"INTRODUCTION"

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Silicon occupies a special position in the hierarchy of elements. On the one hand the tetracovalency of many of its compounds, which show remarkable stability, resembles that of saturated carbon compounds. on the other hand, its lack of ability to form obviously stable multiple-bonded compounds, its poor ability to catenat, its many crystalline compounds, and its ability to expand its coordination sphere are all more characteristic of other elements. Its chemistry may also be said to lie between that of organic and inorganic chemistry. Moreover, silicon is the second most abundant element of earth´s crust and is today the vital component of the microchip technological revolution. That is why there is currently an expanding interest in silicon chemistry.

In this work one have tried to follow this trend and studied some silicon-centered radicals. The corresponding carbon-centered radicals have also been studied and a comparison between the two radicals was attempted.

In order to allow for a fair comparison between carbon and silicon centered radicals, the same substituents were introduced to both of them. The substituents used might be considered of electronic π-type. The substituents may be classified as :

- ✱ Π. donor substituents such as amino group, hydroxy group or fluorine atom.
- ✱ Π. captor substituents such as cyano group.
- ✱ Capto-dative substituents in which a simultaneous substitution by a Π.donor and a Π.captor substituent is effected.

In the first part of this work the influence of substitution on the energetic properties and the geometrical structures of a series including different carbon-centered and silicon-centered free radicals have been studied. The energetic properties were studied in terms of the radical stabilization energy (RSE). This method has been selected since the litrature survey show that, a comparative study between RSE has not been carried yet.

It is well known that methyl radical is planar while the silyl one is pyramidal. This study included an explanation for the factors which induced this difference in structure. The litrature noted that some substituents are capable of deviating the methyl radical from its planarity. Consequently, it is interesting to in study the effects of these substituents on the geometrical structure of the pyramidal silyl radical. Also, it is important to represent a qualitative analysis for the factors behind the similarity or dis-similarity that certain substituent exerts on the silyl and methyl radical. The analysis included studying of the inversion barrier, the extent of interaction between the singly occupied molecular orbital and the lowest unoccupied molecular orbital and measuring of the value of $\hat{h}$.

The second part of this work included a conformational analysis study for the selected radicals. It should be noted that, the conformational analysis of some substituted methyl radicals studied, are already represented in the literature. But, the lack of any studies on the silyl radical counterparts, necessitated the examination of the substituted silyl radicals and the reexamination of the corresponding methyl radicals at the same level of calculations. This have been done by constructing the potential energy surface of these radicals. Through this a to comparison between the height of the rotational barrier of both carbon and silicon- centered radicals was performed. This also enable one to identify the geometry of the stable rotational isomers of the selected radicals. The most important outcome of this study is to be able to predict the conformer of each radical that is accessible experimentally.

Finally to cover a wide range of comparison between both carbon and silicon centered radicals, the specific rate constants for the formation of these radicals were calculated. This has been done using the transition state theory.

The partition functions of the activated complex and of the reactants were calculated from MO calculations at the MNDO level with complete geometry optimization. The activation energy, $\Delta E^{\neq}$, was calculated using the same procedures.

To Sum up, the objectives of this work are :-

1) Studying the effect of different substituents on the energetic properties of both carbon-centered and silicon-centered free radicals.
2) Studying the effect of the same substituents on the geometry and structural properties of the selected radicals.
3) Constructing Potential energy surface and studying the conformational analysis of the studied radicals.
4) Calculating the activation energy and the specific rate constant for the formation of these radicals.