Effect of pH and Cooking Temperature on the Stability of Organophosphate Pesticides in Beef Muscle†

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Temperature and pH stabilities of parent organophosphate pesticides (OPs) were investigated in lean (7.7% fat) beef muscle. Raw (pH 5.5) and pH-adjusted (pH 4.5 and 6.5) meat samples were fortified with mixtures of OPs to 1 ppm. Thermostability of OPs was studied by heating fortified meat samples to an endpoint of 71 or 77 °C. Compounds were extracted from fortified raw and cooked meat samples and analyzed by HPLC on a C_{18} reversed-phase column. Parent OPs were stable in uncooked meat at pH 4.5, and their concentration progressively decreased with increase of pH from 5.5 to 6.5. Combined effects of pH and temperature were more efficient than pH and temperature alone in partly reducing levels of OPs in cooked meat. However, some compounds were susceptible to heat degradation in meat at pH 4.5, whereas others were readily degraded at pH 6.5. Overall, combination of all pHs and cooking temperatures significantly ($p < 0.05$) reduced concentrations of OPs in meat.

Keywords: *Organophosphate pesticides; metabolites; HPLC; stability; beef*

INTRODUCTION

Organophosphate pesticides (OPs) are esters of alcohols with phosphoric acids and are widely used to control pests of plants and animals (Chambers, 1992). The widespread agricultural and animal applications of these chemicals are attributed to their low environmental persistence (Dikshith, 1991). Despite their low persistence, OPs exhibit toxicity to humans and animals and the presence of residues of such compounds in our food supply has raised safety issues. Toxicity of OPs is associated with the anticholinesterase properties of the primary (oxon) metabolites obtained from oxidative desulfuration of the parent molecules (Fukuto, 1987). Oxons are chemically more active than parent OP molecules (organophosphorothionates) and, therefore, react more quickly with acetylcholinesterase enzymes than their corresponding parent molecules (Eto, 1974; Chambers, 1992). The degradation of the OPs and formation of primary (oxon) and secondary (alcohol) metabolites are induced by exposure to high temperature, light, enzymatic systems, microorganisms, and acidic, neutral, and alkaline pHs.

Coulibaly and Smith (1993) investigated the thermostability of OPs in water and beef muscle and found that cooking meat at 70 or 80 °C accelerated the breakdown of the parent molecules. This research confirmed that the formation of secondary metabolites of ronnel, stirofos, fenthion, and parathion was induced by heat treatment. Ishikura et al. (1984) studied the thermal stability of OPs in water and during cooking in boiled rice. Results from this investigation showed that some OPs were heat-degraded, whereas others were removed easily from the aqueous medium by steam distillation. Similarly, Lee et al. (1991) analyzed the thermostability of chlorpyrifos in cooked polished rice and concluded that cooking could reduce the organophosphate by 70%. Walia et al. (1989) investigated the photodegradation of iodofenphos, a broad-spectrum organophosphate insecticide, and indicated that its degradation on soil, glass, and leaf surfaces was accelerated by light. Racke and Coats (1988) reported that the degradation of OPs, including chlorpyrifos in soils, was induced by microorganisms.

Acid- and base-catalyzed oxidative and hydrolytic decompositions of parent OPs also have been studied. Akhtar (1977) investigated the degradation of the insecticide stirofos in buffered aqueous media at pH 5.75, 6.5, 7.4, 8.0, and 9.0. This research showed that the insecticide was hydrolyzed progressively as pH increased. Coburn and Chau (1974) hydrolyzed five OPs (ronnel, crufomate, fenitrothion, parathion, and methyl parathion) using a 10% methanolic potassium hydroxide solution. Similar research indicated that some OPs, including chlorpyrifos, were stable to acid hydrolysis but degraded in alkaline medium (Desmarchelier, 1988). Abou-Assaf and Coats (1987) studied the degradation of [^{14}C]isofenphos at pH 6, 7, and 8 and concluded that formation of [^{14}C]isofenphos oxon was much higher at pH 8 than at pH 6. Macalady and Wolfe (1983) reported that hydrolysis of chlorpyrifos increased progressively as pH was raised from 7 to 12 in distilled water at 25 °C.

Although the catalyzed degradation of OPs in environmental and aqueous systems is well documented, only one study has evaluated the thermostability of OPs and some of their metabolites in beef muscle (Coulibaly and Smith, 1993). That research provided some insight into the thermal stability of OPs, but the final internal temperature of the meat during cooking remains to be investigated. Also, no information is available on the effects of various pHs and the combination of pH and cooking temperature on the stability of OPs in beef muscle.

Therefore, the aims of this work were (1) to evaluate the effects of pH 4.5, 5.5, and 6.5 at room temperature on the stability of six parent OPs in beef muscle and (2) to investigate the cumulative effects of pHs and

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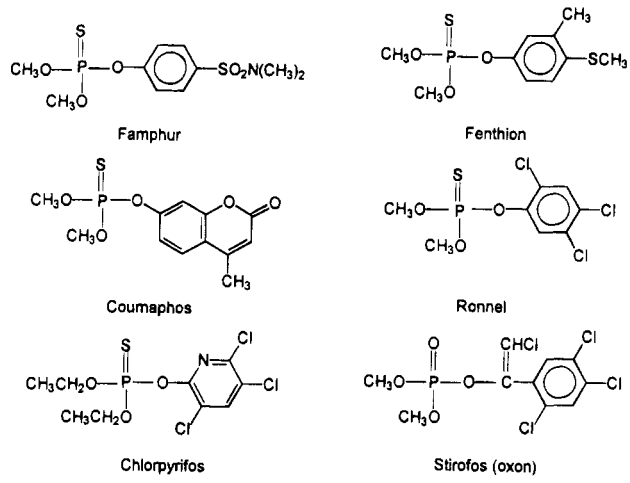

Figure 1. Chemical structures of the parent organophosphate pesticides investigated in this study.

internal cooking temperatures of 71 and 77 °C on the stability of the parent OPs in beef muscle. The selected OPs are approved animal pesticides widely used on beef cattle (USDA, 1993), and the pHs 4.5 and 5.5 fall within the range commonly encountered in fermented beef summer sausages (Acton and Keller, 1974). The choice of pH 6.5 was based upon a previous study which reported that the pH range 5.4–7.0 was expected in muscle foods (Decker and Welch, 1990). Stability of these compounds was studied under normal cooking temperatures for ground beef (Troutt et al., 1992).

EXPERIMENTAL PROCEDURES

Chemicals. Ronnel, fenthion, coumaphos, chlorpyrifos, and famphur standards were purchased from ChemService, Inc. (West Chester, PA), and stirofos was purchased from Supelco, Inc. (Bellefonte, PA). Optima grade ethyl acetate, methanol, acetonitrile, and certified ACS grade sodium hydroxide were purchased from Fisher Scientific (Pittsburgh, PA), and deionized water was obtained from a Sybron/Barnstead PCS unit (Barnstead/Thermolyne, Inc., Dubuque, IA). Citric acid monohydrate was purchased from J. T. Baker Chemical Co. (Phillipsburg, NJ). The chemical structures of the parent OPs are presented in Figure 1.

Sample Preparation. Lean beef (7.7% fat) purchased from a local supermarket was ground to assure sample homogeneity. The meat sample was analyzed for moisture using the air oven method (AOAC, 1990) and for fat content according to the Soxhlet extraction procedure (AOAC, 1990) and frozen at −13 °C until used.

To measure the pH of the meat system, 1 mL of deionized water was added to a 10-g sample in a screw-cap vial (25 × 95 mm). The meat sample was mixed thoroughly with water for 1 min, and pH was measured with a Markson Science Inc. (Phoenix, AZ) pH meter. Raw meat had a pH of 5.5 and did not undergo further pH adjustment. The pH of the meat was adjusted to 4.5 by mixing 0.6 mL of a 1 M solution of citric acid and 0.4 mL of deionized water with the sample. Similarly, pH 6.5 was reached by adding 0.5 mL of a 1 M solution of sodium hydroxide and 0.5 mL of deionized water.

Then meat samples at pH 4.5, 5.5, and 6.5 were spiked with mixtures of the standard OPs using 1000 ppm stock solutions to reach a concentration of 1.0 ppm. The standard solutions were prepared by dissolving single pure (97–99.5%) OPs in optima grade methanol. Each sample then was mixed thoroughly for several minutes, the vials were capped, and the samples were allowed to set for 1 h at room temperature. Three replicate samples were prepared at each pH as noted above. Then the OPs were extracted from meat samples using previously described procedures (Ioerger and Smith, 1993; Coulibaly and Smith, 1993).

Temperature and pH stabilities of the OPs in meat were evaluated by preparing samples as previously described. Adjusted-pH (pH 4.5 and 6.5) and raw (pH 5.5) meat samples were spiked with mixtures of OPs to a 1 ppm concentration. All samples were heated in a water bath held at 81 °C. During cooking in the water bath, a thermocouple was introduced through the cap of each vial to the center of the meat sample to measure the internal temperature. The time necessary for the inside of the meat to reach 71 °C was 4 min and 23 s, and that to reach 77 °C was 7 min and 19 s. Three replicate samples were tested at each pH (4.5, 5.5, and 6.5) and each temperature treatment. Following cooking, samples were cooled to room temperature, and then OPs and pH- and heat-induced derivatives were extracted as previously described.

Extraction and Cleanup Procedure. The OPs were extracted from the meat matrix with a mixture of ethyl acetate–methanol (90:10 v/v) using a modified version of the procedure of Ioerger and Smith (1993). The modification consisted of thoroughly mixing 3.06 g of NaCl with each meat sample and washing the blender with an additional 5 mL of the extraction solvent in the final step. After extraction, the combined filtrates were brought to a final volume of 50 mL with the extraction solvent. Then the total extract was frozen at −13 °C overnight and filtered inside the freezer through Whatman No. 2 paper to remove lipid material. A 10-mL aliquot of the filtrate was placed in a heat block (60 °C) under a gentle stream of nitrogen gas until just dry. The residue was resuspended in 1.0 mL of methanol and passed through a conditioned C_{18} solid-phase extraction (SPE) cartridge (Waters Chromatography, Milford, MA). The SPE cartridge was conditioned by passing 8.5 mL of methanol through the cartridge followed by 8.5 mL of deionized water and discarding the eluted solvents. The OPs were eluted with 4 mL of acetonitrile/water (90:10 v/v), collected, dried on the heat block, and resuspended in 1 mL of methanol. The residue was filtered through a 0.45-μm nylon syringe filter (Alltech Associates, Inc., Deerfield, IL) before HPLC analysis.

High-Performance Liquid Chromatography (HPLC). A Series II Model 1090M Hewlett-Packard HPLC (Palo Alto, CA) with a DR5 binary solvent delivery system was used to analyze the OPs. The compounds were separated on a 250 mm × 4.6 mm Bio-Sil, C_{18} HL-90 analytical column (Bio-Rad Laboratories, Richmond, CA) with a particle size of 5 μm and detected with a scanning UV–visible photodiode array detector. Data storage and processing were performed by a Hewlett-Packard ChemStation (Pascal series).

Liquid Chromatographic Conditions. The parent OPs were separated using the step-gradient mobile phase of Ioerger and Smith (1993). The mobile phase was composed of acetonitrile and water at a flow rate of 1.0 mL/min, and the operating parameters were identical to those used by Coulibaly and Smith (1993). Chlorpyrifos and ronnel were monitored at 202 nm, whereas stirofos, famphur, fenthion, and coumaphos were monitored at 207, 230, 250, and 314 nm, respectively.

Recovery Analysis and Identification. Recovery studies were performed at the 1 ppm fortification level. Three replicate samples were prepared with mixtures of the parent OPs in meat at each pH (4.5, 5.5, and 6.5) and for each pH combined with each temperature (71 and 77 °C). After extraction, each replicate sample of uncooked and cooked meat was injected twice into the HPLC. Similarly, two injections were made from each of the three standard solutions containing a concentration of 1 ppm of all the OPs and their metabolites. Average integrated peak areas of standards and samples were used to calculate the concentrations of each compound (Ioerger and Smith, 1993). Identification involved matching the retention time of each compound from the samples with that of standards and comparing their UV spectra to those of a user-generated library.

Statistical Analysis. A complete nested design (with two recoveries per compound nested in the same replicate sample) was used to analyze the variance of the recoveries for each compound from the meat systems at pH 4.5, 5.5, and 6.5 with and without heat treatment. The means of the recoveries of the OPs were separated according to a Fisher least significant

Table 1. Effects of pH 4.5, 5.5, and 6.5 at Room Temperature (21 °C) on the Recoveries of Parent Organophosphate Pesticides from Raw Meat Samples Spiked to 1 ppm Concentration[a]

	pH 4.5		pH 5.5		pH 6.5	
organophosphate	%	CV[b]	%	CV	%	CV
famphur	79.2[a]	6.8	77.5[a]	4.3	63.0[b]	0.8
fenthion	75.0[a]	10.4	67.0[b]	10.4	64.3[b]	2.0
stirofos	76.3[a]	7.2	71.2[a]	2.0	51.2[b]	4.8
coumaphos	84.5[a]	2.1	78.3[b]	3.9	67.2[c]	2.6
ronnel	70.1[a]	4.4	65.2[b]	3.1	46.5[c]	5.5
chlorpyrifos	77.7[a]	3.8	78.0[a]	10.5	48.0[b]	18.0

[a] Means of three replicates in the same row marked by different letters are significantly different ($p < 0.05$). [b] CV, coefficient of variation.

Table 2. Effects of pH 4.5, 5.5, and 6.5 on the Recoveries of Parent Organophosphate Pesticides from Meat Samples Spiked to 1 ppm Concentration and Cooked to a Final Internal Temperature of 71 °C[a]

	pH 4.5		pH 5.5		pH 6.5	
organophosphate	%	CV[b]	%	CV	%	CV
famphur	60.0[a]	9.8	66.3[ab]	6.2	53.3[b]	13.3
fenthion	50.4[a]	7.6	69.5[b]	3.0	62.8[b]	10.8
stirofos	51.2[a]	13.1	52.6[a]	11.1	43.3[a]	12.2
coumaphos	62.4[a]	6.4	78.4[b]	3.0	64.6[a]	4.1
ronnel	48.8[a]	26.6	43.3[b]	22.0	28.0[b]	18.2
chlorpyrifos	51.0[a]	23.7	46.5[a]	10.0	47.6[a]	23.0

[a] Means of three replicates in the same row marked by different letters are significantly different ($p < 0.05$). [b] CV, coefficient of variation.

difference test (with $p < 0.05$) using Statistical Analysis System (SAS), version 6.07 (SAS Institute, Cary, NC). The objective of this statistical analysis was to compare the stability of the OPs at the three pHs and for each pH combined with each temperature treatment in meat.

RESULTS AND DISCUSSION

Results of previous studies have demonstrated that volatilization was an important pathway for dissipation of OPs, including chlorpyrifos in water and sediment (Knuth and Heinis, 1992) and beef muscle (Coulibaly and Smith, 1993). Therefore, we conducted all of our experiments in closed vials to minimize any possible loss of the volatile compounds. A meat sample was analyzed before and after cooking and found to be free of residues of the parent OPs and their metabolites. Analysis of control meat samples at pH 4.5, 5.5, and 6.5 with and without heat treatment did not show the presence of any OPs or metabolites. The slight increase of the pH (from 5.5 to 5.8) of meat induced by cooking did not significantly affect the stability of the parent OPs. The concentration of 1 ppm used to spike the meat sample in this research was chosen to remain in the range (0–5 ppm) of the tolerance level of OPs in meat and meat products (USDA, 1993).

Table 1 shows the effects of pH 4.5, 5.5, and 6.5 on the stability of the parent OPs in raw meat. The recoveries of fenthion, coumaphos, and ronnel (varying from 70.1 to 84.5%) at pH 4.5 were significantly ($p < 0.05$) higher than those (varying from 46.5 to 78.3%) obtained at pH 5.5 and 6.5. However, no significant differences occurred among the recoveries of famphur, stirofos, and chlorpyrifos in meat at pH 4.5 and 5.5. As the pH was raised to 6.5, recoveries of all the parent OPs were much lower than those observed at the other pHs. These results indicate a progressive pH-induced degradation of the OPs with the increase of pH from 4.5 to 6.5. The stability of stirofos to acid hydrolysis noted in our investigation was reported previously. Akhtar (1977) studied the effects of various pHs on the stability of the insecticide stirofos and its metabolite 2,4,5-trichlorophenacyl chloride in aqueous media. Although the study found the compound to hydrolyze in both acidic and alkaline media, the half-life of its hydrolytic degradation was larger at pH 5.75 than at pH 6.5. Abou-Assaf and Coats (1987) also evaluated the effects of pH 6, 7, and 8 on the stability of [^{14}C]-isofenphos in soil. Their investigation concluded that both acidic and alkaline pHs favored a greater degradation of the organophosphate than pH 7. Similar research showed that hydrolysis of [^{14}C]chlorpyrifos on soil at 35 °C into its metabolite 3,5,6-trichloro-2-pyridinol was higher at pH 6.57 than at pH 4.57 (Getzin, 1981).

Previous studies have attempted to elucidate the mechanism of the alkaline- catalyzed hydrolysis of OPs. O'Brien (1967) indicated that all organophosphates could be hydrolyzed at a rate directly related to the alkalinity of the medium. According to that paper, the hydroxide ion causes the hydrolysis of OPs by nucleophilic attack on the electrophilic phosphorus atom. Qian et al. (1985) also attributed the base-catalyzed hydrolysis of OPs to the same reaction. In addition, these authors reported that hydrogen peroxide ion was chemically more active than hydroxide ion in hydrolyzing OPs in aqueous solutions and soil mixtures, although both ions degrade OPs through the same mechanism.

The presence of hydrogen peroxide in beef and its involvement in oxidative processes have been reported. Decker et al. (1993) showed that an insoluble fraction of beef diaphragm muscle was capable of catalyzing lipid oxidation in the presence of reducing agents such as ascorbate. However, the insoluble fraction/ascorbate-catalyzed oxidation was inhibited by catalase, which suggested the involvement of hydrogen peroxide in the mechanism of oxidation. It appeared that, in the absence of catalase, hydrogen peroxide would likely promote the insoluble fraction-catalyzed lipid oxidation. Therefore, hydrogen peroxide could also be associated with the hydrolytic degradation of parent OPs and their primary metabolites in beef muscle. Other investigations have indicated that metal ions also can hydrolyze OPs. Eto (1974) reported that metal ions such as copper can contribute to the hydrolysis of OPs through the formation of a complex with the sulfur atom. A similar investigation evaluated the catalytic hydrolysis of quinalphos (an organophosphate pesticide) induced by the metal ions of Cu, Fe, Al, K, Ca, and Na (Pusino and Gessa, 1988). This evaluation found that copper-induced hydrolysis of the compound was the major path of its degradation. However, hydrolysis of the organophosphate was catalyzed moderately over time by Fe, Al, and Ca. Consequently, the degradation of the OPs observed in our investigation could have involved hydroxide and hydrogen peroxide ions, Fe^{2+}, or Na^{+}.

Table 2 summarizes the effects of different pHs (4.5, 5.5, and 6.5) on the recoveries of the parent OPs in meat cooked to an endpoint of 71 °C. The recoveries of fenthion and of coumaphos from cooked meat at pH 4.5 (50.4 and 62.4%, respectively) were significantly ($p < 0.05$) lower than those observed at pH 5.5 and 6.5 (between 62.8 and 78.4%). These two parent compounds appear to be susceptible to acid-catalyzed degradation in cooked meat. However, famphur, stirofos, and chlorpyrifos were heat-sensitive in meat at pH 4.5 and 5.5, though no significant differences occurred among re-

Table 3. Effects of pH 4.5, 5.5, and 6.5 on the Recoveries of Parent Organophosphate Pesticides from Meat Samples Spiked to 1 ppm Concentration and Cooked to a Final Internal Temperature of 77 °C[a]

	pH 4.5		pH 5.5		pH 6.5	
organophosphate	%	CV[b]	%	CV	%	CV
famphur	50.4[a]	15.9	60.5[b]	11.8	45.6[a]	19.1
fenthion	48.0[a]	7.6	69.7[b]	2.5	57.4[c]	4.2
stirofos	40.0[a]	26.3	41.0[a]	7.5	39.0[a]	15.0
coumaphos	55.3[a]	12.8	64.6[b]	9.2	61.0[b]	3.6
ronnel	43.7[a]	3.2	40.4[a]	9.6	24.4[b]	9.8
chlorpyrifos	31.7[a]	13.4	67.3[b]	5.9	45.0[c]	11.0

[a] Means of three replicates in the same row marked by different letters are significantly different ($p < 0.05$). [b] CV, coefficient of variation.

coveries within the same compound. The degradation of ronnel and famphur progressively increased as the acidity of the meat system decreased. In summary, famphur and ronnel were susceptible to low acid-catalyzed degradation in cooked meat, whereas fenthion was sensitive to high-acid (pH 4.5) decomposition. These observations suggest that the interactions of all pHs and the internal temperature of 71 °C were more efficient than the pHs alone in degrading the OPs in cooked meat (Tables 1 and 2). In addition, the degradation of most OPs in meat cooked to an internal temperature of 71 °C was greater at pH 6.5 and 4.5 than at pH 5.5.

These results with cooked meat are consistent with a number of previous studies. Heat-induced hydrolysis and oxidation of famphur, fenthion, stirofos, parathion, ronnel, and chlorpyrifos in beef muscle and water have been reported recently (Coulibaly and Smith, 1993). This previous research showed that cooking meat for 2 h in a water bath held at 70 °C promoted hydrolysis of the OPs. Similarly, Sharmila et al. (1989) studied the thermal hydrolysis of methyl parathion in a flooded soil and found the organophosphate compound to disappear more rapidly at 35 °C than at 25 °C.

The results in Table 3 show the effects of pH 4.5, 5.5, and 6.5 on the stability of the parent OPs in meat cooked to an endpoint of 77 °C. The recoveries of famphur, fenthion, and chlorpyrifos from cooked meat at pH 5.5 (between 60.5 and 69.7%) were significantly higher than those (between 24.4 and 57.4%) obtained at pH 4.5 and 6.5. As shown by their recoveries, coumaphos was susceptible to high acid hydrolysis, whereas ronnel exhibited its highest thermal degradation in low-acid (pH 6.5) meat. These observations are consistent with the results obtained during cooking to the endpoint of 71 °C. The recoveries of stirofos (less than 50%) from cooked meat at all three pHs were similar. Therefore, the thermal breakdown of stirofos in meat apparently was caused mostly by the effect of heat. Except chlorpyrifos and fenthion in meat cooked to 77 °C at pH 5.5, recoveries of the OPs were much lower at 77 °C than at 71 °C. Although it is unclear why chlorpyrifos was degraded more at 71 °C than at 77 °C, a correlation was observed between the level of heat applied during cooking and the extent of degradation of the compounds.

Several studies have associated the thermal decomposition of OPs with the level of temperature to which they were exposed. Coulibaly and Smith (1993) indicated that cooking meat fortified with a mixture of OPs or their metabolites in a water bath held at 70 °C caused their degradation. In that study, 2 h of cooking was more efficient than 1 h in decomposing the OPs in meat. During cooking of meat at 70 °C for 2 h, the endpoint temperature was likely higher than that after 1 h. In agreement with our previous study, high-temperature treatment in this study promoted a rapid degradation of the OPs. This observation was made previously by Abou-Assaf and Coats (1987). These co-workers investigated the effects of 15, 25, and 35 °C on the stability of isofenphos, an organophosphate pesticide, and found that the formation of the oxon was greater at 35 °C than at 15 and 25 °C. Although isofenphos was not included in our study, it shares some similarities of chemical structure with the OPs we evaluated. Therefore, studies involving isofenphos can provide some insight on the chemical properties and the degradation of the OPs addressed in this research.

Primary (oxon) and secondary (alcohol) metabolites resulting from the pH- and temperature-catalyzed degradation of the parent OPs were identified tentatively in the meat system. The presence of these metabolites in the matrix is consistent with results of previous studies. Eto (1974) reported that hydrolysis of OPs such as chlorpyrifos and formation of its alcohol metabolite 3,5,6-trichloro-2-pyridinol can occur in an acidic medium. However, the low concentrations of the metabolites observed in the meat system did not readily allow their quantitation and identification. An ongoing investigation is focused on positively identifying these metabolites in cooked meat.

The effect of combinations of each pH and temperature on the decomposition of the OPs in meat was much more significant than the effect of pH alone. The recoveries of the parent molecules from meat showed that 77 °C was more efficient than 71 °C in enhancing the thermal decomposition of the parent molecules. However, fenthion, coumaphos, and chlorpyrifos were more susceptible to high-acid-catalyzed oxidation and hydrolysis than to low-acid-catalyzed reactions in cooked meat. In conclusion, all of the OPs were unstable in raw meat at low acid (pH 6.5) and susceptible to thermal hydrolysis and oxidation in cooked meat in both high and low acid (pH 4.5 and 6.5). Overall, the pHs (4.5, 5.5, and 6.5) generally encountered in cooked beef muscle can significantly decrease (less than 50%) levels of residues of OPs. However, these pHs alone or combined with cooking temperatures could not completely eliminate OPs and their metabolites in meat. The amount of OPs used to spike the meat samples in this study falls within the range of the tolerance level in meat and meat products (USDA, 1993). Consequently, the findings of this investigation can give some insight on the persistence of residues of parent OPs in a real processed or cooked meat product.

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