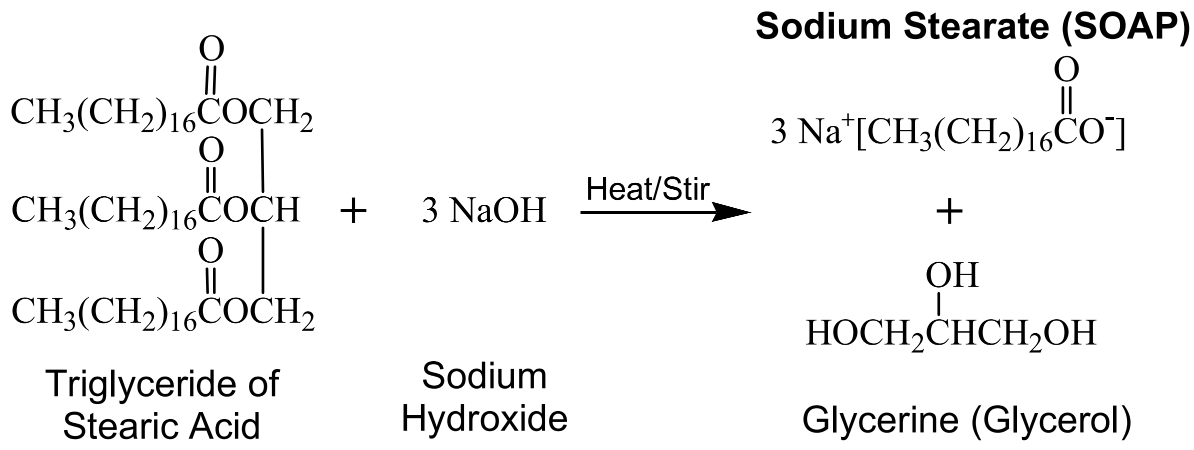
Percent Yield – actual yield divided by theoretical yield times 100

Theoretical Yield – the maximum amount of product that can be produced from the quantities of reactants used; the amount of a given product formed when the limiting reactant is completely consumed

Saponification – the decomposition of triglycerides with aqueous sodium hydroxide

Stoichiometry – application of the laws of definite proportions and conservation of mass to chemical processes; quantitative relationship between compounds involved in a reaction

Reaction: Saponification



Background

Saponification, or soap making, is a very old tradition, dating back to 2800 B.C. However, the chemistry was not described until the 19th century by the French chemist, Chevereul. Early soap makers used animal fat and wood ash (which contains sodium hydroxide and potassium carbonate). Now a wide variety of materials and methods are available to the soap maker. Today, soap making is not only highly visible in the mainstream manufacturing industry (names like Ivory, Dove, Dial), but many specialty product industries center around handmade soaps as well.

An excellent resource including the history, chemistry and manufacture of soaps and detergents is available from the Soaps and Detergents Association Web Site:

http://www.sdahq.org/cleaning/

Related information including stories about soap and detergent companies can be found at:

http://inventors.about.com/library/inventors/blsoap.htm

A brief discussion, with excellent graphical models, of the chemistry of soap making can be found at:

http://antoine.frostburg.edu/chem/senese/101/consumer/faq/making-soap.shtml

Clear directions, including pictures, for making soap are available at the Web Site:

http://www.soapcrafters.com/makebase.htm

Materials (per group of students)

1. Molecular models – many different kits are available or they can be generated from colored Styrofoam balls and toothpicks.
   You will need:
   a. 6 medium-sized black balls for carbon atoms
   b. 9 medium-sized red balls for oxygen atoms
   c. 8 small white balls for hydrogen atoms
   d. 3 small blue balls for sodium atoms
   e. 3 large oblong pieces to represent the hydrocarbon tail of the triglyceride
   f. 28 toothpicks for the bonds between the atoms
2. Periodic Table
3. Calculator or computer spreadsheet program like Microsoft Excel

Procedure

I. Build molecular models of the starting materials.

You can use a representative piece, rather than 18 individual carbon atoms and 35 individual hydrogen atoms, for the long hydrocarbon tail of the triglyceride.

II. Identify the desired product, soap, and the waste byproducts that are generated by the reaction. Convert the starting materials into the products. Use the models to help you visualize the transfer of atoms from starting material to product.

III. Generate a table for the saponification reaction summarizing the following information: (Use of a spreadsheet program to generate the tables and do the calculations is recommended.)

A. List the name and stoichiometric coefficient of each starting material (reagent)

B. For each reagent –

1. List the atomic symbol, atomic mass and quantity (remember to include stoichiometric coefficients) of each type of atom in the reagent.
2. Calculate the sum of the masses of all the atoms in the reagent. If the stoichiometric coefficient is 1, the sum of the masses is the molecular weight of the reagent.

Mass = Quantity of Atoms x Atomic Mass of Atoms

C. Add the masses of the reagents (step B2) to find the total mass of all reagents.

D. For each reagent –

1. Identify the atomic symbol, atomic mass and quantity (remember to include stoichiometric coefficients) of the atoms that are utilized in the product.

2. Calculate the sum of the masses of the atoms utilized in the product.
3. Identify the atomic symbol, atomic mass and quantity (remember to include stoichiometric coefficients) of the atoms that are utilized in the byproduct.
4. Calculate the sum of the masses of the atoms utilized in the byproduct.

E. Add the masses of the atoms from each reagent that are utilized in the product (step D2) to find the total mass of all atoms utilized in the product.

This is the theoretical yield of soap from one mole of the triglyceride reagent. If only one mole of product were produced, the total mass of all the atoms would also be the molecular weight of the product. However, three moles of soap are produced, so the molecular weight (the mass of one molecule) of the soap is 1/3 of the total of all the atoms in the product.

F. Add the masses of the atoms from each reagent that are utilized in the byproduct to calculate the total mass of all the atoms wasted.

G. Calculate the atom economy for the saponification reaction by dividing the total mass of atoms utilized in the product (step E) by the total mass of all the reagents (step C) and multiplying by 100. Since all the products produced are known, you could instead divide by the total mass of products and byproducts.

Questions

1. What is the atom economy for the saponification reaction, assuming 100% yield (3 soap molecules for every triglyceride used)?
2. What is the atom economy if only two soap molecules were made (66% yield) for every triglyceride molecule reacted (include the third soap molecule in the waste instead of the product).
3. What is the theoretical yield (in grams) of soap if 500.0 grams of the triglyceride of stearic acid are used?
4. What are some basic characteristics of reactions that have high atom economy?
5. Do you think it is more important to have high percent yield or high atom economy? Why?
6. BONUS: Describe modifications you would make to the saponification reaction to increase the atom economy.

Student Worksheet **Name**_________________________

Stoichiometric Coefficient, Name of Starting Material	Atomic Symbol, Quantity, Atomic Mass of each atom	Mass (Quantity Times Atomic Mass) of all atoms	Atoms Utilized in Product	Mass of Atoms Utilized in Product	Atoms Wasted in Byproducts	Mass of Atoms Wasted in Byproducts

Calculated Atom Economy: ___________________

Instructional Notes

Estimated Time of Activity: 1-2 Hours

Materials (per group of students)

1. Molecular models – many different kits are available or they can be generated from colored Styrofoam balls and toothpicks. You will need:
   a. 6 medium-sized black balls for carbon atoms
   b. 9 medium-sized red balls for oxygen atoms
   c. 8 small white balls for hydrogen atoms
   d. 3 small blue balls for sodium atoms
   e. 3 large oblong pieces to represent the hydrocarbon tail of the triglyceride
   f. 28 toothpicks for the bonds between the atoms
2. Periodic Table
3. Calculator or computer spreadsheet program like Microsoft Excel

Grade Level: High School, Undergraduate

Considerations and Adaptions

Considerations: This activity was written for high school or undergraduate chemistry students. Be sure the students understand how to calculate molecular weights and use stoichiometric relationships. The calculations are a little tricky since there are three moles of sodium hydroxide and soap per one mole of triglyceride. You may wish to minimize the time involved by providing the molecular formulas and weights [$C_{57}H_{110}O_6$, 891.45 g/mol; NaOH, 40.00 g/mol; $NaC_{18}H_{35}O_2$, 306.45 g/mol]. Use of a spreadsheet is recommended to generate the tables and calculate molecular weights and atom economy. If you wish to introduce the mechanism of the saponification reaction (nucelophilic attack of the hydroxide ions on the carbonyl), you can emphasize that the oxygen from the NaOH is found in the soap product and the oxygen in the glycerine come from the triglyceride. Students will most likely assume the hydroxide ions become the alcohols in glycerine if not told otherwise. The source of the oxygen atoms will not affect the calculation of atom economy. As an extension, you might consider having the students perform the saponification reaction to make their own soap.

Less Advanced: The activity could be adapted for middle school (and possibly late elementary) students by using Legos instead of molecular models (9). Converting Lego trucks to tractors or vice versa provides a more concrete picture of the process of a chemical reaction. Fruit or chewy-candy could be used as an alternative to Styrofoam balls or molecular models.

More Advanced: The atom economy activity is also a relevant prelab exercise for more advanced chemistry students. By providing less detailed procedural information and a more challenging reaction, the process can be easily adapted for more experienced students. For an organic course, the atom economy could be calculated for all of the basic reaction types. Selectivity, percent conversion, productivity, rates, catalysis and electrochemistry are all chemistry topics that would enhance this discussion of atom economy. A detailed study of the mechanisms of Trost's catalysts (10) would be a challenging topic for advanced inorganic chemistry courses.

Sample Table

The following table shows the calculation of atom economy (54.98%) for the combustion of methane.

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$$

Stoichiometric Coefficient, Name of Starting Material	Atomic Symbol, Quantity, Atomic Mass of each atom	Mass (Quantity Times Atomic Mass) of all atoms	Atoms Utilized in Product	Mass of Atoms Utilized in Product	Atoms Wasted in Byproducts	Mass of Atoms Wasted in Byproducts
1 Methane	1C, 12.01, 4H, 1.008	16.04	1C	12.01	4H	4.03
2 Oxygen	4O, 16.00	64.00	2O	32.00	2O	32.00
Totals:		80.04	1C, 2O	44.01	4H, 2O	36.03
Product: 1 Carbon Dioxide	1C, 2O	44.01			Atom Economy:	54.98%

The sample calculations are based on the arbitrary designation of carbon dioxide as the product, and water as the byproduct. Alternatively, water could be the desired product and carbon dioxide (a greenhouse gas) could be considered the waste, giving an atom economy of 85.00%. However, the only truly desired product of combustion is the heat or the work of the expanding gases. If both chemical products are designated as waste, the atom economy is 0%.

Answers to Questions

Use of a spreadsheet to generate the tables and calculate formula weights and atom economy is recommended. A blank Student Worksheet is provided on page 6.

1. **90.89%**, see following table:

Stoichiometric Coefficient, Name of Starting Material	Atomic Symbol, Quantity, Atomic Mass of each atom	Mass (Quantity Times Atomic Mass) of all atoms	Atoms Utilized in Product	Mass of Atoms Utilized in Product	Atoms Wasted in Byproducts	Mass of Atoms Wasted in Byproducts
1 Triglyceride of Stearic Acid	57C, 12.01; 110H, 1.008; 6O, 16.00	891.45	54C, 105H, 3O	802.38	3C, 5H, 3O	89.07
3 Sodium Hydroxide	3H, 1.008; 3O, 16.00; 3Na, 22.99	119.99	3Na, 3O	116.97	3H	3.02
Totals:	57C, 113H, 3Na, 9O,	1011.44	54C, 105H, 3Na, 6O	919.35	3C, 8H, 5O	92.09
Product: 3 Sodium Stearate	54C, 105H, 3Na, 6O	919.35			Atom Economy:	90.89%

2. **60.60%**, see following table:

Stoichiometric Coefficient, Name of Starting Material	Atomic Symbol, Quantity, Atomic Mass of each atom	Mass (Quantity Times Atomic Mass) of all atoms	Atoms Utilized in Product	Mass of Atoms Utilized in Product	Atoms Wasted in Byproducts	Mass of Atoms Wasted in Byproducts
1 Triglyceride of Stearic Acid	57C, 12.01; 110H, 1.008; 6O, 16.00	891.45	36C, 70H, 2O	534.92	21C, 40H, 4O	356.53
3 Sodium Hydroxide	3H, 1.008; 3O, 16.00; 3Na, 22.99	119.99	2Na, 2O	77.98	3H, 1Na, 1O	42.01
Totals:	57C, 113H, 3Na, 9O,	1011.44	36C, 70H, 2Na, 4O	612.90	21C, 43H, 1Na, 5O	398.54
Product: 2 Sodium Stearate	36C, 70H, 2Na, 4O	612.90			Atom Economy:	60.60%

3. 500.0 g SM / 891.45 g/mol SM = 0.5602 mol SM
   0.5602 mol SM * 3 mol soap/1 mol SM = 1.681 mol soap
   1.681 mol soap * 919.35 g soap/3 mol soap = **515.1 g soap**
4. High atom economy characteristically involves rearrangement or addition (e.g. Diels-Alder, Claisen) rather than substitution or elimination processes (e.g. Wittig, Grignard), and makes use of catalytic rather than stoichoimetric reagents. Atom economical reactions incorporate as much of the starting materials as possible into the product, so solvent-free systems are another characteristic feature.
5. Open ended question. Possibilities include:
   High atom economy might be preferred over high yield because it is more efficient and less waste is produced.
   High percent yield might be preferred over high atom economy because more of the product is produced.
   High yield with low atom economy might be preferred if a recyclable byproduct is formed.
6. BONUS: Suggested answers, any logical reasoning is acceptable.
   Using a lower molecular weight base and/or a higher molecular weight triglyceride would reduce the mass of waste and/or increase the mass of the product, thus increasing the atom economy. Considering glycerol (glycerine) a product, rather than a byproduct would remove it from the waste accounting. Making soap directly from the fatty acid rather than the triglyceride would reduce the waste for this reaction, but where does the fatty acid come from?).

References:

(1) Anastas, P. T,; Warner, J. C. *Green Chemistry: Theory and Practice*, Oxford University Press: Oxford, UK, 1998.

(2) Cann, M. C.; Connelly, M. E. *Real World Cases in Green Chemistry*, American Chemical Society: Washington, DC, 2000. See also the University of Scranton's Greening Across the Curriculum Web Site, http://academic.scranton.edu/faculty/CANNM1/organicmodule.html

(3) Ryan, M. A.; Tinnesand, M., Eds. *Introduction to Green Chemistry*, Washington, DC: American Chemical Society, 2002.

(4) Trost, B. M. *Science* **1991,** *254,* 1471-1477.

(5) The Presidential Green Chemistry Challenge is an award program sponsored jointly by the Environmental Protection Agency (Office of Pollution Prevention and Toxics) and the American Chemical Society—Green Chemistry Institute. Introduced in 1995, it is the only program to provide national recognition for green chemistry. The program offers five awards to academic researchers, industry, and government laboratories for innovations in the following categories: 1) academic, 2) small business, 3) alternative reaction conditions, 4) alternative synthesis, and 5) design of safer chemicals. For information about the Presidential Green Chemistry Challenge, refer to the Web Site: http://www.epa.gov/greenchemistry/presgcc.html

(6) Trost, B. M. In *The Presidential Green Chemistry Challenge Awards Program: Summary of the 1998 Award Entries and Recipients*; EPA744-R-98-001, U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics: Washington, DC, 1998; p 2.

(7) Trost, B. M. *Acc. Chem. Res.* **2002,** *35,* 695-705.

(8) For a powerpoint presentation of atom efficiency, with excellent examples, see the Green Chemistry Network Web Site, http://www.chemsoc.org/pdf/gcn/atomeff.ppt

(9) Witzel, J. Eric. *J. Chem. Educ.* **2002,** *79*, 352A-352B.

(10) Trost, B. M. *Acc. Chem. Res.* **2002,** *35,* 695-705.