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DFT study of deoxygenation of cycloaddition products of furan and 2-methylfuran with ethylene in the presence of aluminium chloride

G. Wilfried Kanhounnon, Guy Y. S. Atohoun*, Urbain A. Kuevi, Alice Kpota Houngue, Gaston A. Kpotin and Jean-Baptiste Mensah

Laboratory of Theoretical Chemistry and Molecular Spectroscopy, Faculty of Sciences and Technic, University of Abomey-Calavi, Cotonou-BENIN
** Corresponding e-mail: lacthesmo@fast.uac.bj*

ABSTRACT

With the DFT/B3LYP method and in the LanL2DZ basis set, the study of the cycloaddition of furan and 2-methylfuran with an ethylene molecule, followed by the deoxygenation of the heterobicyclic molecules obtained, have been performed. All the whole reaction process has been modeled in three steps: The molecule adsorption on aluminum chloride considered as catalyst, the cycloaddition of the adsorbed molecules with an ethylene molecule and the elimination of their oxygen atoms by hydrogenation of cycloaddition products. For each of both molecules, the cycloaddition in presence of aluminum chloride has led to a bicyclic compound with a bridge passing by the oxygen atom. The latter reaction of bicyclic compounds with the hydrogen molecule has led to the hydrogenolysis of C-O bonds of those compounds. At the end of the reaction, the products provided by each of the studied molecules were respectively the cyclohexene and the 2-methylcyclohexene with elimination of water molecule. The experimental conditions of temperature and pressure of 373 K and 40 bars are respectively considered in the study.

Key words: DFT/B3LYP, Hydrotreatment, Cycloaddition, Furan, Aluminum chloride.

INTRODUCTION

Generally, hydrocarbons contained in crude oils are mostly heteroatomic molecules whose combustion reaction products are nitrogen oxide, (NOx), sulfur oxide (SO_x) and carbon oxide (CO_x). These gaseous products contribute, greatly, to atmosphere pollution. In addition, a high content of oxygenated hydrocarbons in a fuel induces the increasing of its viscosity and the weakening of its energetic capacity [1–3].

One of the methods recommended for the elimination of the heteroatoms of molecules is the catalytic hydrotreatment. But the process has got difficulties such as: the low activity of catalysts which are generally used (tungsten and molybdenum sulfides), poisoning of the catalysts and the need to perform the reaction at high temperature and under high hydrogen pressure [4]. To overcome these difficulties, two solutions are proposed: the development of new active phases through the promotion of catalysts with transition metals (Fe, Co, Ni) and the development of new supports of catalyst, such as carbon, silica, zeolites, titanium, zirconium and sepiolite [5].

In the same way, we propose, in these works, to examine, by numerical methods of chemistry, an indirect elimination of the oxygen atom of furan and 2-methylfuran molecules, in the presence of aluminum chloride, after the cycloaddition of molecules with a molecule of ethylene, and hydrogenolysis of the bicyclic products obtained at the end of cycloaddition. The experimental conditions of temperature and pressure taken into account in the calculations are respectively 373K (100°C) and 40 bar. At this temperature which is below the melting temperature of aluminum chloride (190°C), the catalysis is heterogeneous and the conditions of hydrotreating are softer than those implemented with the catalyst as molybdenum and tungsten sulfide (250°C to 350°C) [6–8]. The justification of using aluminum chloride as a catalyst is that, the compound is relatively more abundant in the nature and easy to prepare than the noble metals sulfides [9, 10, 11]. Also, we have supposed that, through cycloaddition, the oxygen atom can be more easily removed in the intermediate bicyclic product obtained.

MATERIALS AND METHODS

Two molecules have been studied in this work: furan (a) and 2-methylfuran (b) (Figure 1)

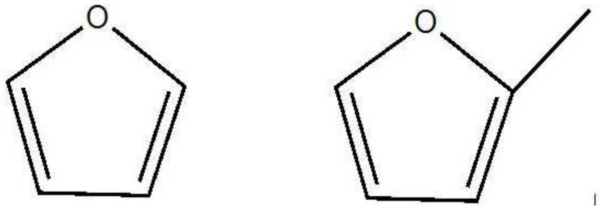


Figure 1: Drawing of studied molecules a) Furan b) 2-methylfuran

The calculations were performed with the Gaussian 09 program [12], using the DFT/B3LYP method [13–15], in the LanL2DZ basic set [16–18], with the Gauss View interface [19]. The main calculations done for each stage of studied chemical transformations are:

- calculations of geometric parameters of the initial and final states, as well as those of the transition state of the studied chemical systems;
- calculations of reaction path
- calculations of thermodynamic parameters such as the reaction enthalpy **(**ΔH) and the Gibbs energy (ΔG)
- and calculations of kinetic parameters as the activation energy (Ea).

The transition states of the different chemical transformations were first calculated by the Berny algorithm, before the reaction paths calculation by IRC algorithm [20]. This makes it possible to check if the calculated transition states are really on the studied reaction pathways [21, 22].

The modeling of the whole of the reaction process was carried out in three successive stages:

- adsorption of molecules on the aluminum chloride used as a catalyst. The geometrical parameters and energy that characterize, at the minimum of adsorption, the studied chemical systems are then determined (Figure 2)
- cycloaddition of adsorbed molecules with an ethylene molecule. It produces a bicyclic compound with a bridge via the oxygen atom (Figure 3)
- elimination of the oxygen atom of the bicyclic intermediate products obtained by the hydrogenolysis of their C-O bonds (Figure 4).

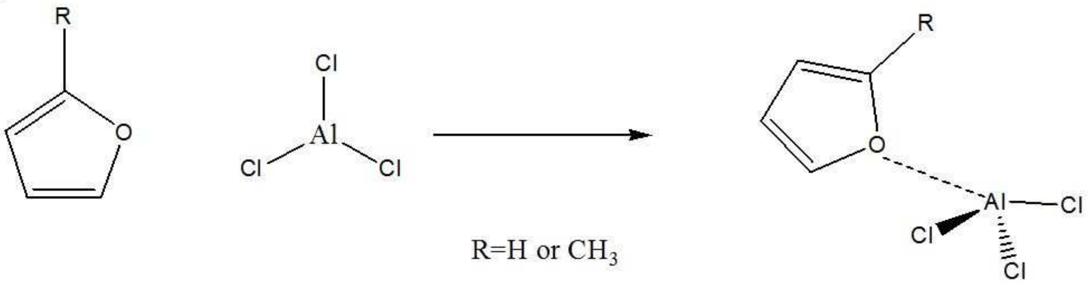


Figure 2: Scheme of molecule adsorption on the aluminum chloride

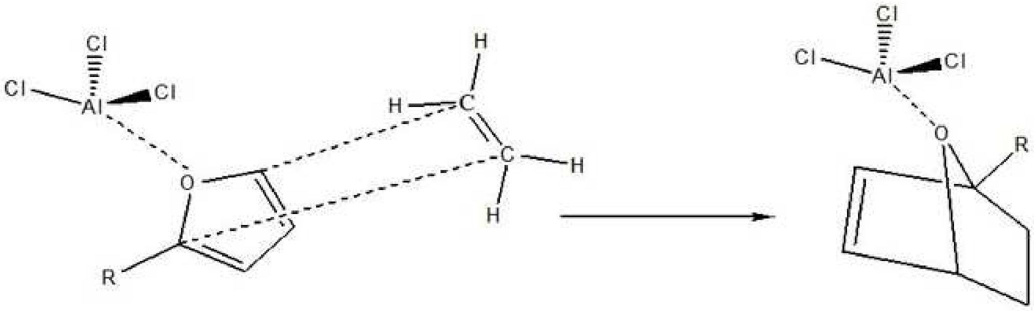


Figure 3: Scheme of the cycloaddition of adsorbed molecule on the aluminum chloride with an ethylene molecule

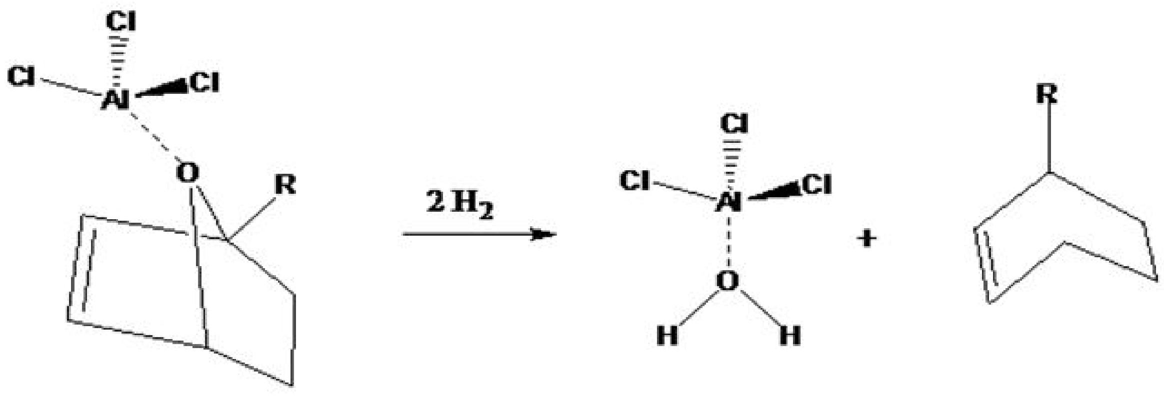


Figure 4: Scheme of the elimination of oxygen atom of bicyclic compound by hydrogenation

Figures representing the planar structures of molecules and systems have been realized using ChemDraw Ultra 8.0 software. For each studied transformation, drawings of chemical systems obtained at each stage are visualized with Gauss View 5.0.8 software.

RESULTS AND DISCUSSION

2-1- Adsorption of molecules on aluminum chloride

Each of both studied molecules was approached to the catalyst (aluminum chloride) and the geometry of the chemical system [molecule-catalyst] obtained was optimized to obtain a minimum (with all positive vibration frequencies) on the Potential Energy Surface (PES) of the system. The calculated geometrical parameters, before and after the adsorption, on the aluminum chloride, of each of both studied molecules, are shown in Table 1. Figure 5 shows the drawing of the complex [molecule-catalyst] for each molecule.

Figure 5: Drawing complex [furan-Catalyst] (a) and [2-methylfuran-catalyst] (b)

Table 1: Geometrical parameters of the studied molecules before and after adsorption

Furan			2-methylfuran		
	Before adsorption	After adsorption		Before adsorption	After adsorption
Distances (Å)			Distances (Å)		
C^7C^8	1.37	1.36	C^7C^8	1.37	1.36
C^5C^6	1.37	1.36	C^5C^6	1.38	1.36
C^5O^9	1.40	1.44	C^5O^9	1.41	1.46
C^8O^9	1.40	1.44	C^8O^9	1.40	1.45
Al^1O^9	-	1.98	Al^1O^9	-	1.97
Al^1Cl^2	2.17	2.21	Al^1Cl^2	2.17	2.21
Al^1Cl^3	2.17	2.21	Al^1Cl^3	2.17	2.21
Angles (°)			Angles (°)		
$O^9Al^1C^{l2}$	94.51	99.82	$O^9Al^1Cl^2$	77.49	101.24
$O^9Al^1Cl^3$	82.67	99.82	$O^9Al^1Cl^3$	117.36	102.96
$Cl^2Al^1Cl^3$	120.00	118.29	$Cl^2Al^1Cl^3$	120.00	115.39
Dihedral (°)			Dihedral (°)		
$C^8O^9C^5C^6$	0.03	-0.38	$C^8O^9C^5C^{13}$	180.00	-179.98

Overall, the values of the geometric parameters of molecules and of catalyst have not so varied after adsorption. But the C-O bonds are slightly stretched in the adsorbed molecules with respect to the isolated molecules. It results in increasing the C-O interatomic distances which went from 1.40 to 1.44 Å for the furan molecule and 1.41 to 1.46 Å for 2-methylfuran. This could help in the C-O chemical bonds breaking in the final stage of the studied reaction process. Also, as shown by the values of dihedral angles that remained around 0 ° and 180 °, both molecules have substantially retained their flatness when adsorbed.

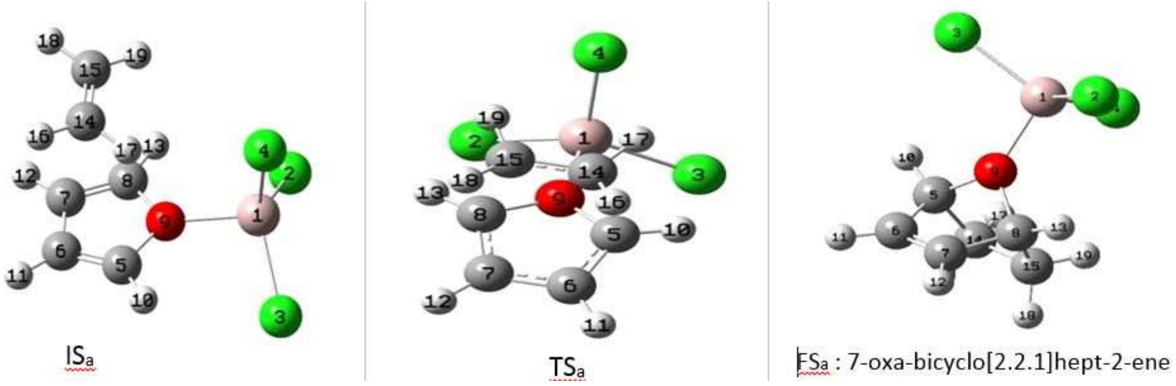
2-2- Cycloaddition of the adsorbed molecules with ethylene molecule

2-2-1- Calculations of geometric parameters

An ethylene molecule was approached to each studied molecules. From the beginning to the end of this process, some geometric parameters of the chemical systems have varied considerably. Their values in the initial state (IS), final state (FS) and transition state (TS) are reflected in the tables 2 and 3. Figures 6 and 7 show the drawings of different chemical systems at the main stages of the cycloaddition.

Table 2: Geometric parameters values of the system [Furan-adsorbed ethylene] in the main stages of the cycloaddition

Distances (Å)	ISa	TSa	FSa	Observations
C^{5}-C^{14}	4.19	2.24	1.56	Formation
C^{8}-C^{15}	4.27	2.24	1.56	Formation
C^{14}-C^{15}	1.35	1.41	1.57	Transformation
C^{5}-O^{9}	1.44	1.45	1.53	Stretching
C^{8}-O^{9}	1.44	1.45	1.53	Stretching
$Al^{1}O^{9}$	1.98	1.94	1.88	Shortening
Angles (°)				
$C^{5}O^{9}C^{8}$	107.07	103.66	95.48	-
$C^{6}C^{5}C^{14}$	83.68	100.83	109.05	-
$C^{7}C^{8}C^{15}$	83.88	100.82	108.95	-
$C^{5}C^{6}C^{7}$	108.36	108.13	107,35	-
Dihedral (°)				
$C^{8}O^{9}C^{5}C^{6}$	-0.38	27.38	51.18	-

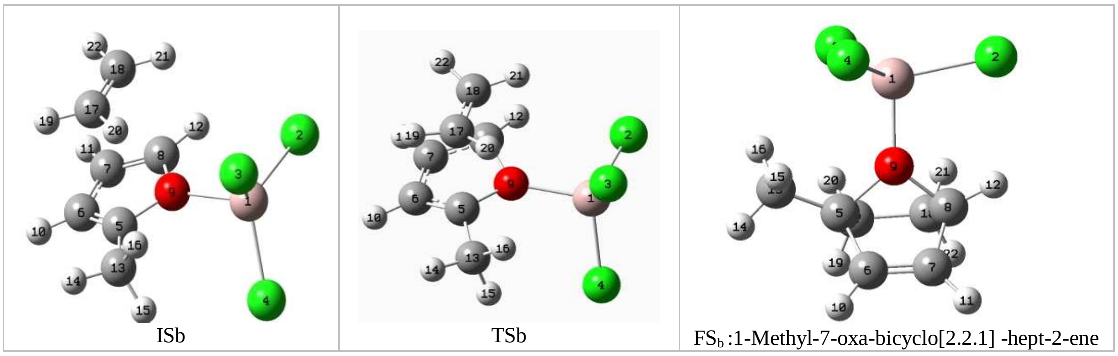


ISa TSa FSa : 7-oxa-bicyclo[2.2.1]hept-2-ene

Figure 6: Drawing complex [furan adsorbed-Ethylene] at the main stage of the cycloaddition

Table 3: Geometric parameters values of the system [2-methylfuran-adsorbed ethylene] at the main stages of the cycloaddition

Distances (Å)	ISb	TSb	FSb	Observations
C^{5}-C^{17}	2.04	1.47	1.59	Formation
C^{8}-C^{18}	2.04	2.18	1.56	Formation
C^{17}-C^{18}	1.35	1.41	1.57	Transformation
C^{5}-O^{9}	1.46	1.47	1.52	Stretching
C^{8}-O^{9}	1.45	1.46	1.51	Stretching
$Al^{1}O^{9}$	1.97	1.94	1.89	Shortening
Angles (°)				
$C^{5}O^{9}C^{8}$	113.08	103.84	98.02	-
$C^{6}C^{5}C^{17}$	98.77	98.60	105.64	-
$C^{7}C^{8}C^{18}$	94.75	100.82	109.06	-
$C^{5}C^{6}C^{7}$	35.01	108.13	108.40	-
Dihedral (°)				
C^{8} $O^{9}C^{5}C^{13}$	-179.98	178.56	174.41	-



ISb TSb FS$_b$:1-Methyl-7-oxa-bicyclo[2.2.1] -hept-2-ene

Figure 7: Drawing complex [2-methylfuran adsorbed-Ethylene] at the main stages of the cycloaddition

At the end of the furan molecule cycloaddition simulation, the value of the interatomic distances C^5-C^{14} and C^8-C^{15} is 1.56 Å. The latter value is close to the standard value of the C-C bond length (1.53 Å). [23] Furthermore, the values of angles $C^7C^8C^{15}$ and $C^6C^5C^{14}$ 109.05 ° and 108.95 °, respectively, show that the C^{14} and C^{15} carbon atoms initially sp^2 hybridized in ethylene molecule are now sp^3 hybridized after the reaction [24]. In addition, during processing, one can notice a more pronounced stretching of the molecule C-O bonds (1.53 Å in the bicyclic product against 1.40 Å in the isolated furan). This stretching weakens these bonds and predisposes them to easier breaking in the further step of the reaction process. The variation of the dihedral angle $C^8O^9C^5C^6$ of 0.03 ° to 51.18 ° justifies that the product formed at the end of reaction is a bicyclic and nonplanar compound with a bridge via oxygen atom: 7-oxa-bicyclo [2.2.1] hept-2-ene (Figure 6). At the end of the cycloaddition, the Al^1O^9 distance is 1.88 Å. This means that the product formed is still adsorbed on the catalyst.

The geometric parameters of the 2-methylfuran molecule varied in the same proportions as those of furan, during the cycloaddition (Table 3). For this molecule, it has also been formed new chemical bonds C-C between it and the ethylene molecule, C-O bonds are stretched at the end of the reaction. The resulting bicyclic product (1-methyl-7-oxa-bicyclo [2.2.1] hept-2-ene) is also adsorbed on the catalyst (Al^1O^9 = 1.89 Å) (Figure 7).

2-2-2- *Thermodynamic and kinetic parameters calculation*

For each simulated cycloaddition reaction, the Gibbs energy (ΔG_r) and the activation energy (E_a) for each reaction path was calculated. The values in kcal/mol obtained for these parameters are shown in Table 5.

Table 4: Gibbs energy (ΔGr) and activation energy Ea of the molecules cycloaddition

	Furan-Ethylene	2-Methylfuran-Ethylene
Ea (kcal/mol)	22	18
ΔGr (kcal/mol)	-25	-28

The fact that Gibbs energies values calculated are negative show that all simulated reactions are thermodynamically favorable ($\Delta G_r < 0$), particularly in the case of 2-methylfuran (ΔG_r) = -28 kcal/mol)**.** The lower activation energy value was obtained for the reaction of this latter molecule. This reaction was more kinetically favored (Table 4).

2-3- *Deoxygenation of bicyclic derivative molecules*

The calculations made at this stage of the work, should allow proposing a way of oxygen atom removing from the furan and 2-methylfuran molecules, via cycloaddition of molecules in the presence of aluminum chloride with an ethylene molecule, followed by hydrogenolysis of C-O bonds of the cycloaddition products. For this, a hydrogen molecule has been approached of each C-O bond of furan bicyclic derivative product. Both hydrogen molecules H^{20}-H^{21} and H^{22}-H^{23} were respectively approached for the first and the second hydrogenolysis of C-O bonds. Similarly, C-O bonds of the bicyclic derivative product of 2-methylfuran were approached by hydrogen molecules H^{23}-H^{24} and H^{25}-H^{26} respectively for the first and second hydrogenolysis. At the main stages of the approaches, the variations of interatomic distances were recorded in Tables 5 and 6. The Figures 8 and 9 show the drawings of the different chemical systems at these main stages.

Table 5: Interatomic distances of 7-oxa-bicyclo [2.2.1] hept-2-ene in both hydrogenolysis

1st hydrogenolysis					2nd hydrogenolysis				
	Beginning	TS	End	Observations		Beginning	TS	End	Observations
H^{20}-H^{21}	0.73	0.81	2.02	Rupture	H^{22}-H^{23}	0.73	0.81	1.87	Rupture
H^{21}-C^{8}	-	1.79	1.10	Formation	H^{22}-C^{5}	-	1.86	1.12	Formation
H^{20}-O^{9}	-	1.67	0.98	Formation	H^{23}-O^{9}	-	1.58	0.98	Formation
C^{8}-O^{9}	1.53	2.99	2.97	Rupture	C^{5}-O^{9}	1.53	3.90	3.69	Rupture

Table 6: Interatomic distances of 1-methyl-7-oxa-bicyclo [2.2.1]-hept-2-ene in both hydrogenolysis

1st hydrogenolysis					2nd hydrogenolysis				
	Beginning	TS	End	Observations		Beginning	TS	End	Observations
H^{23}-H^{24}	0.73	0.82	1.82	Rupture	H^{25}-H^{26}	0.73	0.82	1.83	Rupture
H^{24}-C^{5}	-	1.78	1.11	Formation	H^{26}-C^{8}	-	1.85	1.12	Formation
H^{23}-O^{9}	-	1.60	0.98	Formation	H^{25}-O^{9}	-	1.58	0.98	Formation
C^{5}-O^{9}	1.52	3.04	2.95	Rupture	C^{8}-O^{9}	1.51	3.88	4.87	Rupture

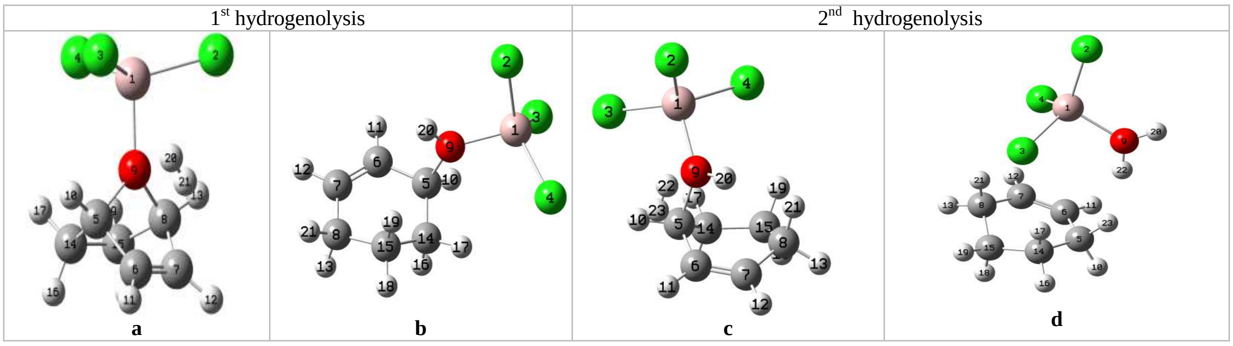

1st hydrogenolysis 2nd hydrogenolysis

Figure 8: Drawings of 7-oxa-bicyclo[2.2.1]hept-2-ene before and after hydrogenolysis: a) First Hydrogenolysis beginning b) First hydrogenolysis end c) Second hydrogenolysis beginning d)second hydrogenolysis end

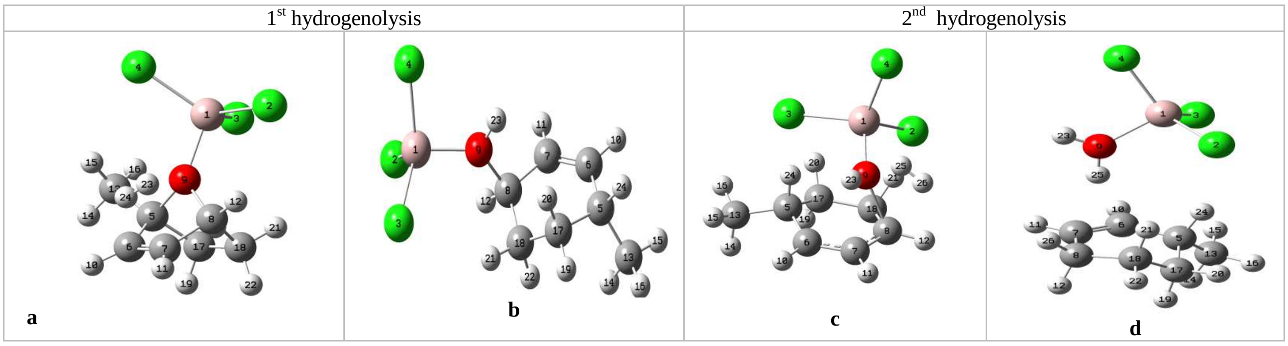

1st hydrogenolysis 2nd hydrogenolysis

Figure 9: Drawings of 1-methyl-7-oxa-bicyclo [2.2.1]-hept-2-ene before and after hydrogenolysis: a) First Hydrogenolysis beginning b) First hydrogenolysis end c) Second hydrogenolysis beginning d)second hydrogenolysis end

In both hydrogenolysis, the distance between the hydrogen atoms of the hydrogen molecule increases substantially, from the beginning to the end of the approach, from 0.73 to over 1.82 Å (Tables 7 and 8). The same observation is done with regard to the C-O bonds lengths of molecules that increase from 1.53 Å to over 2.97 Å for 7-oxa-bicyclo [2.2.1] hept-2-ene and from 1.51 Å to 2.95 Å for 1-methyl-7-oxa-bicyclo [2.2.1] hept-2-ene. All these observations indicate that the bonds of hydrogen molecules and C-O bonds of the bicyclic compounds have been broken during the reactions.

Furthermore, the values of interatomic distances C^{8}-H^{21} and H^{20}-O^{9} were respectively 1.10 Å and 0.98 Å at the end of the first hydrogenolysis, and the values of interatomic distances and C^{5}-H^{22} and H^{23}-O^{9} were respectively 1.12 Å and 0.98 Å at the end of the second hydrogenolysis of 7-oxa-bicyclo [2.2.1] hept-2-ene (Table 5, Figure 8) .These final values of interatomic distances are close to C-H and O-H bonds lengths values given in the literature (1.54 Å and 0.96 Å, respectively) [23]. We can consider that these bonds were formed at the end of the reaction.

The same observations were made for the 1-methyl-7-oxa-bicyclo [2.2.1] hept-2-ene, where the interatomic distances H^{24}-H^{23} and C^{5}-O^{9} were respectively 1.11 Å and 0.98 Å at the first hydrogenolysis and interatomic distances C^{8}-H^{26} and H^{25}-O^{9} were 1.12 Å and 0.98 Å in the second hydrogenolysis (Table 6, Figure 9).

The products obtained after the second hydrogenolysis, were the cyclohexene and the 2-methylcyclohexene, respectively for the furan and the methylfuran bicyclic derivatives. The oxygen atoms of both molecules were removed as a water molecule according to the scheme of Figure 4. The catalysis used can react with the formed water as reaction product. It is known that alumina is produced through this latter reaction [25]. Then when using aluminum chloride for such reaction in which water is formed as reaction product, equipment such as those used for alumina preparation, may be used to contain this possible and energetic reaction.

For each simulated hydrogenolysis, the variation of the Gibbs energy (ΔGr) was calculated as well as the activation energy (Ea) corresponding to each pathway. The values obtained for these parameters are shown in Table 7.

Table 7: Gibbs energy (ΔGr) and activation energy (Ea) of C-O bonds hydrogenolysis of 7-oxa-bicyclo [2.2.1] hept-2-ene (a) and 1-methyl- 7-oxa-bicyclo [2.2.1] hept-2-ene (b) (kcal / mol)

		1st hydrogenolysis	2nd hydrogenolysis
(a)	Ea	13.00	33.00
	ΔG	-38.38	-22.40
(b)	Ea	15.00	32.00
	ΔG	-32.57	-22.22

For both molecules, the first hydrogenolysis was found to be the fastest reaction phase given that the lowest activation energy values were obtained at this stage (Table 7). Accordingly, the second hydrogenolysis step becomes limiting step of the reaction. Also, the Gibbs energies values obtained indicate that the two phases of each reaction are spontaneous reactions (ΔGr<0).

This way of oxygen atom elimination of furan and 2-methylfuran molecules, through their cycloaddition with ethylene in the presence of aluminum chloride, seems advantageous. Indeed, the results of experimental work reported in the literature show that the elimination of the sulfur atom from heterocyclic molecules can be achieved by direct hydrogenolysis of their C-S bonds. The reaction can then lead to an unsaturated hydrocarbon. This is the case of the benzothiophene, whose direct hydrogenolysis leads to the ethyl benzene formation [26]. However, for oxygen or nitrogen heterocycles, it is necessary to hydrogenate first the molecules, until complete saturation of their cycles before the elimination of the heteroatom be easily realized. In the latter case we obtained mainly saturated hydrocarbons. This is the case of benzofuran giving ethyl cyclohexane when so treated [23]. However the octane index of hydrocarbons increases when one goes from the linear and ramified aliphatic compounds to the aromatic compounds while passing by the unsaturated and alicyclic compounds [27, 28].

Before the removal of oxygen atoms of the oxygenated heterocyclic molecules studied in the present work, the preliminary step of cycloaddition allowed not only the increase of number of carbon atoms, but also the obtaining of unsaturated and cyclic compounds. Moreover, it was not necessary to first hydrogenate molecules until total saturation before their deoxygenation. The presence of unsaturated cycle in the final products (cyclohexene and 2-methylcyclohexene) could then contribute to increase the octane index of petroleum cuts that would lend themselves to such transformations. Under the experimental conditions used in this study, we could consider that ethylenic and oxygenated heterocyclic compounds coexisting in oil cuts undergo such transformations (cycloaddition followed by hydrogenolysis). This then would promote the production of fuels of greater octane index.

CONCLUSION

The furan and 2-methylfuran molecules cycloaddition with a molecule of ethylene, in the presence of $AlCl_3$), and the deoxygenation of the molecules produced, were studied by B3LYP/LanL2DZ method of quantum chemistry. The experimental conditions of temperature and pressure of 373 K and 40 bars were respectively considered in the study. For each molecule, the cycloaddition in the presence of the catalyst produces a bicyclic compound with a bridge via the oxygen atom. The subsequent reaction of the hydrogen molecule on the bicyclic compound obtained, enabled the elimination of the oxygen atom of the molecule as water molecule, after hydrogenolysis of these C-O bonds. The obtained products were cyclohexene and 2-methylcyclohexene, respectively. This way of molecules deoxygenation has the advantage of the giving the cyclic compounds with a greater number of carbon atoms and greater fuel octane index. In the experimental conditions considered in this work, we could consider that ethylenic and oxygenated heterocyclic compounds coexisting in oil cuts undergo such transformations. This would then allow an improvement of fuel quality. The work could be continued in this direction. The catalysis used can react with the formed water as reaction product. It is also known that alumina is produced through this later reaction [25]. Then we propose that when using aluminum chloride for such reaction in which water is formed as reaction product, equipment such as those used for alumina preparation, may be used to contain this energetic reaction.

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