Investigation of pyrolysis behavior of carbofuran by pyrolysis-gas chromatography–mass spectrometry

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Abstract

Carbofuran is a kind of carbamate pesticide commonly used on major crops. For understanding of the composition variation versus temperature and pyrolysis mechanism, its pyrolysis behavior was simulated and investigated by pyrolysis-gas chromatography–mass spectrometry (Py-GC–MS). The pyrolysates were directly injected for GC–MS analysis. Totally 86 components were determined based on mass spectra library matching with the aid of the correlation of boiling point (bp) and retention time. It was found that carbofuran was obviously decomposed with the temperature increase. A large number of mono aromatics and polycyclic aromatic hydrocarbons (PAHs) were formed when the temperature was higher than 750 °C, and the higher was the temperature, the more was the content of the corresponding aromatic hydrocarbon. Besides the aromatic hydrocarbons, there were oxygenous and/or nitrogenous compounds produced in the pyrolysis process. Furthermore, the pyrolysis mechanism of carbofuran was proposed based on the determined pyrolysates and their contents variation versus the temperature. The investigation results can provide the useful information for understanding of the thermal behavior of carbofuran and evaluation of the potential influence of the pyrolysates to living thing and the environment.
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1. Introduction

Carbofuran is a broad-spectrum systemic acaricide, insecticide and nematicide included in the general group of the carbamate derivative pesticides. It is widely used in agricultural cultivations and presents a high persistence in raw milk [1], water [2–4], soil [5,6], atmosphere [7,8], or plants [9–12], etc. due to its chemical stability. It exhibits a special refractory character to biodegradation methods. Therefore, the programs focused on its oxidation [13,14], membrane anodic Fenton treatment [15], and photo-assisted Fenton reaction [16], were designed. In fact, a large amount of hazardous substances such as pesticides are handled and stored every day in chemical plants and warehouse as a consequence of their massive use in the agricultural field. It has been reported in the past that fire occurred in a certain number of these installations involving large quantities of chemicals [17]. Over the years, a number of incidents have occurred at several pesticide plants in different parts of the world [17,18]. When the fire occurred, the pesticides and their decomposition products could cause calamitous consequence to living thing and the environment. With respect to these events some studies appeared in the literatures about hazardous combustion products of selected pesticides [17,18]. However, there are questions about pyrolysis behavior of carbofuran with deficiency of the oxidants that may be occurring when on fire of its storage, roasting of the contaminated food, or smoldering of the contaminated tobaccos. For evaluation of the potential influence to the living thing and the environment by the pyrolysates of carbofuran, it is indispensable to investigate its pyrolysis behavior.

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Generally, the pyrolysis product of organic compounds is a complex mixture, which may include different homologues series [19,20]. For separation and determination of the complex pyrolysate, the usually used method is the gas chromatography (GC) conjunction with other detection methods, such as mass spectrometry (MS), infrared spectrometry (IR), nuclear magnetic resonance (NMR), etc., and the most often used technique is pyrolysis-gas chromatography–mass spectrometry (Py-GC–MS). In Py-GC–MS, the pyrolysis components are separated and identified by matching the measured mass spectrum against the standard mass spectra library. The commonly used method is the probability-based match (PBM) algorithm [21,22]. For the complex mixtures, the PBM results can be determined with the aid of correlation of boiling point (bp) and retention behavior [23,24].

In this study, carbofuran was pyrolysed under helium atmosphere at 600, 750, and 900 °C, respectively. The objective is to simulate its pyrolysis behavior with the deficiency of oxidants, and determine the pyrolysis products produced during the pyrolysis process. Totally 86 components were determined with the contents varying from 0.04% to 51.54%. The determined compounds include the residue of carbofuran, the decomposition components, and other compounds produced by the primary or secondary pyrolysis reaction, such as mono aromatics, polycyclic aromatic hydrocarbons (PAHs), and other oxygenous and/or nitrogenous compounds. From the analytical results of the pyrolysates, the pyrolysis mechanism of carbofuran was proposed. The investigation results are useful for understanding of the thermochemical properties of carbofuran and evaluation of the potential influence of the pyrolysates to living thing and the environment.

2. Experimental and data process

2.1. Py-GC–MS experiments

Carbofuran (30 μg) was introduced into the hot microfurnace (SGE International Pty. Ltd., Australia) and immediately heated for 3 s at 600, 750, and 900 °C, respectively, under helium atmosphere. The pyrolysis products were directly injected into the GC–MS system (Agilent 6890 GC equipped with an Agilent 5973 electron impact mass selective detector, Agilent Technology, USA) and separated using an HP-5 capillary column (30 m, 0.30 mm i.d., 0.25 μm film thickness, 5% phenyl-methylpolysiloxane) with helium as carrier gas (flow rate, 2.0 ml/min; constant flow mode). The split rate was 1/2. The temperatures of GC inlet and the MS detector were both controlled at 250 °C. The GC oven was set to 50 °C for the first 5 min, then heated with a rate of 5 °C/min up to 200 °C and held for 15 min. The electron impact ionization was tuned at 70 eV. The mass detection range was 12–450 amu. Fig. 1 shows the total ion current chromatograms (TICs) of the pyrolysates at different pyrolysis temperatures.

In the experiment, carbofuran (99%) was purchased from ICAMA (Institute for Control of Agrochemicals, Ministry of Agriculture, China). Toluene (98%), ethylbenzene (98%), 2-methyl-phenol (98%), fluorene (98%), phenanthrene (99%), and
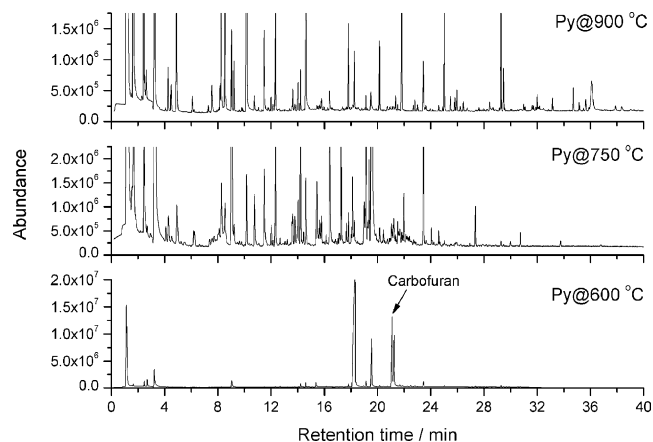

Fig. 1. TICs of the pyrolysis products at different temperatures.

anthracene (99%) were purchased from Shanghai Chemical Reagent Corporation (China Medicine Group, Shanghai, China). The retention times of these reference materials were used for validation of the identification results.

2.2. Data process

The separated components were identified and quantified by the following steps.

2.2.1. Matching the detected mass spectra against standard mass spectra library

The PBM algorithm [21,22], which used a reverse search to verify that peaks in the reference spectrum were present in the unknown spectrum, was used to match the detected mass spectra. The spectral similarity was measured by reverse match factor (R.Match). Generally, there are several tentative components in the "hit list" (the matching list) at a specific peak, and only one of them should be selected as the identified component.

2.2.2. Confirmation of the tentative components

For the tentative components with very similar mass spectra, the correlation of bp and retention behavior of organic compound [23,24] can provide useful information for the identification, i.e., the higher is the bp of a compound in the homologous series, the later is the component elution from the column. For the chemical substances on non-polar column, the bp's of organic homologous are linear with their retention times [23]. In case of that the experimentally measured bp of a compound is unavailable, it can be estimated using the group contributions method [25,26].

2.2.3. Quantification of the identified components

In order to simplify the quantification procedure and conveniently compare the variation of the pyrolysates versus the temperature, the identified components were quantified by normalization of their integration peak areas. Thus, the ratios (%) used in Table 1 were considered as the percentage concentration of the pyrolysates at different temperatures.

Table 1
Identification and quantitation of the pyrolysis products

No.	t_R[a] (min)	Compound	CAS No.[b]	bp[c] (°C)	S[d]	Area (%)		
						600 °C	750 °C	900 °C
1	1.183	Methyl isocyanate	624-83-9	39	3	9.90	8.02	5.48
2	1.263	Cyclopentadiene	542-92-7	42	1	–[e]	7.79	5.77
3	1.622	Benzene	71-43-2	60.3	1	–	6.76	21.16
4	2.421	Toluene[f]	108-88-3	110.8	1	–	5.32	11.64
5	2.694	N,O-Dimethylcarbamate	6642-30-4	103.6	3	0.95	–	–
6	4.064	Ethylbenzene[f]	100-41-4	136.3	1	–	0.66	0.04
7	4.271	p-Xylene	106-42-3	141.3	1	–	1.08	0.82
8	4.484	Phenylethyne	536-74-3	123.4	1	–	0.39	0.51
9	4.896	Styrene	100-42-5	133	1	–	1.81	3.16
10	7.292	Benzaldehyde	100-52-7	162.1	2	–	0.23	0.13
11	7.378	2-Ethyltoluene	611-14-3	165	1	–	0.44	–
12	8.157	Benzonitrile	100-47-0	191	3	–	–	0.42
13	8.256	Phenol	108-95-2	166.2	2	–	2.50	3.34
14	8.543	Benzofuran	271-89-6	178.8	2	–	2.22	5.61
15	9.614	2-Vinyl toluene	611-15-4	163.9	1	–	0.11	–
16	10.166	4-Ethynyltoluene	766-97-2	197	1	–	1.54	9.80
17	10.752	2-Methylphenol[f]	95-48-7	191	2	–	1.33	0.33
18	11.052	2-Methylbenzonitrile	529-19-1	205	3	–	–	0.12
19	11.477	3-Methylphenol	108-39-4	202	2	–	2.13	1.60
20	11.770	4-Methylbenzonitrile	104-85-8	218	3	–	0.50	0.06
21	12.003	2-Methylbenzofuran	4265-25-2	197.7	2	–	0.50	0.23
22	12.142	3-Methylbenzofuran	–	206.7	2	–	0.14	0.17
23	12.329	7-Methylbenzofuran	17059-52-8	206.7	2	–	3.09	1.91
24	12.681	2-(2-Methylallyl)phenol	20944-88-1	241.7	2	–	0.21	–
25	13.586	1-Methylindene	767-59-9	193.0	1	–	0.50	–
26	13.786	2-Methylindene	2177-47-1	202.6	1	–	1.01	0.19
27	14.431	3-Ethylphenol	620-17-7	216.9	2	–	0.37	–
28	14.611	Naphthalene	91-20-3	217	1	0.61	1.63	10.73
29	15.443	1,2-Benzenediol	120-80-9	246.8	2	0.97	2.02	–
30	15.642	4-Methylbenzaldehyde	14-87-0	205	2	–	0.80	0.12
31	15.975	2-Ethenylbenzofuran	7522-79-4	226.2	2	–	–	0.06
32	16.135	Phenol, p-(2-methylallyl)	33641-78-0	259.3	2	–	0.28	–
33	16.401	Dihydrobenzopyran	493-08-3	206.8	2	–	5.16	0.39
34	16.727	1,1-Dimethyl-1H-indene	18636-55-0	216.1	2	–	0.16	–
35	17.033	(1-Methylbuta-1,3-dienyl)benzene	54758-36-0	205.7	1	–	0.18	–
36	17.135	2,3-Dihydroxytoluene	488-17-5	247.9	2	–	0.28	–
37	17.805	1-Methylnaphthalene	90-12-0	243.7	1	0.39	0.66	1.31
38	18.311	Carbofuran phenol	1563-38-8	264.6	2	51.54	1.58	–
39	18.257	2-Methylnaphthalene	91-57-6	241	1	–	0.87	0.99
40	18.996	1H-Indenol	56631-57-3	262.3	2	–	1.35	–
41	19.495	2-Methyl-5-hydroxybenzofuran	–	287.3	2	8.35	30.08	0.51
42	20.134	2-Vinylnaphthalene	827-54-3	248.5	1	0.19	0.57	1.05
43	20.447	2-Allyl-4-methylphenol	6628-06-4	256.8	2	–	0.44	–
44	20.739	1,5-Dimethylnaphthalene	571-61-9	265.2	1	–	0.30	0.12
45	20.939	Naphthyleneethylene	83-32-9	263.1	1	–	–	0.12
46	21.052	2-Methoxy-5-((E)-prop-1-enyl)phenol	19784-98-6	270.8	2	–	0.55	–
47	21.099	Carbofuran[f]	1563-66-2	335.4	2	15.44	–	–
48	21.125	2,6-Dimethylnaphthalene	581-42-0	263	1	–	0.32	0.10
49	21.258	3-Allyl-6-methoxyphenol	501-19-9	264.4	2	9.77	–	–
50	21.365	Biphenyl	92-52-4	254	1	–	0.25	0.26
51	21.531	Diphenylmethane	101-81-5	262	1	–	0.46	0.10
52	21.591	3-Ethylbenzofuran	–	229.6	2	–	0.25	–
53	21.684	2,3-Dimethylbenzofuran	–	234.5	2	0.25	0.53	–
54	21.817	Biphenylene	259-79-0	263.1	1	–	0.30	2.69
55	21.890	2-Ethylbenzofuran	3131-63-3	234.5	2	–	0.20	–
56	21.984	Hexamethylbenzene	87-85-4	265.2	1	–	1.17	–
57	22.403	2,6-Naphthalenediol	581-43-1	326.1	2	–	0.25	–
58	22.696	Acenaphthene	83-32-9	263.9	1	–	–	0.63
59	22.722	1-Methoxy-4-(1-propenyl)benzene	104-46-1	234.5	2	–	0.16	–
60	22.815	o-Phenyltoluene	643-58-3	259	1	–	0.09	0.17
61	23.008	p-Methylbiphenyl	644-08-6	268	1	–	–	0.12
62	23.454	1-Naphthalenol	90-15-3	279	2	–	–	0.24

Table 1 (*Continued*)

No.	t_R[a] (min)	Compound	CAS No.[b]	bp[c] (°C)	S[d]	Area (%)		
						600 °C	750 °C	900 °C
63	23.634	2-Naphthalenol	135-19-3	281.7	2	–	0.16	0.19
64	24.592	Perinaphthene	203-80-5	290.2	1	–	–	0.10
65	25.024	Fluorene[f]	86-73-7	295	1	0.21	0.11	1.69
66	25.477	3,4-Methylenedioxybenzoic acid	94-53-1	311.5	2	–	–	0.25
67	25.816	2,4-Dihydroxy-3,6-dimethylbenzaldehyde	34883-14-2	318.5	2	–	–	0.22
68	25.963	2-Aminofluorene	153-78-6	327.2	3	–	–	0.39
69	26.215	9-Hydroxyfluorene	1689-64-1	320.1	2	–	–	0.09
70	26.448	Fluorene-9-methanol	24324-17-2	337.1	2	–	–	0.17
71	27.619	3-Methylfluorene	2523-39-9	318.1	1	–	–	0.09
72	27.999	2-Methylfluorene	1430-97-3	318.2	1	–	–	0.06
73	29.276	Phenanthrene[f]	85-01-8	340	1	0.23	0.11	1.85
74	29.476	Anthracene[f]	120-12-7	340	1	–	0.05	0.64
75	30.993	9-Vinylanthracene	2444-68-0	364	1	–	–	0.10
76	31.080	9-Methylanthracene	949-41-7	343.4	1	–	–	0.07
77	31.619	1-Methylanthracene	610-48-0	343.4	1	–	–	0.12
78	31.891	2-Methylanthracene	613-12-7	343.4	1	–	–	0.06
79	32.004	4,5-Methylenephenanthrene	203-64-5	353	1	–	–	0.26
80	32.184	2-Phenyl-1H-indene	4505-48-0	343.7	1	–	–	0.06
81	33.149	1-Phenylnaphthalene	612-94-2	370	1	–	–	0.22
82	34.699	Fluoranthene	206-44-0	375	1	–	–	0.38
83	35.145	Pyrene	129-00-0	378.6	1	–	–	0.17
84	35.651	2-Phenylnaphthalene	35465-71-5	370	1	–	–	0.22
85	37.893	2-Methylpyrene	3442-78-2	406.4	1	–	–	0.16
86	38.346	4-Methylpyrene	3353-12-6	406.4	1	–	–	0.17

[a] Retention time.

[b] Chemical Abstract Service Registry Number.

[c] Boiling point obtained from http://chemfinder.cambridgesoft.com (indicated as integer value) or calculated by group contributions method [25,26].

[d] Subclass of the pyrolysis products: (1) aromatic hydrocarbons; (2) oxygenous compounds; (3) nitrogenous compounds.

[e] Not detected.

[f] Compound used as a reference material.

3. Results and discussion

3.1. Identification and quantitation of the pyrolysis products

Fig. 2 shows the chemical structure and standard mass spectrum of carbofuran. It can be seen that the relative abundance at the molecular ion pea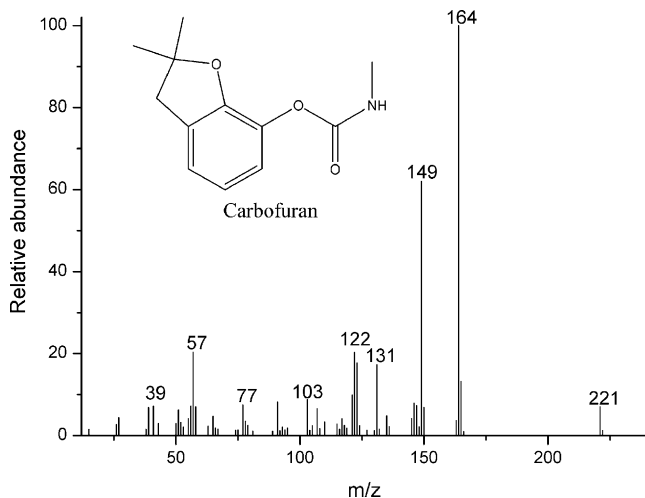k (m/z 221) is very weak, and this can make the identification of carbofuran in GC–MS analysis of a complex mixture to be difficult. It also can be seen that the chemical structure of carbofuran is not very complicated, however, its pyrolysate is very complex that can be seen from the TICs shown in Fig. 1.

Fig. 3 shows the detected mass spectra at the retention times 18.311 and 21.099 min of the pyrolysates at 600 °C, respectively. In the PBM procedure, the R.Matchs for carbofuran

Fig. 2. Plot of chemical structure and standard mass spectrum of carbofuran.
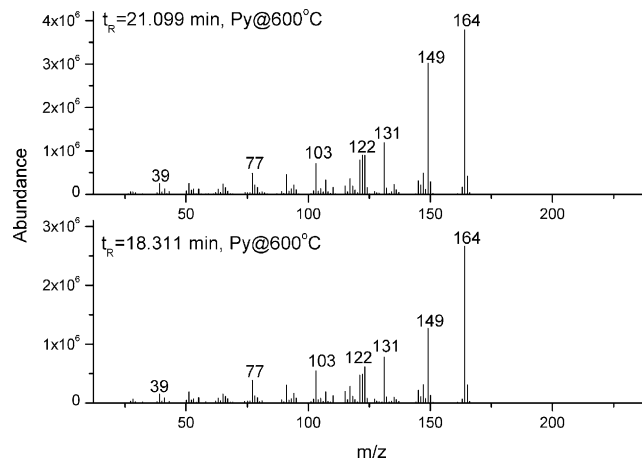

Fig. 3. Measured mass spectra of the pyrolysates at 18.311 and 21.099 min (pyrolysis at 600 °C).

phenol and carbofuran are 947, 956 and 947, 947, respectively. These R.Matchs are all larger than 900, which means very good match. It shows that for the GC–MS analysis of the complex homologous series, the similarity of the detected mass spectra at different peaks makes it difficult to identify the components only by the R.Matchs.

If the bp's of carbofuran and carbofuran phenol are known, the correlation of bp and retention time [23] can provide helpful information for the identification. However, these experimentally measured bp's are not available, but they can be estimated using the group contributions method [24,25]. The estimated bp's of carbofuran phenol and carbofuran are 264.6 and 335.4 °C, respectively. According to the correlation of bp and retention time, the retention time of carbofuran phenol should be less than that of carbofuran. Therefore, the peaks at 18.311 and 21.099 min are corresponding to carbofuran phenol and carbofuran, respectively. The identification of carbofuran also could be validated by the retention time (21.099 min) of the carbofuran reference material.

The above identification results show that the data processing procedure, i.e., PBM search combination with the aid of the correlation of bp and retention time, used in this study is reliable.

The pyrolysates at different temperatures were identified using the similar procedure. The identification results were listed in Table 1. For comparison conveniently, the identified components were divided into three subclasses: (1) the hydrocarbons or aromatic hydrocarbons; (2) the oxygenous compounds; (3) the nitrogenous compounds. The contents of the identified pyrolysis components were calculated and also listed in Table 1. The contents of the 86 determined components varied from 0.04% to 51.54%. It can be seen superficially that the dominant species were nitrogenous and oxygenous compounds when the temperature was lower than 750 °C, and the hydrocarbons or aromatic hydrocarbons were dominant when the temperature was higher than 750 °C. It also can be seen that not a little of the produced PAHs, such as anthracene, phenanthrene, flourene, fluoranthene, and pyrene, etc., are priority toxic substances.
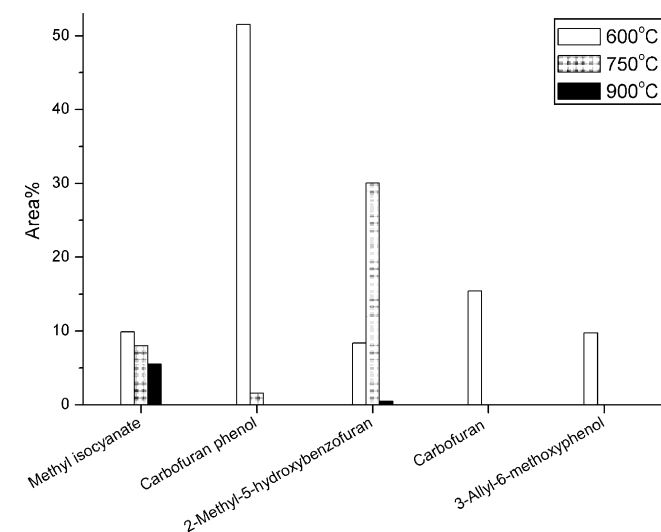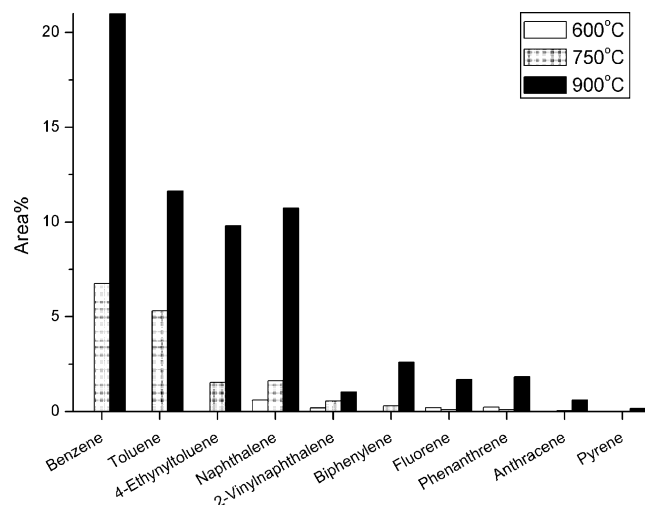

Fig. 5. Contents variation of some representative mono aromatics and PAHs vs. the pyrolysis temperature.

3.2. Contents variation of the representative pyrolysis components

Fig. 4 shows the contents variation of the main thermal decomposition compounds of carbofuran versus the pyrolysis temperature. It can be seen that carbofuran is obviously decomposed at 600 °C with the decomposition ratio being up to 84.56%. When the pyrolysis temperature was higher than 750 °C, carbofuran was fully decomposed. The main decomposition compounds were methyl isocyanate, carbofuran phenol, 2-methyl-5-hydroxybenzofuran, and 3-allyl-6-methoxyphenol. These decomposition compounds could be further pyrolysed with the temperature increase.

Fig. 5 shows the contents variation of several representative mono aromatics and PAHs versus the temperature. It can be seen that most of these aromatic hydrocarbons are produced at higher temperature, i.e., higher than 750 °C in this study. The contents of these compounds increased obviously with the temperature

Fig. 4. Contents variation of the main decomposition compounds vs. the pyrolysis temperature.
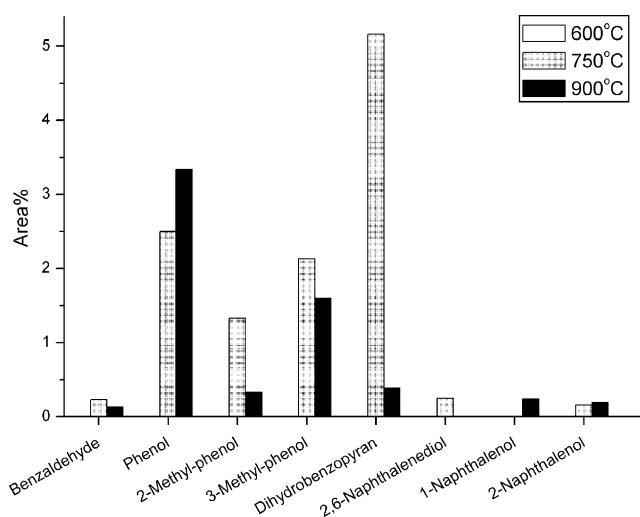

Fig. 6. Contents variation of some oxygenous compounds vs. the pyrolysis temperature.
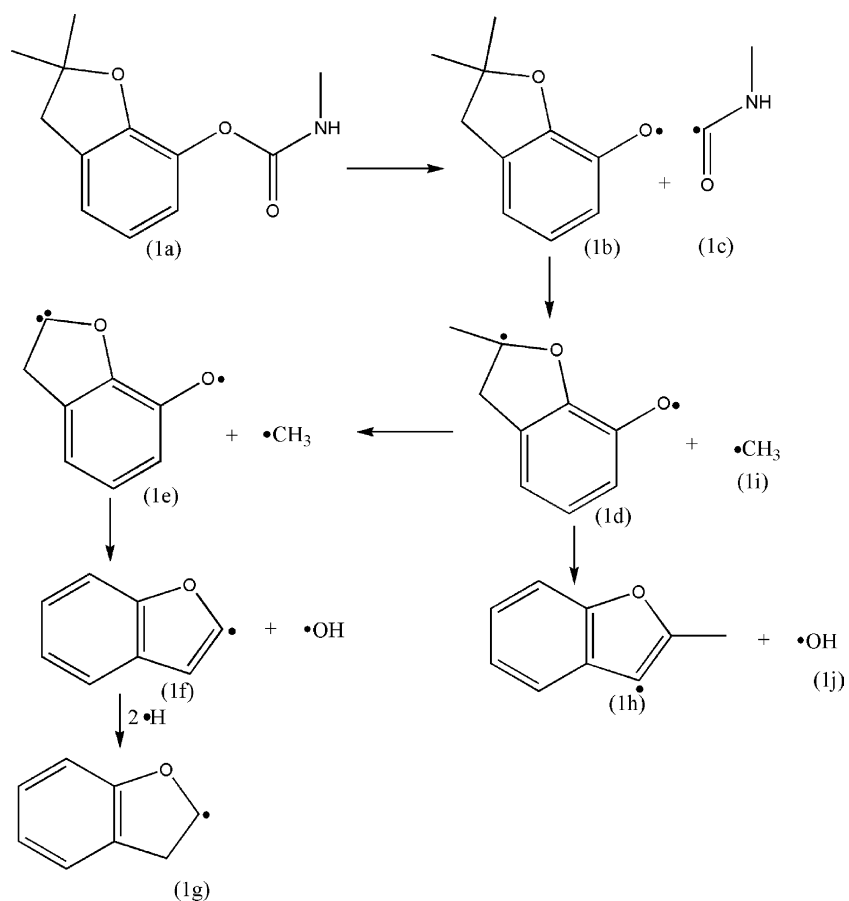
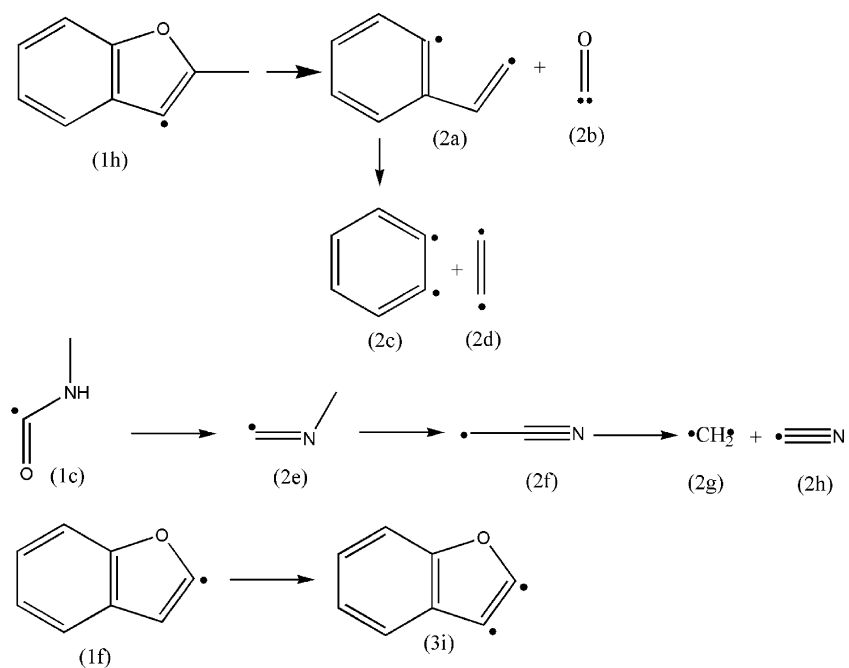Fig. 7. Primary pyrolysis of carbofuran at lower temperature.

Fig. 8. Secondary pyrolysis of the radicals produced during the primary pyrolysis at higher temperature.
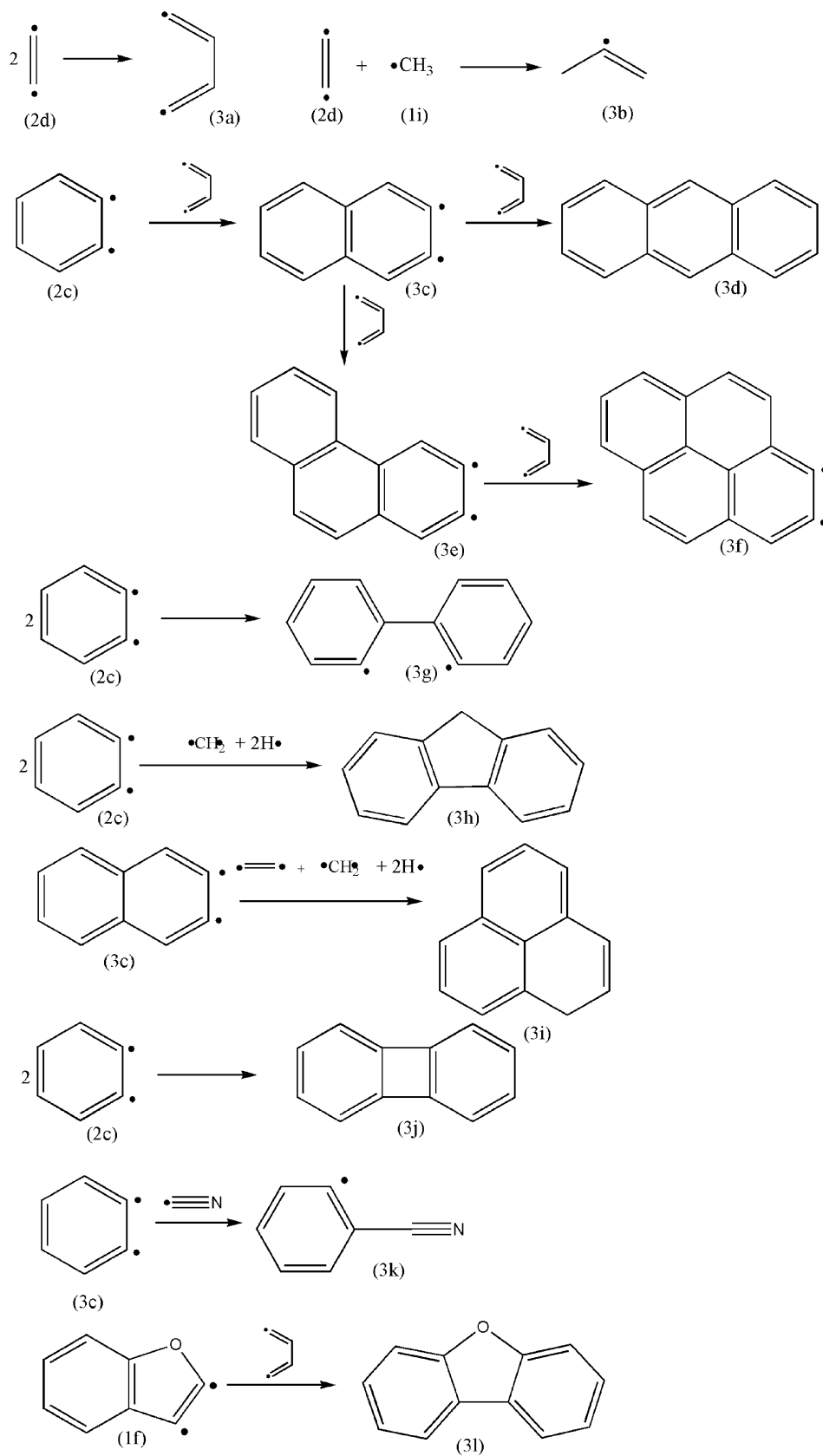
Fig. 9. Polymerization of the radicals produced during the primary or secondary pyrolysis.

increase and had a tendency to decrease with the ring's number increased at a specific temperature.

Besides the decomposition compounds, the mono aromatics, and PAHs, there are other oxygenous and/or nitrogenous compounds that could be seen from Table 1. Fig. 6 shows the contents variation of several oxygenous compounds versus the pyrolysis temperature. It can be seen that these compounds are also produced at higher temperature and their contents vary significantly with the change of temperature.

3.3. Pyrolysis mechanism of carbofuran

Based on the contents variation of the pyrolysis components versus the temperature, the radical chain mechanism, and the reactions of the intermediate radicals [13,15,27–32], the pyrolysis mechanism of carbofuran can be described as followings.

3.3.1. Primary pyrolysis of carbofuran at lower temperature

Carbofuran is firstly decomposed as small radicals or molecules (Fig. 7) [13,15,29]. The radicals can be interacted and transformed as molecules (the decomposition compounds) or other radicals. The nitrogenous and oxygenous compounds that produced at lower temperature, e.g., carbofuran phenol, 2-methyl-5-hydroxybezenofuran, methyl isocyanate, etc., are mainly produced in this pathway. This pathway can also account for the contents variation that shown in Fig. 4.

3.3.2. Secondary pyrolysis of the radicals or components produced during the primary pyrolysis

The radicals or molecules that produced during the primary pyrolysis are further pyrolysed (Fig. 8) [30–32]. Some of the mono aromatics can be produced by the interaction of the radicals. These reactions can account for the contents of the pyrolysis component increase or decrease with the temperature change shown in Figs. 4 and 6.

3.3.3. Polymerization of the radicals produced during the primary or secondary pyrolysis

There are no poly aromatic rings in the chemical structure of carbofuran, whereas there are a number of PAHs identified that shown in Table 1. Therefore, the PAHs should be produced by the polymerization of the radicals or fragments that produced during the primary and secondary pyrolysis. Fig. 9 shows that some of the radicals can be interacted and transformed as new molecules or radicals [30–32]. The PAHs, the mono aromatics, and their oxygenous or nitrogenous derivatives can be produced in this pathway. It can also account for that the contents of the PAHs decreasing with the ring's number increase, and the contents of the oxygenous or nitrogenous compounds are relatively less.

4. Conclusions

The pyrolysis behavior of carbofuran was investigated by Py-GC–MS. The separated pyrolysis components were identified using PBM algorithm with the aid of correlation of bp and retention time. The determined pyrolysis components included the decomposition compounds of carbofuran, and the compounds produced by the primary and secondary pyrolysis reaction, such as mono aromatics, PAHs, and oxygenous or nitrogenous compounds. The contents of the pyrolysis components varied within a wide range with the change of the temperature. The pyrolysis mechanism of carbofuran was proposed. The investigation of the pyrolysis behavior of carbofuran can provide useful information for evaluation of its thermal behavior and the potential influence to living thing and the environment.

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