Reaction mechanism choice using green chemistry principles

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Abstract

Essential industrial processes may threaten the environment despite the restrictions on the standards of rejections. Preserving a safe environment remains a major concern. Industry must look for new technologies, known as "clean" to reduce the environmental impact of their production activities and the consumption of energy and raw materials; This would require following an ecological and durable chemistry known as green chemistry.

The objective of this present work is an initiation with the application of the principles of green chemistry through the calculation of various parameters, namely: carbon efficiency, atom economy, environmental factor, reaction mass efficiency, material recovery parameter, etc.

The work shows the importance of green chemistry principles in searching for a more "clean" reaction way for a given synthesis or production. Indeed, between substitution and addition reaction mechanisms to synthesize tertiobutyl chloride, the results show that the second one proves to be more respectful towards the principles of green chemistry.

Keywords: *Atom economy; Carbon efficiency; Green chemistry principles; Environmental facto; Material recovery parameter; Reaction mass efficiency.*

I. Introduction

Chemical industry developed considerably during the twentieth century. Nowadays, chemistry forms parts of our daily life with the continuous progress in technological innovations. However, the human or ecological consequences are heavy and the challenge of the 21st century is to continue this progress in an economically viable way, by limiting the effects on the man and the environment. With the beginning of 1990, the concept of "Green Chemistry" appeared in the United States. It envisaged the use of principles to reduce and eliminate the use or the generation of harmful substances for the environment, by new chemical processes and ways of "clean" syntheses, i.e. respectful to the environment. The principles of green chemistry make it possible to produce by minimizing waste, by reducing the use of toxic products and by using fast and effective reactions. The twelve principles of green chemistry as introduced by Anastas and Warner [1], and mentioned in different references [2, 3], can be summarized as follows:

- Limit the production of residues to avoid treatments
- Maximize the incorporation of all materials used into the final product.
- Use and manufacture little or no toxic products.
- Replace toxic solvents as well as the intermediaries of syntheses.
- Limit the energy expenditure
- Use renewable resources
- Use catalytic processes
- Reduce the quantity of derivative products
- Conceive biodegradable substances
- Catalytic reagents are superior to stoechiometric reagents.
- Analyze in real-time to prevent the accidents by developing a sourer fundamental chemistry.
- Minimize the potential for chemical accidents, including releases, explosions, and fires.

II. Green chemistry parameters

The whole of the principles of green chemistry led to the implementation of parameters making it possible to assess any process or reaction. A total balance, which represents an average of the separately calculated parameters, makes it possible to quantify the "greenness" of the process. Indeed, the more its value is close to 100%, the more it is respecting the environment.

We note any reaction:

$$a\ A + b\ B \rightarrow p\ P + q\ Q$$

A is the limiting reagent, B the Co-reagent, P the principal product and Q a by-product.
a, b, p and q are the corresponding stoechiometric coefficients. The parameters or factors used are described as follows [1, 4]:

A. Carbon efficiency: This factor measures the absence of disappearance of carbon in the by-products if it is equal to 1:

$$E_C = \frac{p\ nc(P)}{a\ nc(A) + b\ nc(B)} \quad (1)$$

With nc the number of carbons.

B. Atom Economy: it measures the no loss of atoms in by-products during the reaction if it is equal to 1:

$$E_{At} = \frac{p.M(P)}{a.M(A) + b.M(B)} \quad (2)$$

M is the molecular mass (g mol^{-1}).

C. The yield: if the reaction were complete compared to the quantity of limiting reagent, the yield will be equal to 1:

$$\rho = \frac{a\ n(P)}{p\ n(A)} \quad (3)$$

n is the number of moles (mol).

D. Environmental factor E: it measures the importance of the wastes generated during a synthesis. Its ideal value is the smallest possible, while tending towards zero.

$$E = \frac{\sum_i m(dechets)i}{m(produit)} \quad (4)$$

m is the mass(g)

E. Reaction Mass Efficiency EMR : This parameter measures the mass of product per total mass of introduced reagents. It gives an idea on the effectiveness of the reaction.

$$RME = \frac{m(P)}{m(A) + m(B)} \quad (5)$$

F. Material Recovery Parameter MRP: allows to take account of the recycling solvents and/or catalysts used during the reaction and the post-reaction treatments.

$$MPR = \frac{\sum_i m(recyclé)i}{m(total) - \sum_i m(réactif)i} \quad (6)$$

With : m (total)-$\sum_i$ m(reactif)i=m(C)+m(S)+ $\sum_i$ m (Spr)i+ $\sum_i$ m (Rpr)i
C, the catalyst, S: solvent, Spr and Rpr: solvents and post-reaction reagents.

G.Danger: this parameter makes it possible to measure the danger of the reaction:

$$Danger = [1 - \sum_i(coefDanger)]\ \frac{m_i}{m_{total}} \quad (7)$$

The Danger coefficient is defined by the contribution of each pictogram
Coef Danger = (Xn + Xi + C + 5 E + F + 5 F+)/14

With F: flammable, F+ : very flammable, E : explosive, C : corrosive, Xn : harmful, Xi : irritant, O : combustive.
These factors can have the value "1" for a no dangerous reaction, and "0" with dangerous substances.

H. Toxicity: the reaction toxicity is measured by:

$$Tox = [1 - \sum_i(coefTox)]\ \frac{m_i}{m_{total}}$$
(8)

Toxicity coefficient is defined as:
CoefToxicity = (T + 5 T+ + 2 N)/8

T: toxic, T+: very toxic, N: danger to the environment

I. CMR (Mutagen Carcinogen and Reprotoxic): This factor is calculated by:

$$CMR = [1 - \sum_i(coefCMR)]\ \frac{m_i}{m_{total}} \quad (9)$$

With:
CoefCMR=((R40R45R49)+(R46)+(R60R61R62R63)) /3

J. Stoechiometric Factor, FSt : allows to check if the proportions used are stoechiometric:

$$FSt = 1 + \frac{\sum m_{reagents\ in\ excess}}{\sum m_{reagents\ in\ stoechiometric\ proportions}} \quad (10)$$

After the calculation of the parameters, we represent them on a diagram: hexagonal, heptagonal, decagonal, etc. (according to the number of calculated parameters), and we obtain a surface which represents the global assessment and informs about the respect or not of green chemistry. Indeed, the more the surface is full, the more the mechanism or process respects the principles of green chemistry.

III. Results and discussion

In this present work, we calculate the parameters of green chemistry as well as the total assessment for the synthesis of tertiobutyl chloride, using two

different mechanisms: nucleophilic substitution and addition. An Excel worksheet was used, the input data are: the number of carbons in each substance of the reaction, the masses used and obtained, the molar masses, the stoechiometric coefficients and the data on toxicity and the danger of the substances, obtained from the material safety data sheet MSDS (from several online databases, exp: www.inrs.fr/accueil/produits/bdd).
All the parameters quoted above were calculated for each mechanism, and a representative diagram of the global balances of the reactions is given.

A. Nucleophilic substitution

$(CH_3)_3$-C-OH + HCl ↔ $(CH_3)_3$-C-Cl + H_2O

The experiment was carried out in laboratory, in the department of chemical engineering of Constantine3 University. The reaction was carried out with an excess of HCl, and formed water was eliminated by a desiccant, in order to shift the equilibrium in the direction of tertiobutyl chloride production, after the synthesis, the product was separated by solvent extraction and purified by distillation [3]. (For more details on the experimental section and methodology description: http://eduscol.education.fr/rnchimie/chi_org/viollon/TP4.pdf).

B. Electrophilic addition

$(CH_3)_2$- C=CH_2 + HCl → $(CH_3)_3$-C-Cl

In this case the reaction was in stoechiometric proportions. It was instantaneous and complete at 70°C, without catalyst. The desired product required only the purification step [6].
The table below summarizes the quantities used in substitution mechanism. In an Excel worksheet, we represent the calculation cells in green; the others are the input data cells. It is noted that these sheets can be used for other reactions; it is enough to adapt the data to the studied case.

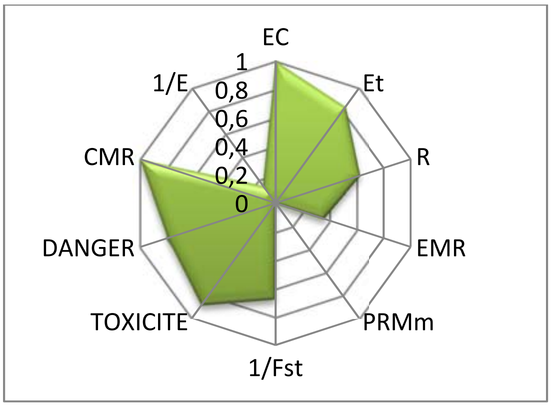
Table 1. Worksheet example (for substitution)

Constituants	Coeff St	n C	M g/mol	m(g)	mol	Xn	Xi	C	E	N	T	T+	F	F+	R40-45-49	R46	R60-61-62-63	Coeff dang	Coeff Tox
A	1	4	74	19.68	0.266	1	1						1					0,0364	0
B	1	0	36.5	23.87	0.654		1	1				1						0,0295	0,129
P	1	4	92.5	15.35	0.166					1				1				0,0474	0,033
Q	1	0	18	4.78	0.266													0	0
Déchets				14.16														0	0
catalyseur				8														0	0
solvant				0			1											0	0
Spr				40							1							0	0,043
Rpr				4														0	0
m recyclé				0														0	0
totaux				115.7															

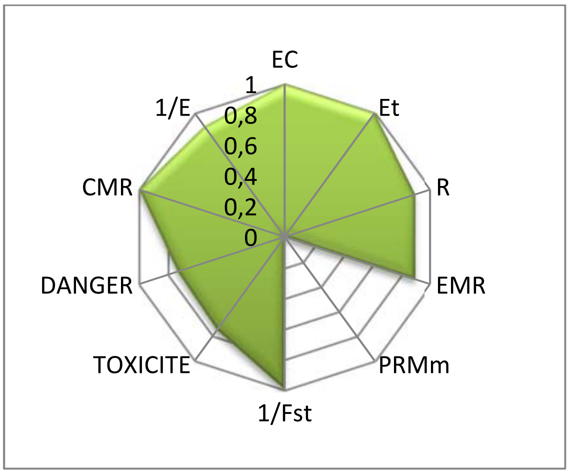
EC	Et	R	EMR	PRMm	1/Fst	TOXICITY	DANGER	CMR	1/E	bilan
1	0.837	0.624	0.35	0	0.675	0.79	0.887	1	0.153	0.632

: calculated cell *: data cell*

The excel sheet developed with all the parameters of the green chemistry makes it possible to calculate the balance of each reaction and also to plot the decagonal diagram (for the ten calculated parameters) for the two reactions as follows:



a)Substitution



b) Addition

Figure 1. Decagrams for the two mechanisms

According to these results, the addition is more respectful of the green chemistry principles than substitution, with a global balance of 81.64% against 63.2%. The advantage of the addition as a mechanism of production in this case, is its best yield, considering it as a complete reaction, its mass efficiency and especially its environmental factor, which is the key factor for every process since it means less wastes, its atom economy because it does not produce by-products and finally its stoechiometric factor: the reaction occurs without excess. Addition mechanism is a "green" solution much more that substitution. Note that this study only compares the two mechanisms, and we could do more effort in the choice of substances, especially to replace the HCl that has a high coefficient of toxicity.

IV. Conclusion

Thus, it is possible to improve the assessment of a production by choosing a greener mechanism, or by seeking an alternative: a less pollutant way, less expensive and with fewer stages, while preserving the principles of green chemistry, such is the current stake of every process. The new process of production of ibuprofen with fewer stages and cleaner process than the usual one is a concrete example [7]. Indeed the industrial world is ever getting more interested in green chemistry, especially the pharmaceutical industries which have an E-Factor much higher than that of oil industry [8, 9].

The introduction of green chemistry as course study will be valuable to industry [4]; indeed its principles can be learned easily through practical works, where the student must better know the products handled by exploiting their material safety data sheets and calculating the various parameters of green chemistry, to see where improvements could be made. He will be aware of the fact to improve the environmental impact of its handling, and to always search for the "greenness" way, especially as calculations are simple and the mean of each parameter is easy to assimilate.

If "green chemistry" principles and technologies, have recently made their ways in chemistry classroom pedagogy, in several universities in the world [10], this is not the case of Algeria. In fact, the teaching of these principles concerns only a few levels in chemistry or organic chemistry course, with only few applications.

Education institutions have to start with gradual introduction of GC principles applications at the first graduation levels, to progressively achieve Master and research level applications on processes, and include it as a key design parameter.

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