دراسة نظرية لتجزئة بعض المبيدات في الطور الغازي

أطروحة مقدمه

من قبل

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إلى

إلى مجلس كلية العلوم- جامعة بابل بوصفها جزء من متطلبات نيل درجة الدكتوراه فلسفة في علوم الكيمياء .

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Theoretical study for degradation of some pesticides in gas phase

A thesis submitted by

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الله لا إله إلا هو الحي القيوم لا تأخذه سنة ولا نوم له ما في السماوات

وما في الأرض . من ذا الذي يشفع عنده إلا بإذنه يعلم ما بين أيديهم وما

خلفهم ولا يحيطون بشيء من علمه إلا بما شاء وسع كرسيه السماوات والأرض

ولا يؤوده حفظهما وهو العلي العظيم*

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Abstract

The photodegradation have been theoretically studied for some pesticides Captan ,Carbaryl and Methomyl in gas phase through reacting them with hydroxyl free radical simulating their degradation in aqueous solution using UV light and some oxidants.

Quantum methods like Semi-empirical and ab initio have been used by using two reliable well-known programs Hyperchem٧.٥ and Gaussian٠٣W, which they include most of Quantum mechanics treatments.

Chemical reactivity and chemical interaction have been studied for pesticides 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 by free hydroxyl radical.

Stability strength of main bonds, which have highest probability in first cleavage step of pesticide, have been studied. The probable transition states stability to get up the first cleavage step have been studied through surface potential energy, zero point energy, and first negative frequency of molecular vibration spectrum.

Activation energy and rate constant of cleavage reaction step are calculated for the three molecules . total energy, heat of formation and vibration spectrum have been calculated for all reactions component that's probable to be formed during the complete degradation of pesticides into essential minerals. The reactions that have the highest probability to occur with lowest value of activation energy are studied by comparing relatively to others competitive reactions, in order to estimate reasonable mechanisms of completely degraded pesticides in gas phase. Additionally, calculation over all

change in enthalpy of reactions has been done. Both vibration and electronic spectrum have been studied theoretically, and compared with practical spectrums. A close relation between the theory and experimental spectrum, which support the theoretical study has been found.

From this study that's found:

The activation energy of peroxide dissociation into its two moles of hydroxyl radical is equal to ٥٣.٦٠٥ kCal mol$^{-١}$.

The first degradation reaction step of Captan is endothermic reaction have been carried out through $N_{١٠}$—$S_{١٤}$ bond to give up three major component THID, $SCCl_{٢}$ and OCl* . the activation energy of this reaction step is ٩٧.٢٤١ kCal.mol$^{-١}$. rate constant of cleavage step reaction is ٢.٥٠ x ١٠^{٨}s$^{-١}$. enthalpy change value of overall reaction for Captan is -٢٦٠٧٣.١٧٨ kCal.mol$^{-١}$. Forty one moles of hydroxyl radical are needed to convert Captan into simple non toxic moieties produced from this reaction like $H_{٢}CO_{٣}$, $H_{٢}O$, $H_{٢}SO_{٤}$, HOCl, $H_{٢}$, $NH_{٣}$ and OCl*.

The first degradation reaction step of Carbaryl is exothermic reaction bond to give up two major components α-Naphthol and through $C_{٩}$—$O_{١٣}$ carbamic acid radical. the activation energy of this reaction step is ١١٦.٣٩١ kCal mol$^{-١}$. rate constant of cleavage step reaction is equal to ٢.٢٥ x ١٠^{١١} s$^{-١}$. the enthalpy change value of overall reaction for Carbaryl degradation is equal to -٣٧١.٦٧٤ kCal mol$^{-١}$. Ten moles of hydroxyl radical are needed to convert Carbaryl into simple non toxic moieties like $CO_{٢}$, $H_{٢}CO_{٣}$, $H_{٢}O$, $HNO_{٣}$ and $H_{٢}$. hydroxylation reactions, which may compete with the first step, are the major competitive reactions. In addition, the product of these reactions can inter the same path degradation reaction to produce different hydroxylation products of naphthalene products.

The first degradation reaction step of Methomyl is exothermic reaction through $O_{٨}$—$N_{١٠}$ bond to give up two major components NHTME and carbamic acid radical. the activation energy of first reaction step is ١٠٩.٦٤٨ kCal mol$^{-١}$. rate constant of cleavage step reaction is ١.٣٢٧ x ١٠^{١١} s$^{-١}$. the enthalpy change value of overall reaction for Methomyl degradations equal to -١٧٠١.٢٥٢ kCal mol$^{-١}$. Thirteen moles of hydroxyl radical needed to convert Methomyl into simple non toxic moieties produced from this reaction like $CO_{٢}$, $H_{٢}CO_{٣}$, $H_{٢}O$, $H_{٢}SO_{٤}$, $HNO_{٣}$ and $H_{٢}$.

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Abbreviations

CODE	FULL NAME STRUCTURE
THPI:	١,٢,٣,٦-tetrahydrophthalimide
٣-OH THPI	*cis/trans*-٣-hydroxycyclohex-٤-ene-١,٢-dicarboximide
٥-OH THPI	*cis/trans*-٥-hydroxycyclohex-٣-ene-١,٢-dicarboximide
٤,٥diOHHHPI	٤,٥-dihydroxycyclohexane-١,٢-dicarboximide
THPAM	(*cis/trans*-١,٢,٣,٦-tetrahydrophthalamic acid) epoxide٧oxabicyclo[٤.١.٠]heptane٣,٤dicarboximide
DDVP	Dichloroviyl dimethyl phosphate
MP٢	Moller-Plesset Perturbation Second Version
STO	Slater- type orbital
G	Gaussian type function
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
PM٣	Parameterizes method third version of Hyperchem
FTIR	Fourier Transition Infrared Spectrophotometer
UHF	Unrestricted Hartree-Fock
RHF	Restricted Hartree-Fock
CBS-Q	Complete basis set –Quadratic method
ZINDO	Zerner Intermediate Neglect Differential Overlap
THID	٣a,٤,٧,٧a-Tetrahydro-isondole-١,٣-dione
$SCCl_{٢}$	Thiophosgen
٥HTHID*	*cis/trans*-٥-hydroxy٣a,٤,٧,٧a-Tetrahydro-isondole-١,٣-dione,٦radical.
٥O,٦HTHID	٥oxy,٦hydroxy٣a,٤,٧,٧a-Tetrahydro-isondole-١,٣-dione
CDCCA*	٢, Carboxy, ٤,٥Dihydroxy- Cyclohexane Carboxy acid Amide radical.
CDCCA	٢,Carboxy,٤,٥Dihydroxy- Cyclohexane Carboxy acid Amide .
THCHA	٢,٤,٥-Trihydroxy-Cyclohexane carboxy acid Amide
FA*	Form acid radical
THCH	١,٢,٤,٥Tetrahydroxy-Cyclohexane
FAM*	Form amid radical
FAMA	Form amid acid
HFAMA*	Hydroxyl Form amid acid radical
CA	Carbonic acid
A*	Amine radical
HA	Hydroxyl Amine

AM	Ammonia
OTHCH*	١-Oxy,٢,٤,٥Trihydroxy-Cyclohexane
OTHCH	١-One,٢,٤,٥Trihydroxy-Cyclohexane
DODHCH*	١,٢-Dione,٤,٥Dihydroxy-Cyclohexane radical
DODHCH	١,٢-Dione,٤,٥Dihydroxy-Cyclohexane
HTOCH*	٥-Hydroxy,١,٢,٤,-Trihydroxy-Cyclohexane radical
HTOCH	٥-Hydroxy,١,٢,٤,-Trihydroxy-Cyclohexane
TOCH*	١,٢,٤,٥TetrOne-Cyclohexane radical
TOCH	١,٢,٤,٥TetraOne-Cyclohexane
HOTOCH*	١-Hydroxy,١-Oxy,٢,٤,٥Trihydroxy-Cyclohexane radical
TOHA*	٢,٤,٥Tri one Hexanoic Acid-٦,radical
TOHA	٢,٤,٥Tri one Hexanoic Acid
HTOHA	٦-Hydroxy,٢,٤,٥Trione Hexanoic Acid
DOPA	٣,٤Dione Pentanoic Acid
٢OPA	٢,One Propanoic Acid
EA*	Ethanoic Acid radical
EA	Ethanoic Acid
HEA	Hydroxy Ethanoic Acid
ET*	Ethanaldehyde radical
M*	Methyl radical
ME	Methanol
FO	Formaldehyde
OME*	Oxy methanol radical
FOA	Formic acid
OCl*	Hypochlorite radical
HTP·	Hydroxyl -Thiophosegen radical
CMS*	Chloro methyl- sulfide radical
HCA	Hypochloric acid
HCMS	Hydroxyl, Chloro methyl sulfide
HHSDCM	Hydroxy, hydroxy sulfide, dichloro -methane
CHSDHM	Chloro, hydroxy sulfide, dihydroxy -methane
CHHSM*	Chloro, hydroxyl, hydroxy sulfide- methyl radical
HSCF	Hydroxysulfide, chloro-formyl
CFOA*	Chloroformic acid radical
CFOA	Chloroformic acid
HS*	Hydroxy sulfide radical
CDHM*	Chloro, dihydroxy- methyl radical
DHDCM	DiChloro, dihydroxy- methane
DHS	Dihydroxy sulfide
*OHS	Oxy, hydroxy- sulphide radical
SD	Sulfide dioxide
SUA*	Sulfurous acid radical

SUA	Sulfurous acid
١HN	١,Hydroxy-Naphthaline
CAA*	Carbamic acid radical
٤HCA	٤,Hydroxy-Carbaryl
DHN	١,٤,Dihydroxy-Naphthaline
DHCA	٥,٦,Dihydroxy Carbaryl
١,٥,٦THN	١,٥,٦TrihydroxyNapthaline
HMCA	Hydroxyl methyl Carbamic acid
HMCAA*	Hydroxyl methyl Carbamic acid radical
MHA	Methyl Hydroxyl- Amine
MO*A	Methyl Oxy- Amine
MHA*	Methyl Hydroxyl -Amine radical
DHA	Di Hydroxyl -Amine
HA*	Hydroxyl- Amine radical
MAZ	Methyl Azo
NA	Nitrous Acid
DHO*A	Di Hydroxyl oxy- Amine
NTA	Nitric Acid
NHTAME	N-Hydroxyl thio acetimidic acid methyl ester
NHAA	N-Hydroxyl - acetimidic acid
MTH*	Methane -thiol radical
HMS	Hydroxyl, Methyl -Sulfide
HAED*	١-Hydroxyl Amine Ethan-١,١-diol-(N,radical)
DHAED	١,١-DhydroxylAmine Ethan-١,١-diol
NDHAE*O	N,N-Di hydroxyl Amine- Ethanol radical
NHFA*	N, Hydroxyl- formimidic acid radical
ETO	Ethanol Triol
DHA*	Di hydroxyl- Amine radical
THA	Tri hydroxyl -Amine
E*DO	Ethane radical diol
MTO*	Methyl triol radical

الخلاصة:

لقد تم دراسة التكسير الضوئي نظريا لبعض المبيدات(الكابتين والكارباريل والميتوميل) بوساطة تفاعل هذه المبيدات مع جذر الهيدروكسيل الحر في الطور الغازي محاكاة لما يحصل من تكسر المبيدات في الطور السائل بوجود الأشعة فوق البنفسجية و بعض الموكسدات.

استخدمت طرق الكم (Semi-empirical & ab initio) المحملة ضمن البرنامجان المعروفان (HyperChem٧.٥ & Gaussian٠٣W) اللذان يعتمدان على تطبيقات ميكانيك الكم لغرض أجراء الحسابات النظرية الخاصة بهذه الدراسة.

تم احتساب الفعالية الكيميائية و التأثر الكيميائي لكل من جزيئة المبيد و الجذر الحر المهاجم على التوالي من خلال حسابات سطوح جهد الطاقة والشحن الذرية وأطوال الأواصر و المجال الكهربائي و الاوربيتالات الجزيئية المشغولة العليا و الاوربيتالات الجزيئية غيرالمشغولة الدنيا و ذلك لبيان المواقع الفعالة ذات الاحتمالية الأكبر في مهاجمة الجذر الحر لها .

تم مقارنة استقرار و قوة ثبات الأواصر الرئيسة ذات الاحتمالية ألكبرى في بدء تكسر جزيئة المبيد و دراسة الحالات الانتقالية المحتملة التكون لحدوث خطوة بدء التكسر لجريئة المبيد بوساطة حسابات سطح جهد الطاقة و طاقة نقطة الصفر و التردد الأول الموجب لطيف ألجزيئه الاهتزازي .

احتسبت طاقة تنشيط التفاعل و ثابت السرعة لتفاعل خطوة بدء التكسر للجزيئات الثلاثة . تم احتساب الطاقة الكلية والتغير بمحتوى حراري التكوين والطيف الاهتزازي لمكونات جميع التفاعلات المحتمل حدوثها خلال عملية التكسر الكلية لجزيء المبيد إلى المكونات الأساسية . درست ومحصت التفاعلات ذات الاحتمالية الكبرى التي تمتلك قيمة دنيا من طاقة التنشيط مقارنة بمثيلاتها من التفاعلات المنافسة لها (الاحتمالات الأخرى)لغرض استنتاج الإلية الواضحة لتكسر المبيدات في الطور الغازي ,إضافة إلى احتساب التغير الكلي بالمحتوى الحراري المرافق لتكسر جزيء المبيد. و دراسة وتشخيص الأطياف الاهتزازية و الالكترونية نظريا و مقارنتها مع النتائج العملية التي أجريت و قد وجد أن هنالك تقاربا بالنتائج .

وجد ان طاقة التنشيط أللازمة لتوليد جذور الهيدروكسيل من جزيئة البيروكسيد مساوية إلى٥٣.٦٠٥ كيلو سعره$^{-١}$. خطوة بدء التكسر لمبيد الكابتين هو تفاعل ماص للحرارة يتم من خلال كسر الآصرة ($N_{١٠}$—$S_{١٤}$) بطاقة تنشيط مساوية إلى ٩٧.٢٤١ كيلو سعره مول$^{-١}$. تتولد ثلاث مكونات رئيسة من التفاعل وهي *OCl و THIDو$SCCl_٢$. ثابت سرعة التفاعل المحسوب يساوي $١٠^{٨}$ x ٢.٥٠ ثا$^{-١}$. إلية التكسر الكلي لمول واحد من الكابتين تتطلب واحد وأربعون مولا من جذور الهيدروكسيل الحرة . التغير الكلي بالمحتوى الحراري المرافق للتكسر الكلي يساوي ٢٦٠٧٣.١٧٨- كيلو سعره مول$^{-١}$. المكونات الناتجة عن عملية التكسر للكابتين هي $H_٢CO_٣$و$H_٢O$ و$H_٢SO_٤$ وHOCl و$H_٢$ و $NH_٣$ و*OCl .

خطوة بدء التكسر لمبيد الكارباريل هو تفاعل باعث للحرارة يتم من خلال كسر الآصرة ($C_٩$—$O_{١٣}$)بطاقة تنشيط مساوية الى ١١٦.٣٩١ كيلو سعره$^{-١}$. تتولد مكونتان رئيستان من التفاعل وهي Carbamic acid radical & ١-Naphthol.

ثابت سرعة التفاعل المحسوب يساوي $١٠^{١١}$ x ٢.٢٥٢ s$^{-١}$ الية التكسر الكلي لمول واحد من الكارباريل تتطلب عشرة مول من جذور الهيدروكسيل الحرة . التغير الكلي بالمحتوى الحراري المرافق للتكسر الكلي يساوي٣٧١.٦٧٤- كيلو سعره مول$^{-١}$.

المكونات الناتجة عن عملية التكسر للكارباريل هي$H_٢CO_٣$ و$H_٢O$ و$HNO_٣$ و$H_٢$ و $CO_٢$. تفاعلات استبدال الهيدروكسيل على الحلقة الاروماتية هي التفاعلات المنافسة لتفاعلات تكسير الكارباريل والتي تولد ناتجا مختلفا يتضمن معوضات الهيدروكسيل للنفثالين.

خطوة بدء التكسر لمبيد الميتوميل هو تفاعل باعث للحرارة يتم من خلال كسر الآصرة ($O_٨$—$N_{١٠}$) بطاقة تنشيط مساوية إلى ١٠٩.٦٤٨كيلو سعره مول$^{-١}$.تتولد مكونتان رئيستان من التفاعل وهي NHTME وCarbamic acid radical . ثابت سرعة التفاعل المحسوب يساوي $١٠^{١١}$ x ١.٣٢٧ ثا$^{-١}$. إلية التكسر الكلي لمول واحد من الميتوميل تتطلب ثلاثون مولا من جذور الهيدروكسيل الحرة . التغير الكلي بالمحتوى الحراري المرافق للتكسر الكلي يساوي - ١٧٠١.٢٥٢ كيلو سعره مول$^{-١}$,المكونات الناتجة عن عملية التكسر الكلي للميتوميل هي $CO_٢$ و$H_٢CO_٣$ و$H_٢O$ و$H_٢SO_٤$ و $HNO_٣$ و$H_٢$.

CHAPTER ONE

INTRODUCTION

١- ١ GENERAL INTRODUCTION

For a long time ago and until recent year, the use of pesticides is widespread in agriculture, the levels of these compounds in air, soil, and in aqueous media have increased significantly. therefore, pesticides constitute major pollutants of aquatic environment, and their presence is of cretin concern because of their potential toxicity towards animals and human being . they are only partially eliminated by biological and chemical degradation (١). presently, several hundred pesticides of various chemical natures are used all over the world for agricultural and non-agriculture purposes. Many of these pesticides are utilizing in amounts over ٥٠ ton/year (٢).

Relatively high pesticides contamination levels, are found in ground waters and surface water: ٠.١—٠.٣ µg/L in US ground waters, and ٠.٠٣-٠.٥ µg/L European ground waters. to protect the quality of drinking and surfaces waters, priority lists of pesticides discharged in the aquatic environment have been established by the European community with very drastic tolerance limits(٣). therefore, there is an increasing interest in the developments of simple cheap and rapid methods for the destruction of organic pesticides in water.

Photochemical reactions have been extenensively used directly and indirectly for pesticides degradation. direct photodecomposition processes can be used whenever organic pesticides absorb light sufficiently in the UV region (٢٥٠—٣٠٠nm) (٤-٦). Indirect photochemical processes of pesticides degradation and other organic pollutants have been improved. In most indirect photochemical methods, UV irradiation of pesticides in aqueous solutions is performed in the presence of $H_٢O_٢$, $Fe^{٣+}$, or $H_٢O_٢$ / $Fe^{٢+}$ (٧-١٢).

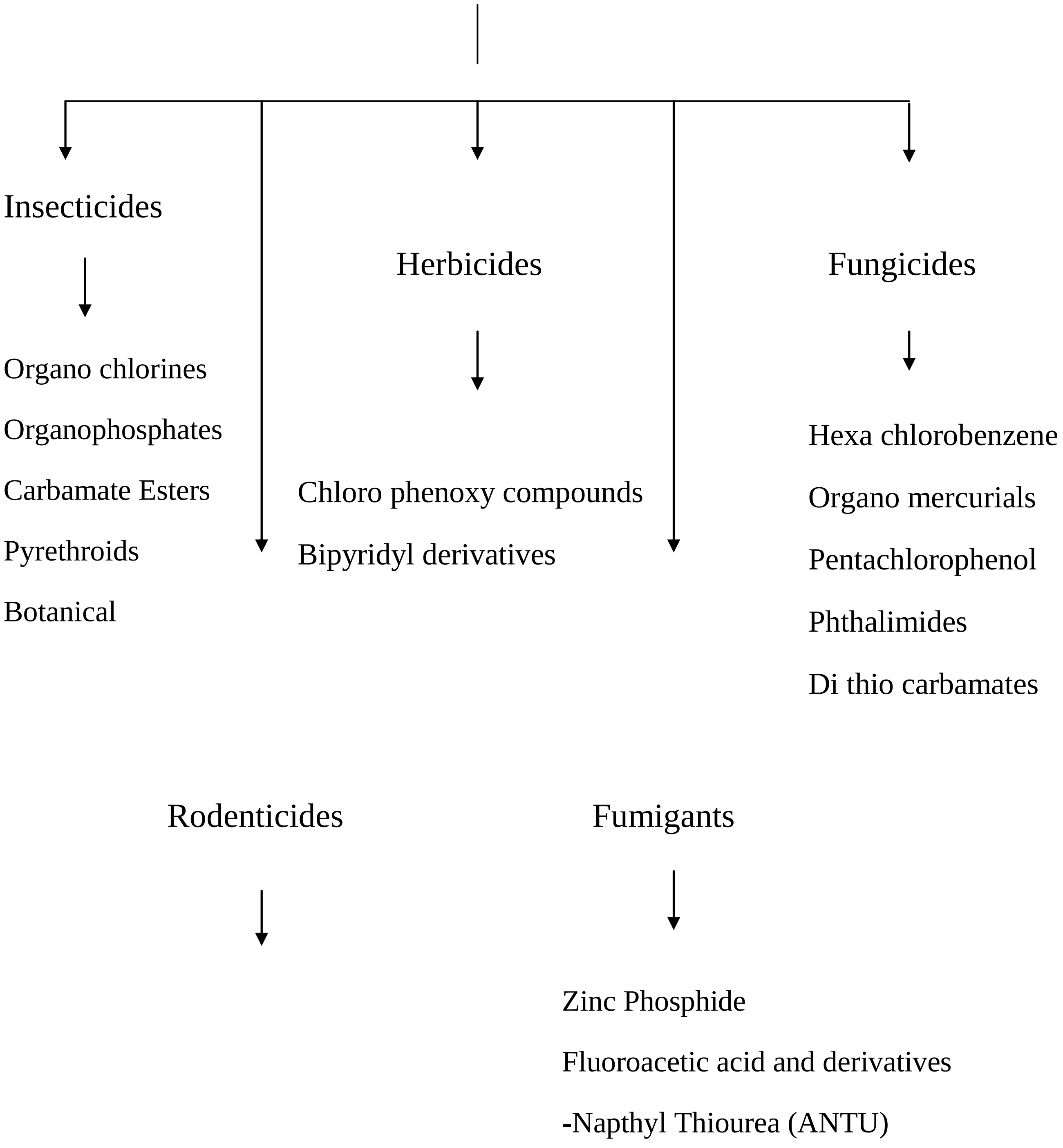
These technologies based on the use of advanced oxidation process, in which very oxidizing reactive free radicals, mainly OH* species generated in gas phase or aqueous solutions and produce rapid photo degradation of organic pollutants (١٣).

The most chemical process is complex, it consists of a number of coupled elementary reactions. the complex reactions are divided into several classes opposing, or reversing reaction, consecutive reaction, paralleled reaction, ionic reaction, and mixed reactions (١٤, ١٥).

١-٢ Pesticides

Pesticides are chemicals (organic or inorganic), either naturally, or synthesis products, they have been used to kill pests(١٦). They are classified according to target as: insecticides target harmful or destructive insects, herbicides target weeds, fungicides target fungi, rodenticides target rodents and acaricides target acarose (mites). The basic classes of pesticides are listed in scheme (١-١)(١٧) .

Basic Classes of Pesticides



Phosphine

Ethylene dibromide

Dibromochloropropane

Scheme (١-١) classification of pesticides according to main groups.

Chemical structures of pesticides are differing within categories as well as between categories. Thus, toxicity to humans can vary widely within each group. Pesticides have been used for long time ago to reduce economical losses caused by organism. Environmentally important because these biocidal chemicals deliberately released (applied) across broad areas with the intention to cause mortality of selected pest populations. The historical uses of pesticides have shown in Table (١-١) (١٨).

Table (١-١) History of pesticides uses

A- PESTICIDE USE: AN OLD PRACTICE	
١٠٠٠ BC	Chinese used sulfur as a fumigant
١٨٠٠s	Europeans used sulfur as a fungicide to control powdery mildew on fruit
٢٠٠١s	Sulfur still used in California today
١٦th century	Japanese mixed poor quality whale oil with vinegar to spray on rice paddies to prevent development of insect larvae by weakening the cuticle
١٧th century	century Water extracts of tobacco leaves were sprayed on plants to kill insects Nux vomica, the seed of Strictness

	nuxmomica (strychnine) used to kill rodents
B- PESTICIDE USE : AN NEW PRACTICE	
٢٠th century	Sulfuric acid (١٠٪) used to destroy dicotyledonous weeds without harming monocotyledonous cereal grains and other cultivated plants with waxy coat on leaves
١٩٢٠s	Public concern because some treated fruits and vegetables were found to contain pesticide residues
Post WWII	Pesticide development and use increased dramatically in agriculture and public health. Widespread use of pesticides for insect control to prevent transmission of diseases such as typhus, river blindness and malaria Need to make risk/benefit decisions

U.S. Productions of Pesticides (annual; approximate):

- ٦٠٠ million pounds of insecticides
- ٦٨٠ million pounds of herbicides
- ١٠٠ million pounds of fungicides

Total Production = approx. ١.٥ billion pounds .Approximately ١/٣ used in U.S., remainder is exported. Economics of Pesticide Use can be summarized in figure (١-٢).

- Can only afford to target ٨٠-٩٠٪ of pest population.
- Too improbable and costly to eradicate ١٠٠٪.

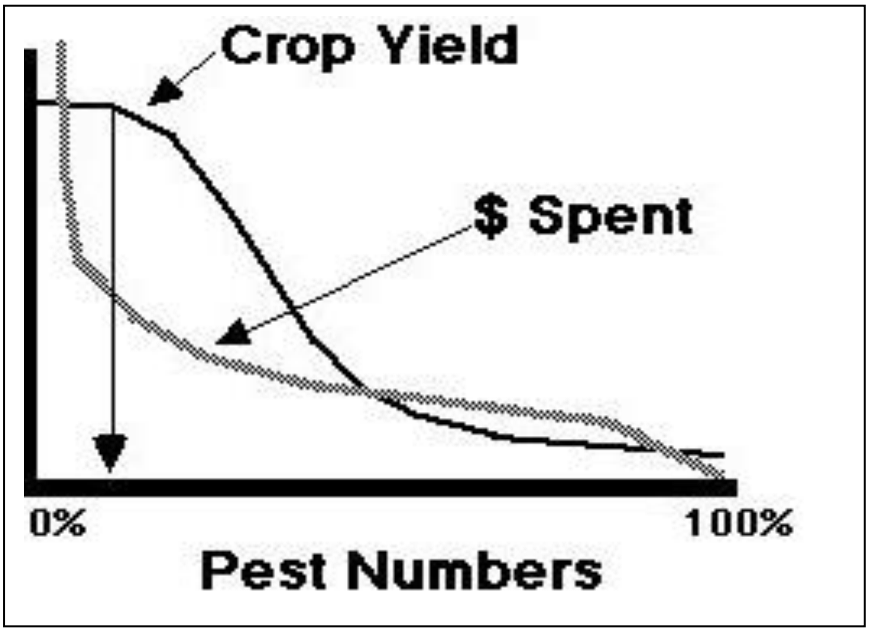


Figure (١-١) Economics uses of Pesticide.

Standard preservation techniques have been recommended by different government organizations for the storage of water samples in containers or after liquid-liquid extraction(١٩, ٢٠). Studies on alternative pesticide stabilization techniques, including the use of freeze-drying, have been published(٢١). The results obtained with this technique show that the stability of the compounds depends on their water solubility and vapor pressure. Other papers have demonstrated that solid-phase extraction (SPE) is a good alternative to the storage of pesticides preconcentrated from water samples(٢٢-٢٥). In general, many pesticides are quite stable, except for compounds such as captan, carbofuran, fenamiphos, trifluraline, due to their physico-chemical properties and sample pre concentration conditions.

The loss of pesticides in water can be due to several processes ,that's including hydrolysis, photolysis, biodegradation and oxidation. Indeed, the US Environmental Protection some examples of degradation processes include hydrolysis and photochemical degradation on SPE cartridges, hydrolysis catalyzed by graphitized carbon black (GCB) surface, hydrolysis by residual water and biodegradation on GCB material (٢٦,٢٧) .

١-٢-١ Captan

Captan is synthetic chemical fungicides. It belongs to the group's related chemicals called "Phthalimides"(٢٨). Captan characteristics and various nomenclature are shown in table (١-٢).

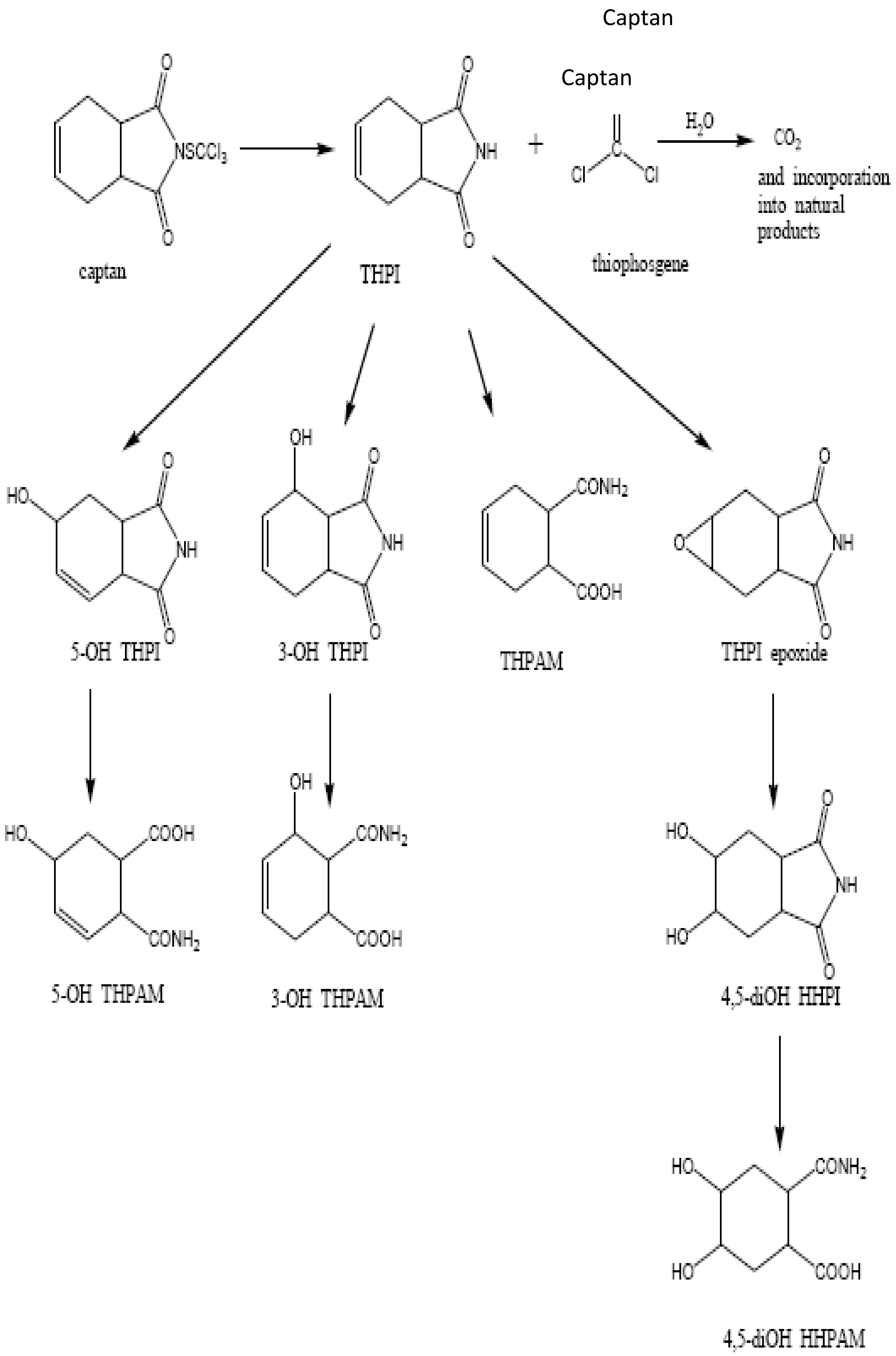
The half-life, assuming a quantum yield of ١ and using experimental extinction values, was estimated to be about ٨٨٠ days(٢٩). The following types of formulation are available: suspension concentrate (SC), wettable powder (WP), dustable powder (DP) and water dispersible granule (WG).

Table (١-٢) Identity of Captan, and its characteristics with various nomenclature

Iso common name	Captan
Chemical name	IUPAC:[N-(tri chloromethyl thio)cyclohex-٤-ene-١,٢-dicarboximide] CAS:٣a,٤,٧,٧a-tetrahydro-٢-[(tri chloro methyl) thio]-١H-isoindole-١,٣(١,٣(٢H)dione
Synonyms /trade names	SR-٤٠٦, Merpan,Vanicide ٨٩,Orthocidide
Molecular formula	$C_٩H_٨Cl_٣NO_٢S$
Molecular weight	٣٠٠.٥٩ gm/mol
Appearance	Colorless crystal, white solid cream.
Melting point	١٧٢ °C
Relative density	١.٧١ gm/mol
Vapor pressure	$٤.٢*١٠^{-٦}$ Pa at ٢٠ °C
Half life at ٢٥ °C	١٢ hours at pH٤ ٢.٦ hours at pH٧ too fast to measure at pH ٩
Half life at ٤٠ °C	١.٧ hours at pH٤ ٠.٥١ hours at PH٧ too fast to measure at pH ٩
Solubility at ٢٠ °C mg/kg solvent	Purified water :٤٠٩ Water buffered pH ٥ :٤٠٨ Water buffered pH ٧:٥.٢ Hexane ٠.٠٤ Octan-١-ol ١ Methanol ٤ Xylenes ٩ Ethyl acetate ٢٥ Acetonitrile ٣١

١-٢-١-١ Metabolism and Environmental Fate

The metabolism of Captan in goats and hens proceeds by cleavage of the N-S bond to form THPI and a derivative of the -$SCCl_{٣}$ side chain. THPI and -$SCCl_{٣}$ undergo further metabolism through independent pathways. The carbon of the side chain becomes incorporated into Thio-Tri Chloro Methan TTCM and natural products. the cleavage partner THPI is oxidized to form THPI epoxide which is subsequently hydrolyzed to form ٤,٥-diOH THPI, or hydroxylated at the cyclohexene ring to form ٣-OH and ٥-OH THPI. The hydrolysis of THPI and its hydroxylated derivatives results in the formation of the corresponding THPAM derivatives. The proposed metabolic pathway in livestock is shown in Scheme (١-٢) (٣٠).



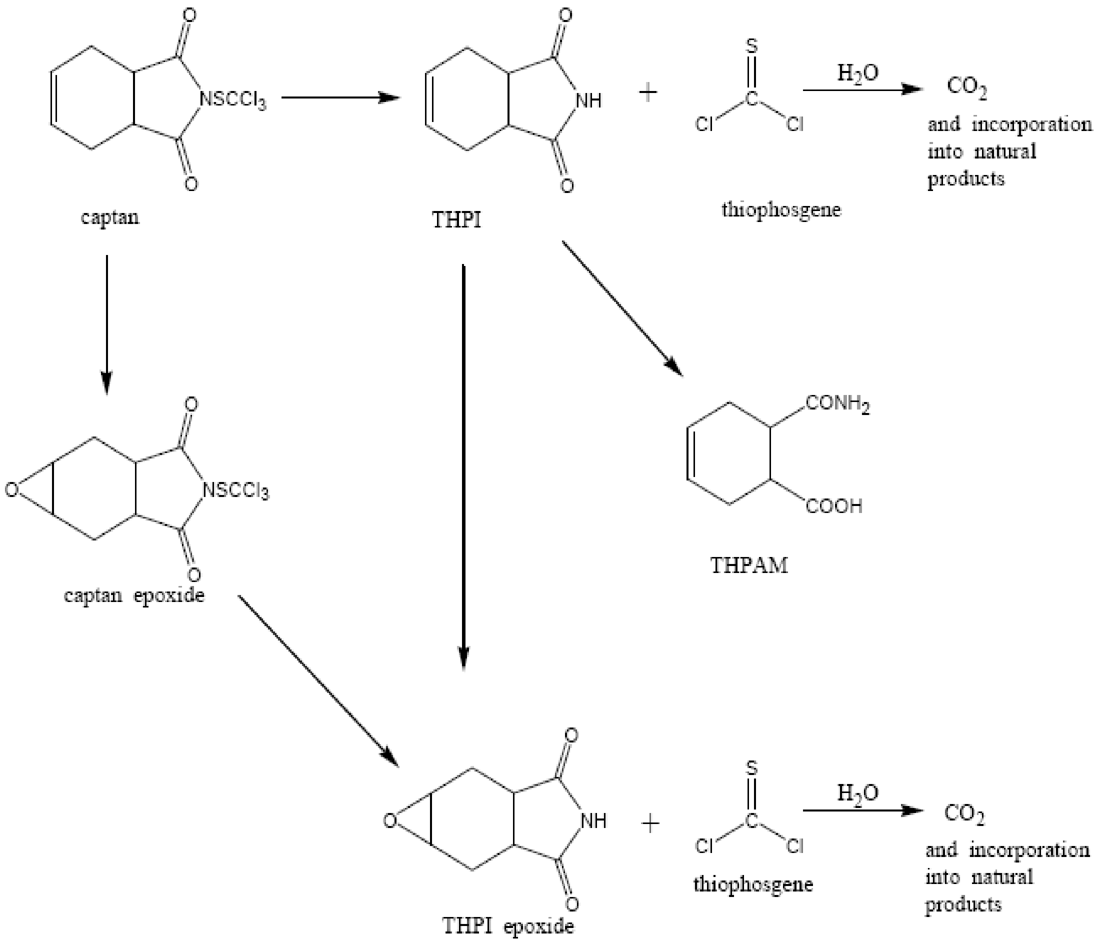
Scheme (١-٢) Proposed metabolic pathways of Captan in livestock.

١-٢-١

-٢ Plant metabolism

In apples, tomatoes and lettuce most of the residue was presence on the surface of the leaves and fruit, mainly as unchanged captan. Metabolism in the plants includes cleavage of the thio-indole bond to form THPI and derivatives of the -$SCCl_{٣}$ side chain. The carbon of the side chain is incorporated into natural products, and THPI is further metabolized to form THPAM. Captan is also oxidized to captan epoxide which undergoes hydrolysis to form THPI epoxide. The proposed

metabolism in plants is shown in Scheme (١-٣)(٣١).

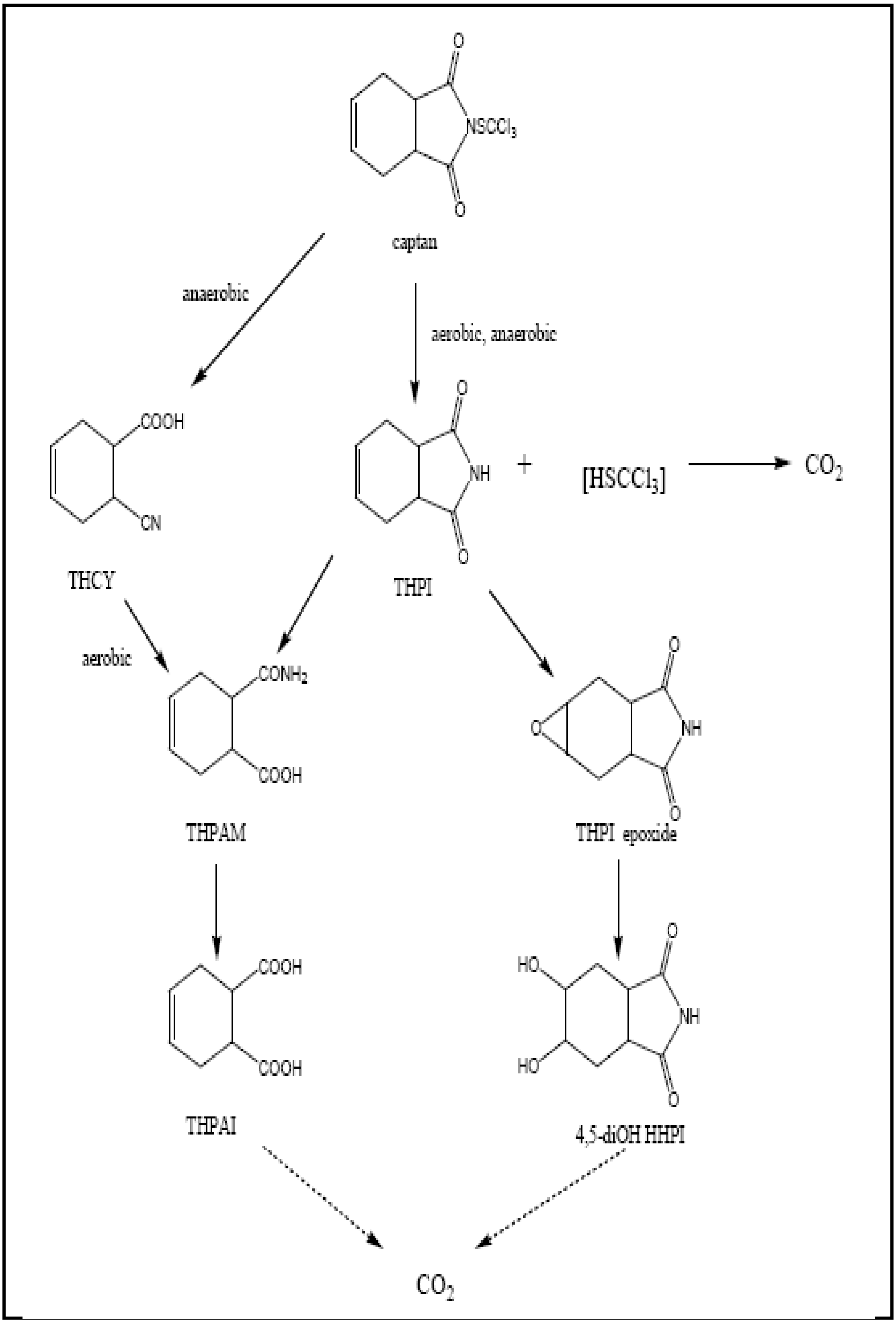


Scheme (١-٣) Proposed metabolic pathways of Captan in plants.

١-٢-١-٣ Soil degradation

The aerobic degradation of [*trichloromethyl*-^{١٤}C]captan on Visalia sandy loam (sand ٥٥٪, silt ٣٣٪, clay ١٢٪; pH ٧.٧; organic matter ٠.٧٪; CEC ٩.١ meq/١٠٠ g), and Greenville sandy loam (sand ٥٨٪, silt ٣٠٪, clay ١٢٪; pH ٧.٢; organic matter ١.٢٪; CEC ٧.٧ meq/١٠٠ g) at ٢٥°C in the dark have been studied (٣٢,٣٣). Captan applied at a rate equivalent to ٨.٨ mg/kg to the Visalia soil, and ٤.٦-٦.١ mg/kg to the Greenville soil, and incubated for periods up to ٣٠ days. In both Visalia sandy loam and Greenville, sandy loam the major product was $^{١٤}CO_{٢}$, which accounted for ٥٠-٥٩٪ of the applied radioactivity after ١-٣ days and reached ٨١-٩٠٪ after ٢٨-٣٠ days incubation. The other compound detected was thiocarbonic acid, which accounted for at most ١.١٪ of the applied radioactivity (٣٤).

The anaerobic soil degradation of [*carbonyl*-^{١٤}C] captan was studied on Oakley loamy sand soil (sand ٨٥٪, silt ٦٪, clay ٩٪; pH ٧.٣; organic matter ١.٤٪; CEC ٧.٥ meq/١٠٠ g) at ٢٥°C in the dark with an initial captan concentration of ٦.٢ mg/kg. No Captan detected after ٧ days of incubation. Compounds identified were THPI, THCY, THPAM and THPAL. The cyano acid THCY not observed under aerobic conditions. Less than ٩٪ of the applied radioactivity converted to $^{١٤}CO_{٢}$ over a period of ٩ months. Extracts from the anaerobic soil that contained THCY added to Oakley soil under aerobic conditions. The THCY rapidly degraded with ٩٨٪ loss occurring within ٧ days (٣٥,٣٦). The proposed metabolisms of captan in soil are shown in Scheme (١-٤) (٣٧) .



Scheme (١-٤) Proposed metabolic pathways of Captan in soil.

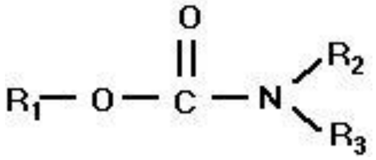
١-٢-١-٤ Captan Photolysis

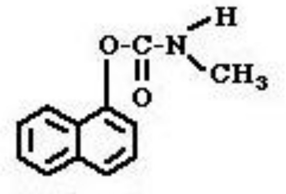
The half-life of [*trichloromethyl*-^{١٤}C] captan in Greenville sandy loam soil exposed to sunlight was ١٥ days while the half-life for the dark control soil was ٢٠ days(٣٨). The photochemical half-life was estimated to be ٥٤ days. Most of the radioactivity was accounted for as captan and carbon dioxide, with the remainder present as bound residues and unidentified compounds. In irradiated samples on day ٢١ captan accounted for ٣٦-٤٠٪, $^{١٤}CO_{٢}$ for ٤٩-٥١٪, bound residues for ٧٪, acid-released residues for ٢-٥٪ and unidentified residues for ١.٤٪ of the applied radioactivity. In dark control soil samples captan accounted for ٥٠-٥٦٪ and $^{١٤}CO_{٢}$ for ٣٣-٤٠٪ of the applied radioactivity. The natural sunlight photolysis of [*cyclohexene*-^{١٤}C] captan at ٢٥°C have been studied on the surface of Greenville sandy loam soil treated at ٤.٤٨ kg ai/ha (٣٩). The half-lifes for photolysis were ١٣٠ and ٢٣٦ hours for the light and dark conditions respectively, resulting in an estimated photochemical half-life of ٢٨٧ hours. Products present at >٣٪ were identified by HPLC and TLC. The major components formed under both light and dark conditions were THPI, THPI epoxide, THCY, THPAM and THPAL.

١-٢-٢ Carbamates:

The 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 ٤٠ years(٤٠). The general formula of the carbamate insecticides is :

CARBAMATES





Carbaryl

Where R^{١}, R^{٢}, and R^{٣} are hydrogen, alkyl or aryl groups.

Three classes of carbamate pesticides is known. The carbamate ester derivatives, used as insecticides (and nematocides), are generally stable and have a low vapour pressure and low water solubility. The carbamate herbicides (and sprout inhibitors) have the general structure R^{١}NHC(O)OR^{٢}, in which R^{١} and R^{٢} are aromatic and/or aliphatic moieties. Carbamate fungicides contain a benzimidazolegr.

In general, the vapor pressure of the carbamates is low; Nevertheless, they will evaporate or sublimate slowly at normal conditions. temperature may lead to volatilization of carbamates from water and soil. However, distribution via air will be a minor factor. The aqueous environment will be an important route of transport for highly soluble carbamates. The light absorption characteristics of carbamates contribute to their rapid decomposition (by photodegradation or photodecomposition) under aqueous conditions. Thus, the hazards of long-term contamination with carbamates seem small.

Carbamate insecticides mainly applied on the plants, and can reach the soil, while carbamate nematocides and herbicides applying directly to the soil. Several factors influence the biodegradation of carbamates in soil, such as volatility, soil type, soil moisture, adsorption, pH, temperature, and photodecomposition. Because the different carbamates have different properties, it is clear that each should be evaluation on its own merits, and no extrapolation of results made from one carbamate to another. One carbamate may be easily decomposion, while another may strongly adsorbed on soil. Some leach out easily and may reach groundwater(٤١). In these processes, the soil type and water solubility are of great importance. Furthermore, it should be recognizing that this not only concerns the parent compound but also the breakdown products or metabolites.

Photodegradation of *N*-methyl carbamates absorb radiation available in the solar region (lambda = ٣٠٠ nm) and hence, would be expected to undergo photo-oxidation as well as metabolic degradation(٤٢). The fate study of various *N* -methyl carbamates when solutions were sprayed on bean foliage and exposed to sunlight or artificial light (lambda = ٢٥٤ nm). It is not entirely clear whether the products they observed resulted solely from a photochemical reaction or from absorption followed by enzymatic attack (٤٣).

١-٢-٢-١ Carbaryl

Carbaryl (١-naphtyl methyl carbamate), was first synthesized by Dr. A. J. Lambrech in ١٩٥٣ and introduced as an agricultural insecticide in ١٩٥٨. Since then it is one of the most widely used insecticides in the world against fruit, vegetable, cereals, timber forest, cotton; domestic animals and livestock insects. Carbaryl ($C_{١٢}H_{١١}NO_{٢}$) can use for the control of a variety of pests on fruit, vegetables, cotton and other crops. Between ١٠٠ and ٢٠٠ ton are use annually in Canada. the solubility of carbaryl in water is ٤٠ mg/L at ٣٠°C; its vapour pressure at ٢٦°C is less than ٠.٧ Pa .the log octanol-water partition coefficient reported to range from ٢.٣١ to ٢.٨٦ therefore, carbaryl is not likely to bioaccumulate significantly(٤٤-٤٦). Carbaryl identity and physical properties are showing in table (١-٣) (٤٧) .

Tabel(١-٣) Identity of Carbaryl and its characteristics with various nomenclature .

Density/Specific Gravity	١.٢٣٢ at ٢٠°C
Melting point	١٤٥°C, decompose at boiling point
Molecular weight	٢٠١.٢٢gm/mol
Vapor pressure	٤.١X١٠-٢ mPa at ٢٣.٥°C
Synonyms /trade names(some of)	ARILAT, ARYLAM, ATOXAN, BERCEMA NMC٥٠, CAPROLIN, CARBAMIC ACID, METHYL-, ١-NAPHTHYL ESTER, Carbamine, Carbaril **(Italian), CARBATOX,** VIOXAN, **UC** ٧٧٤٤**,** Tricarnam, SEVIMOL, ١-**NAP**HTHYL N-METHYLCARBAMATE
Molecular formula	$C_{١٢}$-$H_{١١}$-N-$O_{٢}$
Iso common name	Carbaryl
Appearance(colour/form)	Colorless solid, Colorless to light-tan crystals,or White or gray ... solid
Chemical name	IUPAC: CAS: ١-naphthyl N-methyl carbamate
Stability, and Half live below ٧٠° C	Stable to heat, light, acids; hydrolyze in alkaline solutions
Solubility at ٢٠ °C g/kg solvent	Water ١٢٠; dimethylformamide ٤٠٠-٤٥٠, dimethyl sulfoxide ٤٠٠-٤٥٠, acetone ٢٠٠-٣٠٠, cyclohexanone ٢٠٠-٢٥٠, isopropanol ١٠٠, xylene ١٠٠ .

Degradation of carbaryl in water is influenced by temperature, light, and pH. It rapidly hydrolyzed to ١-naphthol in neutral and alkaline waters; half-lives at ٢٠°C of ١٠.٥ days, ١.٨ days and ٢.٥ hours reported at pH ٧, ٨ and ٩, respectively. Hydrolysis is much slower in acidic waters; half-lives of ١٥٠٠ days at pH ٥ and ٢٧°C and ٤٠٦ days at pH ٦ and ٢٥°C have been reported. Carbaryl is degraded in soil, undergoing photolysis, hydrolysis and microbial action. It is moderately mobile in the soil and may leach to groundwater(٤٨, ٤٩).

Carbaryl is very readily absorbed by the gastrointestinal tract and rapidly metabolized. An oral dose of carbaryl (quantity unspecified) was ٥٣٪, and ٨٢٪ absorbed in rats in ٢٠ minutes and one hour, respectively. Metabolites of carbaryl eliminated in the urine, exhaled breath, faeces and bile. Urinary metabolites identified in two human volunteers administered single doses of ٢ mg/kg carbaryl included ١-naphthol and its glucuronide and sulphate conjugates, ٤-hydroxycarbaryl and a minor amount of ١-naphthyl methylimido carbamate-O-glucuronide. Recovery of ٢٦٪ and ٢٨٪ of the administered dose in the urine reported within four days. Carbaryl crosses the placental barrier in rats and mice(٥٠, ٥١).

The acute toxicity of carbaryl is due to its ability to inhibit cholinesterase activity. However, because carbaryl rapidly metabolized, its acute oral toxicity is low, and toxic effects are rapidly reversible. The acceptable daily intake (ADI) of carbaryl in drinking water has been established by the Food and Agriculture Organization (FAO) and the World Health Organization (WHO) as ٠.٠١ mg/kg per day, based on the no-observed-adverse-effect levels of ٠.٠٦ mg/kg per day in human volunteers and ١٠ mg/kg per day in rats(٥٢-٥٥).

١- ٢- ٢- ١- ١ Environmental fate of Carbaryl

In the environment, Carbaryl breaks down primarily through hydrolysis and microbial degradation to ١-naphthol and carbon dioxide. Carbaryl degrades in distilled water with a half-life of ٣.٢ hours at pH ٩ and ١٢.١ days at pH ٧. Carbaryl is stable in acidic water with a half-life of ١٦٠٠ days at pH ٥. Carbaryl is degraded by photolysis in water, with a half-life of ٢١days. Scientists observed that carbaryl in river water (pH ٧.٣-٨), exposed to natural and artificial light, degrades completely within ٢ weeks.

Carbaryl has low solubility in water and sorption to soil particles depends on the organic matter content of the soil. Carbaryl is moderately mobile in soils and can be found in the groundwater and surface water due to its widespread use and persistence under acidic conditions(٥٦, ٥٧).

Air-- Carbaryl dissolved in water has low potential to volatilize. The low vapor pressure for carbaryl suggests that evaporation from treated surfaces will be minimal.

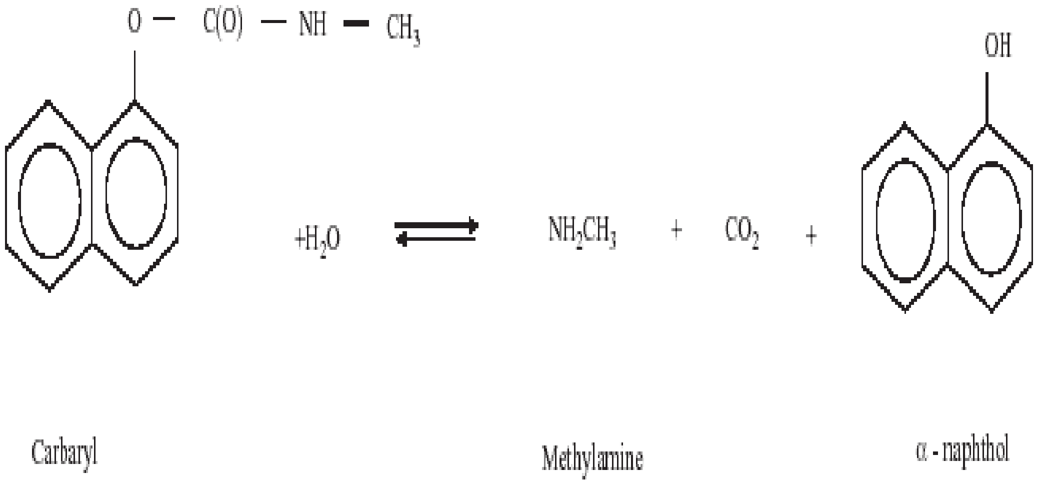
Soil-- The half-life of carbaryl ranges from ٤ days in aerobic soils to ٧٢.٢ days in anaerobic soils. Carbaryl degrades more rapidly in aerobic soils due to microbial action.

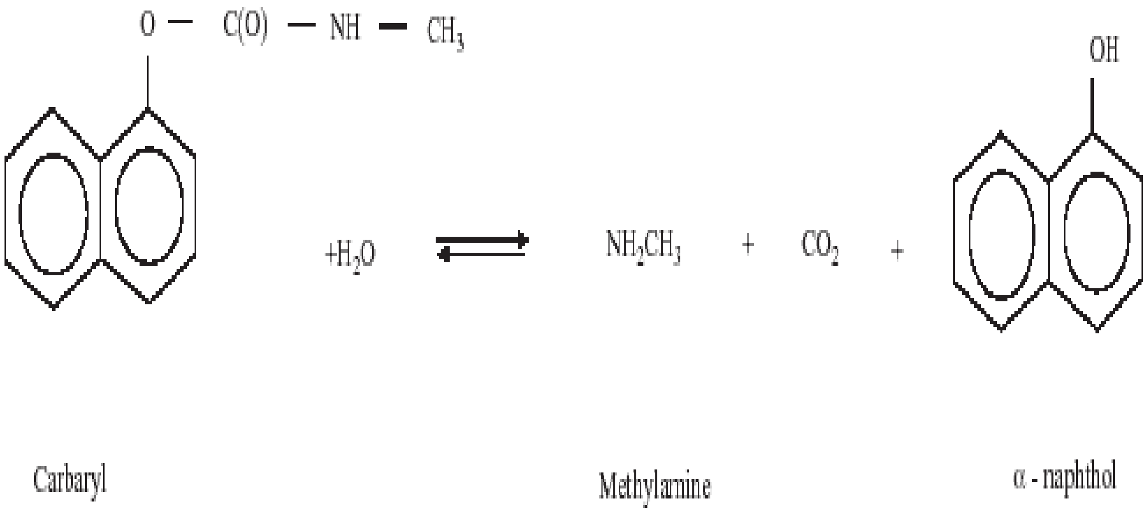
Carbaryl degrades nearly twice as fast as in flooded soils compared to dry soils due to hydrolysis and microbial action.

Plants-- Scientists observed ٥٩.١٪ of Carbaryl remaining ١ week after injection into bean plants and only ٦.٩٪ after ٢ weeks.

The mean foliar half-life of Carbaryl on plants is ٣.٢ days. Carbaryl is slowly taken up by plants and broken down through hydrolysis producing ١-naphthol, ٤-hydroxycarbaryl, ٥-hydroxycarbaryl and methylol-carbaryl(٥٨-٦٠).

As a relatively short degradation period, and a wide safety margin. In the past, it reported that Carbaryl degrades in short time in water, soil and on various plants as in the following equation(٦١-٦٤).





ethomyl

t is used
ops and
carb per
cide (٦٥).

Methomyl is classified as highest-hazard pesticides, ranked by the UC Environmental Health Policy Program(٦٦). The substance is very toxic to aquatic organisms, therefore special attention should be given to birds and honey bees. this substance does enter the environment under normal use (٦٧).

Thiodicarb is rapidly and extensively absorbed, via gastrointestinal tract in rats (>٧٠٪, based on excretion data) and distributed. Excretion occurs primarily as volatile components (acetonitrile and $CO_{٢}$) in expired air about ٤٠٪ and in urine about ٣٠٪. less than ١٠٪ excreted in faeces. The acute toxicity is high oral LD ٥٠-٥٩ mg/kg as well as during inhalator exposure . acute dermal LD ٥٠ is greater than ٢٠٠٠ mg/kg . It is not a skin or an eye irritant but it is a skin sensitizer. Classification for acute toxicity is needed and the proposed risk phrases are: T; R٢٣/R٢٥ (Toxic by inhalation and if swallowed)" and R٤٣ "May cause sensitization by skin contact". Repeated exposures resulted in decreased body weight and food consumption, alterations in haematological parameters, haemolytic anemia, haemosiderosis and extramedullary haematopoiesis, as well as signs of cholinergic effects .The identity and physical properties of Methomyl are showing in table (١-٤) (٦٨).

Tabel(١-٤) Chemical and physical properties of methomyl

Iso common name	Methomyl
Chemical name	IUPAC: Ethanimidothioic acid N-{{(methylamino)carbonyl}oxy}-, methyl ester. Methyl-N-{(methylamino)carbonyloxy}ethanimidothioate S-Methyl-N-(methylcarbamoyloxy)thioacetimidate
Molecular formula	$C_٥H_{١٠}N_٢O_٢S$
Molecular weight	١٦٢.٢ gm/mol
Appearance	White solid crystals
Melting point	٧٨ °C
Density/Specific Gravity	١.٣ g/cm^٣ ٢٠ °C
Stability, and Half life below ٧٠ °C	Stable to heat, light, acids; hydrolyze in alkaline solutions. Slow hydrolyze in highly temperature solutions.

١-٢-٢-٢-١ Environmental fate of Methomyl

The metabolism of Methomyl in fruits after foliar application clearly understood. The residue definition proposed for both monitoring and risk assessment expressed as other metabolite needs to consider in the residue definition due to its potential contribution to the toxicological burden. Ultimate degradation products of thiodicarb are acetonitrile and carbon dioxide, the last being reincorporated in endogenous plant materials. No expected residues are to be present in following crops.

١-In animal, the metabolism of thiodicarb is extensive and no carbamate related compound is present in edible animal commodities. There is no need for defining a residue definition for animal products, or to monitor residues resulting from the representative uses of thiodicarb in these products.

٢-In grapes and cereals, supervised residue trials support the establishment of Methomyl residual levels (MRLs) at ١ and ٠.٠٥ mg/kg respectively.

٣-In wine, the residue transfer is limited and the residue level in wine is not expected to be higher than ٥٠ % of the residue level in raw grapes (٦٩).

The risk assessment carried out for the representative uses supported by the applicant indicated 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.

Two major metabolites were identified under dark anaerobic condition .methyl,N[Nmethyl,N(methylaminothio)carbamoyloxy]thioacetamidate, and acetonitrile. photolysis may contribute slightly to the environmental degradation of thiodicarb being acetonitrile the only major soil photolysis metabolite. Thiodicarb is very low to persistent in soil under aerobic laboratory conditions. Whereas not triggered by the directive, field dissipation studies are available for thiodicarb formulated either as water flowable or slow release pellets. Thiodicarb is low to high mobile and is Methomyl very high mobile in soil. In sterile buffer, solutions at ٢٥°C thiodicarb and Methomyl degradation are pH dependent. The main product of thiodicarb hydrolysis is Methomyl ntribution of aqueous photolysis to the environmental degradation of thiodicarb and methomyl is deemed negligible. Thiodicarb is not ready biodegradable. In water/sediment systems, thiodicarb degrades very fast to Methomyl in the water phase (DTd). Degradation of Methyomyl was also fast with half-lifes between ٣.٥ to ٥ days in the total systems (٧٠) .

١-٢-٢-٢-٢ Degradation of Methomyl

The ultrasonic degradation of the wastewater simulated by addition of Methomyl to distilled water. The reaction degradation results show that the Methomyl has converted into inorganic materials in ٣٥ minutes, and the degradation dynamics is first order reaction. On increasing the concentration of Methomyl, the degradation rate decreases, $Fe^{٢+}$ and $H_٢O_٢$ can both accelerate degradation, the action of $Fe^{٢+}$ being stronger than that of $H_٢O_٢$. When the saturation gas in the solution is changed, the destruction rate follows the order: $Ar > O_٢ > air > N_٢$. IR study shows that the reaction products are $SO^{٢-}_٤$, $NO^-_٣$ and $CO_٢$(٧١,٧٢).

The degradation of Methomyl in aqueous solution by UV- irradiation in the presence of $TiO_٢$ 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. Under our conditions, complete disappearance of ١.٢٣×١٠^{-٤} mol. $l^{-١}$ of pure pesticide occurred within ٤٥ min of illumination and ٨٠٪ TOC removal occurred in less than ٤ h.

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). In order to be sure that the photocatalytic results were consistent, hydrolysis and photolysis tests performed. Photocatalysis used as excellent new advanced oxidation technology (AOT) to eliminate Methomyl present in water(٧٣).

١-٣ Potential Energy surface:

A potential energy surface is generally used within the adiabatic or Born-Oppenheimer approximation in quantum mechanics and statistical mechanics to model chemical reactions and interactions in simple chemical and physical systems. There is a natural correspondence between potential energy surfaces as they exist (as polynomial surfaces) and their application in potential theory, which associates and studies harmonic functions in relation to these surfaces(٧٤).

The activation energy in chemistry is the threshold energy, or the energy that must be overcome in order for a chemical reaction to occur. Activation energy may otherwise be denoted as the minimum energy necessary for a specific chemical reaction to occur. The activation energy of a reaction is usually denoted by E_a.

Known as the collisional model, there are three necessary requirements in order for a reaction to take place: Molecules must collide to react. If two molecules simply collide, however, they will not always react; therefore, the occurrence of a collision is not enough. The second requirement is that there must be enough energy (energy of activation) for the two molecules to react. This is the idea of a transition state; if two slow molecules collide, they might bounce off one another because they do not contain enough energy to reach the energy of activation and overcome the transition state (the highest energy point). Lastly, the molecules must be oriented with respect to each other correctly. For the reaction to occur between two colliding molecules, they must collide in the correct orientation, and possess a certain, minimum, amount of energy. As the molecules approach each other, their electron clouds repel each other. Overcoming this repulsion requires energy (activation energy), which is typically provided by the heat of the system; i.e., the translational, vibrational, and rotational energy of each molecule, although sometimes by light (photochemistry) or electrical fields (electrochemistry). If there is enough energy available, the repulsion is overcome and the molecules get close enough for attractions between the molecules to cause a rearrangement of bonds(٧٥).

At low temperatures for a particular reaction, most (but not all) molecules will not have enough energy to react. However, there will nearly always be a certain number with enough energy at any temperature because temperature is a measure of the average energy of the system individual molecules can have more or less energy than the average. Increasing the temperature increases the proportion of molecules with more energy than the activation energy, and consequently the rate of reaction increases. Typically the activation energy is given as the energy in kilojoules, or kilocalories needed for one mole of each reactants to react.

١-٣-١ Mathematical formulation

The Arrhenius equation gives the quantitative basis of the relationship between the activation energy and the rate constant at which a reaction proceeds. From the Arrhenius equation(٧٦) , the activation energy can be expressed as:

$$E_a = -RT \ln(k/A) \qquad (١-١)$$

where *A* is the frequency factor for the reaction, *R* is the universal gas constant, and *T* is the temperature (in kelvins). The higher the temperature, the more likely the reaction will be able to overcome the energy of activation. A is a steric factor, which expresses the probability that the molecules contain a favorable orientation and will be able to proceed in a collision. In order for the reaction to proceed and overcome the activation energy, the temperature, orientation, energy, of the molecules must be substantial; this equation manages to sum up all of these things. A general rule of thumb is that raising the temperature by ١٠ kelvins doubles the rate of a reaction, in the absence of any other temperature dependent effects, due to an increase in the number of molecules that have the activation energy(٧٧).

To compute rate of reaction using results derived from transition state theory the equation, that's used for calculating reaction rates is(٧٨)

$$K(T) = K_B T/hC^\circ * e^{-\Delta G^\circ/RT} \qquad (١-٢)$$

This equation is another class of Arrhenius equation to calculate rate constant of reactions according to the sum of free energy for reaction species. K_B is Boltizman constant, **h** is blank constant, and C° concentration of reactant (use C° = ١ for the concentration) (٨٢).Difference in free energy of reaction achieved by the summation of energies for reaction components(٧٩) .

١-٣-٢Transition states

The transition state along a reaction coordinate is the point of maximum free energy, where bond-making and bond-breaking are balanced. Transition states are only in existence for extremely brief (١٠$^{-١٥}$ s) periods of time. Figure(١-٢) show the relationship between activation energy (E_a) and enthalpy of formation (ΔH) with and without a catalyst(٨٠).

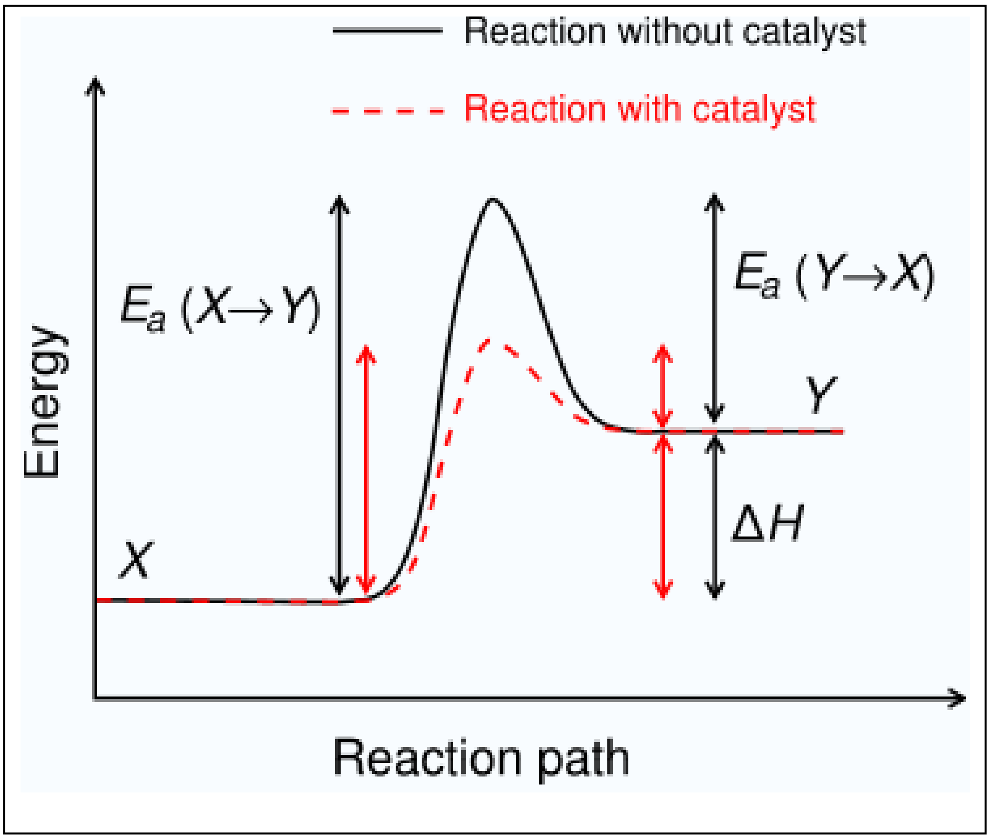


Figure (١-٢) relation shipe between the activation energy and enthalpy formation.

The highest energy position (peak position) represents the transition state. With the catalyst, the energy required to enter transition state decreases, there by decreasing the energy required to initiate the reaction.

The energy required to reach the transition state is equal to the activation energy for that reaction. Multi-stage reactions involve a number of transition points, here the activation energy is equal to the one requiring the most energy. After this time the molecules move apart again with either original bonds reforming, or the bonds break and new products form. This is possible because both possibilities result in the release of energy (shown on the enthalpy profile diagram, Figure (١-٢), as both positions lie below the transition state). A substance that modifies the transition state to lower the activation energy is termed a catalyst. It is important to note that a catalyst increases the rate of reaction without being consumed by it. In addition, while the catalyst lowers the activation energy, it does not change the energies of the original reactants nor products. Rather, the reactant energy and the product energy remain the same and only the activation energy is altered (lowered)(٨١).

١-٤ Computational Chemistry:

Computational chemistry is a branch of chemistry that uses the results of theoretical chemistry incorporated into efficient computer programs to calculate the structures and properties of molecules and solids, applying these programs to real chemical problems. Examples of such properties are structure, energy and interaction energy, charges, dipoles and higher multipole moments, vibrational frequencies, reactivity or other spectroscopic quantitities, and cross sections for collision with other particles. The term computational chemistry is also sometimes used to cover any of the areas of science that overlap between computer science and chemistry. Electronic configuration theory is the largest subdiscipline of computational chemistry(٨٢).

Theoretical chemistry may be defined as a mathematical description of chemistry, whereas computational chemistry is usually used when a mathematical method is sufficiently well developed that it can be automated for implementation on a computer. the words exact and perfect do not appear here, as very few aspects of chemistry can be computed exactly. Almost every aspect of chemistry can be described in a qualitative or approximate quantitative computational scheme.

Molecules consist of atoms (nucleis and electrons), so the methods of quantum mechanics apply. Computational chemists often attempt to solve the non-relativistic Schrödinger equation, with relativistic corrections added, although some progress has been made in solving the fully relativistic Schrödinger equation. It is, in principle, possible to solve the Schrödinger equation, in either its time-dependent form or time-independent form as appropriate for the problem in hand, but this in practise is not possible except for very small systems. Therefore, a great number of approximate methods strive to achieve the best trade-off between accuracy and computational cost. Present computational chemistry can routinely and very accurately calculate the properties of molecules that contain no more than ١٠-٤٠ electrons. The treatment of larger molecules that contain a few dozen electrons is computationally tractable by approximate methods such as density functional theory (DFT). There is some dispute within the field whether the latter methods are sufficient to describe complex chemical reactions, such as those in biochemistry. Large molecules can be studied by semi-empirical approximate methods. Even larger molecules are treated with classical mechanics in methods called molecular mechanics(٨٣) .

Both are chemists and physicists together develop algorithms and computer programs to predict atomic and molecular properties and reaction paths for chemical reactions. Computational chemists, in contrast, may simply apply existing computer programs and methodologies to specific chemical questions. There are two different aspects to computational chemistry:

١-Computational studies can be carried out in order to find a starting point for a laboratory synthesis, or to assist in understanding experimental data, such as the position and source of spectroscopic peaks.

٢-Computational studies can be used to predict the possibility of so far entirely unknown molecules or to explore reaction mechanisms that are not readily studied by experimental means.

Thus computational chemistry can assist the experimental chemist or it can challenge the experimental chemist to find entirely new chemical objects. Qualifying energetic materials (EM) and formulations for military use is a tedious, expensive and hazardous process. It may be possible to replace much of the redundant Empirical testing of EM, either in service or under consideration, by computer simulation. Therefore, accurate theoretical models of EM performance and stability can (٨٤):

- Accelerate research and development of new materials with improved performance and handling characteristics.
- Reduce maintenance costs for energetic materials in service
- Reduce risk to personnel testing, handling or using energetic materials.

Several major areas may be distinguished within computational chemistry(٨٥) :

- The prediction of the molecular structure of molecules by the use of the simulation of forces to find stationary points on the energy hypersurface as the position of the nuclei is varied.
- Storing and searching for data on chemical entities.
- Identifying correlations between chemical structures and properties.
- Computational approaches to help in the efficient synthesis of compounds.
- Computational approaches to design molecules that interact in specific ways with other molecules.

١-٤-١ Schrödinger Equation

Schrödinger equation proposed by the Austrian physicist Erwin Schrödinger in ١٩٢٥, describes the space- and time-dependence of quantum mechanical systems. It is of central importance to the theory of quantum mechanics, playing a role analogous to Newton's second law in classical mechanics(٨٦) .

Schrödinger's equation for molecular systems can only solved approximately. The approximation methods can be categorized as either DFT or *ab initio* or semiempirical. Semiempirical methods use parameters that compensate for neglecting some of the time consuming mathematical terms in Schrodinger's equation, whereas ab initio methods include all such terms. The parameters used by semiempirical methods can derived from experimental measurements or by performing ab initio calculations on model systems. The differences between these methods can describe in more detail in table (١-٥) that is showing their practical differences(٨٧).

Table (١-٥) Practical characteristics Comparisons of *ab intio* and Semiemperical methoeds.

AB-INITIO	SEMIEMPIRICAL
Limited to tens of atoms and best performed using a supercomputer.	Limited to hundreds of atoms.
Can be applied to organics, Organo-metallic, and molecular fragments (e.g. catalytic components of an enzyme).	Can be applied to organics, Organo-metallics, and small Oligomers (peptide, nucleotide, saccharide).
Can be used to study ground, transition, and excited states (certain methods).	Can be used to study ground, transition, and excited states (certain methods).
Specific implementations include HyperChem, GAMESS and GAUSSIAN.	Specific implementations include AMPAC, MOPAC, and ZINDO.

In the mathematical formulation of quantum mechanics, each system is associated with a complex Hilbert space such that each instantaneous state of the system is described by a unit vector in that space. This state vector encodes the probabilities for the outcomes of all possible measurements applied to the system. As the state of a system generally changes over time, the state vector is a function of time. The Schrödinger equation provides a quantitative description of the rate of change of the state vector(٨٨) .

١-٤-٢ Solutions of the Schrödinger equation

Analytical solutions of the time-independent Schrödinger equation(٨٩) can be obtained for a variety of relatively simple conditions. These solutions provide insight into the nature of quantum phenomena and sometimes provide a reasonable approximation of the behavior of more complex systems (e.g., in statistical mechanics, molecular vibrations are often approximated as harmonic oscillators). Several of the more common analytical solutions include:

- The free particle
- The particle in a box
- The particle in finite potential well
- The particle in a ring
- The particle in a spherically symmetric potential
- The particle in quantum harmonic oscillator
- The hydrogen atom or hydrogen-like atom
- The particle in ring wave guide
- The particle in a one-dimensional lattice (periodic potential)

For many systems, however, there is no analytic solution to the Schrödinger equation. In these cases, one must resort to approximate solutions. Some of the common techniques are:

- Perturbation theory
- The variational principle underpins many approximate methods (like the popular Hartree-Fock method which is the basis of the post Hartree-Fock methods)
- Quantum Monte Carlo methods
- Density functional theory
- Discrete delta-potential method

١-٤-٣ Molecular structure

Molecular formula can represent a number of molecular isomers. Each isomer is a local minimum on the energy surface (called the potential energy surface) created from the total energy (electronic energy plus repulsion energy between the nuclei) as a function of the coordinates of all the nuclei. A stationary point is when the derivative of that energy with respect to all displacements of the nuclei is zero. A local minimum is when all such displacements lead to an increase in energy. The local energy that is lowest is called the global energy and corresponds to the most stable isomer. If there is one particular coordinate change that leads to a decrease in the total energy in both directions the stationary point is a transition structure and the coordinate is the reaction coordinate. This process of determining stationary points is called geometry optimisation(٩٠) .

The determination of molecular structure by geometry optimisation became routine only when efficient methods for calculating the first derivatives of the energy with respect to all atomic coordinates became available. Evaluation of the related second derivatives allows the prediction of vibrational frequencies if harmonic motion is assumed. In some ways more importantly it allows the characterisation of stationary points. The frequencies are related to the eigenvalues of the matrix of second derivatives (the Hessian matrix). If the eigenvalues are all positive, then the frequencies are all real and the stationary point is a local minimum. If one eigenvalue is negative (an imaginary frequency), the stationary point is a transition structure. If more than one eigenvalue is negative the stationary point is a more complex one and is of little interest. If it found, it is necessary to move the search away from it to continue looking for local minima and transition structures.

The total energy is determined by approximate solutions of the time-dependent Schrödinger equation, usually with no relativistic terms included, and making use of the Born-Oppenheimer approximation which, based on the much higher velocity of the electrons in comparison with the nuclei, allows the separation of electronic and nuclear motions, and simplifies the Schrödinger equation. This leads to evaluating the total energy as a sum of the electronic energy at fixed nuclei positions plus the repulsion energy of the nuclei. A notable exception is certain approaches called direct quantum chemistry, which treat electrons and nuclei on a common footing. Density functional methods and semi-empirical methods are variants on the major theme. For very large systems the total energy is determined using molecular mechanics(٩١) .

١-٤-٤ Ab initio methods

The term "ab initio" is Latin for "from the beginning". This name had given to computations, which derived directly from theoretical principles. Most of the time, this is referring to an approximate quantum mechanical calculation. The approximations made are usually mathematical approximations, such as using a simpler functional form for a function or getting an approximate solution to a differential equation.

An accurate ways of determing the total energy to predict molecular structures is *ab intio* methods. 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. It means that a particular approximation is carefully defined and then solved as exactly as possible. 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). Figure (١-٣) showing various *ab initio* electronic structure methods in terms of energy(٩٢).

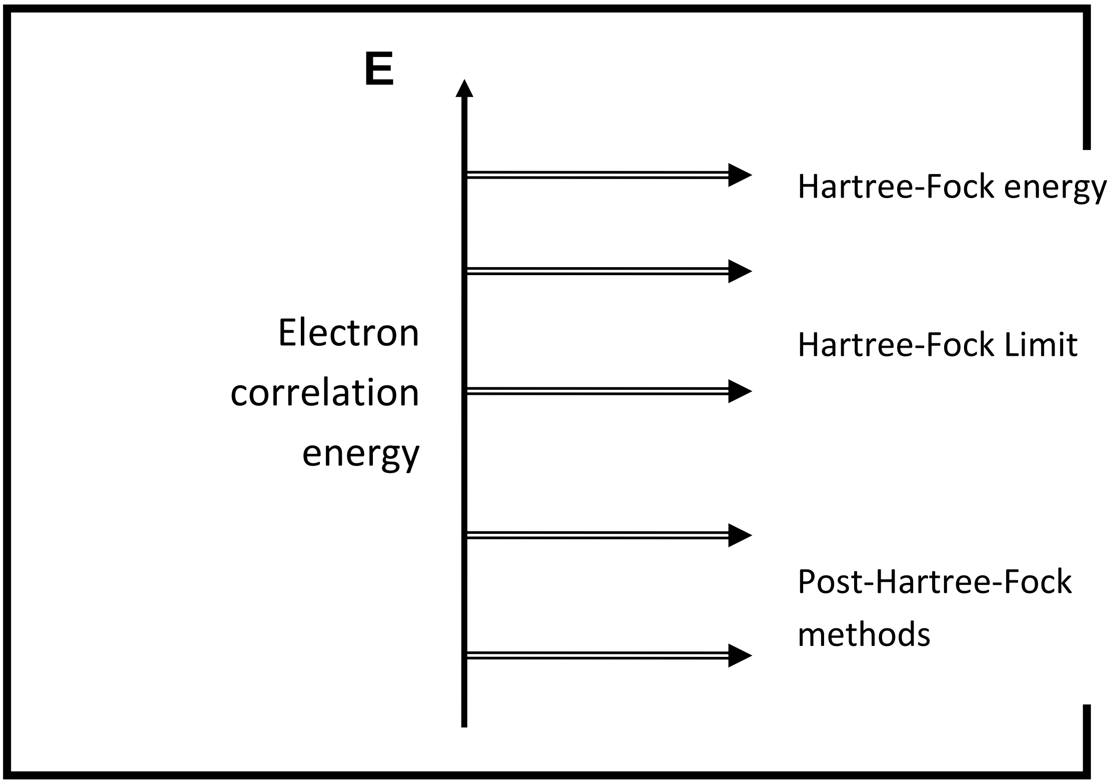


Figure (١-٣) Various *ab initio* electronic structure methods in terms of energy.

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. Many types of calculations, known as post-Hartree-Fock methods, begin with a Hartree-Fock calculation and subsequently correct for electron-electron repulsion, referred to also as electronic correlation. As these methods are pushed to the limit, they approach the exact solution of the non-relativistic Schrödinger equation. In order to obtain exact agreement with experiment, it is necessary to include relativistic and spin orbit terms, both of which are only really important for heavy atoms. In all of these approaches, in addition to the choice of method, it is necessary to choose a basis set. 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 (the method) and a basis set(٩٣) .

The Hartree-Fock wave function is a single configuration or determinant. In some cases, particularly for bond breaking processes, this is quite inadequate and several configurations need to be used. Here the coefficients of the configurations and the coefficients of the basis functions are optimised together.The total molecular energy can be evaluated as a function of the molecular geometry, in other words the potential energy surface(٩٤) .

Electronic structure methods, particularly ab initio calculations, are capable of consistent predictions with high accuracy (± ٢٠ kJ/mol) over a wide range of systems(٩٥) . a critical prerequisite for the successful modeling of energetic materials. Accuracy is related to its number of atoms per molecules.

Ab initio molecular orbital computations can provide accurate quantitative predictions of chemical properties for a wide range of molecular systems. However, they place a considerable demand on computer resources. The choice of theoretical method and basis set determine the duration of the calculation; thus, a sophisticated method and a large basis set will provide more accurate results, but will also require more computer resources. Hence timely calculations on large molecules (*n* ~ ١٠-٣٠ atoms) may only be possible using the basic theory (*i.e.*, Hartree Fock approximation) with minimal basis sets, whereas calculations on chemical reactions between simple diatomic molecules can be performed with state-of the-art model chemistries. For very large systems (*n* ~٥٠ atoms or more), timely results are only possible with less sophisticated models.

١-٤-٤-١ Basis Sets

Basis set is an assortment of mathematical functions used to solve a differential equation. In quantum chemical calculations, the term .basis set. is applied to a collection of contracted Gaussians representing atomic orbital, which are optimized to reproduce the desired chemical properties of a system. Standard ab initio software packages generally provide a choice of basis sets that vary both in size and in their description of the electrons in different atomic orbital. Larger basis sets include more and a greater range of basis functions. Therefore, larger basis sets can better refine the approximation to the true molecular wave function, but require correspondingly more computer resources. Alternatively, accurate wave functions may obtain from different treatments of electrons in atoms. For instance, molecules containing large atoms (Z > ٣٠) are often modeled using basis sets incorporating approximate treatments of inner-shell electrons, which account for relativistic phenomena. Minimal basis sets contain the minimum number of AO basis functions needed to describe each atom (e.g., ١s for H and He; ١s, ٢s, ٢px, ٢py, ٢pz for Li to Ne). An example of a minimal basis set is STO-٣G, which uses three Gaussian-type functions (٣G) per basis function to approximate the atomic Slater-type orbital . Although minimal basis sets are not recommended for consistent and accurate predictions of molecular energies, their simple structure provides a good tool for visualizing qualitative aspects of chemical bonding. Improvements on minimal basis sets described below and illustrated in Figure (١-٤).

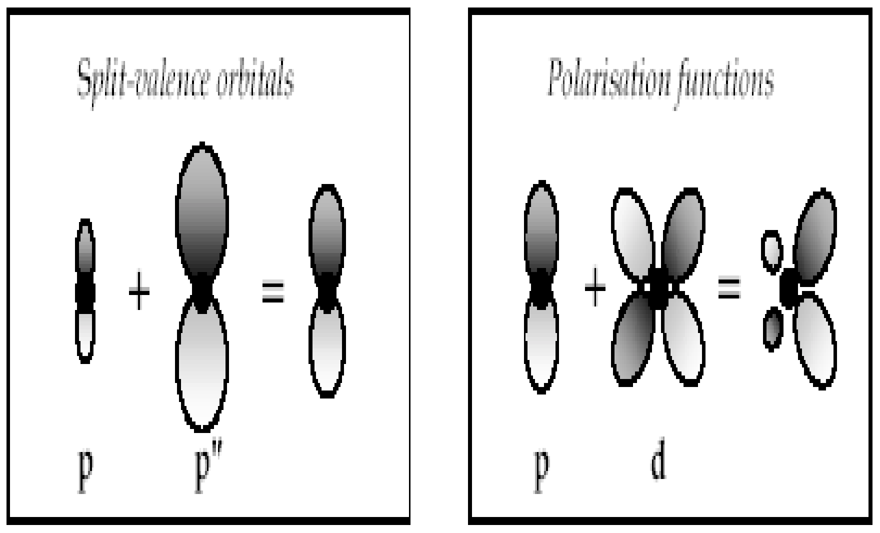


Figure (١-٤) Basis set improvements.

١-٤-٤-١-١ Split valence basis sets

Split valence basis sets are additional basis functions (one contracted Gaussian plus some primitive Gaussians) that are allocated to each valence atomic orbital. The resultant linear combination allows the atomic orbital to adjust independently for a given molecular environment. The number of functions assigned to valence orbital characterizes split valence basis sets. Double zeta, basis sets use two basis functions to describe valence electrons, triple zeta, use three functions, and so forth. Developed Basis sets (٩٦) are denoted by the number of Gaussian functions used to describe inner and outer shell electrons. Thus ٦-٢١G describes an inner shell atomic orbital with a contracted Gaussian composed of six primitive Gaussians, an inner valence shell with a contracted Gaussian composed of two primitives, and an outer valence shell with one primitive. Other split-valence sets include ٣-٢١G, ٤-٣١G, and ٦-٣١١G.

١-٤-٤-١-٢ Polarized basis sets

Polarization functions can be added to basis sets to allow for non-uniform displacement of charge away from atomic nuclei, thereby improving descriptions of chemical bonding. Polarization functions describe orbital of higher angular momentum quantum number than those required for the isolated atom (*e.g.*, *p*-type functions for H and He, and *d*-type functions for atoms with Z > ٢), and are added to the valence electron shells. For example, the ٦-٣١G (d) basis set constructed by adding six d-type gaussian primitives to the ٦-٣١G description of each non-hydrogen atom. The ٦-٣١G (d,p) is identical to ٦-٣١G(d) for heavy atoms, but adds a set of Gaussian *p*- type functions to hydrogen and helium atoms. The addition of *p* orbitals to hydrogen is particularly important in systems where hydrogen is a bridging atom.

١-٤-٤-١-٣ Diffuse basis sets

Species with significant electron density far removed from the nuclear centers (*e.g.*, anions, lone pairs and excited states) require diffuse functions to account for the outermost weakly bound electrons. Diffuse basis sets recommended for calculations of electron affinities, proton affinities, inversion barriers and bond angles in anions. The addition of diffuse s- and p-type gaussian functions to non-hydrogen atoms is denoted by a plus sign as in ٣-

٢١+G. Further addition of diffuse functions to both hydrogen and larger atoms is indicated by a double plus.

١-٤-٤-١-٤ High angular momentum basis sets

Basis sets with multiple polarization functions are now practical for many systems and, although not generally required for Hartree-Fock calculations, are useful for describing the interactions between electrons in electron correlation methods .Examples of high angular momentum basis sets include: ٦-٣١G (٢d) - two *d*-functions are added to heavy atoms; . ٦-٣١١G (٢df, pd). besides the (٣١١) valence functions, two *d* functions and one *f* function are added to heavy atoms, and *p* and *d* functions to hydrogen; . ٦-٣١١G(٣df, ٢df, p) - three *d* functions and one f function are added to atoms with *Z* > ١١, two *d* functions and one *f* function to first-row atoms (Li to Ne) and one *p* function to hydrogen. High angular momentum basis sets augmented with diffuse functions represent the most sophisticated basis sets available. As its known, energetic molecules have a complicated electronic structure due to the presence of nitro groups. Therefore, the most accurate *ab initio* studies of energetic materials would be produced by reasonably sophisticated polarized split-valence basis sets augmented with high angular momentum and diffuse atomic orbital. However, the size of the optimum basis set, when its especially used with electron correlation methods(٩٧) will ultimately be determined by the size of the energetic molecule, the amount computing power available, and the time allotted for the studies.

١-٤-٤-٢ Electron correlation

Hartree-Fock theory is a single-particle approximation, and therefore cannot adequately treat the correlated motion of electrons that occur due to electron-electron interactions. Neglect of electron correlation has blamed for systematic HF errors such as underestimated bond lengths and overestimated vibrational frequencies.

Calculations added to HF-SCF theory to remedy these errors are termed electron correlation, or post-HF methods. There are three general types of electron correlation treatments: configuration-interaction (CI) methods, Møller-Plesset (MP) perturbation theory, and density functional theory (DFT).

١-٤-٤-٢-١ Configuration-interaction

A HF wave function of a molecule has one determinant; therefore, it can only describe only one electronic configuration in a molecule. This approximation is so restrictive that HF theory cannot predict dissociation of the simplest molecule, the hydrogen dimer, into its neutral atomic components. However, correct dissociation behavior is restored when extra configurations, corresponding to electronically excited states, are added to the wave function . Configuration-interaction methods incorporate excited state configurations into the wave function by constructing new determinants from the original HF determinant. New determinants created by replacing one or more occupied orbitals with unoccupied (virtual) orbitals of higher energy. The number of replacements within the determinants designates the level of CI. For instance, single substitution (CIS) switches one pair of occupied and virtual orbitals and is equivalent to a one-electron excitation. Higher-order calculations include CID (double substitutions), which generates determinants where two orbital pairs are

Switched; CISD, which adds singly and double-substituted determinants; and CISD (T), with single, double and triple excitations. The theoretical limit of this expansion - a full CI calculation - forms the molecular wavefunction as a linear combination of the HF determinant and all possible substituted determinants.

١-٤-٤-٢-٢ Møller-Plesset perturbation

For typical molecules, most of the ground-state energy originates from one-electron HF contributions. Møller-Plesset perturbation theory assumes that the effects of electron correlation are minor, and can be described by small corrections (perturbations) to the HF solution. Essentially, MP methods assume the true molecular Hamiltonian can divided into two parts:

$$\hat{H}_{mol} = \hat{H}_{one\text{-}e} + \lambda \, \hat{P}_{many\text{-}e} \qquad (\text{١-٣})$$

Where $\hat{H}_{one\text{-}e}$ denotes single-electron energy contributions that can be solved exactly by HF-SCF, and $\hat{P}_{many\text{-}e}$ represents contributions due to electron correlation. The coefficient λ is used to generate power series expansions of the energy and the molecular wavefunction:

$$E_{mol} = E^{(D)} + \lambda^{\text{١}} E^{(\text{١})} + \lambda^{\text{٢}} E^{(\text{٢})} + \lambda^{\text{٣}} E^{(\text{٣})} + \ldots \qquad (\text{١-٤})$$

$$\Psi_{mol} = \Psi^{(D)} + \lambda^{١} \Psi^{(١)} + \lambda^{٢} \Psi^{(٢)} + \lambda^{٣} \Psi^{(٣)} + \dots \qquad (١-٥)$$

These series are then substituted back into the molecular Schrödinger equation with the modified Hamiltonian (١-٣), and each term is evaluated in turn. The first two energy terms constitute the HF energy

$$E_{HF} = E^{(D)} + E^{(١)} \qquad (١-٦)$$

In addition, they are used to evaluate $\psi^{(١)}$, which is composed of a linear combination of substituted determinants

$$\Psi^{(١)} = \Sigma_n b_n \Psi_{S, D, T\dots} \qquad (١-٧)$$

With coefficients *bi* that are inversely proportional to the difference in energy between the ground state and the associated excited states. That is, substituted wave functions close in energy to the ground state make larger contributions to the perturbation expansion. The first-order correction to the wave function, $\psi^{(١)}$, is then used to calculate the second-order correction to the total energy $E(٢)$, and so on, back and forth, until the desired order of correction is achieved(٩٨) . Møller-Plesset theory designated by the order of the perturbative corrections. Since the second-order energy term $E(٢)$ is the first-order correction to the HF energy, the designation begins at MP٢, and continues with MP٣,MP٤, MP٥, and so forth .

١-٤-٥ Semi-empirical methods

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.

Semi-empirical methods follow what are often called empirical methods where the two-electron part of the Hamiltonian is not explicitly included. For π-electron systems, this was the Hückel method proposed by Erich Hückel, and for all valence electron systems, the Extended Hückel method proposed by Roald Hoffmann(٩٩) .

Several semi-empirical methods are available and appear in commercially available computational chemistry software packages such as HyperChem and Chem٣D(١٠٠) . Some of the more common semi-empirical methods can be grouped according to their treatment of electron-electron interactions.

The good side view of semiempirical calculations is much faster than the ab initio calculations. The bad side of semiempirical calculations is that the results can be eratic. If the computed molecule is similar to molecules in the database used to parameterize the method, then the results may be very good. If the computed molecule is significantly different from anything in the parameterization set, the answers may be very poor.

Semiempirical calculations have been very successful in the description of organic chemistry, where there are only a few elements used extensively and the molecules are of moderate size. However, semiempirical methods have devised specifically for the description of inorganic chemistry as well (١٠١).

١-٤-٦ Molecular Mechanics

Large molecular systems can be modelled successfully while quantum mechanical calculations are entirely avoided. Molecular mechanics simulations, for example, use a single classical expression for the energy of a compound, like the harmonic oscillator. All constants appearing in the equations must be obtained before hand from experimental data or ab initio calculations.

The database of compounds used for parameterization - (the resulting set of parameters and functions is called the force field) - is crucial to the success of molecular mechanics calculations. A force field parameterized against a specific class of molecules, like proteins, would be expected to only have any relevance in case of describing other molecules of the same class.

The atoms in molecules model developed by Richard Bader was developed in order to effectively link the quantum mechanical picture of a molecule, as an electronic wavefunction, to chemically useful older models such as the theory of Lewis pairs and the valence bond model. Bader has demonstrated that these empirically useful models are connected with the topology of the quantum charge density. This method improves on the use of Mulliken charges(١٠٢) .

The basic assumptions of typical molecular mechanics (١٠٣) methods listed below.

١- Each atom (i.e., electrons and nucleus) represented as one particle with a characteristic mass.

٢-A chemical bond represented as a .spring, with a characteristic force constant determined by the potential energy of interaction between the two participating atoms. Potential energy functions can describe intermolecular bond stretching, bending and torsion, or intermolecular phenomena such as electrostatic interactions or van der Waals forces.

The potential energy functions rely on empirically derived parameters obtained from experiments or from other calculations. Current molecular mechanics models characterized by the set of potential energy functions used to describe the chemical forces. These force fields depend upon the following

١- Atomic displacements (i.e., bond lengths);

٢- Atom types, that is, the characteristics of an element within a specific chemical context (e.g., a carbonyl carbon versus a methyl carbon); and

٣- One or more parameter sets relating atom types and bond characteristics to empirical data.

١-٤-٧ Types of Calculations

There are several types of calculations in HyperChem٧.٥٢ such as single point, transition state, IR, UV, geometry optimization or minimization, MM, and molecular dynamics.

١-٤-٧-١ Single Point

A single point calculation gives the static properties of a molecule. The properties include potential energy, derivatives of the potential energy, electrostatic potential, molecular orbital energies, and the coefficients of molecular orbitals for ground or excited states. The input molecular structure for a single point calculation usually reflects the coordinates of a stationary point on the potential energy surface, typically a minimum or transition state.

One type of single point calculation is that of calculating vibrational properties distinguished as a vibrations calculation in HyperChem. A vibrations calculation predicts fundamental vibrational frequencies, infrared absorption intensities, and normal modes for a geometry optimized molecular structure.

A single point calculation can be used also to determine energies for ground and excited states, using configuration interaction, to predict frequencies and intensities of an electronic ultraviolet-visible spectrum.

١-٤-٧-٢ Geometry Optimization

Carrying out a geometry optimization (minimization), HyperChem starts with a set of Cartesian coordinates for a molecule and tries to find a new set of coordinates with a minimum potential energy, It should be appreciated that the potential energy surface is very complex, even for a molecule containing only a few dihedral angles. Since minimization calculations cannot cross or penetrate potential energy barriers, the molecular structure found during an optimization may be a local and not a global minimum. The minimum represents the potential energy closest to the starting structure of a molecule. Researchers(١٠٤) frequently use minimizations to generate a structure at a stationary point for a subsequent single point calculation or to remove excessive strain in a molecule, preparing it for a molecular dynamics simulation.

١-٤-٧-٣ Transition State Search

A potential energy surface may contain saddle points; that is, stationary points where there are one or more directions in which the energy is at a maximum. A saddle point with one negative eigen value corresponds to a transition structure for a chemical reaction of changing isomeric form. Transition structures also exist for reactions involving separated species, for example, in a bimolecular reaction

$$A + B \rightarrow C + D \qquad (١-٨)$$

Activation energy or the energy of the transition structure relative to reactants can be observed experimentally. However, the only way that the geometries of transition structures can be evaluated is from theory. Theory also can give energetic and geometry parameters of short-lived reaction intermediates.

Transition state search algorithms rather climb up the potential energy surface, unlike geometry optimization routines where an energy minimum is searched. The characterization of even a simple reaction potential surface may result in location of more than one transition structure, and is likely to require many more individual calculations than are necessary to obtain equilibrium geometries for either reactant or product. Calculated transition structures may be very sensitive to the level of theory employed. Semi-empirical methods, since they are parameterized for energy minimum structures, may be less appropriate for transition state searching than ab initio methods are. Weak “partial” bonds, that is, normally characterize transition structures being broken or formed (١٠٥). In these cases, UHF calculations are necessary, and sometimes even the inclusion of electron correlation effects.

١-٤-٧-٤ Molecular Dynamics

A molecular dynamics simulation samples phase space (the region is defined by atomic positions and velocities) by integrating numerically Newton’s equations of motion. Unlike single point and geometry optimization calculations, molecular dynamics calculation account for thermal motion. Molecules may contain enough thermal energy to cross potential barriers. Molecular dynamics calculations provide information about possible conformations, thermodynamic properties, and dynamic behavior of molecules (١٠٦).

١-٤-٧-٥ Langevin Dynamics

Molecules in solution undergo collisions with other molecules and experience frictional forces as they move through the solvent. Using Langevin dynamics, you can model these effects and study the dynamical behavior of a molecular system in a liquid environment. These simulations can be much faster than molecular dynamics. Instead of explicitly including solvent molecules, the Langevin method models their effect through random forces applied to the molecule of interest to simulate collisions, and frictional forces added to model the energy losses associated with these collisions. Langevin dynamics simulations can be used to study the same kinds of problems as molecular dynamics time dependent properties of solvated systems at non-zero temperatures. It is possible to decouple the time scales of molecular motion and focus on just the slow modes associated with conformational changes, for example, or to follow the rapid bond stretching motions leading to chemical reaction, while incorporating the influence of molecular collisions. Langevin dynamics has been used to study solvent effects on the structural dynamics of the active site of the enzyme lysozyme, conformational equilibria and the dynamics of conformational transitions in liquid alkanes, and temperature effects on a system of interacting quantum harmonic oscillators (١٠٧).

١-٤-٨ HyperChem٧.٥٢ Philosophy

HyperChem٧.٥٢ is a versatile molecular modeler and editor and a powerful computational package. It offers many types of molecular and quantum mechanics calculations.The philosophy of HyperChem٧.٥٢ associated with back end computations is one which is intended to instill confidence, as far as is possible, in the scientific results emanating from HyperChem٧.٥٢. This philosophy is one of openness about the product, the calculations being performed, the science embodied in the product. Apart from protecting the proprietary code associated with a commercial product, Hypercube wishes to document and describe as fully as is possible the calculations that

HyperChem٧.٥٢ performs. There should be no mystery about the scientific results obtained with HyperChem٧.٥٢(١٠٨) .

١-٤-٩ View of Gaussian ٠٣W program

Gaussian٠٣W program is the latest in the Gaussian series of electronic structure programs. Designed to model a broad range of molecular systems under a variety of conditions, it performs its computations starting from the basic laws of quantum mechanics. Gaussian ٠٣W is used by chemists, physicists and engineers for research in established and emerging areas of chemical interest, studying molecules and reactions of definite or potential interest, including both stable species and compounds which are difficult or impossible to observe experimentally: short-lived intermediates, transition structures and the like(١٠٩) .

G٠٣W predicts the energies, molecular structures, vibrational frequencies-along with the numerous molecular properties that are derived from these three basic computation types-for systems in the gas phase and in solution, and it can model them in both their ground state and excited states. Chemists apply these fundamental results to their own investigations, using Gaussian ٠٣ to explore chemical phenomena like substitute effects, reaction mechanisms, and electronic transitions(١١٠) .

Gaussian٠٣W compute molecular energies by modeling the electronic wave function using a variety of methods ranging in accuracy and corresponding computational cost(١١١) :

١- Low-cost semi-empirical methods, allowing energies to be predicted for molecules containing tens of thousands of atoms.

٢-Hartree-Fock theory, the well-proven first-level method applicable to a wide range of compound types and system sizes.

٣-Methods which include the electron correlation effects neglected by less expensive approaches, ranging from those based on Møller-Plesset perturbation theory to the highly accurate Quadratic Configuration Interaction and Coupled Cluster methods including triple substitutions.

Gaussian٠٣W is capable of predicting many properties of molecules and reactions, including molecular energies and structures, bond and reaction energies, spectroscopic (IR, UV, Raman, NMR) properties, reaction pathways. Computation can be carried out on molecules in the gas phase or in solution. Molecules in their ground and excited states can be calculated, too. Gaussian٠٣W provides insight into chemical properties for experimental research chemists, leading to better understanding of chemical phenomena(١١٢).

١-٥ Historical survey of theoretical photodegradation for pesticides

Heterogeneous photocatalytic methods are the best from several methods that used to run of the toxic materials from our environment (pollution of air, surface water, ground water, and soil)(١١٣). Semiconductor catalysis have used by Gratzel in ١٩٨٧ that's he studied the complete mineralization of ٤-nitrophenyl-ethyl-phosphate on Nb-dobed $TiO_{٢}$(١١٤).

Harad reported at ١٩٨٩ that organic pesticides are libel to the photo catalyzed decomposition into completely mineralized products by using semiconductors suspension solutions(١١٥).

Lu has investigated several factors in ١٩٩٣ affected on photo-catalyzed reaction for toxic compound decomposition using a glass photo reactor coated with $TiO_{٢}$ and ٢٠W black-light tungsten fluorescent tube (١١٦).

Aaron has developed new electrochemical and photochemical methods in ٢٠٠١ for the decontamination of natural water containing significant concentrations of aromatic pesticides. The electrochemical method based on the electro-Fenton process, i.e. the simultaneous reduction of $O_{٢}$ and $Fe^{٣+}$ ions. Hydroxyl (OH^{*}) radicals are electro synthesized in aqueous solutions, followed by complete mineralization of the initial pollutants. Either the photochemical methods involve a direct photodegradation reaction of pesticides by UV light, or indirect photodegradation processes including $H_{٢}O_{٢}$ photolysis or photo-Fenton reagents ($H_{٢}O_{٢}$ / $Fe^{٣+}$)(١).

Hussien and Naman have studied in ٢٠٠١-٢٠٠٢ the effective concentration of $H_{٢}O_{٢}$ of $TiO_{٢}$, mixed semiconductor, various sensitizers, UV light, and temperature on photodegradation of pesticides DDVP. They showed that these insecticides could be photodegraded into chloride ion, water, carbon dioxide, and other compounds in aqueous solution containing semiconductor powder suspension, $H_{٢}O_{٢}$ and using ultraviolet light. The addition of $H_{٢}O_{٢}$ in the presence of semiconductor suspension would increase the efficiency of the photodegradation process(١١٧,١١٨).

Evgenidou have studied in ٢٠٠٣ the photo catalytic degradation of a pesticides by using two types of photo catalysts ($TiO_{٢}$ and ZnO), in the absence as well as in the presence of an oxidant ($H_{٢}O_{٢}$). Thy found the activation energy Ea for $TiO_{٢}$ system was ٣٦ kj /mol and for the ZnO systemwas١٣.٣ kJ $mol^{-١}$ (١١٩).

Suara Kalid has studied in ٢٠٠٤ the transition state of insecticide Dichlorovos photodegradation with hydroxyl radical by using world theoretical programming. She's found reasonable mechanisms of degradation, and she calculate the activation energy of reaction that's was equal to ٢٤.٥ $kJmol^{-١}$. All results have executed Hyperchem٧.٥ program(١٢٠).

In addition to Kaldh Samawi has studied in ٢٠٠٦ the Energetic properties of complexes by using The PM٣ and ab-initio method at high level are used for calculating the relative energies , charge density and surface potential of twenty-two ligands to investigate the reactive sites of these ligands. All results have executed Hyperchem٧.٥ program (١٢١).

١-٦ The aim of the present work

In present work, the theoretical study of photodegradation for some pesticide through the quantum treatment and calculation of the electronic and geometrical structure of these pesticides and their reaction with hydroxyl radical. the present work goals are:

١. To find out a reasonable mechanism of photo degradation for Captan, Carbaryl, and Methomyl by hydroxyl radical in gas phase.

٢. To study the initial attack on substrate molecule which is believed to be the most important step in determine the subsequent reaction steps by usage of an advanced molecular package, HyperChem٧.٥, ٢٠٠٣, Gainesville, Florida, USA.

٣. To calculate rate constant of first cleavage reaction step for pesticides by using Gaussian ٠٣W: IA٣٢W-G٠٣RevD.٠١ ١٣-Oct-٢٠٠٥.

٤. Investigation of the possible mechanism for this photo degradation reaction by using two main quantum methods, PM٣ and *ab intio*.

٥. Reporting the results of large basis set *ab intio* molecular orbital calculation with an adequate correlation treatment (e.g. MP٢) for the reactions. Results of structures, energetic, thermodynamics, and vibrations frequencies of reactants, products, intermediates, transition states .

٦. Studying the vibration analysis ,and UV-visible transitions for pesticides molecules, theoretically and comprise with the experimental result that's output from spectrophotometers analysis instruments.

٧. To present the research outcomes at the College of Science University of Babylon.

Chapter Two

Practical Part

٢-١ Chemicals

Chemicals have been used are listed in Table (٢-١) according to its producer companies.

Chemicals names	Purity %	Company
Captan	٥٠ (W/W)	VAPCO
Carbaryl	٨٥ =	Premier
Methomyl	٩٠ =	Blue Field
Dimethyl Sulfoxid	٩٦.٤ Analar	Fluka

٢-٢ Apparatus

Two different type computers have used as following

A-For simple small basis set calculations, computer that is used are:

Pentium IV computer

Processor ٢.٤ GB

Hard Disk ٨٠ GB

RAM ٠.٧٥٦GB

UBS ١٢٠٠s

B-For complex large basis set calculations, computer that is used are:

Pentium IV computer

Processor ٣.٢ GB

Hard Disk ٢٠٠ GB

RAM ٢GB

UBS ٣٦٠٠s

Two different Spectrophotometers have used as following

A-FTIR spectrophotometer-(shimadzu) -٢٠٠٢-Japan

B-UV-Visible spectrophotometer-(shimadzu) LBC-١٦٠٠-٢٠٠٢-Japan

٢-٣ Programs used in Calculation

Sophisticated universal molecular modeling software has been used. These software are known for their best quality, flexibility, and easy of use and they have ٣D visualization, animation with quantum chemical calculation, molecular mechanics, and dynamics.

١.HyperChem puts more molecular modeling tools at finger tips than any other windows programs(١٢١). Two versions have been used of HyperChem ٦.٠٣ and ٧.٥٢ (Gainesville University, Florida, USA-

٢٠٠٣). the ٧.٥٢ programs incorporates even more powerful, computation chemistry tools than ever HyperChem ٦.٠٣, as well as newly incorporates models, additional basis sets, new drawing capabilities and more (١٢٢).

٢.Gaussian٠٣W (Carnegie Mellon University IA٣٢W-G٠٣RevD.٠١ ١٣-Oct-٢٠٠٥), which puts more molecular modeling performance tools than HyperChem ٧.٥٢ . Various thermo chemical values are computed in Gaussian٠٣W. These quantities have been calculated according to quantum mechanics concepts, such as partition functions. These calculations including the enthalpy change and Gibbs free energy for a reaction, the heat of formation of a molecule and absolute rates of reaction are worked out(١٢٣,١٢٤).

The calculation of the rate constant of main reactions, and some of vibrational analysis calculations at higher basis sit. The calculations are summarized as follow:-

١. Single point calculations to determine the total energy of the molecule, and properties for a given fixed geometry.

٢. Geometry Optimization calculation employs energy minimization algorithms to locate stable structure.

٣. Vibrational frequency calculations find the normal vibrational modes of an optimization structure. The vibrational spectrum displayed and the vibrational motions associated with specific transitions can be animated.

٤. Transition state searching locates the metastable structure corresponding to transition state using either eigen vector following or synchronous transition methods molecular properties are then calculated.

٥. UV spectrum calculation using configuration interaction (١٠x١٠) between HOMO and LUMO.

٦. Rate constant calculation using RMP٢/٦-٣١١++g(٢d,٢p)//RHF/٦-٣١G(D) geom=connectivity.

٢-٤ Routs of Calculations

The following steps were used to achieve the calculations.

٢-٤-١ -Building and Displaying Molecules

HyperChem and G٠٣W tools have been used to build and display molecules. Since HyperChem has a flexible graphical interface, the construction monitor of molecules. By using the Drawing tool, drawing a two-dimensional (٢D) representation of a molecule, and then use the Model Builder to generate a three-dimensional (٣D) structure. The Model Builder adds implicit hydrogen to the molecule at ours request. Also the manipulate individual bonds, bond geometries, angles, torsions and atomic charges during model building (using the Constrain commands on the Build menu) or after model building (using the Set commands on the Edit menu).

٢-٤-٢ Optimizing the Structures of Molecules

To calculate the properties of a molecule, must be generate a well-defined structure. A reliable calculation often requires a structure that represents a minimum on a potential energy surface. HyperChem and G٠٣W contain several geometry optimizers to do this. The optimized geometry of defined structure, submitted to single point calculation.

Two different methods were used for configuration interaction; semiemirical PM٣ method, and ab initio with different basis set.

٢-٤-٣ Investigating the Reactivity of Molecules

The reactivity of molecules and their functional groups have been done by using molecular orbital energies, coefficients, and nodal properties from single point quantum mechanics calculations to investigate some issues such as the relative reactivity of different molecular subsistent, region selectivity of reactions, and site-selectivity of nucleophiles and electrophiles.

٢-٤-٤ Viewing Orbital and Electronic Plots

Orbital wave functions have been plotted by using the results of semiempirical calculations. It is interesting to view both the nodal properties and the relative sizes of the wave functions. Orbital wave functions can provide chemical insights. Also the plot of electrostatic potential, the total charge density, or the total spin density determined during a semi-empirical calculation.

٢-٤-٥ Bond Breaking

Quantum mechanical calculation of molecular dynamics trajectories can simulate bond breaking and formation. the appearance or disappearance of bonds can not seen, only (elongation of bonds to maximum scale). Selection to the required bond or the distance between two bonded atoms. A distance exceeding a theoretical bond length may refer to bond breaking through reaction. the required energy can calculated before the angles torsion between three atoms in same way.

٢-٤-٦ Configuration Interaction (CI)

Configuration Interaction (or electron correlation) have been used to improve energy calculations using PM٣ for these electron configurations and to predict electronic spectra of molecules. The Configuration Interaction treatment provides a ground state and some excited state energies. Vibrations spectrums (Infrared spectrum) calculated by PM٣ method. Electronic spectrum (UV Visible) is calculated by single excited state using single point calculation. Properties written at log file. Spectrum chart calculation exported at suitable name file.

٢-٤-٧ Transition State Searching

By merging all components files structures of a reaction in a new file page. Reaction Map from setup menu used for the synchronous transit method from compute menu to match reactants and products to connect atoms in reactants and products. Started log file before running synchronous transition state. Stopping log file and saving it. Total energy values have been estimated from log file for transition state. Energy barrier (activation energy of reaction) calculated by achieving the energy difference between the transition state and the summation energy values of reactants as in following equation:-

$$\Delta E_{reaction} = E_{TS} - \Sigma E_{reactants} \qquad (٢\text{-}١)$$

٢-٤-٨ Rate constant calculation

For each reaction component, the input file (*.gif) were prepared for Gaussian ٠٣ program. The input file should contain instructions referring to the kind of computation to be perform, comments, and the molecular description using z-matrix or XYZ-coordinates. The output file is designated to be named with the filename "gausjob.out".

By achieving the difference in free energy values of reaction components in Hartree unites at ٢٩٨.١٥K°, which converted by factor (**٦٢٧.٥٠٩٥**) into kcal $mol^{-١}$. Using rate constant equation to calculate rate constant of desired reaction.

٢-٥ Computation Details of Present Work

The second order Møller–Plesset perturbation theory (MP٢) used together with various basis sets. These basis sets could be categorized as following:

١. Minimum basis sets: STO-٣G (d). (HyperChem٧.٥٢)
٢. Large basis sets: ٦-٣١G (d, p), ٦-٣١++G (d, p). (HyperChem٧.٥٢)
٣. Very large basis sets: such as ٦-٣١١++G(٢d,٢p). (HyperChem٧.٥٢)
٤. RMP٢(Full)/٦-٣١١++G(٢df,٢p) ٦D ١٠F// ٦-٣١١++G(٢d,٢p). (G٠٣W)
٥. UMP٢(Full)/٦-٣١١++G(٢df,٢p) ٦D ١٠F// ٦-٣١١++G(٢d,٢p). (G٠٣W)
٦. G٢MP٢. (G٠٣W)

Some of these basis sets such as STO-٣G(d) ٦-٣١G(d,p), ٦-٣١++G(d,p) were chosen for geometry optimization, while others were used for MP٢ calculations for intermediates, products, and transition states. They give good result in an acceptable time. the neglecting of very large basis sets for transition states due they require three months to fulfill the calculation of one molecule as well as they give the same results in comparison with large basis sets. In other words the bigger is not always better as well as they are time consuming in addition to that they either give values of the same accuracy for this type of reaction or they give value of less accuracy. The Correlation Exchange Functions (CEF) has used for optimization, atomic charge, and geometry calculations. They give similar results of MP٢ calculation but they behaved badly during transition state calculation. Through semiemprical calculation, we used PM٣ method with a microstate option which represents a type of configuration interaction methods for enhancing the ΔH_f value for structures. Also PM٣ method have been used for IR, UV, and Transition state calculation.