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ARTICLE

Reduction of Dichlorvos and Omethoate Residues by O_2 Plasma Treatment

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A practical, inexpensive, and green chemical process is greatly needed for degrading pesticides in food and environmental water. In this work, the impact of O_2 plasma treatment on reduction of dichlorvos (DDVP) and omethoate in maize was determined by gas chromatography (GC). The main plasma-induced degradation mechanisms were investigated through identification of intermediates or products during O_2 plasma treatment for DDVP and omethoate on solid surfaces by gas chromatography/mass spectrometry (GC/MS). The results clearly demonstrate that O_2 plasma treatment is significantly effective in the degradation of original DDVP and omethoate, and the degradation efficiency mainly depends upon related operating parameters and chemical structures of pesticides. Moreover, GC/MS analyses show that DDVP and omethoate molecules are degraded into less-toxic compounds, and the plasma degradation mechanisms for pesticides can be dominated by a free-radical reaction. It is concluded that O_2 plasma has the potential to reduce pesticide residues in agricultural products.

KEYWORDS: Reduction; dichlorvos residues; omethoate residues; degradation mechanisms; O_2 plasma treatment

INTRODUCTION

Organophosphorus (OP) pesticides, a group of cholinesterase-inhibiting insecticides, have been used extensively as an alternative to organochlorine compounds in both agricultural and residential environments, and their use is expected to increase at least in the near future because of their broad spectrum of insecticidal activity and effectiveness. However, their extensive and indiscriminate use on agricultural production, postharvest, storage, and transportation may result in the presence of such pesticides ubiquitous in the diet (as residues on treated raw agricultural commodities that can be ultimately found in the human diet) and drinking water (as residues found in environmental water, such as groundwater, that can be used for drinking water sources) (*1*−*4*). Overexposure to OP pesticides had the potential to pose a health risk to adults, particularly in children, along the food-chain transfer. The toxic effects of OP pesticides including alterations in metabolism, reproduction, mutagenicity, carcinogenesis, neurotoxicity, and endocrine-disrupting effects have become a serious environmental concern as well as a public health priority (*5*−*7*). Furthermore, the fact cannot disregarded that "cocktail effects" of pesticides can lead to higher adverse effects on human health through the combined effects of multisite use of several pesticides (*8*, *9*). For these reasons, there is urgent demand in research and development of the efficient and effective reduction methods for food and environmental water polluted with OP pesticides.

The chemical oxidation processes (such as photocatalysis, ozonation, and hydrolysis), physical method (such as ultrasonic irradiation and ionizing radiation), and biological method appear to be the most popular degradation methods for OP pesticides (*10*−*15*), but their efficiency is somewhat limited or undesired because toxic compounds are sometimes formed as well. In addition, the lack of chemistry control and the failure of expeditious and complete decomposition and detoxification of trace pesticides have been a major hurdle to overcome. To resolve these challenges, nonthermal plasmas (NTPs) as an innovative tool have been proven to be effective for the degradation of OP molecules in some literature (*16*−*21*). The main characteristic of NTPs is its high electron temperatures (10^5 K); i.e., the electrons are preferentially excited with the energies of 1−10 eV, whereas the bulk gas (contained the more massive reactive species) temperature remains at ambient temperature. Therefore, a significant energy savings can be realized. In general, most covalent bond energy equals 3−6 eV. As such, this energy-savings potential is a primary reason why most organic molecules can easily be destroyed by NTPs, in which high-energy electrons collide with the molecules of the background gas or pollutants, and secondary electrons and highly reactive species were produced by mechanisms of ionization, excitation, and dissociation (*22*). As a result, NTPs are good sources of highly reactive species and plasma electrons that are capable of reacting with and decomposing chemical pollutants to yield safer products. Similarly, under selective experimental conditions when OP pesticide molecules

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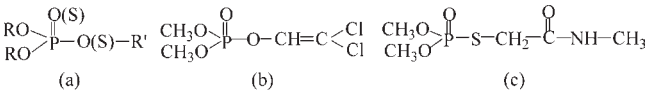

Figure 1. Chemical structures of the (a) general structure of OP pesticide, (b) DDVP (phosphate ester pesticide), and (c) omethoate (phosphorothioic acid ester pesticide).

are exposed to O_2 plasma, high-energy electrons generated from plasma provide sufficient energy to dissociate the molecules of the feed gas or OP pesticide, produce free radicals (e.g., ·O and ·OH) and excited-species-initiated chemical reactions, which are normally not able to occur at low temperatures, and then promote various desired conversions of OP pesticides to liberate unharmful or less hazardous compounds. In addition, UV and irradiate light derived from NTPs may also enhance the degradation efficiency of OP pesticides. When the OP pesticide absorbs UV light, it can be degraded through bond scissions or oxidations that take place in its electronically excited states. Therefore, a combination of physical and chemical unit processes of NTPs is very attractive and actually employed to ensure the reduction of OP pesticide residues. However, no literature was found in examining the degradation efficiency of OP pesticides in agricultural products by O_2 plasma.

OP pesticides are still widely used in China and the rest of the world, where the conditions of use have raised concerns. Around 10 000 tons of DDVP and 8000 tons of omethoate are applied annually to agricultural crops in China. DDVP is the common name of an *O*-2,2-dichlorovinyl-*O*,*O*-dimethyl phosphate, with the molecule formula of $C_4H_7Cl_2O_4P$, molecule mass of M = 220.98 g mol^{-1}, and CAS registry number 62-73-7. In animal studies, the acute oral LD_{50} in rats is between 56 and 80 mg/kg and its acceptable daily intake (ADI) is 0.004 mg kg^{-1} day^{-1}. Recently, it has been reported that exposure to DDVP affects glucose metabolism and produces hyperglycemia (*7*). Omethoate is a phosphorothioic acid ester, with the International Union of Pure and Applied Chemistry (IUPAC) name of *O*,*O*-dimethyl-*S*-methyl-carbamoyl-methylthiophosphate, the molecule formula of $C_5H_{12}NO_4PS$, molecule mass of M = 213.2 g mol^{-1}, and CAS registry number 1113-02-6. The oral LD_{50} of omethoate in rats is approximately 50 mg/kg of body weight, and its acceptable daily intake (ADI) is 0.0003 mg kg^{-1} day^{-1}. As a metabolite of dimethoate (the use of dimethoate on crops can lead to residues of omethoate in treated produce), omethoate has clear mutagenic potential and allergic disorders (*9*). The chemical structures of DDVP and omethoate are listed in **Figure 1**.

The objective of this study was to investigate whether DDVP and omethoate could be degraded by O_2 plasma treatment. DDVP and omethoate were employed as the target pesticides because of their extensive use in China. This work focused on examining the degradation effectiveness of DDVP and omethoate in maize subject to the influence of various O_2 plasma-operating parameter factors by gas chromatography (GC) analysis. To clarify the major plasma degradation reactions as well as degradation mechanisms, O_2 plasma was applied to perform the degradation of DDVP and omethoate on solid substrates. Identification of the formation of intermediates and products after plasma treatment was also analyzed by gas chromatography/mass spectrometry (GC/MS). To the best of our knowledge, this is the first time to study the reduction of OP pesticides by O_2 plasma and reveal the chemical reaction and plasma degradation mechanisms for OP pesticides. As such, this work has scientific significance for crop protection and other practical applications involving agricultural and food chemistry.

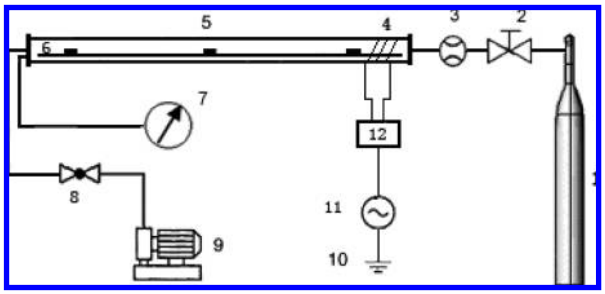

Figure 2. Schematic diagram of the plasma reactor: (1) gas bottle, (2) valve, (3) mass flow meter, (4) inductance coil, (5) reaction chamber, (6) sample, (7) vacuum gauge, (8) electromagnetism valve, (9) vacuum pump, (10) grounding protection, (11) rf generator, and (12) matching system.

MATERIALS AND METHODS

Reagents and Materials. DDVP and omethoate standard (99.0−99.5% purity) were provided by the Institute of Environmental Protection and Monitoring, Ministry of Agriculture of China. The stock solutions of DDVP and omethoate were prepared in acetone at a concentration of 100 μg/mL. The solutions, stored in the dark and in the refrigerator at 4 °C, were used no more than 12 h after they were made to ensure that no degradation occurred prior to O_2 plasma treatment. DDVP purchased from the Hubei Shalongda Chemical Co. with a purity of 80% and omethoate purchased from Hebei Chemical Co. with a purity of 40% were employed for simulation to maize. All organic solvents were purchased from Xi'an Chemical Co. and redistilled before using. Maize was purchased from a local market.

Plasma Generator. **Figure 2** shows the schematic diagram of the plasma treatment system employed in this research. It consists of four parts: gas inlet, reaction chamber, vacuum pump, and power supply (SY-500W, 13.56 MHz) and matching network (SP-II matcher), which are made by the Science Academy of China. The reaction chamber is a cylindrical Pyrex glass tube (1000 mm in length and 45 mm in diameter), where inductively coupled radio-frequency (rf) discharge is initiated.

Pesticide Degradation Procedures. In the plasma degradation of the pesticide test series, the central design was applied to determine the degradation efficiency of pesticide residues and to evaluate the effects of plasma factors on the reduction of pesticides in maize. First, maize purchased from market was randomly selected and fortified with DDVP and omethoate aqueous solution at normal farm concentration by spray. Then, the maize samples were dried at room temperature for 24 h and positioned onto a glass plate (100 × 35 mm) at the distance of 20 cm (discharge zone), 45 cm (afterglow zone), and 70 cm (remote zone) from the center of the induction coil in the Pyrex glass tube of the reactor. Afterward, the maize samples were exposed to O_2 oxygen plasma for treatment times of 30, 60, 90, and 120 s at discharge power levels of 30, 60, 90, and 120 W with different O_2 flux. Each maize sample was withdrawn from the plasma reaction chamber immediately after plasma treatment. The extraction of pesticide residues were carried out according to a standard method of grains established by the Ministry of Agriculture of China (GB/T19649-2005), with some modifications. DDVP and omethoate residues in maize with different plasma treatment conditions were detected and quantified using GC analyses.

In the second series, to clarify the plasma degradation mechanisms for pesticides, the DDVP and omethoate standard solutions at a concentration of 100 μg/mL were spin-coated onto glass slides (20 × 20 mm). The glass slides were positioned on a glass plate (100 × 35 mm) at the distance of 20 cm (discharge zone), 45 cm (afterglow zone), and 70 cm (remote zone) from the center of the induction coil in the Pyrex glass tube of the reactor. Then, the samples were exposed to O_2 oxygen plasma at the optimal plasma degradation condition based on the previous investigation. After plasma treatment, each sample was withdrawn from the plasma reaction chamber immediately and dissolved in an ultrasonic bath of acetone for 5 min, with a metered volume at 2.0 mL for GC/MS analyses. Additionally, the well-known radical scavenger, *tert*-butanol, was used to evaluate the role of radicals derived from O_2 plasma on the degradation of

Table 1. Mean Recovery and Relative Standard Deviation (RSD) for Pesticides Fortified in the Maize Sample at Various Fortification Levels (n = 6)

pesticides	concentration (μg/mL)	recovery (%)	RSD (%)
DDVP	0.1	98	2.8
	1.0	102	3.3
	10.0	103	3.1
omethoate	0.1	91	3.9
	1.0	92	2.7
	10.0	89	1.5

pesticides. At the same conditions, 100 μL of *tert*-butanol was coated onto the glass slides (20 × 20 mm), which was parallel to the corresponding glass slides, with pesticide samples in the same glass plate. They were then exposed to O_2 oxygen plasma. The degradation efficiency of plasma treatment alone was compared to *tert*-butanol + plasma treatment to estimate the contribution of the radicals generated in O_2 plasma. Each sample was manipulated 3 times to ensure the reproducibility. Identification of intermediates and products as well as the pesticide residues were detected by GC/MS and GC, respectively.

Chromatographic Analyses. DDVP and omethoate residues were detected and quantified using a shimadzu-2010 gas chromatograph (GC) equipped with a flame photometric detector (FPD). GC conditions: RTX-225 high-performance capillary columns of 30 m × 0.32 mm × 0.25 μm. The rate of the temperature rise is 70 °C (1 min) → 30 °C/min → 170 °C (3 min) → 4 °C/min → 225 °C → 25 °C/min → 250 °C (1 min). Injector and detector temperatures were 250 and 280 °C, respectively. Nitrogen was used as the GC carrier gas, and gas flow through the column was 80 mL/min. Sample solution (2.0 μL) was injected in a split ratio of 1:10, and the quantification of pesticide was performed using an external standard. Each sample was injected twice during GC analysis to monitor the reproducibility. The degradation efficiency of OP pesticides was described with the remaining fraction by calculating the ratio of the pesticide concentration at a given time (C_t) to the initial one (C_0) prior to plasma treatment. The remaining fraction η was calculated from the equation as follow:$\eta = \frac{C_t}{C_0} \times 100\%$.

The intermediates or products formed during plasma degradation of OP pesticides are determined by GC/MS. GC/MS analyses were performed on an Agilent Technologies 6890 gas chromatograph, equipped with a HP-5MS column (30 m × 0.25 mm inner diameter × 0.25 μm) coated with 5% phenyl/95% methylpoly siloxane, coupled to a MSD 5973 selective mass detector (Agilent Technologies). The oven temperature program is 60 °C (held for 2 min) ramped at 20 °C/min to 270 °C (held for 5 min); the injector port temperature was 150 °C. Helium was used as a carrier gas at a flow of 1 mL/min. The temperatures of the ion source and interface were set at 230 and 280 °C, respectively. A 1.0 μL sample was injected for detection, and a split ratio of 1:10 was used. MS conditions: electron energy, 70 eV; collect current, 300 μA; source temperature, 150 °C. Identification and confirmation of the pesticides were based on their GC retention times and a comparison of their sample mass spectrum to the characteristic ions in the standard mass spectra.

Recovery Experiments and Detection Limits. Maize samples were fortified at 0.1, 1.0, and 10.0 μg/mL, respectively, by adding DDVP and omethoate pesticides. The recovery assays were replicated 6 times, and the data are presented in **Table 1**. The limits of detection (LODs) for DDVP and omethoate, by considering a signal-to-noise (S/N) ratio of 3, were determined to be 0.005 and 0.011 mg/L, respectively. The quantity of each OP was calculated with the use of the external standard method.

Statistical Analysis and Quality Assurance. Quality control and quality assurance measures were incorporated in the analytical scheme. In this study, the effects of variable plasma treatment conditions including different discharge power, plasma treatment time, and variance distance from the induction coil on the degradation of DDVP and omethoate were designed on the basis of the preliminary orthogonal experiment. Each sample was analyzed 3 times to ensure reproducibility. To determine whether the differences between plasma treatment conditions influenced the degradation efficiency and the differences between DDVP and omethoate were statistically significant, a one-way analysis of variance (ANOVA) test was performed by Statistical Package for the Social Sciences (SPSS, version 13.0). When significant differences were found at a 95% confidence level ($p < 0.05$), the least significant difference (LSD) test was performed among means.

RESULTS AND DISCUSSION

Degradation of DDVP Residues in Maize at Different O_2 Plasma Treatment Conditions. To evaluate reduction efficiency of DDVP residues in maize under different O_2 plasma treatment conditions, the samples were positioned at the distance of 20 cm (discharge zone), 45 cm (afterglow zone), and 70 cm (remote zone) from the center of the induction coil in the Pyrex glass tube of the reactor. Then, they were exposed to the O_2 plasma for treatment times of 30, 60, 90, and 120 s at discharge power levels of 30, 60, 90, and 120 W with difference O_2 flux. The reduction efficiency of DDVP by the O_2 plasma was investigated from the remaining fraction as a function of the treatment time, discharge power, and O_2 flux, respectively.

Effects of the Treatment Time on the Reduction of DDVP in Maize. The diagram of the remaining fraction of DDVP residues in maize at the distance of 20 cm (discharge zone), 45 cm (afterglow zone), and 70 cm (remote zone) as a function of the treatment time is plotted in **Figure 3a**. It can be noticed that the remaining fraction of DDVP decreases sharply with an increasing plasma treatment time up to 120 s, regardless of the sample position. This indicates that the treatment time is the most influential parameter and the longer treatment time can speed up the reduction efficiency of pesticide. Almost 90% of the initial amounts of DDVP is removed after 120 s in the discharge zone. Furthermore, treatment in the discharge zone shows noticeable effects compared to those in the afterglow and remote zones with statistical significance ($p < 0.05$). It is anticipated that DDVP residue levels would be reduced considerably by O_2 plasma treatment and the interaction between the pesticide molecule and active species has almost completed within 120 s.

Effects of the Discharge Power on the Reduction of DDVP in Maize. The remaining fraction of DDVP residues versus discharge power at the above-mentioned distances is shown in **Figure 3b**. It is interesting to mention the diminution of its degradation as the discharge power varies from 30 to 60 W. Further increasing the discharge power enhances degradation of DDVP, and then it tends to remain stable beyond 90 W; i.e., the degradation efficiency of 120 W is the greatest in the discharge zone, whereas the degradation efficiency of 60 W was the lowest in the remote zone. Therefore, the degradation efficiency appears to undulate with an increasing discharge power. ANOVA analysis also indicates that removal efficiency of DDVP is significantly effective in discharge power by O_2 plasma treatment conducted at 30, 90, and 120 W than at 60 W with statistical significance ($p < 0.05$) but not in the case of 30 and 90 W, 30 and 120 W, and 90 and 120 W ($p > 0.05$). At this point, the result agrees well with our previous experimental results about the distribution of electrons, ions, and oxygen radicals in O_2 plasma. In our previous experiment (*23*), across all power levels, we observed a similar trend for all created active species between density and power. When the discharge power ranges from 0 to 30 W, the electron energy is increased to remain in the peak values of 11.0 eV in the discharge zone, whereas it declined from 30 to 60 W because of colliding with each other, and then it is augmented rapidly above 60 W. As a result, the discharge power ranges from 0 to 30 W and leads to the enhancement of the possibility for the pesticide molecule to experience the dissociation by collision with electrons and the probability of reactions between them is also promoted. When the discharge power varies from 30 to 60 W, electrons cannot carry the necessary energy to perform a dissociation collision because of their relatively high recombination rate; consequently, the

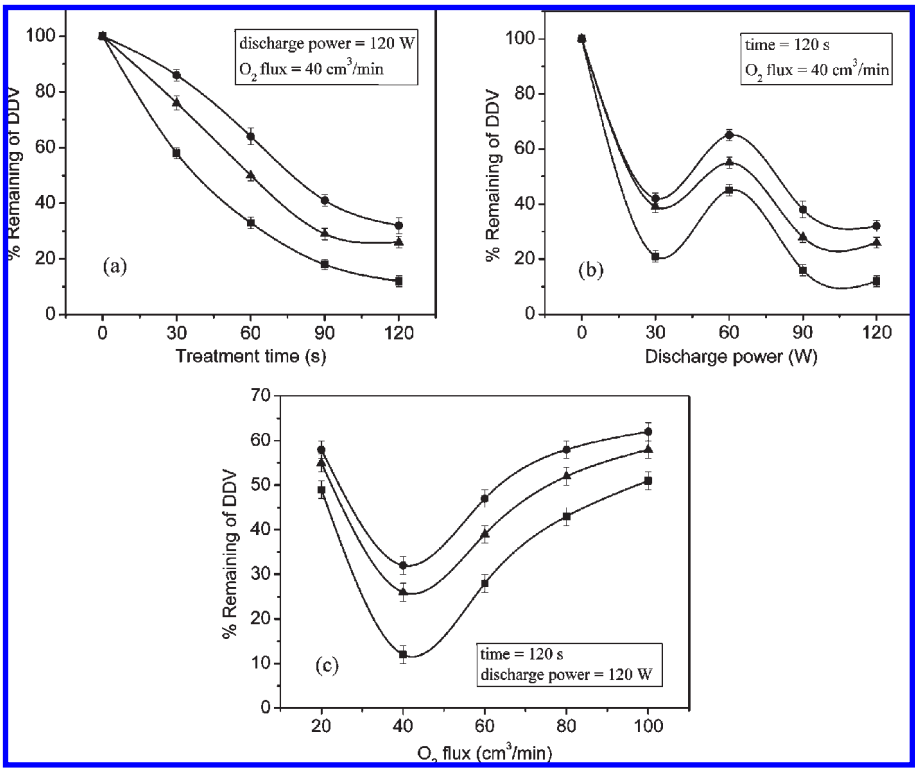

Figure 3. Effects of (a) treatment time, (b) discharge power, and (c) O_2 flux on the reduction of DDVP in maize at the (■) discharge zone, (▲) afterglow zone, and (●) remote zone. Error bars are standard deviations of three replicates.

average energy of mass of active species (secondary electrons and radicals) is declined as well as the probability of degradation reactions. As the discharge power further increased, the average energy of electrons is increased because the increase of the discharge power can extend the action sphere of the plasma inner electronic field. Besides high-energy electrons directly providing energy to pesticide molecules, they can provide energy to feed gas (O_2) to form a large number of free radicals, such as oxygen radicals, which are considered highly active and instable and can also react with pesticide molecules through the free-radical reaction. The initial concentration of ·O radicals is the highest in the discharge zone and decreased with the increase of the distance to the remote zone. It implies that the contact area between pesticide- and plasma-active species increases as well as the reaction probability. According to the above results, it can be concluded that the treatment time and discharge power are both important factors for the reduction of DDVP and the optimum O_2 plasma treatment conditions are 120 W after 120 s of treatment time to obtain the best reduction of DDVP residues in maize. Therefore, for the subsequent investigation of effects of O_2 flux on the removal of DDVP, two plasma treatment conditions are fixed.

Effects of O_2 Flux on the Reduction of DDVP in Maize. **Figure 3c** displays the remaining fraction of DDVP as a function of O_2 flux. As shown in **Figure 3c**, it is obvious that the reduction efficiency increased initially but decreased later with the increase of O_2 flux. The results can be explained by the fact that the constant energy is obtained in the reaction system, when the discharge power and treatment time are fixed. Thus, the different effects can be related to the average energy of reaction species, which increases with the enhancement of the O_2 flux in the range of 20−40 cm^3/min, and subsequently, different drawdown appears (40−100 cm^3/min). O_2 flux at 40 cm^3/min was shown to be a more noticeable plasma degradation efficiency of DDVP than other flux with statistical significance ($p < 0.05$); however, there was no significant difference with the O_2 flux in the case of 20 cm^3/min and 60, 80, and 100 cm^3/min ($p > 0.05$). For the same reason, at low O_2 flux, the number of active species colliding with the pesticide molecule is less than that at high flux, whereas the average energy of reaction species is higher than that at high flux. As a result, the probability of each reaction species colliding with the pesticide molecule increases; therefore, degradation increases. Similarly, at high O_2 flux exceeding 40 cm^3/min, the concentration of reaction species is large but the average energy and residence time are relatively low; therefore, the action on pesticide molecules is comparatively weak. Consequently, when O_2 flux is changed, while other conditions are fixed, the action on pesticide molecules is the combining effects of the average energy and the amount of reaction species and their residence time.

Degradation of Omethoate Residues in Maize at Different O_2 Plasma Treatment Conditions. The second phase of this work was to evaluate reduction efficiency of omethoate residues in maize under different O_2 plasma treatment conditions and compare the differences with DDVP. The samples were positioned at the distance of 20 cm (discharge zone), 45 cm (afterglow zone), and 70 cm (remote zone) from the center of the induction coil in the Pyrex glass tube of the reactor, and they were also exposed to the O_2 plasma for treatment times of 30, 60, 90, and 120 s at discharge power levels of 30, 60, 90, and 120 W with different O_2 flux. Similarly, the reduction efficiency of omethoate by the O_2 plasma was investigated from the remaining fraction as a function of the above-mentioned operating parameters.

Effects of the Treatment Time on the Reduction of Omethoate in Maize. The disappearance of omethoate residues in maize at the above-mentioned distance versus time is plotted in **Figure 4a**. A similar trend is observed with omethoate to those found in DDVP in this study. The reduction efficiency of omethoate was increased as the treatment time increased at all distances. In O_2 plasma treatment at the distance of 20 cm (discharge zone), almost 95% of omethoate is removed after

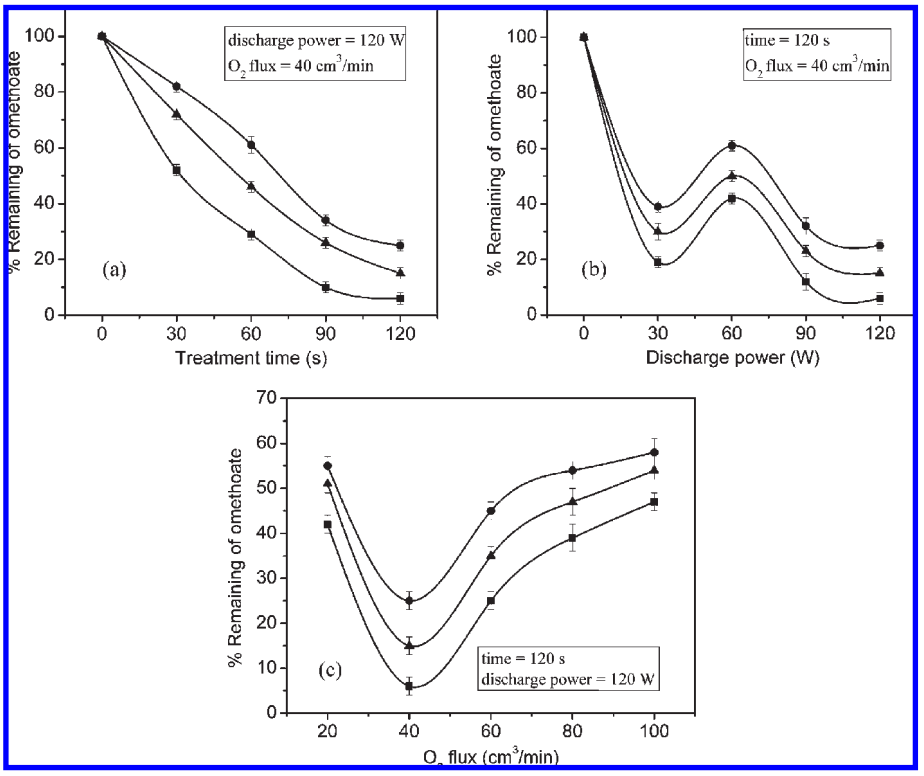

Figure 4. Effects of (a) treatment time, (b) discharge power, and (c) O_2 flux on the reduction of omethoate in maize at the (■) discharge zone, (▲) afterglow zone, and (●) remote zone. Error bars are standard deviations of three replicates.

120 s, whereas it is reduced only about 19% at the distance of 70 cm (remote zone) after 30 s. Clearly, the longer plasma treatment time can also help improve reduction efficiency of omethoate, and the interaction between pesticide and active species has almost completed within 120 s. However, treatment in the discharge zone is notably effective compared to those in the afterglow and remote zones with statistical significance ($p < 0.05$). This is most likely due to a higher intensity of reactive species (electrons, ions, radicals, etc.) in the discharge zone than that in the afterglow and remote zones.

Effects of the Discharge Power on the Reduction of Omethoate in Maize. **Figure 4b** displays the variation in the remaining fraction of omethoate in maize over the discharge power at the mentioned distance. It can be seen that increased discharge power cause a degradation of omethoate over 60 W, whereas a different trend is observed between 0 and 30 W regardless of the sample position. The degradation of omethoate of 120 W discharge power in the discharge zone is the greatest, whereas 60 W in the remote zone is the least effective. The different effects can be related to the average energy of reaction species increasing with the enhancement of the discharge power in the range for 0−30 W, and subsequently, a different fall trend appears (30−60 W). Over 90 W, the probability of each reaction species colliding with pesticide enhances; therefore, degradation increases. It is anticipated that residue levels would be reduced considerably by the O_2 plasma treatment if the discharge power is increased beyond 60 W. Moreover, ANOVA results indicate that reduction efficiency of omethoate by the O_2 plasma process is significantly effective in discharge power treatments conducted at 30, 90, and 120 W than 60 W with statistical significance ($p < 0.05$) but not in the case of 30 and 90 W, 30 and 120 W, and 90 and 120 W ($p > 0.05$). Therefore, the optimum plasma treatment conditions for the reduction of omethoate is also at 120 W discharge power and 120 s treatment time. The subsequent investigation should be taken under the optimum plasma treatment conditions.

Effects of O_2 Flux on the Reduction of Omethoate in Maize. The remaining fraction of omethoate residues versus O_2 flux at the above-mentioned distances is presented in **Figure 4c**. The degradation increases initially but decreases later with increasing O_2 flux. As the same reason in the previous discussion, at low O_2 flux, the average energy and residence time of reaction species are higher than that at high flux; thus, the probability of each reaction species colliding with pesticide enhances, and therefore, degradation increases. At higher O_2 flux over 40 cm^3/min, the number of reaction species is large but the average energy and residence time is lower; therefore, the action on pesticide is relatively small. The result shows more noticeable plasma reduction efficiency of omethoate at O_2 flux of 40 cm^3/min compared to others ($p < 0.05$) but no significant difference in the case of 20 cm^3/min and 60, 80, and 100 cm^3/min of O_2 flux ($p > 0.05$).

Comparison of the Effects of Distance on the Degradation of DDVP and Omethoate in Maize. The degradation fraction of DDVP and omethoate residues in maize versus the distance is plotted in **Figure 5**. The results indicate that O_2 plasma degradation of DDVP and omethoate in the discharge zone are more effective with 88 and 94% degradation fraction, respectively, compared to those in afterglow and remote zones ($p < 0.05$). This can be explained by the fact that the intensities of various species including electrons, ions, and free radicals are decreased with the increase of the distance far from the discharge zone. Furthermore, the degradation behavior of DDVP and omethoate appears to differ. Besides plasma treatment parameters, the chemical structure of pesticide is the dominant factor for the persistence because it influences the chemical stability during the degradation reaction. The results also indicate that the reduction of omethoate shows higher effects than that of DDVP during O_2 plasma treatment in all distances with statistical significance ($p < 0.05$). This is probably due to the fact that S of the P−S bond in the omethoate molecule possessing smaller electronegativity than O of P−O in the DDVP molecule results in a difference activity of

reaction initiated by the electron attacking the P atom. Moreover, the bond energy of P−S is less than that of the P−O bond. According to the above results, it is clearly demonstrated that O_2 plasma treatment is significantly effective in the degradation of original DDVP as well as omethoate in maize. Furthermore, the interaction between active species and the omethoate molecule is more effect than that of the DDVP molecule. Notwithstanding, we cannot ignore the fact that, besides degrading pesticides, a certain amount of DDVP and omothoate on the surface of maize can be reduced by evaporation during O_2 plasma treatment.

Identification of Intermediates and Possible Degradation Mechanisms. When a new treatment process is considered, not only the reduction of the target compound is of interest but also the formation of reaction byproducts and degradation of mechanisms are of great importance. The optimum pesticide degradation of plasma treatment conditions (120 W discharge power, 120 s treatment time, and 40 cm^3/min oxygen flux) was taken to provide a favorable condition for identification and evolution of degradation intermediates. DDVP and omethoate spin-coated on glass slides (20×20 mm) were exposed to the O_2 oxygen plasma at the optimal plasma degradation conditions. After plasma treatment, identification of intermediates and products of detailed GC/MS analysis was performed in this research. **Table 2** displays GC/MS data of the identification of intermediates and products of DDVP and omethoate along with their retention times and the characteristic ions of the mass spectra. Three byproducts for DDVP and four byproducts for omethoate have been identified as possible degradation intermediates using GC/MS.

From **Table 2**, C_1, C_2, and C_3 were detected as O_2 plasma degradation intermediates of DDVP and C_1, C_3, C_5, and C_7 were detected as those of omethoate. C_1 was identified as *O*,*O*-dimethyl phosphonic ester, with more than 90% matching.

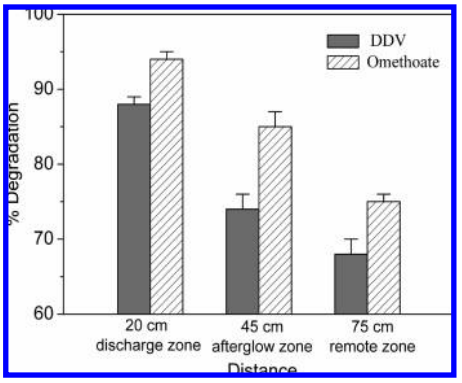

Figure 5. Comparison of effects of the distance on degradation of DDVP and omethoate in maize. Applied treatment time, 120 s; discharge power, 120 W; O_2 flux, 40 cm^3/min. Error bars are standard deviations of three replicates.

The ions at *m*/*z* 109 and 79 are characteristic of the phosphate esters and belong to the groups $[(CH_3O)_2P(O)]^+$ and $[CH_3O-P-OH]^+$, respectively. C_2 was identified as 2,2-dichlorovinyl *O*-methylphosphate with more than 70% matching and exhibited the $[M]^+$ ion at *m*/*z* 207 that corresponds to the loss of a methyl group (M-14) from DDVP and the characteristic ions of $[CH_3OP(OH)_2]^+$, $[CH_3OP(O)OH]^+$, $[CH_3O-P-OH]^+$, $[P(OH)_2]^+$, and $[OP-OH]^+$ at *m*/*z* 96, 95, 79, 65, and 64, respectively. C_3 was identified as *O*,*O*,*O*-trimethyl phosphoric ester with more than 70% matching and exhibited the $[M]^+$ ion at *m*/*z* 140, 110, 95, and 79 that belong to the groups $[(CH_3O)_3P(O)]^+$, $[(CH_3O)_2P(OH)]^+$, $[CH_3OP(O)OH]^+$, and $[CH_3O-P-OH]^+$, respectively. As shown in **Table 2**, omethoate was mainly converted into C_1 and C_3, just like in the case of DDVP. C_5 and C_7 were also detected in the O_2 plasma degradation of omethoate. C_5 was identified as *O*,*O*,*S*-trimethylphosphorothiate and exhibited the $[M]^+$ ion at *m*/*z* 156, 141, 126, 110, 95, and 79. C_7 was identified as *N*-methyl-2-sulfanylacetamide and exhibits a peak at *m*/*z* 105, which corresponds to the molecular ion $[M]^+$, and the characteristic ions at *m*/*z* 73 and 58 that correspond to the loss of HS− and $HSCH_2$− fragments, respectively.

On the basis of the distribution of intermediates by the aid of GC/MS analyses, theory of organic chemical mechanisms, and bond energies (*24*) (**Table 3**), we propose the possible O_2 plasma degradation mechanisms for DDVP and omethoate. It can be seen from panels **a** and **b** of **Figure 6** that the dominated O_2 plasma degradation mechanisms for DDVP and omethoate are free-radical-reaction-initiated through (i) one-electron transfers to the π bond within either P═O or C═C (pathway I) and (ii) free-radical attacks to pesticide molecules (pathway II). It is interesting to notice that C_1 and C_3 are identified as intermediates during O_2 plasma degradation of DDVP and omethoate, and they are also detected as identified intermediates during advanced oxidation of various OP pesticides (*25*−*28*). The formations of C_1 and C_3 because of the cleavage of either the P−O or P−S bonds resulting in several intermediates are proposed to arise by attack of one electron, followed by various radicals, such as hydroxyl and methyl radicals. C_2 as another intermediate of O_2 plasma degradation of the DDVP molecule is formed through the carbon atom of the methoxy group attacked by the hydroxyl radical, followed by the elimination of the methoxy group. The complete mineralization of DDVP degradation by O_2 plasmas produces PO_4^{3-}, CO_2, Cl^-, etc. Consider the omethoate molecule, the scission of the P−S bond leads to the formation of $\cdot SCH_2C(O)NHCH_3$ radicals that are the precursor of C_1 and C_7. Cleavage of the C−S bonds followed by the rearrangement of methyl radical is evident from the detections of C_5. Continuous cleavage of the P−S bond within the C_5 molecule, followed by adding the methoxy group could lead to the formation of C_1 and C_3. C_5 and C_7 are also identified as main intermediates of the degradation of dimethoate (*25*). Hydrogen sulphide, although not detectable for omethoate, is proposed as one of the possible

Table 2. GC/MS Retention Times (R_t) and Special Characteristics of DDVP and Omethoate Identified Intermediates

	pesticide/intermediate	R_t (min)	characteristic ions (*m*/*z*)
DDVP	C_1, *O*,*O*-dimethyl phosphonic ester	3.82	109, 95, 80, 79
	C_2, 2,2-dichlorovinyl *O*-methylphosphate	4.73	207, 96, 95, 79, 65, 64
	C_3, *O*,*O*,*O*-trimethyl phosphoric ester	5.12	140, 110, 95, 79
	C_4, DDVP	8.02	220, 185, 145, 109, 79
omethoate	C_1, *O*,*O*-dimethyl phosphonic ester	3.78	109, 95, 80, 79
	C_3, *O*,*O*,*O*-trimethyl phosphoric ester	4.64	140, 110, 95, 79
	C_5, *O*,*O*,*S*-trimethylphosphorothiate	5.60	156, 141, 126, 110, 95, 79
	C_6, omethoate	9.62	213, 156, 141, 126, 110, 79, 58
	C_7, *N*-methyl-2-sulfanylacetamide	9.87	105, 73, 58

Table 3. Average Bond Energies (KJ/mol, 298.15 K, 100 kPa)

bond	bond energy	bond	bond energy
C−H	414	P−O	502
C−O	351	P═O	755
C−C	347	P−H	318
C═C	620	P−S	230
C−Cl	331	P−C	264
O−H	460	S−C	289

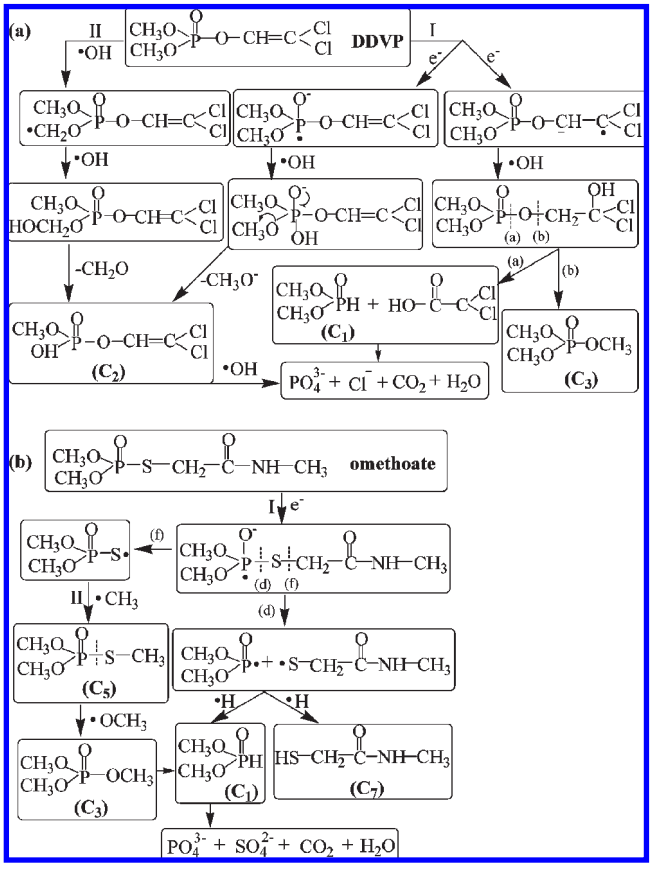

Figure 6. Potential degradation pathways of (a) DDVP and (b) omethoate during O_2 plasma treatment.

intermediates that can be further transformed to sulfate. Finally, this can proceed to form PO_4^{3-}, H_2S, SO_4^{2-}, CO_2, Cl^-, etc. Therefore, the relative significance of the C−O or C−S cleavage versus P−O or P−S cleavage depends upon not only energies provided by reactive species derived from O_2 plasma but also the nature of the leaving group during plasma degradation processing. In short, the key step for plasma degradation is that high-energy electrons can provide enough energy to cleave chemical bonds by reacting with feed O_2 gas or OP pesticide molecules to form high intensities of various free radicals initiated by the free-radical chain reaction, and then OP pesticides are decomposed ultimately to form a series of less toxic molecules than parent pesticide molecules.

To verify the important role of the free radicals in O_2 plasma degradation of DDVP and omethoate, a well-known radical scavenger, i.e., *tert*-butanol, was employed (*29*). **Figure 7** shows the comparison of effects on the degradation of OP pesticides (DDVP and omethoate) by O_2 plasma alone and O_2 plasma + *tert*-butanol. Decreased degradation of DDVP and omethoate are demonstrated by the presence of *tert*-butanol. As shown in **Figure 7**, a significant decrease of the degradation fractions of DDVP and omethoate is observed in the presence of *tert*-butanol

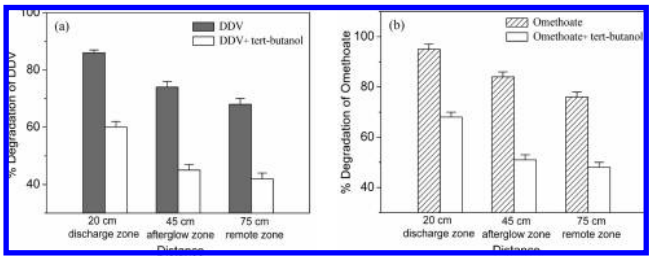

Figure 7. Comparison of effects on the degradation of DDVP and omethoate by O_2 plasma alone and O_2 plasma + *tert*-butanol. Applied treatment time, 120 s; discharge power, 120 W; O_2 flux, 40 cm^3/min. Error bars are standard deviations of three replicates.

compared to that in the absence of it during O_2 plasma treatment ($p < 0.05$) and the O_2 plasma degradation efficiency is greatly retarded with the distance far from the discharge zone. This is probably due to *tert*-butanol molecules scavenging the radicals formed in O_2 plasma when OP pesticides are exposed to O_2 plasma in the presence of *tert*-butanol. Accordingly, this radical scavenger could diminish the degradation reaction between the radicals and OP pesticide molecules. In this case, the result is similar to that in our previous study, in which the intensities of electrons decreased quickly, but those of radicals declined slowly from the discharge zone to the remote zone. When *tert*-butanol molecules are added to the OP pesticides treated by O_2 plasma processing, they can scavenge radicals derived from O_2 plasma and lead to a slow down of the degradation reaction between these radicals and OP pesticide molecules. These results can be reasonably inferred that O_2 plasma degradation mechanisms of OP pesticides are dominated by the free-radical mechanisms. Therefore, it is believed that O_2 plasma degradation of DDVP and omethoate through the formation of intermediates, followed by the generation of radicals, induces pesticide molecules to decompose into small ones. However, to draw a more detailed plasma degradation mechanism for these pesticides, further points are still needed to be clarified.

From what has been mentioned above, we can come to the conclusion that the plasma-induced degradation reactions of DDVP and omethoate molecules are demonstrated in this study. Our results indicate that O_2 plasma is capable of degrading DDVP and omethoate residues completely in maize in a very short exposure time and the optimum plasma treatment conditions for the reduction of these two widely used OP pesticides are 120 W of discharge power, 120 s of treatment time, and 40 cm^3/min of O_2 flux. Moreover, the removal effectiveness of DDVP is lower than that of omethoate because of their chemical structures. Identification of intermediates during O_2 plasma treatment appears to be a necessary process to best understand the mechanisms of plasma degradation. Therefore, the major degradation products formed during O_2 plasma treatment of DDVP and omethoate were identified, and the reaction pathways were examined. It has been verified that most of the identified intermediates are less toxic compounds than the parent compounds and O_2 plasma degradation mechanisms for OP pesticides can be dominated by the free-radical reaction, which is confirmed by adding radical scavenger. Because the degradation reactions are based on reactive species derived from O_2 plasma (such as excited atoms, radicals, etc.), a wide range of chemical contaminants in agricultural products can be reduced by O_2 plasma. As such, the application of O_2 plasma challenges the conventional methods for the degradation of pesticides because of its crucial advantages, such as high efficiencies, low cost, and without causing secondary pollution. Further work needs to be carried out to elucidate

plasma degradation mechanisms in detail and to ascertain that new pesticides introduced recently in agricultural products may also be degraded by O_2 plasma.

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