

Higher Chemistry Principles to Production Unit

Additional notes for teachers: Percentage yield and atom economy

Industrial chemists evaluate synthetic routes and their associated economic and environmental costs by calculating the relative efficiency of the chemical reactions involved. Percentage yield provides a means of comparison of the theoretical and actual quantity of product, and historically has been the main means of evaluating reaction efficiency. More recently, however, calculation of 'atom economy' has become a more important means of comparing the efficiency of chemical reactions.

The concept of 'atom economy' was developed by Professor Barry Trost at Stanford University and derives from the principles of 'green chemistry'. Green chemistry is the design of chemical products/processes that reduce or eliminate the use or generation of hazardous substances. Historically, the chemical industry responded to environmental legislation by treatment, rather than prevention of waste. However, with waste treatment costs becoming increasingly economically unviable, chemical manufacturers are being forced to consider the economic benefits of applying the principles of green chemistry.

Atom economy is a measure of the proportion of reactant atoms which are incorporated into the desired product of a chemical reaction. Calculation of atom economy therefore also gives an indication of the proportion of reactant atoms forming waste products.

Chemists commonly calculate percentage yield (Equation 1) to ascertain the efficiency of a particular reaction.

Equation 1

$$\% \text{ yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

ADDITIONAL NOTES: ATOM ECONOMY

Using this strategy, a reaction proceeding with 100% yield of desired product is deemed to be perfectly efficient. However, calculation of percentage yield provides no information about the extent to which unwanted products are formed in the reaction pathway. In the chemical industry there are many examples of highly 'efficient' reactions that generate waste far greater in mass and volume than the desired product.

With the inadequacies of calculating percentage yield clearly established, Trost developed an equation for atom economy (Equation 2).

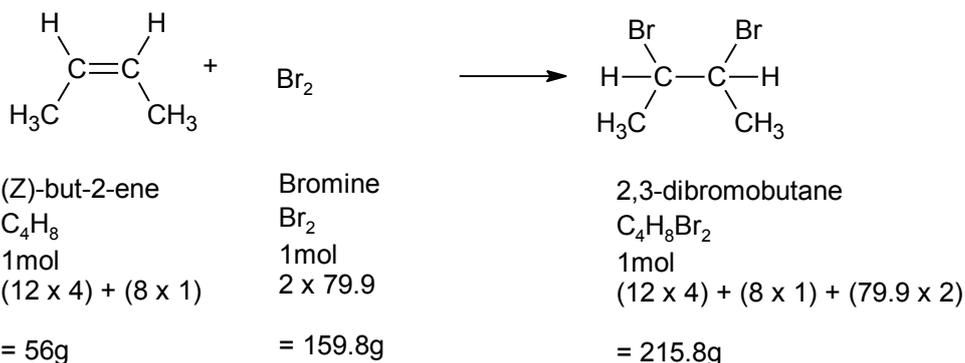
Equation 2

$$\% \text{ atom economy} = \frac{\text{Mass of desired product(s)}}{\text{Total mass of reactants}} \times 100$$

13,000 tonnes per annum of the painkiller Ibuprofen have been produced since its introduction in the 1980s. Initially, Boots used a six-step production process with an overall atom economy of just 40.1%. In the 1990s the Hoechst Celanese Corporation (in collaboration with Boots) developed a new, improved three-stage process to producing Ibuprofen with an atom economy of 77.4%. This improvement in atom economy resulted in a reduction in the quantity of unwanted by-products, and therefore in significant environmental and economic cost savings.

The atom economy of a reaction depends on the reagents used and the type of chemical reaction involved. Most chemical reactions can be classified as rearrangement (eg migration of an alkyl group), addition (Example 1), substitution (eg chlorination of methane) or elimination (eg dehydration). Rearrangement and addition reactions are atom economical by their very nature, since they simply involve reactant atoms being repositioned within the same molecule or incorporated within a second molecule. Substitution reactions, however, involve replacement of one group with another and therefore have intrinsically poor atom economy. Elimination reactions (Example 2) are also inherently atom uneconomical since eliminated atoms are always lost as waste. In developing an atom economical reaction pathway, therefore, the industrial chemist may well prefer rearrangement and addition reactions over less environmental friendly substitution and elimination reactions.

Example 1: Addition reaction – halogenation of an alkene



Total mass of reactants = 56 g + 159.8 g = 215.8 g

(Note: Product mass is also 215.8 g)

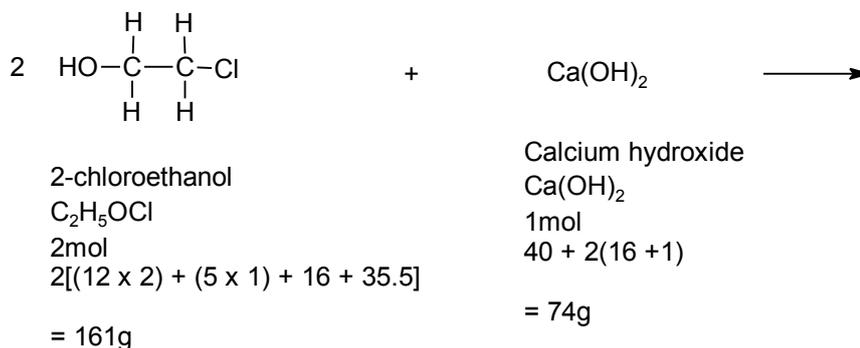
Mass of desired product (2,3-dibromobutane) = 215.8 g

$ \text{\% atom economy} = \frac{\text{Mass of desired product(s)}}{\text{Total mass of reactants}} \times 100 $
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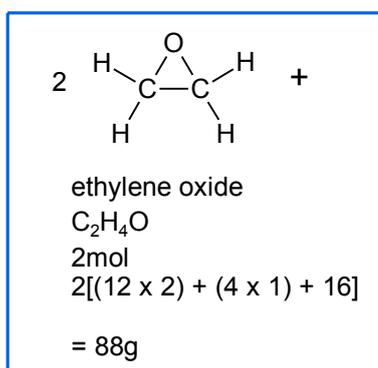
$$\text{\% atom economy} = \frac{215.8}{215.8} \times 100 = \mathbf{100\%}$$

This process is 100% atom efficient, with all the reactant atoms included within the desired product.

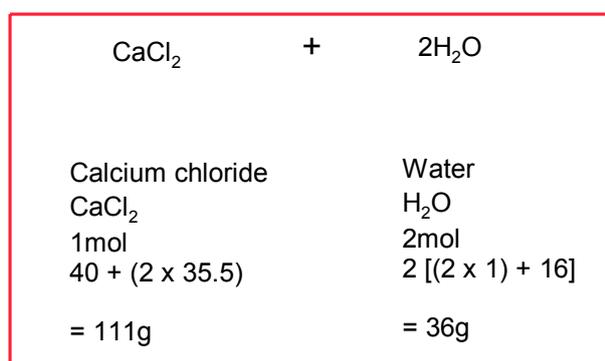
Example 2: Elimination reaction



Desired Product



Waste Products



Total mass of reactants = 161 g + 74 g = 235 g
 (Note: Total product mass = 235 g)

Mass of desired product ethylene oxide = 88 g

$$\% \text{ atom economy} = \frac{\text{Mass of desired product(s)}}{\text{Total mass of reactants}} \times 100$$

$$\% \text{ atom economy} = \frac{88}{235} \times 100 = \mathbf{37.4\%}$$

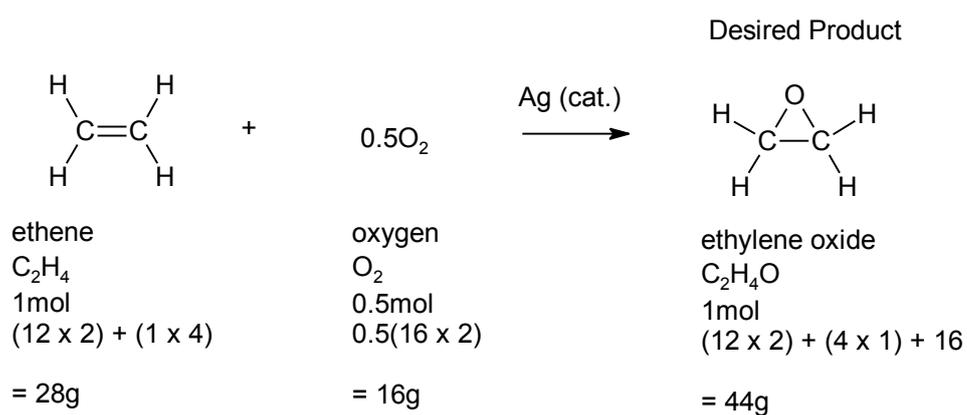
This elimination reaction is therefore only 37.4% atom efficient, with the remaining 62.6% in the form of unwanted waste products (calcium chloride and water).

Catalysts have a crucial role in improving the atom economy of chemical reactions. They allow the development of more effective synthetic reaction routes, which produce fewer waste products, and can be recovered and reused

time and again. Catalysts also allow reactions to be run at lower temperature, reducing energy costs.

The dramatic effect of a catalyst on improving atom economy is illustrated in Example 3. The introduction of a silver catalyst into the ethylene oxide production process in Example 2 improves the atom economy of the reaction from 37.4% to 100%. Although the silver catalyst is initially costly, it can be reused many times in the process.

Example 3: Use of catalyst in ethylene oxide production



Total mass of reactants = 28 g + 16 g = 44 g

(Note: Total product mass = 44 g)

Mass of desired product ethylene oxide = 44 g

$\% \text{ atom economy} = \frac{\text{Mass of desired product(s)}}{\text{Total mass of reactants}} \times 100$

$$\% \text{ atom economy} = \frac{44}{44} \times 100 = \mathbf{100\%}$$

Atom economical approaches have become increasingly popular in the last decade due to the rising cost of raw materials (particularly petrochemicals) and increasing awareness of environmental concerns. Energy consumption, raw material costs, the nature of waste products/pollutants and the value of the final product are also factors that will influence the selection of a particular synthetic route.