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Theoretical Degradation Study of Methomyl

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ABSTRACT

Quantum calculation methods have been used, that is packaged on two reliable well-known programs Hyperchem7.5 and Gaussian03W to achieve the theoretical calculations of degradation for Methomyl. Chemical reactivity and chemical interaction have been studied for pesticide molecules and the attached species (hydroxyl free radical), by calculating the surface potential energy, atomic charge, bond length, electrostatic potential and molecular orbital to estimate the highest probable active sites in pesticides to be degraded .Twenty one different chemical structures and four different probable transition state stabilities to get the first step have been studied through surface potential energy, zero point energy, and first negative frequency of vibration spectrum. Activation energy and rate constant of cleavage reaction step are calculated for all reaction components that is probable to be formed during the complete degradation into simple molecular structure. Thirty of different chemical reactions have been studied to estimate the reactions that have the highest probability to occur with lowest value of activation energy by comparing relatively to others competitive reactions, in order to estimate reasonable mechanisms of completely degraded. They found the first degradation step of methomyl is exothermic through O_8—N_{10} *bond to give up two major components. The activation energy of first step is 109.648 kcal* mol^{-1} *and rate constant of first degraded step is* 1.327×10^{11} s^{-1}. *The enthalpy change value of overall reaction for methomyl degradation is equal to -1701.252 kcal* mol^{-1}. *Thirteen moles of hydroxyl radical needed to convert methomyl into simple moieties like* CO_2, H_2CO_3, H_2O, H_2SO_4, HNO_3 *and* H_2.

Keywords: Methomyl, quantum calculation methods, degradation, computational chemistry, DFT, Ab-initio, semiemprical.

INTRODUCTION

Methomyl (Thiodicarb) is a mixture of (Z) - and (E)-isomers that is used as a foliar spray, to control many insects on field crops, fruit crops and vegetables. Thiodicarb used only as insecticide and molluscicide [1]. Methomyl is classified as highest-hazard pesticides, ranked by the UC Environmental Health Policy Program [2]. The substance is very toxic to aquatic organisms and this substance does enter the environment under normal use [3,4] . Ultimate degradation products of thiodicarb are acetonitrile and carbon dioxide, the last being reincorporated in endogenous plant materials[5].The risk assessment carried out for the representative uses supported and an acute risk resulting from the consumption of wine and table grapes. Under dark aerobic conditions in soil, methomyl was the only major metabolite of thiodicarb. Photolysis may contribute slightly to the environmental degradation of thiodicarb being acetonitrile is only major soil photolysis metabolite. Thiodicarb is very low to persistent in soil under aerobic laboratory conditions. The field dissipation studies are available for thiodicarb formulated either as water flow able or slow release pellets. Thiodicarb is low to high mobile and methomyl is very high mobile in soil. In sterile buffer solutions at 25°C thiodicarb and methomyl degradation are pH dependent. The main product of thiodicarb hydrolysis is methomyl. In water/sediment systems, thiodicarb degrades very fast to methomyl in the water phase (DTd). Degradation of methomyl was also fast with half-life is between 3.5 to 5 days in the total systems [6] .On increasing the concentration of methomyl the degradation rate decreases and Fe^{2+} and H_2O_2 can both accelerate degradation. IR study shows that the reaction products are SO^{2-}_4, NO^-_3 and CO_2 [7, 8].

The degradation of methomyl in aqueous solution by UV- irradiation in the presence of TiO_2 showing that mineralization to carbon dioxide, water, sulfate and ammonia took place during the process. The rate of photodecomposition of methomyl measured using high performance liquid chromatography (HPLC), while its mineralization was followed using ion chromatography (IC), and total organic carbon (TOC) analysis. The identification of reaction intermediate products carried out using coupled techniques HPLC-MS (electro spray ionization in positive mode) and a degradation pathway was proposed. Three main intermediates identified resulting from: i) the rupture of the ester bond (or the N–O bond), ii) the hydroxylation of methyl group borne by the nitrogen atom and iii) the product resulting from the decarboxylation of the oxidized hydroxylated methyl group (photo-Kolbe reaction)[9].

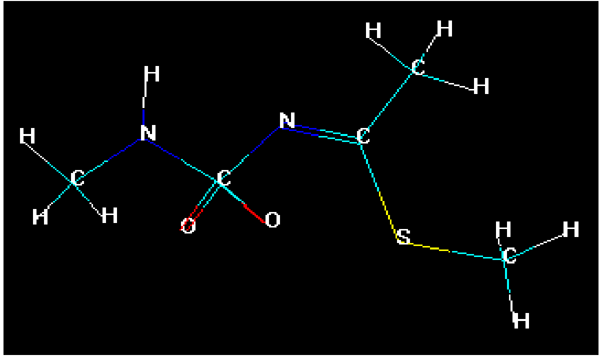
The present work tend to study the reaction of methomyl with hydroxyl radical theoretically through the quantum calculation treatment of the electronic and geometrical structure of this pesticide with their reliable transition states and also to find out a reasonable mechanism of degradation reaction in gas phase[10].

MATERIALS AND METHODS

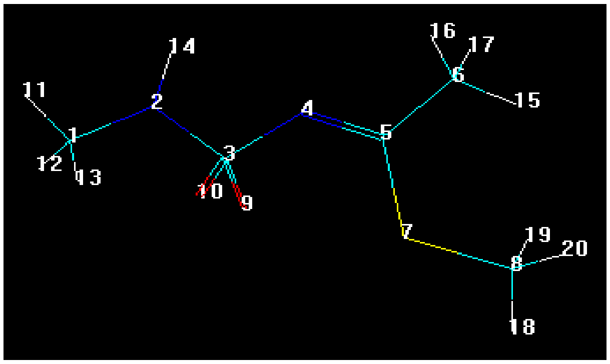
DFT, *ab initio* and PM3 methods have been used for evaluation of electronic energies, heat of formation and electrostatic potential of methomyl and *OH. The geometries of intermediates and final molecules have been optimized at /6-311++G(2df,2p) (5d,7f) and PM3 level. Polarized spilt valence 6-311++G(2df,p) 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 [11]. 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 step, using RMP2/6-311++g(2d,2p)//RHF/6-31G(D)(12).

RESULTS AND DISCUSSION

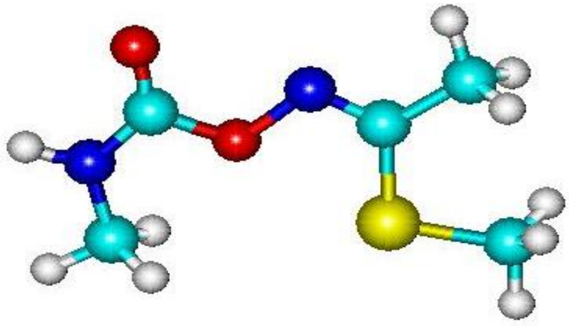
Free hydroxyl radical is used as initiator for sequences of degradation reactions. It is generated from peroxide molecule by photolysis reactions. Electronic features investigations of methomyl have been done through the calculation of atomic charge and molecular orbital interaction to predict the active site of reaction in methomyl molecules toward OH^* radicals. Electronic features of methomyl molecules were concluded from geometry optimization which calculated at MP2/6-311++GDP//6-31GDP large function level of theory as shown in Figure 1. The electrostatic interaction approximated by atomic charge and a frontier orbital, can be concerned for the reactive atoms, which are possibly sharing in the reaction. The atoms of N_5, O_8, O_9, and N_{10} have a negative charge, that is equal to -0.845, -0.618, -0.635, and -0.240 respectively. The atoms of C_7, C_{11}, and S_{16} have a positive charge, that is equal to +1.236, +0.094, and +0.311 respectively. Therefore, oxygen atoms of hydroxyl radical can attach to the positive charge atoms C_7, is most probable in methomyl molecule than other positive atoms, while hydrogen atoms at hydroxyl radical attacks the atom with negative charges. The total potential energy surface of free methomyl is -534183.783 kcal mol^{-1}. Bond length of methomyl bonds N_5—C_7, C_7—O_8 , C_7==O_9, O_8—N_{10} and C_{11}—S_{16} are 1.349, 1.376, 1.201, 1.448, and 1.760 Angsroms respectively.



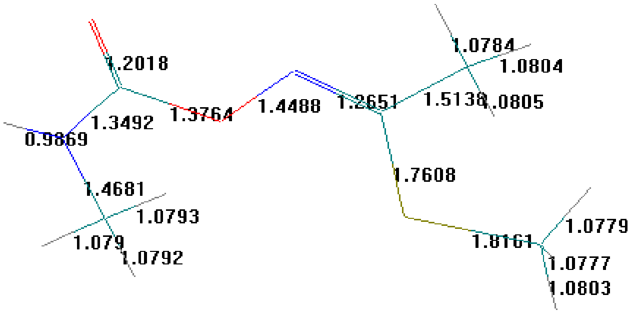
Atomic symbol



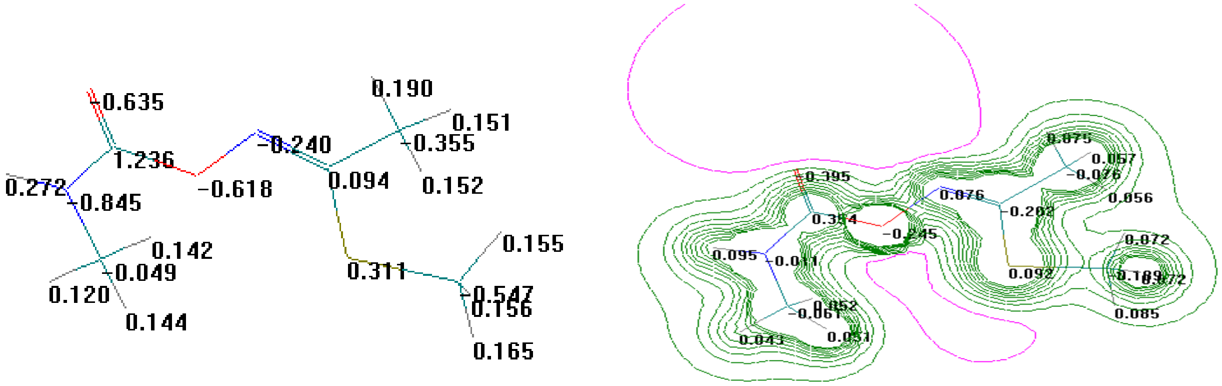
Atomic serial



Atomic Ball view



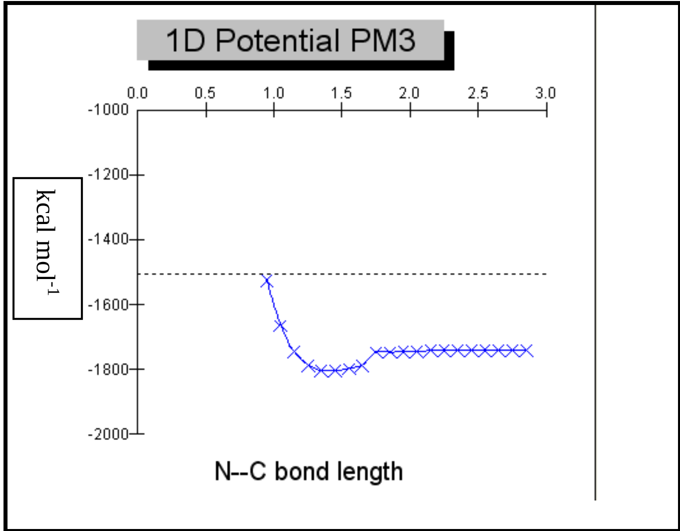
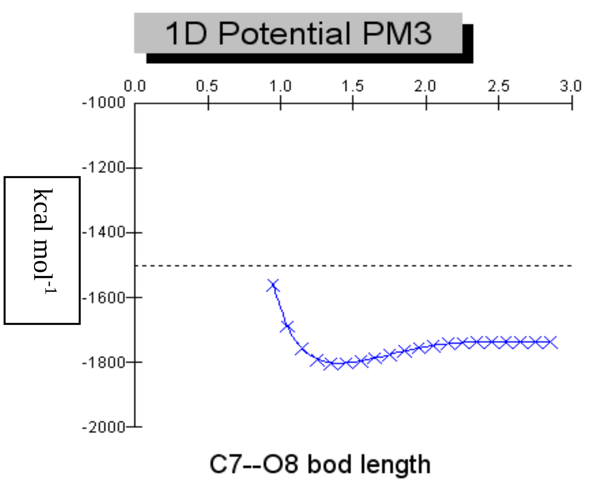
Bond length(A°)

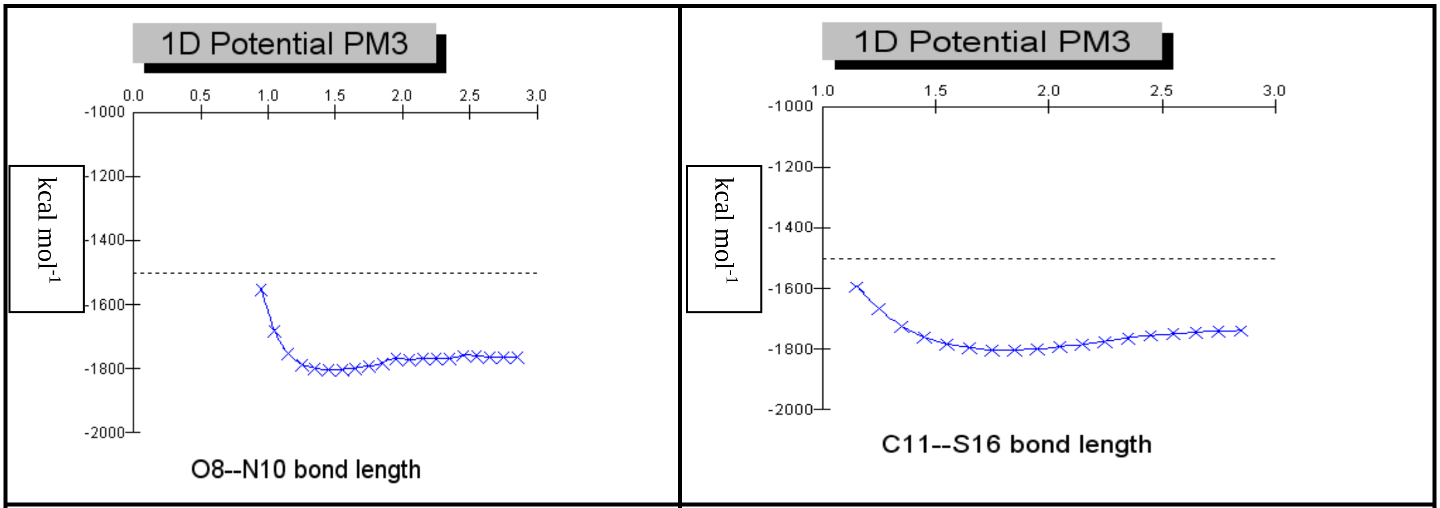


Atomic charge (coulomb) Electrostatic field

Figure 1. Geometry optimization of methomyl molecule calculated at MP2/6-311++GDP//6-31GDP level of theory

Bond strength has been measured for the main important bonds. Figure 2. illustrates the stability of bonds N_5—C_7, C_7—$O_{8,}$ O_8—N_{10}, and C_{11}—S_{16} calculated by PM3 Method. By comparing these bonds, we found the N_5—C_7, and C_7—O_8 as lowest stable rather than other bonds because they break down at 1.2 A^o with -1750 kcal mol^{-1} and 2 A^o with -1780 kcal mol^- respectively.

	
A-N_5—C_7 Bond potential	B-C_7—O_8 Bond Potential

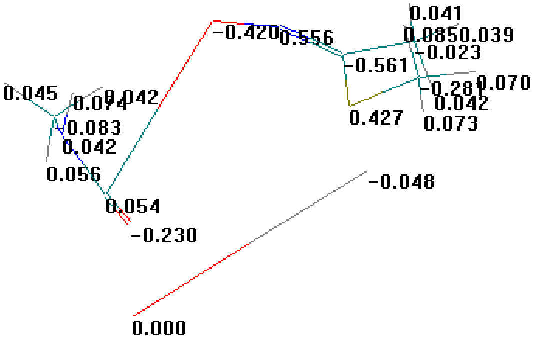


C- O_8—N_{10} Bond Potential | D- C_{11}—S_{16} Bond Potential

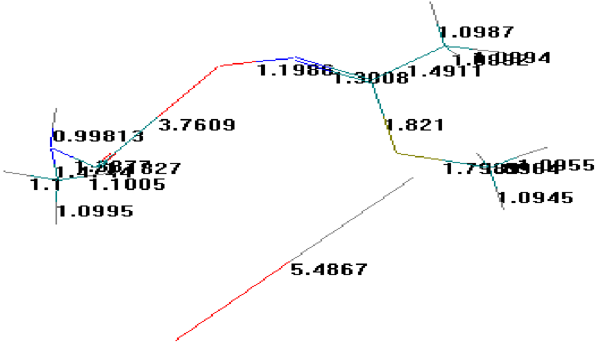
Figure 2. Potential energy stability of Methomyl bonds

Calculations of the atomic charge and molecular orbital prediction involved the most probable active site of methomyl toward hydroxyl radical. The most stable product which may occur in one-step. Negative charge atom of hydroxyl radical attached with largest positive charges atom in methomyl.

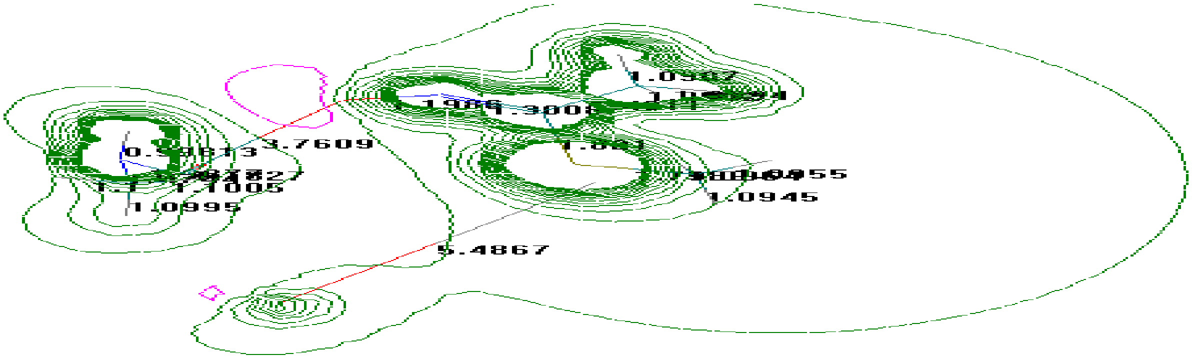
Figure 3. Shows the overlap interaction of electrostatic potential of both reactants, since the most original electronic properties will change. The net atomic charges of oxygen and hydrogen atom in hydroxyl radical are changed from -0.336, 0.336 to 0.00, and -0.048 respectively. The atoms N_5, O_8, O_9, and N_{10} have new charges, due to this interaction and bond lengths of methomyl are changed. Bond length of hydroxyl radical showed a similar behavior where bond length of O—H bond was changed from 0.9906 to 5.4867 A°. The initial assumption to above data is that oxygen atoms of OH^* radical preferred attacks to C_7, in large ratio of probability than the double bond (N_{10}==C_{11}) and other active site. Hydrogen atom of OH^* radical preferred to attach to the atoms O_8, O_9, and N_{10} rather than the other active site in methomyl molecule. Investigation show that bond C_7—O_8 with high potential than other bonds due to the interaction of methomyl molecules with OH radical. This bond may be more favorable to be a good site for cleavage reaction step. different results have been got more than mentioned in literature[13], that the O_8—N_{10} bond was the effective bond for first step reaction.



Atomic Charge(coulomb)



Bond Length(A°)

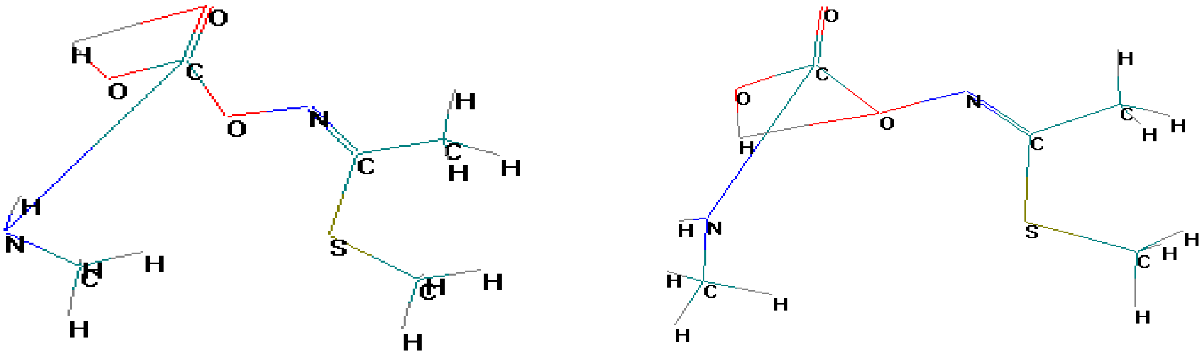


Electrostatic Potential

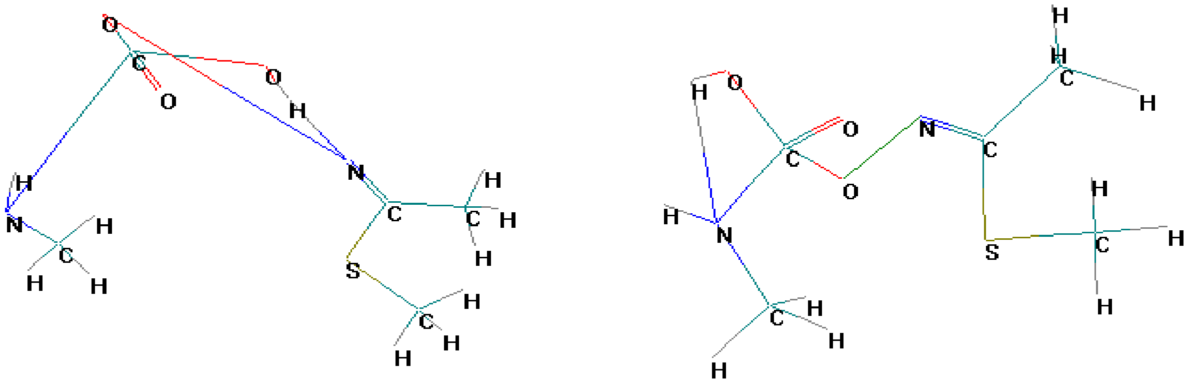
Figure 3. semiemprical calculation of Electronic features for the reaction of methomyl with hydroxyl radical

The reaction of methomyl with OH* occurs at different directions, either the hydroxylation reaction on methyl group which is of low importance than degradation reaction of methomyl molecules by hydroxyl radicals into simple fine moieties like CO_2. The same thing was happened for the products of first reaction therefore the degradation reaction will have the same final products i.e. SO_4^{2-}, NO^-_3 and CO_2 [14,15]. Four different transition states were proposed, based upon the above investigations that lead to the real path of degradation.

Figure 4 shows the geometries and the sites of N_5, C_7, O_8, O_9, and N_{10}.All four proposed transition state structures have been optimized and IR-tested.



A- TS1 B- TS2(real)



C-TS3 D-TS4

Figure 4. Geometrical wire form view of proposed transitions states Calculate at 3-21G** level of theory

Table 1. Represents the calculation of energetic values and IR-frequency of the proposed transition state. The investigated bond length of C_7—O_8, and N_{10}—O_8 bonds which they showed different new lengths relatively through the interaction of methomyl with radical in transition state, which are expected to yield cleavage through bond C_7—O_8.

Table1. Optimized Geometry and IR frequency of Proposed Transition State Calculate at 3-21G** level of theory

Transition State	Length of C_7-O_8A^o	Length of N_{10}-O_8A^o	Potential Energy Surface Kcal/mol	Zero point energy Kcal/mol	IR-frequency
TS1	1.361	1.433	-49613.961	102.331	+
TS2	1.380	1.448	-49616.623	107.085	-
TS3	1.179	6.097	-5212.759	96.9139	+
TS4	1.361	1.433	-49613.961	102.331	+

TS2 is the real transition state because it has the lowest Potential Energy Surface value and highest Zero point energy value than other states [16]. The test of theoretical vibration spectra calculation showed that TS2 has negative frequency. Evidence refers that the cleavage step can occurs through TS2 transition state.

According to the above evidences, the calculated energy barrier value of first cleavage reaction step is 109.647 kcal mol^{-1} (260.985 nm) for methomyl that is done by one mole of hydroxyl radical (calculation carried out by G03W program). Scheme1.represent the suggested mechanism of first cleavage step for methomyl.

Methomyl + OH^{*} → NHTME + Carbamic acid radical

$$\Delta H_{rea} = -24.566 \text{ kcal mol}^{-1}$$

Scheme 1. suggested mechanism of first cleavage step for Methomyl

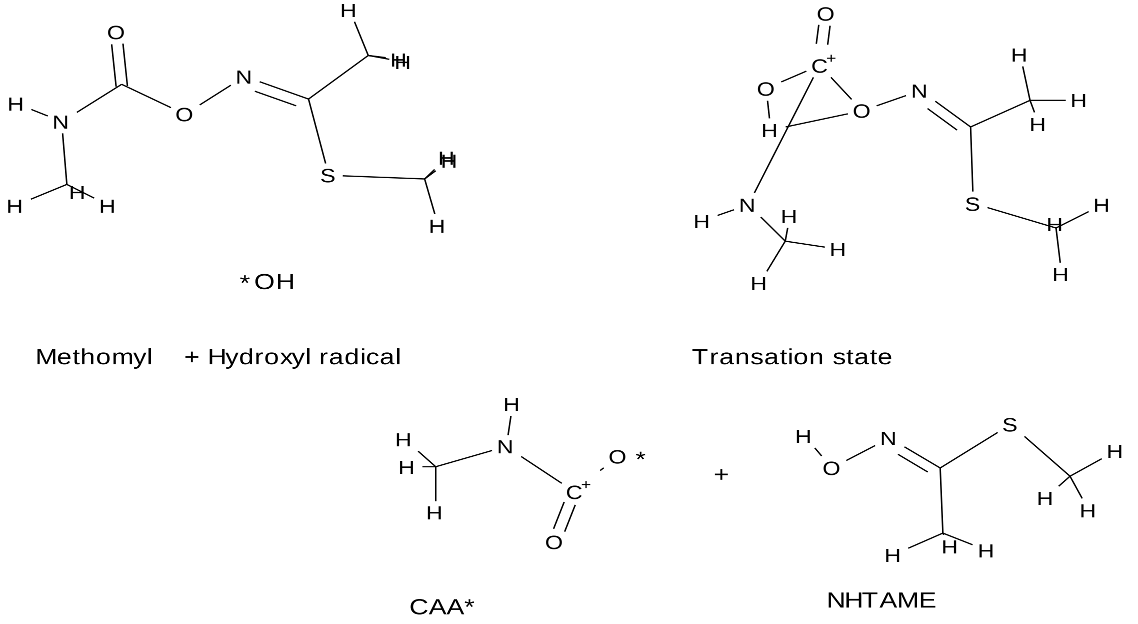


Table 2. represents the thermodynamics values of reaction components .The enthalpy change of reaction equal to $\Delta H_{298.15K}$= 231.834 kcal mol^{-1}.The Gibbs free energy of reaction equal to $\Delta G_{298.15K}$=2.2785 kcal/mol. The reactions rate is equal to 1.32724 x 10^{11} s^{-1}.

Table 2. Thermodynamics Calculation values of Methomyl Cleavage Reaction Component, using G03W program

Reaction components	ΔH^o(Hartree)	ΔG^o (Hartree)
Methomyl	-851.069977	-851.121003
*OH	-75.369868	-75.390067
CAA*	-282.122717	-282.161121
NHTAME	-644.305174	-644.346318

The last calculation of the cleavage step produces two main fragment molecules. Therefore, the prediction involved the full degradation of NHTME and carbamic acid radical from previous calculations because both of them are major pollutant components in Carbamate pesticides [17]. Tables 3 and 4 represent the energies and investigated degradation reaction of NHTME respectively.

Table 3. The total energies of proposed structures of NHTME degradation calculated at MP2/3-1G* level

Code Structure	ΔH_f° (kcal mol^{-1})	Total Energy(kcal mol^{-1})	IR- frequency
Methomyl	-32.149	-42504.414	+
NHTAME	-8.685	-25468.473	+
NHAA	-55.977	-24507.686	+
MTH*	21.447	-8072.285	-

HMS	-56.898	-15236.284	-
HAED*	-92.446	-31629.808	-
DHAED	-130.555	-38753.570	+
NDHAEO*	-57.410	-31594.772	-
NHFA*	-9.721	-20664.729	-
ETO	-164.428	-27954.053	+
DHA*	-14.633	-17933.676	-
THA	-48.430	-25053.126	-
EDO*	-89.088	-20793.060	-
MTO*	-134.936	-24127.862	-

Table 4. Energetic values of proposed reactions for N-Hydroxy-thioacetimidic methyl ester degradation calculated at MP2/3-1G* level

Reactant	Product	Energy Barrier (kcal mol^{-1})	$\Delta H°_{reac}$(kcal mol^{-1})
Methomyl + OH*	CAA*+NHTME	+109.647	-24.566
NHTME + OH*	MTH* +NHAA	+23.754	-26.805
MTH* + OH*	HMS	+7.086	-79.306
HMS + OH*	DHS + M*	+68.829	-8.875
DHS + OH*	OHS* + H_2O	+37.664	-35.211
OHS*	SD + H*	+74.929	+90.110
SD + OH*	SUA*	+94.486	-81.626
SUA*	SUA	+13.022	+15.477
SUA + OH*	H_2SO_4	+5.521	-92.631
M* + OH*	ME	+18.641	+83.631
NHAA + OH*	HAED	+17403.275	-37.428
	NDHAE*O	+968.163	-2.393
	NHFA*	+1043.019	-9.454
NDHAEO*+ OH*	DHAED	+1.093	-74.106
DHAED + OH*	ETO + DHA*	+88.844	-49.471
	THA + E*DO	+160.556	-7.928
DHA*	HNO_2 + H*	+50.778	-11.699
HNO_2 + OH*	$(HO)_2$-NO *	+32.518	-13.249
$(HO)_2$-NO *	HNO_3 + H*	+246.370	-37.392
ETO + OH*	ME + M*TO	+58.088	-163.467
M*TO	CA + H*	+39.338	+40.823
ME + OH*	ME * + H_2O	+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_2O	+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

Over all degradation reaction mechanism of N-Hydroxy-thioacetimidic methyl ester can summarized into ten main reactions.

NHTME+ OH^* → MTH^* + NHAA (2)
ΔH_{rea} = -26.805 kcal mol^{-1}
MTH* +2 OH* → DHS + M* (3)
ΔH_{rea} = -88.181 805 kcal mol^{-1}
DHS + 3OH* → H_2SO_4 + H_2O + H* (4)
ΔH_{rea} = -103.881 805 kcal mol^{-1}
M* + OH* →ME (5)
ΔH_{rea} = 83.631 805 kcal mol^{-1}
NHAA + 3OH* → ETO +DHA* (6)
ΔH_{rea} = -125.971 805 kcal mol^{-1}
DHA* + OH*→ HNO_3 + 2H* (7)
ΔH_{rea} = -62.340 kcal mol^{-1}
ETO + OH*→ ME +M*TO (8)
ΔH_{rea} = -163.467 kcal mol^{-1}
M*TO → CA + H* (9)
ΔH_{rea} = +40.823 kcal mol^{-1}
2{ME + 4OH* → CA+ $2H_2O$ + 2H*} (10)
2X {ΔH_{rea} = -208.421 kcal mol^{-1}}
4{H* + H* → H_2 } (11)
4X {ΔH_{rea} = -117.601 kcal mol^{-1}}

NHTME+20 OH* → $3H_2CO_3$ +$5H_2O$ +H_2SO_4 + HNO_3 + $4H_2$ (12)
ΔH_{rea} = -1333.437 kcal mol^{-1}

Equation 12 represents the overall degradation reaction of N-hydroxy-thioacetimidic methyl ester.

Degradation reactions of Methomyl in gas phase by using hydroxyl radicals can be summarized in three main steps. First step is the cleavage step of Methomyl (equation 1), which is exothermic reaction to produce main degraded components. This reaction will promote other reactions too. This means that one of them will degrade as in (equation 12) to represent the second step. Equation 10 represent the degradation reaction for second component of methomyl into carbamic acid radical (CAA*). Reaction of hydrogen free radical will represent the fourth exothermic reaction step. The overall reactions of methomyl is summarized as

Methomyl + OH * → NHTME + CH3-NH-COO * (1)
ΔH_{rea} = -24.566 kcal mol^{-1}
NHTME+20OH*→$3H_2CO_3$+$5H_2O$+H_2SO_4+HNO_3+$4H_2$ (12)
ΔH_{rea} = -3963.643 kcal mol^{-1}
CH3-NH-COO*+9OH*→CO_2+H_2CO_3+HNO_3+$3H_2O$+4H* (10)
ΔH_{rea} = -108.049 kcal mol^{-1}
2X{H* + H* → H_2 } (13)

$2X\{\Delta H_{rea} = -117.601 \text{ kcal mol}^{-1}\}$

$$\text{Methomyl} + 30\, OH^* \rightarrow CO_2 + 4H_2CO_3 + 2HNO_3 + H_2SO_4 + 8H_2O + 6H_2$$

$$\Delta H_{\text{overall reaction}} = -1701.252 \text{ kcal mol}^{-1} \quad (14)$$

Finally, simple moieties were produced from this reaction like CO_2, H_2CO_3, H_2O, H_2SO_4, HNO_3, and H_2, which are in good agreement with literature.

CONCLUSION

- The activation energy of exothermic first degradation reaction step of methomyl is 109.647 kcal mol^{-1} (260 nm). The suggested equation of cleavage reaction is:

$$\text{Methomyl} + OH^* \rightarrow \text{NHTME} + \text{Carbamic acid radical}$$

$$\Delta H_{\text{reaction}} = -24.566 \text{ kcal mol}^{-1}$$

- The calculated rate constant of first cleavage reaction step is $1.33 \times 10^{11}\ s^{-1}$. The enthalpy change value of overall reaction for methomyl degradations is equal to -1701.252 kcal mol^{-1}. The degradation equation of methomyl is:

$$\text{Methomyl} + 30OH^* \rightarrow + CO_2 + 4H_2CO_3 + 2HNO_3 + H_2SO_4 + 8H_2O + 6H_2$$

APPLICATIONS

The electronic and geometrical structure of the pesticide, methomyl with hydroxyl radical and their reliable transition states can be theoretically calculated by the quantum calculation treatment.

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