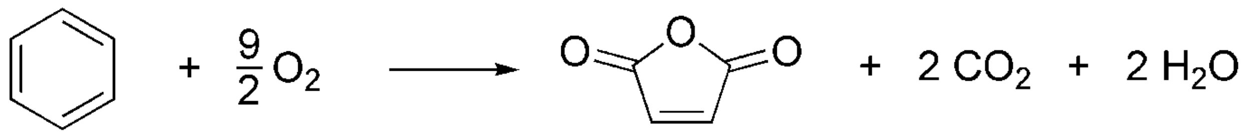
Tutorial questions (1st lesson)

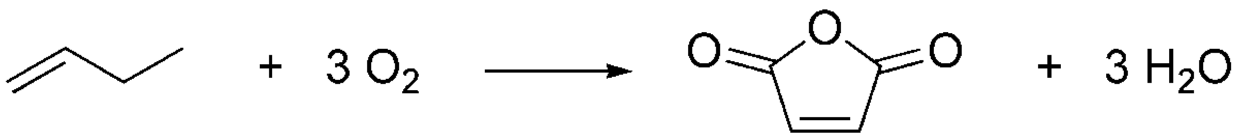
Maleic anhydride may be prepared using two routes:

Oxidation of benzene:



Catalyst: V_2O_5 + MoO_3 on alumina, Typical chemical yield: 65%

Oxidation of but-1-ene:



Catalyst: V_2O_5 + P_2O_5 on alumina, Typical chemical yield: 55%

Questions:

(a) Assuming that each reaction is performed in the gas phase only, and that no additional chemicals are required, calculate

(i) the atom economy

(ii) the effective mass yield of both reactions. You should assume that O2, CO2 and H2O are not toxic.

(iii) E-factor. Consider that the by-products are completely oxidized to CO_2 and consider CO_2 being a waste. It means that in the oxidation of benzene 35% is converted solely to CO_2 and in the oxidation of butane 45% .

(b)Which route would you recommend to industry? Outline the factors which might influence your decision.

Basic terms:

$$\text{Chemical Yield} = \frac{\text{mols (g) pdt obtained}}{\text{mols (g) pdt possible}} x100\%$$

$$\text{Atom Economy} = \frac{MW_{\text{desired pdt}}}{\sum MW_{\text{starting materials}}} x100\%$$

- How much of the reactants remain in the final product
- Does not account for solvents, reagents, reaction yield, and reactant molar excess

$$\text{Atom Efficiency} = \text{(\% Yield)(Atom Economy)}$$

Effective mass yield:

$$\text{EMY} = \frac{\text{Product (Kg)}}{\text{Hazardous reagents (Kg)}} x100\%$$

- What is hazardous and what not? Depends on the person, who decides…
- Ignores stoichiometry

$$\text{E - Factor} = \frac{\text{Total Waste (Kg)}}{\text{Product (Kg)}}$$

- Typically split into organic and aqueous waste
- Smaller is better

Answer:

Atom economy:

$$\text{Atom Economy} = \frac{MW_{\text{desired pdt}}}{\sum MW_{\text{starting materials}}} x100\%$$

Benzene oxidation:

RMM of reactants = 78 + (4.5 x 32) = 222
RMM of desired product = 98
∴Atom economy =44 %

But-1-ene oxidation
RMM of reactants = 56 + (3 x 32) = 152
RMM of desired product = 98
∴Atom economy =64 %

Effective mass yields:

$$\text{EMY} = \frac{\text{Product (Kg)}}{\text{Hazardous reagents (Kg)}} x100\%$$

EMY =mass of non-benign reagents/mass of maleic anhydride x 100 %

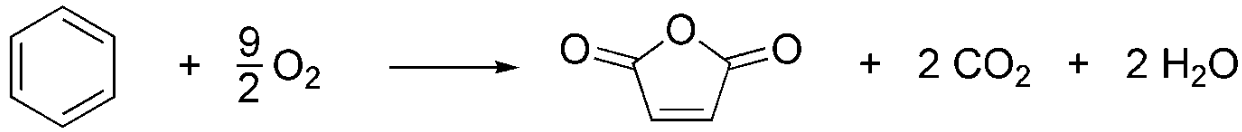
Benzene Oxidation
100 g benzene (1.28 mol) would give 81.5 g maleic anhydride (0.83 mol, 65 %):

EMY = [81.5 / 100] x 100 % = 81.5 %

But-1-ene Oxidation
100 g but-1-ene (1.79 mol) would give 96.3 g maleic anhydride (0.98 mol, 55 %):
EMY = [96.3/ 100] x 100 %= 96.3 %

E-factor

$$\text{E - Factor} = \frac{\text{Total Waste (Kg)}}{\text{Product (Kg)}}$$

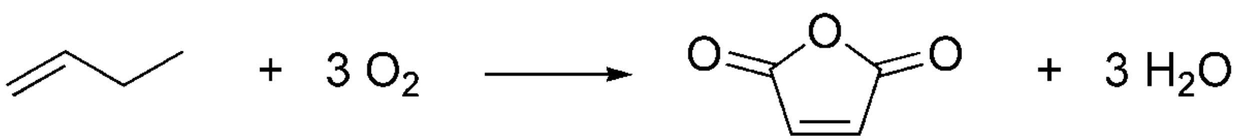


Benzene Oxidation

100 g benzene (1.28 mol) would give

1) (65%) 81.5 g maleic anhydride (0.83 mol, 65 %) + 73.3 g CO_2 (1.67 mol, 65%)
2) (35%) $C_6H_6 + 15/2\ O_2 \rightarrow 6\ CO_2 + 3\ H_2O$ 118.4 g CO_2 (2.69 mol, 35%)

E-factor = (73.3+118.4)/81.5 = 2.35



But-1-ene Oxidation

100 g butene (1.79 mol) would give

1) (55%) 96.3 g maleic anhydride (0.98 mol, 55 %)
2) (45%) $C_4H_8 + 6\ O_2 \rightarrow 4\ CO_2 + 4\ H_2O$ 141.4 g CO_2 (3.2 mol, 45%)

E-factor = (141.4)/96.3 = 1.46

The butene oxidation route would appear to be greener (higher atom economy, a higher effective mass yield, a lower E-factor). It also avoids the use of the toxic reagent benzene (we would therefore expect its waste stream to be less hazardous).

However, without a full life cycle analysis (which would take into account the environmental impact of producing both benzene and butene) a definitive answer is not possible.