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Degradation of 2.2 dichlorovinyl dimethyl phosphate (DDVP) in aqueous solution, by gamma radiation.

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ABSTRACT/RESUME

Abstract: *The degradation of the 2.2 dichlorovenyl dimethyl phosphate in aqueous suspension with gamma irradiation was studied. The solution was irradiated to absorbed doses varying from 0.1 to 10 kGy, using a 60Co gamma source. The results showed that the dichlorvoswas completely degraded at the dose of 10kGy. Some by-products formed during the radiation degradation process wereidentified by gas chromatography associated to mass spectrometry (GC-MS), among them, Phosphoric acid trimethyl ester (C1); 2,chloroethenyl dimethyl ester phosphoric acid (C2) and o-methyl o-propyl isopropylphosphonate (C3).A degradation pathway for DDVP is proposed based on the identified by- products.*

I. Introduction

Pesticides are chemical substances that are widely used against plant pests and diseases [1]. In recent decades, the environment is continuously polluted as a consequence of the rapid growth of various industrial and agricultural activities [2], leading to contamination of surface and ground waters [3-4].Organophosphorus compounds aredetected in soils years after application, and frequently detected withconcentrations varying from ng/L to µg/L [5], they can persist in the environment for long period of time [6]. Their removal from water is in urgent; they become a problem to the ecosystem because of residues that remain in the environment and their removal from water is urgent [7]. They are extremely toxic acting on acetylcholinesterase activity [8-9] and affect pancreatic and hepatic glucokinase activity [10].

Different decomposition ways of organo-phosphates such as hydrolysis, photolytic oxidation, microbial degradation and other biological processes were studiedby several authors [11]. Among the various techniques developed for pesticide degradation, gamma irradiation appears to be a very promising one. It is known as an efficient method for the destruction of various pollutants in water [12-13].

The dichlorvos (DDVP), is one of the most widely used pesticides in locust control in Algeria. To better understand the phenomenon that occurs in aqueous media, the degradation of DDVP in aqueous suspension under gamma irradiation has been investigated.The aim of the present work is to determine the effect of absorbed dose on the degradation of DDVP in aqueous solution and the main by- products formed by using GC-MS technique.

II. Materials and methods

II.1. Reagent and pesticide

Dichlorvos (2.2 dichlorovenyl dimethyl phosphate), analytical grade97% purity, purchased from LIMARU (Belgium), was used without further purification. All solventssupplied by MERCK, Darmstadt, Germany were HPLC-grade (acetonitrile, toluene). Phosphate buffer pH 7 and anhydrous sodium sulfate were supplied by Fluka. Stock solution of dichlorvos (0.75 g/l) was prepared in deionized water, protected from light and stored at 4^0C.

II.2. Irradiation procedure

Glass vials containing 10 ml of DDVP stock aqueous solution ($C_{0=}$ 0.75g/l) were irradiated with C_o-60gamma rays at the doses of 0.1, 0.5, 2, 4, 6, 8 and 10kGy. Irradiation was conducted at room temperature at a dose rate of 11.40Gy /min.

II.3. Extraction procedure

A liquid-liquid extraction was performed to concentrate the pesticide after irradiation. A volume of 10ml of stock solution was poured into theseparatory funnel and mixed with10ml of toluene as a solvent extractor. Then 5% (w/v) of sodium chloride salt was added in order to enhance the extraction [8-14]. The extraction was performed by bubbling helium gas through capillary into the solution during 30mn. After the phase separation was observed, the upper organic phase was passed through a layer of anhydrous sodium sulfate in view to fixe remaining water. The organic phase was then distilled in a rotary evaporator at $93^0C \pm 1^0C$ to dryness and finally re-dissolved again in 1ml of toluene and analyzed by GC-MS.

II.4. HPLC Analysis

DDVP content in the solutions prior and after irradiation was measured by liquid chromatography, on an Agilent 1100 chromatograph equipped with a diode array UV/ Vis detector.The detection was realized at 215nmwavelength, using an Eclips XDB-C18 column (5µm,4.6 x 250 mm), temperature of the oven was 25^0C. The mobile phase consisting of a mixture of acetonitrile and waterin volume proportionsof 50:50(v/v), at 1ml/min flow rate with injection volume of 20 µl.

II.5. GC-MS Analysis

The identification of by-products was carried out on irradiated solutions of DDVP with an initial concentration of C_0=0.75g/l. GC-MS analyses were performed on a Perkin Elmer Autosystem XL Gas chromatography and Turbo Mass Gold Mass spectrometer Detector, equipped with a 5% diphenyl / 95% polysiloxane column of 30m length and 0.25mm id; 0.25µm film thickness . The separation of by-products was conducted under the following chromatographic conditions: injector temperature 280^0C, Oven temperature program from 60^0C (2min) to 160^0C (3min) followed by 25 ^0C to 220^0C (3min) at the rate of 15^0C/min and isotherm at 280^0C during 1min. Helium was used as carrier gas at a flow rate of 1ml/min and the injected volume of 1,2µl. The MS operated in electron impact ionization mode with a potential of 70eV.

III. Results and Discussion

III.1. Radiation effect on pH of the solution

According to previous studies, pH appears to play an important role during the radiation process [15]. The pH can changes the ionization form of certain analytes and thereby it will affect their water solubility and extractability.

The results showed that irradiation decreased the solution pH from 3.08 at the absorbed dose of 0.1kGy to 2.21at 10kGy(Fig.1). It is well known that acidic solutions are favorable for oxidation of dichlorvos [16].

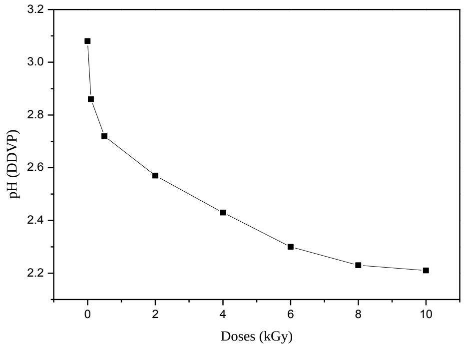


Fig 1. *Irradiation effect on pH of the DDVP aqueous solution.*

III.2. Dependence of the pesticide degradation on the absorbed dose

The variation of the DDVP concentration as a function of the absorbed irradiation dose is represented on figure 2. The fit of the curve showed that the concentration in the solution decreased exponentially with the absorbed dose according to the following function:

$$C = C_0\, e^{-D/Dt}$$

Where,

C: concentration of DDVP after irradiation;
C_0: initial concentration of stock solution;
D: irradiation dose;
D_t: dose constant (or the characteristic dose).

The characteristic dose determined by the best fit procedure from experimental data was1.31 ± 0.09 kGy. The absorbed dose corresponding to 50% degradation of the pesticide was estimated to be 0.90 ± 0.06 kGy. Thus, the corresponding exponential function can be written as following:

$$C = 5.68\ \ e^{-D/0.9}$$

with a correlation coefficient of: $R^2 = 0.9963$.

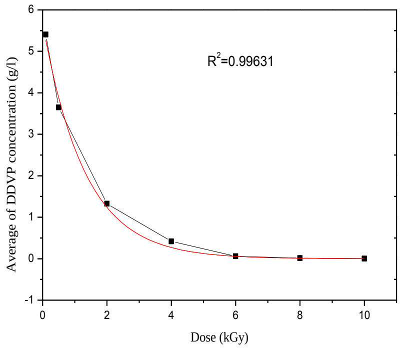


Fig 2. *Decrease in DDVP concentration with absorbed radiation dose.*

Exposition to gamma rays of ^{60}Co at a dose rate of 11.40Gy /min; experimental values (dots), and best-fit exponential function (solid line)**.**

This drastic decrease of DDVP concentration with the increase of radiation dose denotes that gamma radiation is efficient in degrading the DDVP. Similar results were reported by[17]. A degradation rate of 33% was observed at 0.1kGy, 65% at 0.5kGy and 99 % degradation was reached at the dose of 8kGy. The dichlorvoswas completely degraded at the dose of 10kGy.

III.3 Identification of radiolytic degradation products

The identification of radiolyticdegradation products of DDVP was done by GC-MS chromatography analysis. Figure 3 shows the chromatographic profile of DDVP solution irradiated at 4kGy. The peak of DDVP appears at retention time of 6.82min.The peaks corresponding to the retention times of 4.62min, 5.99min and 7.55min (Fig.4) were attributed to the radiolytic degradation products of DDVP.The identification program of *(National Institute of standard and Technology)* NIST, *National Bureau of Standards(*NBS) libraries have identified the radiolytic products formed with a fit value higher than 75% in all cases.The mass spectra of these products are shown on Figure 5.

Figure 4 shows the mass spectra of DDVP, with a good matching (83%) using NIST and NBS library.

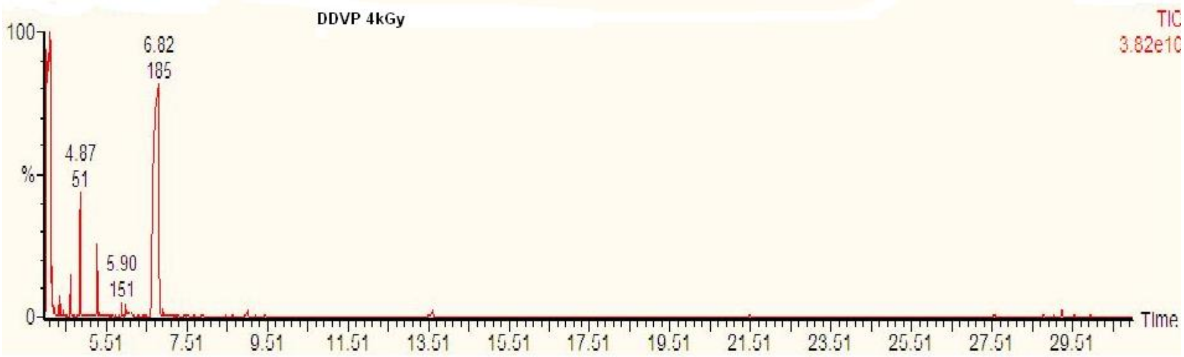


Fig.3:*GC-MS spectrum of irradiated DDVP aqueous solution at4kGy*

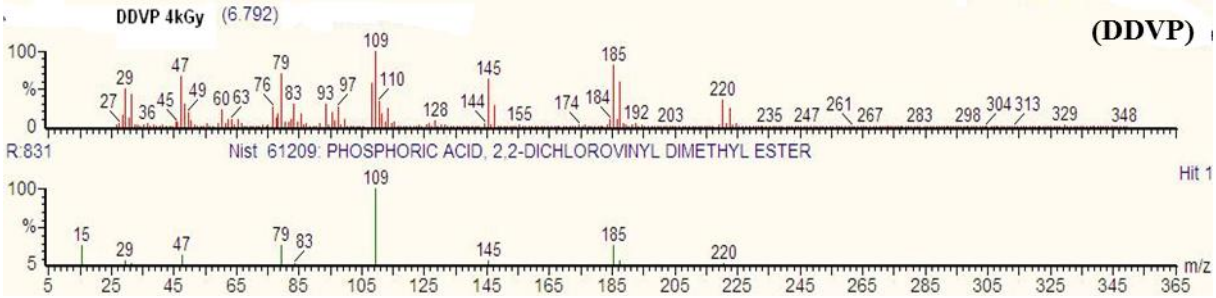


Fig.4. *GC-MS Mass spectra of DDVP*

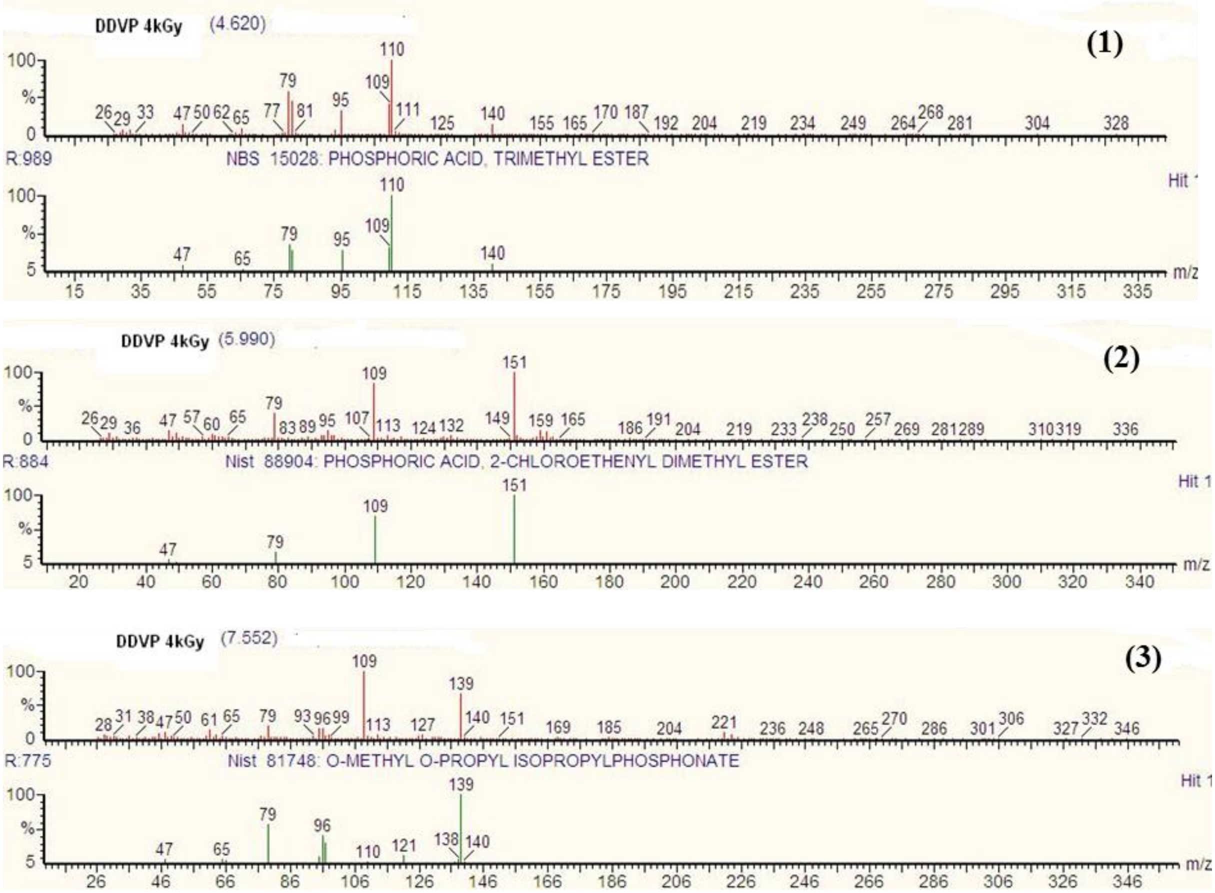


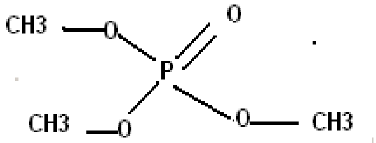
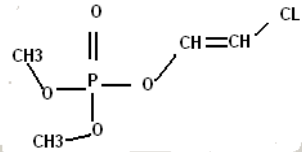
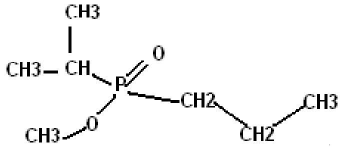
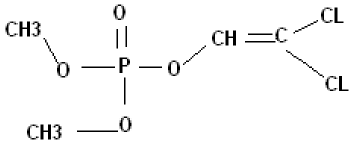
Fig 5. *Mass spectra of radiolytic decomposition of DDVP.*

Figure 5 shows the mass spectra of the radiolytic decomposition products of DDVP. The compounds identified are the (1): Phosphoric acid, trimethyl ester; (2):2, chloroethenyl dimethyl ester phosphoric acid and (3): o-methyl o-propyl isopropyl phosphonate with a good matching corresponding to 98.9% and 88.4% respectively using NIST and NBS libraries.

The identified by-products of DDVPare summarized in table 1 along with their retention times and the molecular weight.

Table 1. *Identified by-products of DDVP.1-Phosphoric acid, trimethyl ester; 2- 2,chloroethenyl dimethyl ester phosphoric acid; 3- o-methyl o-propyl isopropylphosphonate.*

Product n°	Retention time (min)	MW (m/z)	Chemical Structure

1	4.62	140	
2	5.99	186	
3	7.55	180	
DDVP	6.79	220	

III.4. Primary reactions of degradation of aqueous solution

The degradation of organic compounds in aqueous solution by gamma radiation, involves the indirect effect via water-radiolysis products, mainly the oxidative species $OH^{\bullet}$ and $O_2^{\bullet-}$[18], formed as follow [19]:

$$H_2O \rightsquigarrow e + H_2O^{\bullet+} \quad (1)$$

$$H_2O \rightsquigarrow H_2O^{*} \rightarrow H^{\bullet} + OH^{\bullet} \quad (2)$$

The hydroxyl radical $OH^{\bullet}$ is derived mainly from positive ions formed by ionization of water:

$$H_2O^{\bullet+} + H_2O \rightarrow H_3O^{+} + OH^{\bullet} \quad (3)$$

The peroxy radical $O_2^{\bullet-}$ results from the interaction of the hydrated electron $e^-_{aq}$with the oxygen dissolved in water, according to the reaction (4):

$$e^-_{(aq)} + O_2 \rightarrow O_2^{\bullet-} (4)$$

The hydrated electron e^-_{aq} results from the solvation of an electron that was ejected during ionization. The rate of degradation is related to the formation of $^{\bullet}OH$ radicals, which are the critical species in the degradation process [20]. When organic compounds are present in reaction solution, they can trap rapidly the $^{\bullet}OH$ radicals [16], leading to the production of oxidized intermediates. In the presence of air, other species might contribute to the oxidation of the organic molecules. Hydroxyl radicals ($OH^{\bullet}$), generated through water oxidation, are known to be the most oxidizing species [12].

3.5 Mechanism of Degradation of DDVP in Aqueous Solution by Gamma Irradiation

It is well known that $OH^{\bullet}$radicals react rapidly and non-selectively with organic molecules leading to the production of numerous intermediates [21].

The primary mechanism for the degradation under gamma radiation of DDVP via hydroxyl radical attack is hydrogen abstraction.

The formation of phosphoric acid trimethyl ester as a compound **(C_1)** identified on the pathway (1), exhibited $[M]^+$ ion m/z = 140 that corresponds to the loss of fragment of methyldichlorine ketone m/z = 99 [M-99] from DDVP. The **Phosphoric acid trimethyl ester** has been identified as a metabolite of a photocatalytic oxidation of DDVP elsewhere [22-23].

In the second path, the parent compound loses the chlorine ion leading to the formation of **2, chloroethenyl dimethyl ester phosphoric acid,** which was identified as the Compound **(C_2).** The loss of chlorine ion is due to the capture of the hydrated electron **($\acute{e}_{aq}$)**, which is a strong reducing agent. The carbon-chlorine bonds breaks rapidly through a dissociative electron capture process [24]. The GC-MS analysis showed the formation of $[M]^+$ ion m/z =185 that corresponds to the release of chlorine ion [M-36] from DDVP, which is a rapid process [15].

Following this, begins the third transformation which involves, thanks to the presence of hydrated electron **($\acute{e}_{aq}$)** and hydrogen radical $^{\bullet}H$, the release of the second chlorine ion from the compound**C_2.**

The GC-MS analysis showed [M_{C2}-36] with m/z =150 formed from the **2,chloroethenyl dimethyl ester phosphoric acid** identified as the Compound **C_2**, through elimination of Chlorine ion considered as the first moiety of **C_3**.

Due to the abundant concentration of $^{\bullet}$H, isopropyl group was formed by two sequential addition (pathway 3) of the radical$^{\bullet}$H on the R-CH=CH_2 first, followed by the transfer of methyl group (-$CH_3^{\bullet}$) on the unsaturated bond of the first moiety of the molecule.

Methyl and methoxy groups could come from the decomposition of molecular organic or intermediates under photocatalytic technique [25]. Then, further transformations were obtained through the loss of methoxy group (-O-CH_3) by the attack of OH$^{\bullet}$ radical. The rupture of P-OCH_3O bond results in the formation of the unsaturated ion.

The hydrogen abstraction pathway constitutes a major route for OH$^{\bullet}$ radical reaction [26]. Thus, the propyl group could be formed by simultaneous addition reaction series of hydrogen abstraction from hydroxyl radicals OH$^{\bullet}$and the transfer of methyl groups into the second moiety (pathway3) and then results in the formation of the third intermediates compound **(C_3)** identified as **o-methyl o-propyl isopropylphosphonate.**

According to the literature, the first degradation product of DDVP, the **Phosphoric acid trimethyl ester,**has been identified by [23-15].To our knowledge, the presence of the two other radiolytic products C_2 and $C_3$was not reported previously in the literature.

Based on the intermediates products identified, the possible radiation degradation pathway of DDVP in water is proposed on figure 6.

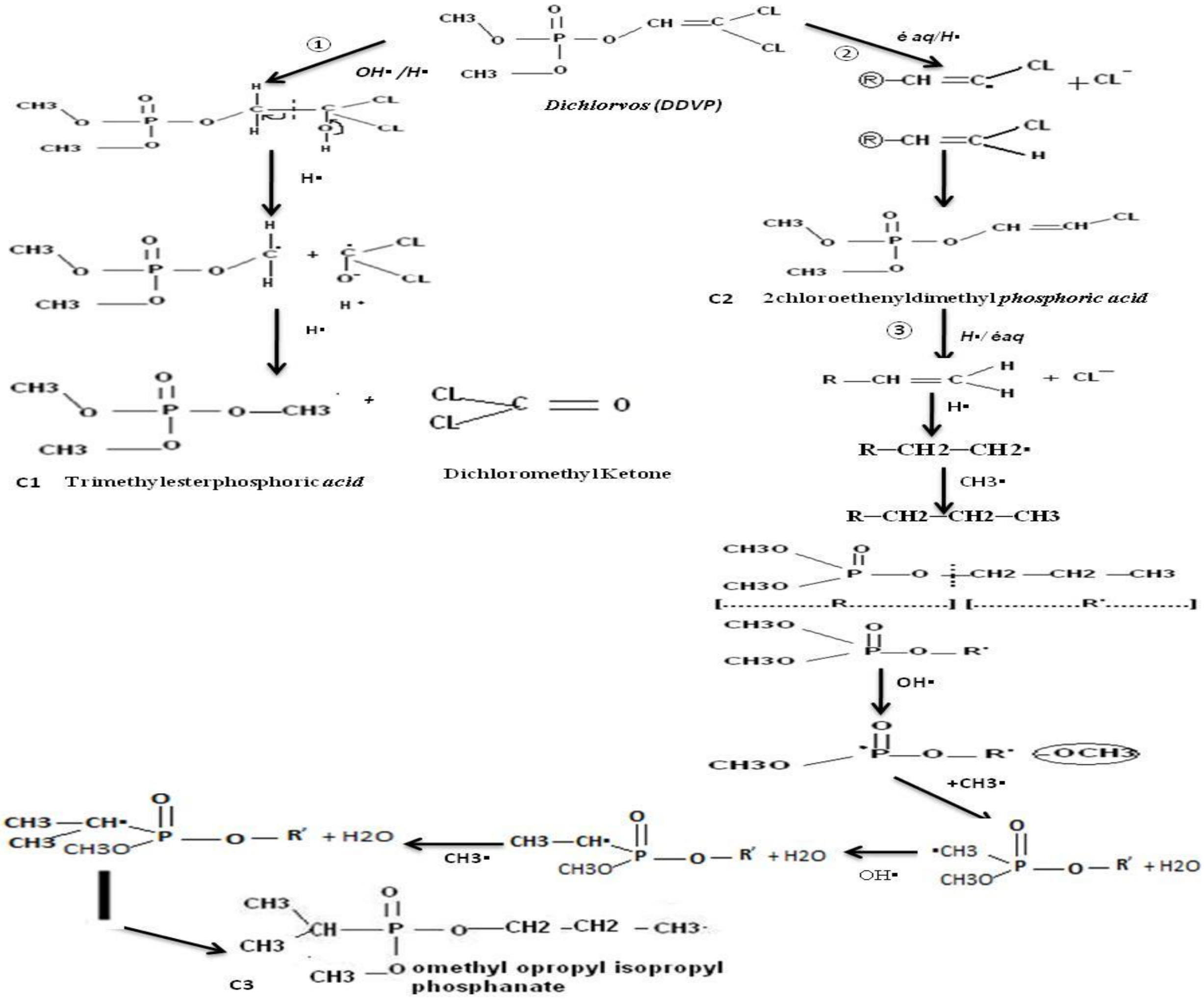


Fig.6. *Tentative reaction pathway during the degradation by gamma radiation of DDVP in aqueous solution*.

IV. Conclusion

In the present work, a solution of DDVP in aqueous solution at a concentration of 0.75g/l was exposed to a large dose range of gamma radiation. The pesticide was completely degraded at the absorbed dose of 10kGy. The results showed that the radiation process acidifies the pH of the solution. The major degradation products formed during the degradation of DDVP were identified and a reaction pathway was proposed.

HPLC analysis showed the formation of three main radiolysis products of the pesticide, which were identified by GC-MS analysis. The major by-products formed during the degradation of DDVP by gamma radiation were identified. The possible degradation pathway for DDVP in aqueous solution is also proposed in scheme. Gamma radiation has been proved to be a promising method and an alternative technique for the degradation of organic compounds.

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