

Photodegradation of carbaryl by hydroxyl radical theoretically

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Abstract

Carbaryl has been degraded in vacuum with hydroxyl radical theoretically using UV light. Different calculation methods like semi-empirical, ab-initio and DFT that's included quantum mechanics package programs. Optimized structures for all suggested chemical species have been carried out to estimate the reactivity and all chemical properties in the estimated reactions. The probable transition states have been studied through surface potential energy, zero point energy, and first negative frequency of vibration spectrum. Energetic values of all reactions and rate constant of cleavage reaction step are calculated. Total energy, heat of formation and vibration spectrum have been calculated for all suggested reactions component.

First degradation reaction of carbaryl is exothermic reaction through C₉-O₁₃ bond to give up two major components α -naphthol and carbamic acid radical by activation energy equal to 116.391 kCal mol⁻¹. Rate constant of cleavage step reaction is equal to 2.25 x 10¹¹ s⁻¹. Enthalpy change value of overall degradation reaction equal to -371.674 kCal mol⁻¹. Ten moles of hydroxyl radical are needed to convert carbaryl into simple molecular moieties like CO₂, H₂CO₃, H₂O, HNO₃ and H₂.

Key words: - carbamates, carbaryl, quantum calculation methods, photo degradation, computational chemistry, DFT, ab-initio, semi-empirical.

Introduction

Carbamates are those mainly used in agriculture, as insecticides, fungicides, herbicides, nematocides, or sprout inhibitors. In addition, they used as biocides for industrial or other applications and in household products. A potential use is in public health vector control. Thus, these chemicals are part of the large group of synthetic pesticides that have been developed, produced, and used on a large scale in the last forty-five years (Abdel and Fahmy 1977). The aqueous environment will be an important route of transport for highly soluble carbamates (Uyanik 1999, and Suntio *et al.* 1988). The light absorption characteristics of carbamates contribute to their rapid decomposition (by photodegradation or photodecomposition) under aqueous conditions. One carbamate may be easily decomposing, while another may strongly adsorbed on soil. Some leach out easily and may reach groundwater (Cranmer 1986, FAO/WHO 1974, Carpenter *et al.* 1961, and U. S. Environmental Protection Agency 2003).

Degradation of carbaryl in water is influenced by temperature, light, and pH. It rapidly hydrolyzed to α -naphthol in neutral and alkaline waters; half-lives at 20°C of 10.5 days, 1.8 days and 2.5 hours reported at pH 7, 8 and 9, respectively. Hydrolysis is much slower in acidic waters; half-lives of 1500 days at pH 5 and 27°C and 406 days at pH 6

and 25°C have been reported (DeLeeuw *et al.* 1992, Taylor 1999, Dorsett *et al.* 1996, and Dronskowski 2005).

The programs used in computational chemistry are based on many different quantum-chemical methods that solve the molecular Schrödinger equation associated with the molecular Hamiltonian. This does not imply that the solution is an exact one. They are all approximate quantum mechanical calculations. If numerical iterative methods have to employed, the aim is to iterate until full machine accuracy is obtained (the best that is possible with a finite word length on the computer) (Jensen 1999). The simplest type of ab initio electronic structure calculation is the Hartree-Fock (HF) scheme, in which the coulombic electron-electron repulsion is not specifically taken into account. Only its average effect is included in the calculation. As the basis set size is increased the energy and wave function tend to a limit called the Hartree-Fock limit. This is set of functions, usually centred on the different atoms in the molecule, which are used to expand the molecular orbitals with the LCAO ansatz. Ab-initio methods need to define a level of theory and a basis set (HyperChem 5.0 user manuals 1996, and Leach 2001). Semi-empirical quantum chemistry methods are based on the Hartree-Fock formalism, but make many approximations and obtain some parameters from empirical data. They are very important

in computational chemistry for treating large molecules where the full Hartree-Fock method without the approximations is too expensive. The use of empirical parameters appears to allow some inclusion of correlation effects into the methods (Bury 1997).

The present work tend to study the theoretical reaction of carbaryl with hydroxyl radical from the quantum calculation treatments of the electronic and geometrical structure of this pesticide with their reliable transition states, also to find out a reasonable mechanism of photodegradation reaction in gas phase.

Calculation details

DFT, ab-initio and PM3 methods have been used for evaluation of electronic energies, heat of formation and electrostatic potential of carbaryl and $\cdot\text{OH}$. The geometries of intermediates and final molecules have been optimized at /6-311++G(2df,2p) (5d,7f) and PM3 level. Polarized spilt valence 6-311++G(2df,p) and 6-311++G(d,p) basis functions were employed for HF calculation while B3-LYP was used for DFT calculation. Single point MP2 calculation were performed on the optimized structures using 6-31G(d), 6-311G(d), 6-311++G(d,p) and 6-311++G(2df,2p) for high accuracy. The Polak-Ribiere method was used for optimization algorithm (Korzeniewski and Kowalchuk 1991). Theoretical vibrational frequencies of large molecules were carried on at PM3

method in addition to calculation of zero point energy, ZPE, to compute the relative quantum mechanical energies. Rate constant calculation are carried for first reaction cleavage step, using RMP2/6-311++g(2d,2p)//RHF/6-31G(D) (Fleming 1976).

Results and discussion

Investigation of carbaryl characteristics towards degradation reaction by hydroxyl radicals will be predicted through several evidences achieved from aspects of potential energy surface for chemical processes. Chemical reactivity investigations of Carbaryl have been carried out through the calculation of atomic charge, and molecular orbital interaction to guess the site of reaction in carbaryl molecules toward OH radicals (Mount, and Oehme 1981). Electrostatic potential calculation also illustrate the active sites of carbaryl which lead to transition state formation during the interaction with hydroxyl radical (International Agency for Research on Cancer 1976). Geometry optimization of carbaryl molecules calculated at 3-21G** small function basis sets while their energies calculated at MP2/6-311++G** high level of theory as shown in Figure 1. The atoms of, O₁₃, N₂₀, C₂₁, and O₂₆ have a negative charge, that is equal to -0.823, -0.848, -0.049, and -0.654 respectively. The atoms of C₉, and C₁₉ have a positive charge, that is equal to +0.425, and +1.241 respectively. Figure 2 shows the negative charge of oxygen of hydroxyl radical can attack the positive

charge atoms in carbaryl molecule. The same manner the proton of hydroxyl radical attacks the negative charge atoms in carbaryl molecule. The total energy of free carbaryl is $-415034.494 \text{ kCal mol}^{-1}$. Bond length of carbaryl bonds C₉-O₁₃, O₁₃-C₁₉, C₁₉=O₂₆, C₁₉-N₂₀, and N₂₀-C₂₁ are 1.395, 1.363, 1.211, 1.343, and 1.467 Å respectively. These bond calculations give another evidence form the bond strength point of view which usually refers to most probable bond that prone to broken out faster than the other bonds. As a general guess, the longest bond will most probable break faster than the others. From the electrostatic potential diagram, viewing the contour map in several planes will help in

observing the general form of the charge distribution. From above evidence, atomic charges indicate that large negative values (sites for electrophilic attack) are likely to occur. The largest negative atomic charge occurs on the nitrogen, but the most negative values of the electrostatic potential occur at the oxygen lone pair sites. A protonation reaction mostly favours to occur at these sites. This illustrates the value of electrostatic potential compared to simple atomic charges in predicting reactivity. However, the largest negative value of the electrostatic potential is not necessarily adjacent to the atom with the largest negative charge.

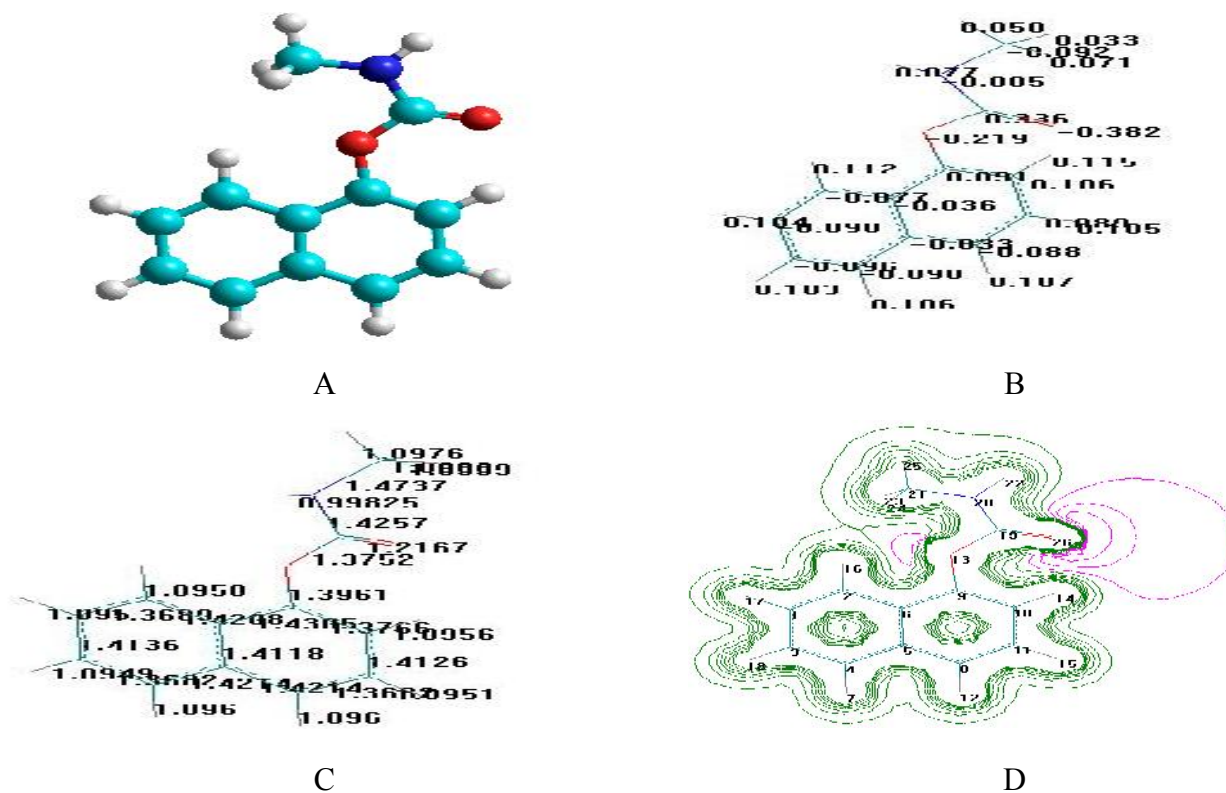


Figure (1) Optimized geometry of Carbaryl calculated at MP2/6-311++GDP level of theory. A- Balls and cylindrical view. B- Charge of atoms. C- Bond length (Å). D- Electrostatic potential.

The bond stability of carbaryl bond, which shows high tendency for breaking, can be studied through a comparison as shown in figure 3. The bond C₉-O₁₃ (1.395 Å) has less stability than other bonds in carbaryl because

it's stable until -2820 kcal/mol. Therefore, carbaryl may be cleaved through this bond to give its major moieties, which are carbamic acid radicals, and 1-naphthol.

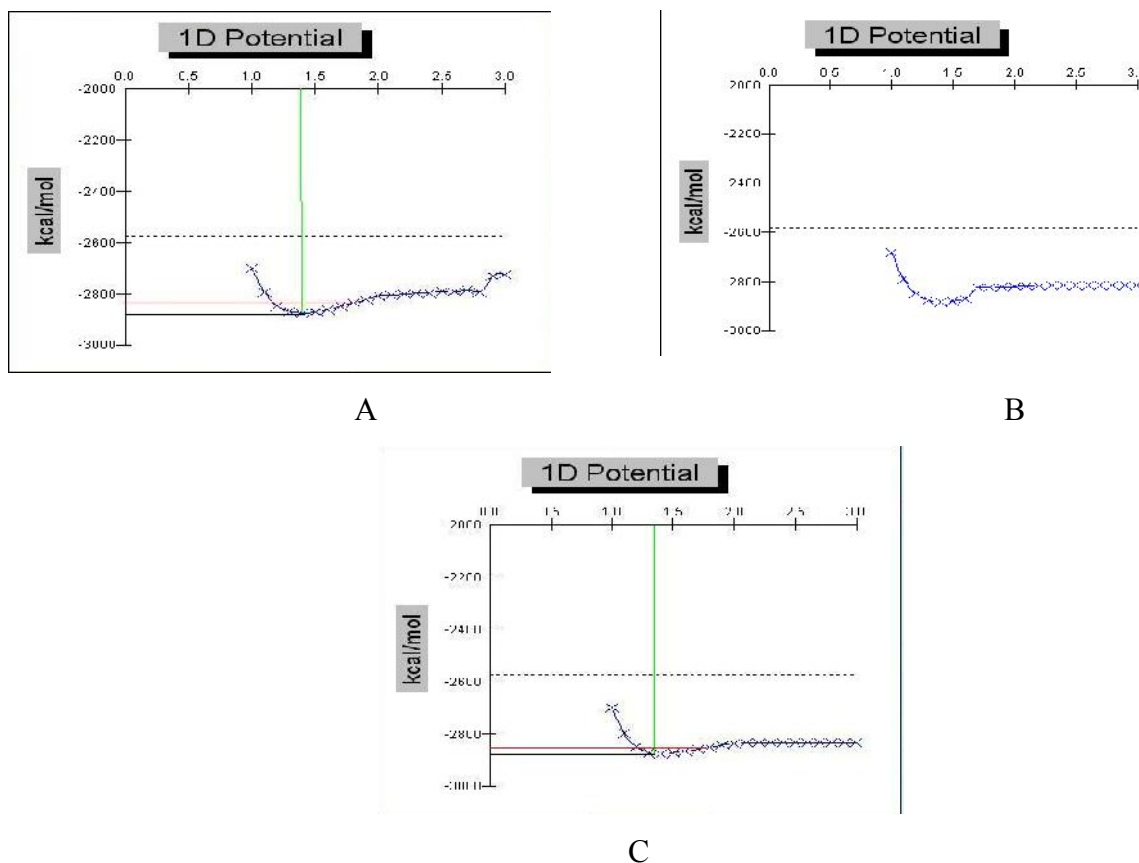


Figure (2) Potential energy stability of carbaryl bonds, calculated by PM3 method. A- C₉-O₁₃ length bond is 1.39589 Å. B- C₁₉-N₂₀ length bond is 1.34335 Å. C- O₁₃-C₁₉ length bond is 1.36327 Å (-2890kCal/mol).

Energies calculation of the carbaryl reaction yields straightforward, well-defined information about the likely products. Electrophilic, aromatic substitutions are an example of this type of reaction. Other

reactions are controlled kinetically, and the most stable product is not the major one which is observed. In these cases, we must look at the reactant side of the reaction coordinate to discover factors determining the

outcome. Development an analysis of reactivity may fulfil in terms of two factors: an electrostatic interaction approximated by atomic charges and a frontier orbital

interaction. Figure 3 described the total change in electronic features of carbaryl through reaction with hydroxyl radical.

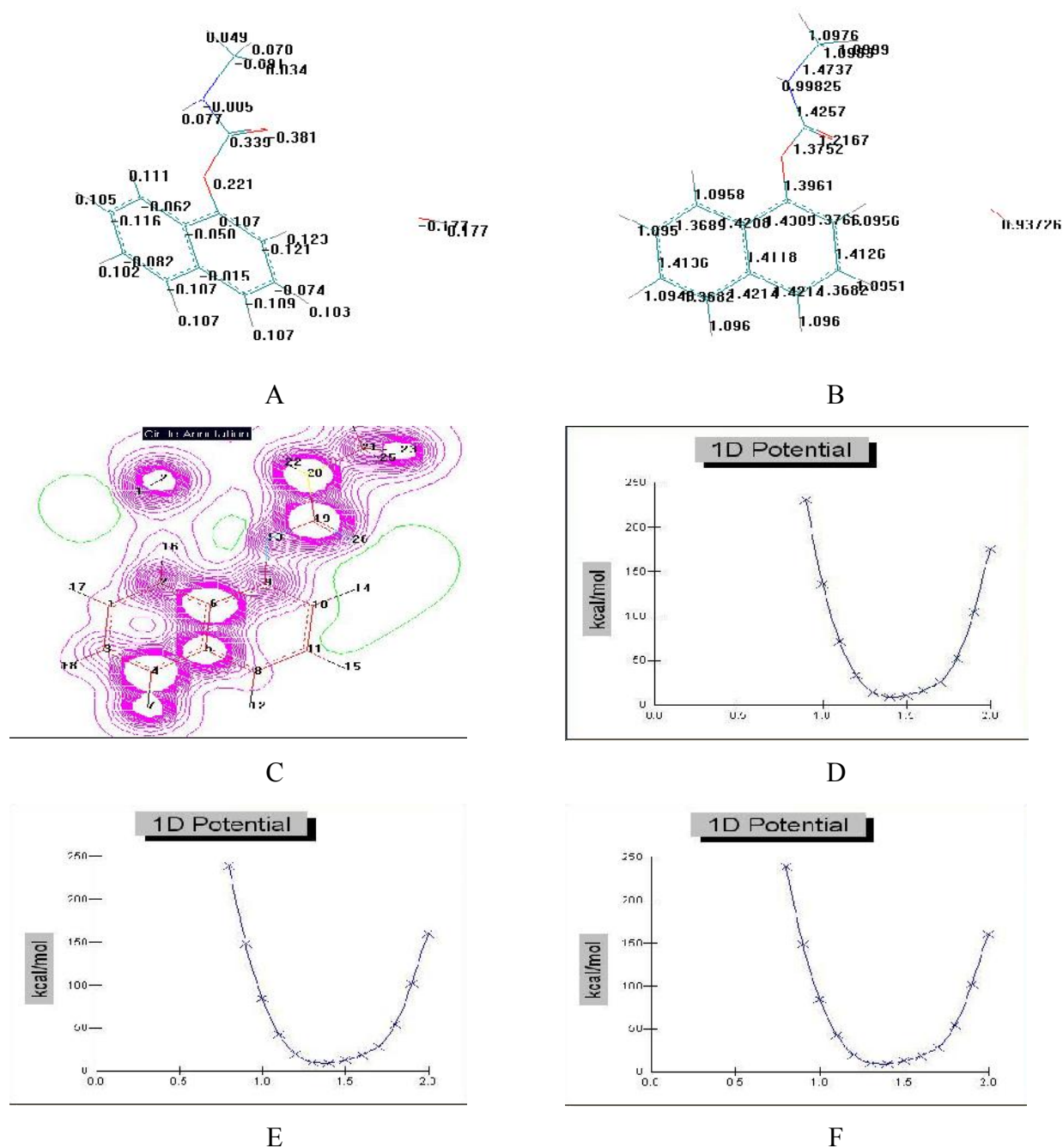


Figure (3) Electronic features of carbaryl reaction with hydroxyl radical, calculated by PM3 method. A- Atomic Charge. B- Bond Length. C- Electrostatic Potential. D- Bond length C₉-O₁₃(Å). E- Bond length O₁₃-C₁₉(Å). F- Bond length C₁₉-N₂₀(Å).

The overlap interaction investigations of electrostatic potential for both reactants were carried out. The atoms O₁₃, N₂₀, C₂₁, and O₂₆ have a negative charge, that is equal to -0.221, -0.005, -0.091, and -0.381 respectively. The atoms C₉, and C₁₉ have a positive charge, that is equal to +0.107, and +0.339 respectively. The length of carbaryl bonds C₉-O₁₃, O₁₃-C₁₉, C₁₉=O₂₆, C₁₉-N₂₀, and N₂₀-C₂₁ are 1.3961, 1.3752, 1.2167, 1.4257, and 1.4737 angstrom respectively. Bond length of hydroxyl radical shows the same behaviour where bond length of O-H is changed from 0.99067 into 0.93726 Å.

The initial assumption from above data, showed that the oxygen atoms of radical preferred to attach to C₉, C₁₉, and aromatic ring is in large ratio than other active site in carbaryl. Hydrogen atom of radical preferred to attach to O₁₃, N₂₀, and O₂₆ in large ratio than other active site in carbaryl molecule. The potential energy surface of C₉-O₁₃ bond

which show a high effectiveness than other bonds, due to the interaction of carbaryl molecules with OH radical. This bond may be more favourable to be a good site for cleavage of carbaryl. Its good agreement with literatures (International Agency for Research on Cancer 1976). The reaction of carbaryl takes place in different directions, the first one is the hydroxylation reaction on methyl group, and aromatic ring. The second reaction is degradation reactions of carbaryl molecules by hydroxyl radicals into small moieties like CO₂. The same things happen for the products of first reactions therefore the degradation reaction will include several types of products. Four transition states have been proposed, based upon the above investigations lead us to the real path of degradation. Figure 4 shows the geometries stick view of these states. Different attachment sites are suggested for hydroxyl radical to interact. These sites are at C₉, C₁₉, N₂₀, O₁₃, and O₂₆.

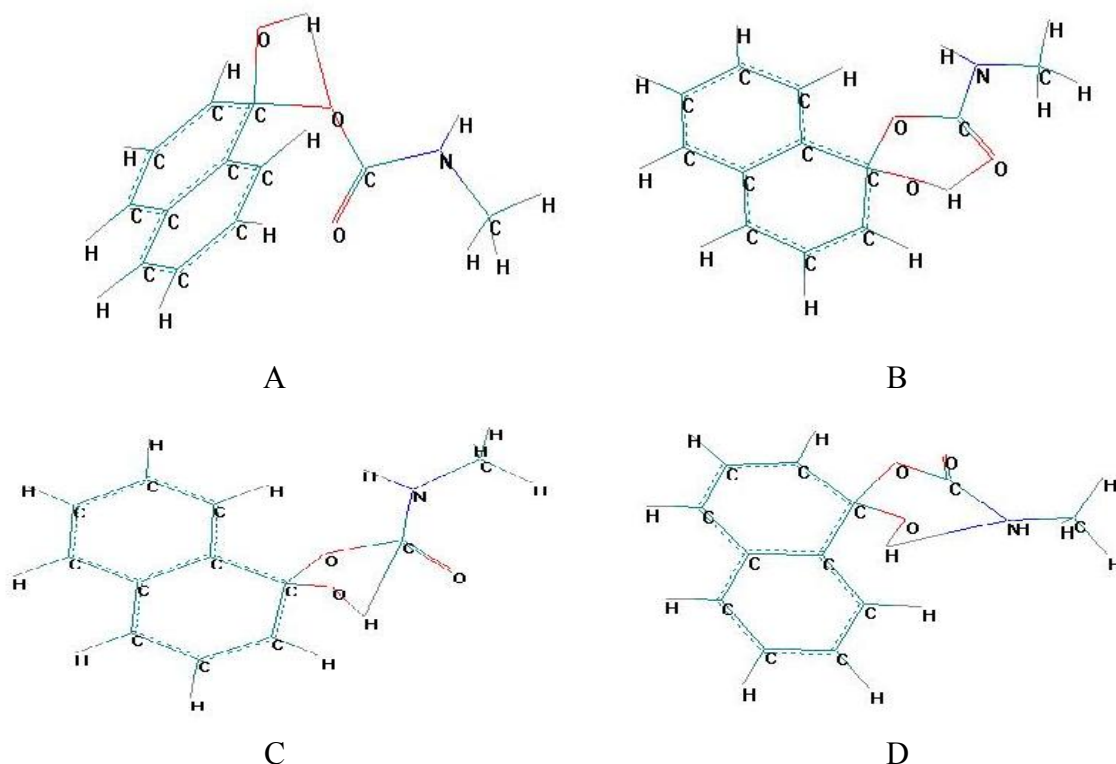


Figure (4) Wire frame view of proposed transitions states, calculated by PM3 method at CI(4x4). A-Test-carbaryl-OH-TS1.B-Test-carbaryl-OH-TS2.C-Test-carbaryl-OH-TS3.D-Test-carbaryl-OH-TS4 (REAL).

Were shown in table 1 represented the calculation of energies and IR- frequencies of proposed transition state. Investigation refers all bonds showed the same ratio of length

difference relatively to the interaction structure of carbaryl with radical in transition state, which that expected to yields cleavage through bond C₉-O₁₃.

Table (1) Optimized geometry of proposed transition state calculated at 3-21G** level of theory.

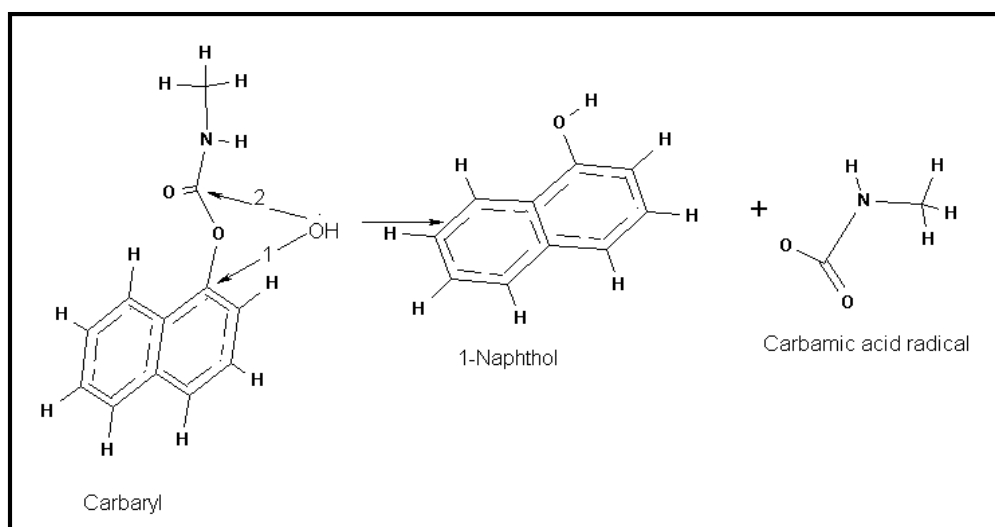
Transition States	RC ₉ -O ₁₃ A°	RO ₁₃ -C ₁₉ A°	PES kcal mol ⁻¹	ZPE kcal mol ⁻¹	IR frequency
TS1	1.4397	1.3659	-61095.812	135.399	+
TS2	1.46445	1.35757	-61095.454	135.256	+
TS3	1.4422	1.38418	-61089.800	135.199	+
TS4	1.42263	1.37477	-61090.622	138.992	-

TS4 has a medium potential energy surface value than others transition states with negative value of first frequencies and its

have higher ZEP value than other states. The test of vibration frequency calculation showed that only TS4 has one negative frequency,

which may enhance the evidence that the cleavage step occurs through TS4. There are two different paths probable for hydroxyl radical to attack carbaryl. In the first path the $\cdot\text{OH}$ attacks directly to naphthalene ring, while in the second path it attacks to C_{19} atom of carbamic acid. This conclusion based on calculation of activation energy barrier which required for producing the products according

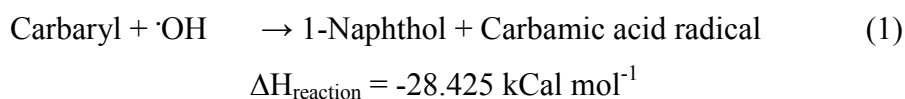
to this probability. Scheme (1) described the reaction probability. Energy barrier calculation for the first path is equal $116.390 \text{ kCal mol}^{-1}$ (245.865 nm), while the energy barrier calculation of for the second path is equal $+197.600 \text{ kCal mol}^{-1}$. Therefore the first path probability assumption is the most credible.



Scheme (1) Probabilities of hydroxyl radical's attached on carbaryl.

According to the above evidence, the cleavage reaction step occurs for carbaryl by one hydroxyl radical, calculation carried out

by configuration interaction method. The suggested cleavage reaction can be writing as follow:



Reaction rate of the cleavage step has been calculated by G03W program. Table (2) represents the thermodynamics values of reaction component. The enthalpy change of

reaction equal to $\Delta H_{298.15\text{K}} = 2.1963 \text{ Kcal/mol}$. The Gibbs free energy of reaction is equal to $\Delta G_{298.15\text{K}} = 1.96536 \text{ kCal mol}^{-1}$. The reaction rate, K value is equal to $2.2520 \times 10^{11} \text{ s}^{-1}$.

Table (2) Thermodynamics calculation of carbaryl cleavage reaction components using G03W program

Reaction components	$\Delta H_{298.15K}$ (Hartree)	$\Delta G_{298.15K}$ (Hartree)
Carbaryl	-664.798721	-664.852429
$\cdot\text{OH}$	-75.369868	-75.390067
Naphthol	-458.038932	-458.079502
Carbamic acid radical	-282.126159	-282.159862

There are other reactions that may be competed with the first step. Hydroxylation reactions are the major competitive reactions. In addition, the product of these reactions can enter the same path degradation reaction; finally these reactions will produce different hydroxylation products of naphthalene products. The hydroxylation reaction may

occur with different species to produce hydroxylation products which depend on the number of hydroxyl radical inter the reaction. Both Table (3) and (4) are summarized the calculations of energies for chemical structures and investigated hydroxylation reaction of carbaryl reactions respectively.

Table (3) Energetic values, and IR frequencies of proposed structures for carbaryl Hydroxylation reactions calculated at MP2//3-1G* level.

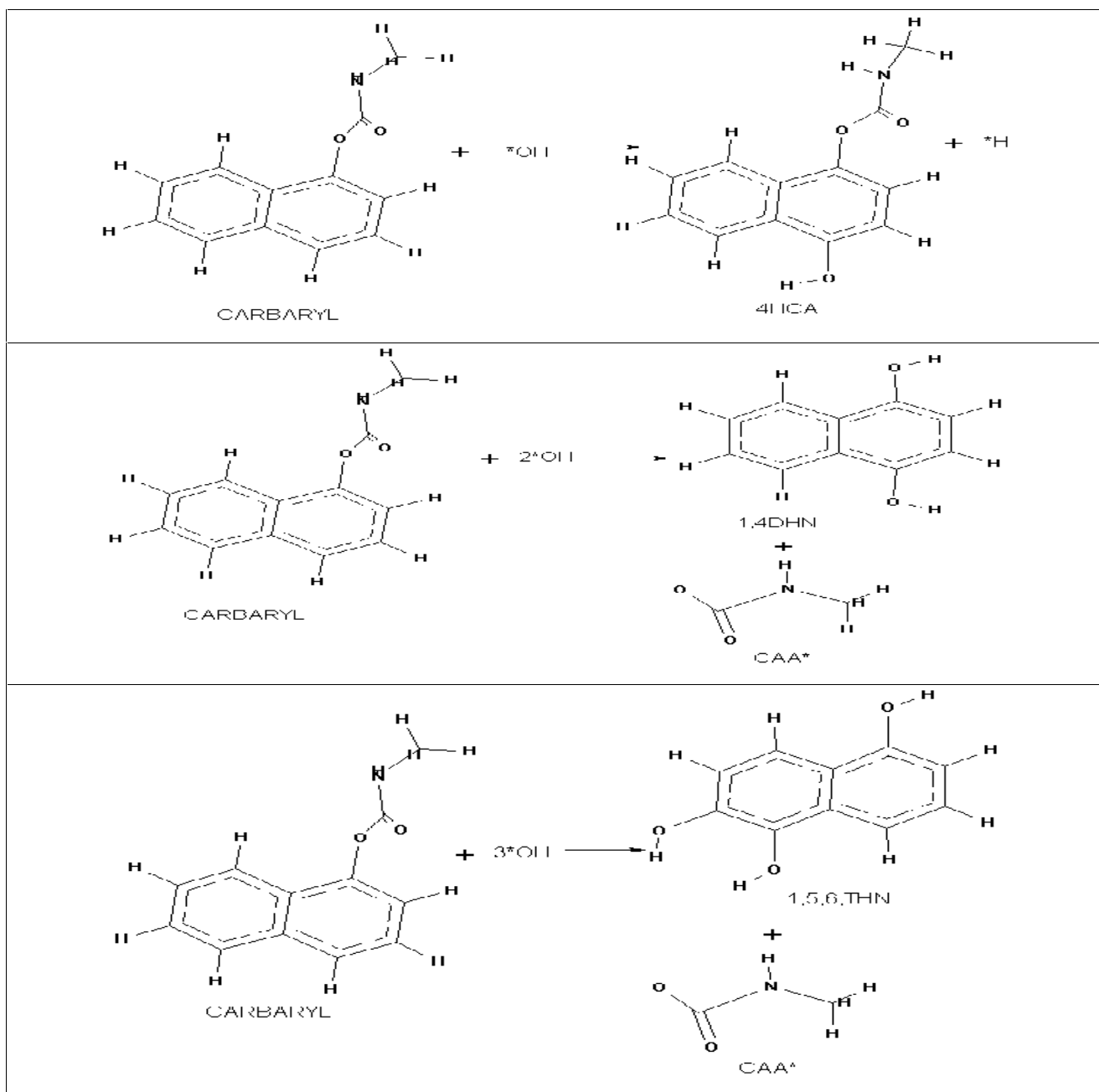
Code Structure	ΔH_f° kCal mol ⁻¹	Total energy kCal mol ⁻¹	IR- Frequency
Carbaryl	-44.0816227	-53976.911143	+
1-Naphthol	-21.0145811	-36941.367367	+
$\cdot\text{CAA}$	-54.9189992	-24153.049049	-
4-HCA	-94.0219698	-60758.926352	+
DHN	-63.3993534	-43715.827001	+
DHCA	-132.0640491	-67529.043294	+
THN	-105.0164497	-50489.51897	+
HMCA	-93.3557813	-60758.260164	+
HM \cdot CAA	-80.9338471	-30911.13876	-

Table (4) Energy barriers of hydroxylation reactions calculated at MP2//3-1G* level.

Reactant	Products	Energy Barrier kCal mol ⁻¹	$\Delta H_{\text{reaction}}$ kCal mol ⁻¹
Carbaryl + $\cdot\text{OH}$	HCA	+11.035	-45.388
	HMCA + $\cdot\text{H}$	+29847.771	+1.858
	naphthol+CAA	+116.390	-61066.121
Carbaryl+2 $\cdot\text{OH}$	DHN +CAA	+11.877	-27.226
	DHCA	+64.773	-93.785
	1-naphthol+HM \cdot CAA	+88.659	-59.790
Carbaryl+3 $\cdot\text{OH}$	THN +CAA	+568.556	-118.739

Aromatic substitution of carbaryl occurs into 4-HO-carbaryl by one free radical or 5,6-di-HO-carbaryl by two free radicals. Degradation of both of them yields carbamic acid radical in addition to 4-HO-Naphthol, and 5,6-di-HO-naphthol respectively. Aliphatic hydroxylation of carbaryl occurs into methyl group of carbaryl. Degradation

yield 1-naphthol, and hydroxyl methyl carbamic acid radical. Scheme (2) represents the hydroxylation subside reaction that occurs within the degradation reaction of carbaryl. These reaction probabilities depend on the lowest energy barrier values to occur at highest ratio yields.



Calculation of degradation reaction of carbamic acid radical refers to cleavage step which produces two main fragment molecules. Focusing on the step because its products

represent the major pollutant component in carbaryl. Both Table (5) and (6) are representing the energies of degradation reaction for carbamic acid radical respectively.

Table (5) Energetic values and IR- frequencies of proposed structures for carbamic acid radical degradation calculated at MP2/3-1G* level.

Code Structure	ΔH_f° kCal mol ⁻¹	Total energy kCal mol ⁻¹	IR-Frequency
MHA	-17.882	-15001.551	+
MO·A	1.590	-14628.499	-
MHA·	4.621	-14625.468	-
DHA	-27.013	-18299.635	+
HA·	6.632	-11180.335	+
MAZ	2.243	-14274.268	+
NA	-14.92	-17580.393	+
DHO·A	-27.216	-24678.334	-
NTA	-44.830	-24342.369	+

Table (6) Energetic values and IR- frequencies of proposed structures for carbamic acid radical degradation calculated at MP2/3-1G* level.

Reactant	Products	Energy barrier kCal mol ⁻¹	ΔH_f° kCal mol ⁻¹
CAA·	CO ₂ + MA·	+273.270	-22.715
CAA·+ ·OH	CO ₂ + MHA	+ 4.028	-64.374
MHA + ·OH	MO·A + H ₂ O	+911.467	-35.047
	MHA·+ H ₂ O	+9132.534	-31.916
	DHA + ·M	+9255.131	-64.843
	HA·+ME	+9209.609	+51.472
MO·A	MAZ + ·H	+12.933	+52.745
MAZ+ ·OH	NA+ ·M	+68.570	+9.785
NA + ·OH	DHO·A	+32.518	-13.249
DHO·A	NTA + ·H	+246.370	-37.392
M·+ ·OH	ME	+18.641	+83.631
ME + ·OH	ME·+ H ₂ O	+21.009	-13.023
ME·	FO + ·H	+25.374	+21.569
FO + ·OH	·OME	+644.861	-94.308
·OME	FOA + ·H	+8.407	+62.782
FOA + ·OH	FOA+ H ₂ O	+19.737	-4.562
FOA·	CO ₂ + ·H	+15.338	-0.216
FOA·+·OH	CA	+9.088	-76.668
·H+ ·H	H ₂	-0.003	-117.601

*IR and Heat of formation calculated by PM3/CI methods

The overall mechanism of carbamic acid radical degradation can be summarized into three main reactions as in following equations:-



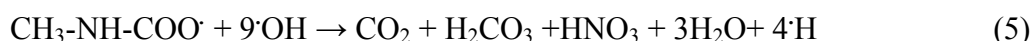
$$\Delta H_{\text{rea}} = -36.891 \text{ kCal mol}^{-1}$$



$$\Delta H_{\text{rea}} = -50.641 \text{ kCal mol}^{-1}$$



$$\Delta H_{\text{rea}} = -20.578 \text{ kCal mol}^{-1}$$



$$\Delta H_{\text{rea}} = -108.049 \text{ kCal mol}^{-1}$$

Equation 5 represented the overall degradation reaction of carbamic acid radical.

Degradation reactions of carbaryl by hydroxyl radicals in gas phase may generally be divided into three main steps. First step is the cleavage step of carbaryl (equation 1), which is exothermic reaction to produced main degraded components. This reaction will promote the last other reactions to occur. These components, one of them will degrade

as in (equation 5) to represent the step two. Combination reaction of hydrogen free radical will represent the third exothermic reaction step. The overall reaction of carbaryl can be summarized in three main steps to produced general equation for degradation as shown follow:



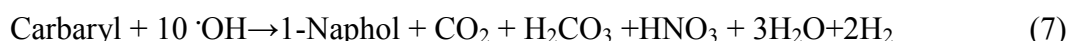
$$\Delta H_{\text{rea}} = -28.425 \text{ kCal mol}^{-1}$$



$$\Delta H_{\text{rea}} = -108.049 \text{ kCal mol}^{-1}$$



$$\Delta H_{\text{reaction}} = -117.601 \text{ kCal mol}^{-1} \times 2$$



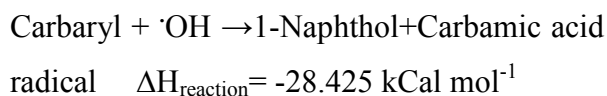
$$\Delta H_{\text{overall reaction}} = -371.674 \text{ kCal mol}^{-1}$$

The enthalpy changed value of the overall reaction for carbaryl degradation indicates that this reaction is exothermic. Finally, a simple moieties was produced from this

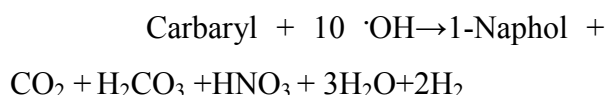
reaction like CO_2 , H_2CO_3 , H_2O , HNO_3 and H_2 .

Conclusion

The first degradation reaction step of carbaryl can be written as in following equation:



The activation energy of this step is 116.390 kcal mol⁻¹ (245.865 nm) and rate constant of cleavage step reaction is 2.2520 x 10¹¹ s⁻¹. The enthalpy change value of overall reaction for carbaryl degradation is equal to -371.674 kCal mol⁻¹. Hydroxylation reactions may be a major competitive step with the first step. The equation of overall degradation reaction is:



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التجزئي ء الضوي للكارباريل بوساطة جذر الهيدروكسيل نظريا

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الخلاصة

تم تكسير الكارباريل في الفراغ بوساطة جذر الهيدروكسيل الحر نظريا باستخدام الأشعة فوق البنفسجية. استخدمت طرق حسابية مختلفة مثل الشبة التجريبية والحسابات الأساسية ونظرية دالة الكثافة المحملة ضمن برامج ميكانيك الكم. تم إيجاد التراكيب الهندسية المثلى لجميع الأصناف الكيميائية المقترحة لغرض تخمين الفعالية الكيميائية والخواص الكيميائية لجميع التفاعلات. تم دراسة الحالات الانتقالية المحتملة من خلال سطوح جهد الطاقة الكامنة وطاقة نقطة الصفر والتردد الخيالي الأول. تم احتساب القيم الطاقية وحواجز الطاقة للتفاعلات الكيميائية لجميع التفاعلات وكذلك إيجاد ثابت سرعة خطوة تفاعل البدء. احتسبت الطاقة الكلية وحرارة التكون والطيف الاهتزازي لجميع مكونات التفاعلات المقترحة.

خطوة بدء التكسر لمبيد الكارباريل هو تفاعل باعث للحرارة يتم من خلال كسر الأصرة (C₉—O₁₃) بطاقة تنشيط مساوية إلى 116.391 كيلو سعرة⁻¹. تتولد مكونتان رئيستان من التفاعل وهي Carbamic acid radical & 1-Naphthol. ثابت سرعة التفاعل المحسوب يساوي $2.252 \times 10^{11} \text{ s}^{-1}$. الية التكسر الكلي لمول واحد من الكارباريل تتطلب عشرة مول من جذور الهيدروكسيل الحرة. التغير الكلي بالمحتوى الحراري المرافق للتكسر الكلي يساوي 371.674- كيلو سعرة⁻¹. المكونات الناتجة عن عملية التكسر للكارباريل هي H₂O و H₂CO₃ و HNO₃ و H₂ و CO₂. تفاعلات استبدال الهيدروكسيل على الحلقة الاروماتية هي التفاعلات المنافسة لتفاعلات تكسير الكارباريل والتي تولد ناتجا مختلفا يتضمن معوضات الهيدروكسيل للنفثالين.

الكلمات المفتاحية:- المتيوميل ، طرق حسابات الكم ، التجزوء ، دالة الكثافة الوظيفية ، الكيمياء الحاسوبية