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What Would Be the Molecularity of A Reaction Having Two Rate Determining Steps? A Conceptual Analysis

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Abstract One of the conclusions of C Stegelmann's, *JACS* article titled "Degree of Rate Control: How Much the Energies of Intermediates and Transition States Control Rates" is that the 'degree of control of reaction' is a concept similar to the concept of the 'rate determining step' but more direct to apply and much more widely applicable ***(since there is rarely a single rate determining step)***. Thus, an important inference from this JACS article is that a reaction having two or more rate determining steps in its multistep mechanism is in the realm of possibility. Can we write the molecularity of such reactions (that is a reaction having two or more rate determining steps)? The answer to this question and its implication is probed in this conceptual analysis. An important spin-off, of the answer to this question is that, the age-old classic substitution nucleophilic unimolecular i.e., S_N^1 reaction between tertiary butyl bromide and water being termed as 'unimolecular' in many textbooks and the entry in the Wikipedia is incorrect. The authors are of the opinion that this article should be discussed when S_N^1 reaction is taught at undergraduate level.

Keywords: *Molecularity, Rate determining Step, Elementary reaction, & SN1 reaction*

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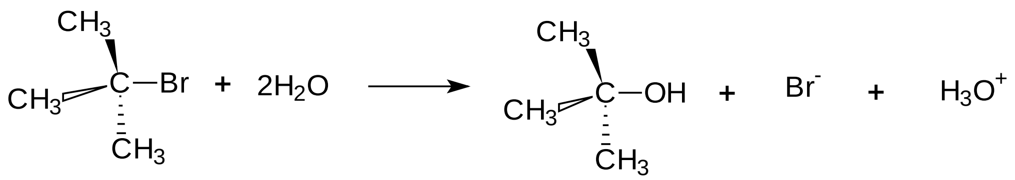
1. Introduction

The pre-requisite to comprehend this article is to revisit the defination of elementary step and molecularity of reaction (See the supporting information). An "elementary step" or "elementary reaction" is one which occurs as a result of the direct collision of molecules, ions or atoms as shown by the balanced equation. The molecularity of a reaction is the number of reacting species involved in an elementary step. The well-known S_N^1 reaction between tertiary butyl bromide and water (I) has a three-step mechanism [1].

In other words, this S_N^1 reaction is not an elementary reaction. If it is not an elementary reaction, molecularity term should not be used. but we still term it as unimolecular. It is explained as follows:

The first step of this reaction mechanism is the formation of tertiary butyl cation (II) and this step is the slow rate determining step (the other fast two steps of this mechanism are not written; since it is not required).



(I)

Figure 1. Hydrolysis of tertiary butyl bromide

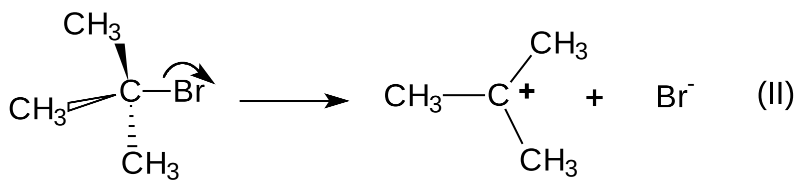


Figure 2. The slow rate determining step of the reaction between tertiary butyl bromide and water

The molecularity of the above slow rate determining elementary reaction is one and the molecularity of this (I) particular S_N^1 'substitution nucleophilic *unimolecular***'** is unimolecular. Here the molecularity of the slow rate determining step is treated as the molecularity of the reaction (I). The following simple analogy explains why the molecularity of slow step is taken as the molecularity of reaction (I).

Let us say a group of students is assigned the simple task of transferring books from Shelf A to Shelf B in a library.

A → Student1 → Student2 → Student3 → Student4 → Student5 → Student6 → B

Student 1 is able to transfer the books from Shelf A to Student 2 at 15 books per minute, Student 2 is able to transfer the books to Student 3 at 16 books per minute, Student 3 is able to transfer the books to Student 4 at 15 books per minute, ***Student 4 is able to transfer the books to Student 5 at 2 books per minute*,** Student 5 is able to transfer the books to Student 6 at 16 books per minute, and finally Student 6 is able to transfer the books to Shelf B at 16 books per minute. No matter how fast the books are transferred by Student 1, Student 2, Student 3, Student 5 and Student 6, the rate at which the books are transferred from Shelf A to Shelf B is determined by Student 4, who is able to transfer only 2 books per minute. In other words, Student 4 is deciding or strongly influencing the rate at which books are transferred from Shelf A to Shelf B. The same argument holds good for a slow step in the mechanism of a reaction occurring in many steps.

We may then wonder "If Student 2 is able to transfer 3 books per minute, which is comparable to the rate at which Student 4 is transferring the books, then which student corresponds to the slow rate determining step?" This is tantamount to a reaction having two rate determining steps. Stegelmann, Andreasen and Campbell [2] conclude that 'degree of control of reaction' is a concept similar to the concept of the 'rate determining step' but more direct to apply and much more widely applicable (since there is rarely a single rate determining step). Stegelmann, Andreasen and Campbell [2] clearly reflect that a reaction can have more than one rate determining step. In such a situation – where two steps have similar rates of reaction and therefore can both be considered to be rate-determining – what would be the molecularity of the reaction? If one of the slow rate determining steps has, for example, 2 reactant species and the other slow rate determining step has 1, then will the molecularity be 2 or 1? We can only say that the molecularity of one of the rate determining steps is 2 and that of the other is 1. We cannot define the overall molecularity of the reaction. The nomenclature 'molecularity of a reaction' fails in this situation. In other words, it is meaning-less to use molecularity of a reaction. Its high time we do away with the term molecularity, somewhat similar to doing away with the term pseudo-unimolecular [3].

An important point to be noted is that the defination of molecularity holds good only for elementary reactions [4,5], and the S_N^1 reaction between tertiary butyl bromide and water (I) is NOT AN elementary reaction. A number of texts. [6,7,8,9] describe this reaction as 'substitution nucleophilic *unimolecular'*. Is this correct? The answer appears to be an unequivocal 'no'. As already explained, the molecularity of the slow (rate-determining) step of a multi-step reaction mechanism is considered to constitute the molecularity of the overall reaction. Where a multi-step reaction mechanism has more than one step with a comparably slow rate, a decision cannot be made as to which of these would define the molecularity of the overall reaction. On these grounds, describing this S_N^1 reaction as 'unimolecular' appears to be incorrect in the context of a reaction having two comparably-slow steps. The nomenclature of 'molecularity of a reaction' is, we would argue, not meaningful for reactions which are not elementary reactions, especially in the context where more than one step can be considered rate-determining. On this basis, we consider that the textbooks [6,7,8,9] and the Wikipedia [1] entry which describe the S_N^1 reaction between tertiary butyl bromide and water as 'substitution nucleophilic *unimolecular'* are incorrect.

2. Conclusion

Reactions which have more than one rate determining step, the nomenclature 'molecularity of a reaction' is meaningless. In view of the preceding conclusion, the well-known S_N^1 reaction between tertiary butyl bromide and water being termed as 'unimolecular' in many textbooks and the entry in the Wikipedia is incorrect. One should be mindful of the fact that term molecularity is meant for for elementary reactions and well-known S_N^1 reaction between tertiary butyl bromide and water (I) is not an elementary reaction. Further, the authors would like to reiterate that this conceptual article should be discussed in the undergraduate classroom when S_N^1 reaction of hydrolysis of tert-butyl chloride is being taught.

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Conflict of interest statement

The authors declare no conflicts of interest

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Author Contributions

Sanjeev Rachuru, Jagannadham Vandanapu, David Geelan & Adam A Skelton contributed equally for the the article. Malleli Murali, Sateesh Kuna and J. Bhargavilakshmi contributed towards collecting resources such as books and articles for this work.

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Supporting Information

Meaning of Molecularity and Elementary reaction which is well known and taught in high Schools; this is only a revisit to these terms for better comprehension of the article

A balanced (or stoichiometric) equation shows the reactants that are present at the beginning of the reaction and products present at the end of the reaction. It is not common that reactants are converted into products in one step as suggested by the stoichiometric equation. A reaction like

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g) \quad (1)$$

occurs as a result of direct collision between NO and O_3. Such reactions, which occur as a result of direct collision between reactants as indicated in the balanced equation are described as ‘elementary reactions’; but most reactions do not occur this way. Reactants are typically converted into products thorough several steps. For instance, consider the reaction

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g) \quad (2)$$

The impression that may be gathered from balanced equation (2) is that two molecules, one each of NO(g) and CO_2(g), are formed when one molecule of NO_2(g) collides with one molecule of CO(g); but this is not true. The experimental data suggest that the reaction occurs in two steps. First, two molecules of NO_2 collide and as a result of this an oxygen atom from one molecule is transferred to other. The resulting NO_3 then collides with CO. The two steps are represented as:

$$\text{Slow step } NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g) \quad (3)$$
$$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g) \quad (4)$$

It can be seen that addition of these steps (3) & (4) leads to overall balanced reaction (2). Each of the two steps (3) and (4) is called an ‘elementary step’ of reaction (2). Thus, we can define an ***“elementary step”*** or reaction as one which occurs as a result of the direct collision of molecules, ions or atoms as shown by the balanced equation. All the steps of the reaction are collectively known as the ***“mechanism of the reaction”***.

Each step of the mechanism may involve a different number of reacting species, and this number of reacting species is described as the ***“molecularity”*** of that step. Molecularity is defined only for an elementary step [1,2]. For instance, the molecularity of elementary step (3) is two and the molecularity of elementary step (4) is again two. Speaking of the molecularity of the overall reaction (2) does not make sense, since it is not an elementary reaction (But the molecularity of slow step among (3) and (4) is taken as molecularity of the overall reaction). It does, however, make sense to speak of the molecularity of reaction (1), because it is an elementary reaction occurring as a direct collision between NO(g) and O_3(g). Thus, the molecularity of this reaction is two.

Additional examples of elementary reactions include:


(5)

$2HI \rightarrow H_2 + I_2$ (6)

$2NO + O_2 \rightarrow 2NO_2$ (7)

Since reactions (5), (6) and (7) are elementary reactions, their molecularities are one, two and three, and they are termed unimolecular, bimolecular and termolecular reactions respectively.

1. I. N. Levine, "Physical Chemistry," 6/e, 2009, pp. 531.
2. P. Atkins and J. De Paula, "Physical Chemistry," 10/3, 2014, pp. 842.