

Thermal Decomposition of Diphenethyl Carbonate by Pyrolysis-Gas Chromatography/Mass Spectroscopy

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To develop thermal stable flavour, a flavour precursor of diphenethyl carbonate was synthesized by the transesterification of dimethyl carbonate and phenethyl alcohol with potassium carbonate as a catalyst. The thermal decomposition behaviour and pyrolysis products of diphenethyl carbonate were investigated by on-line pyrolysis-gas chromatography/mass spectroscopy (Py-GC/MS). Pyrolysis-gas chromatography/mass spectroscopy was used for the qualitative and quantitative analysis of the pyrolysis products at 300, 500 and 700 °C. It was found that the amount of phenethyl alcohol increased rapidly with the increase of temperature, but the amount of 2-phenethyl- β -phenylpropionate decreased sharply. Phenethyl alcohol was the main product at 700 °C. The typical pyrolysis mechanism of diphenethyl carbonate mainly included: the cleavage of the C-O single bonds of ester group and phenylethyloxy group and the recombination of radicals at three temperatures.

Key Words: Diphenethyl carbonate, Flavour precursors, Pyrolysis, Phenethyl alcohol, Pyrolysis-gas chromatography/mass spectroscopy.

INTRODUCTION

Phenethyl alcohol, because of its inherent rose flavour, has been widely used as additives in tobaccos. But the volatility limited its wide application in the high temperature processing. It has been suggested that phenethyl alcohol might be incorporated into the tobacco as part of a compound that upon burning of the tobacco, the compound is decomposed to yield phenethyl alcohol.

A variety of carbonate esters as flavour precursors have been developed and proposed for incorporation into tobacco products^{1,2}. However, the synthesis and application of phenethyl carbonate have been rarely reported.

Pyrolysis, in combination with gas chromatography and mass spectrometry (Py-GC/MS), has been extensively used in smoke chemistry to assess the potential effect of individual cigarette components on smoke composition^{3,4}. Stotesbury *et al.*^{5,6} predicted tobacco additives behaviour in a burning cigarette through

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pyrolysis. Wan-cui Xie *et al.*^{7,8} investigated the decomposition process and pyrolysis products of glycosides to study the possibility used as flavour additives in high temperature processing. Sufang Wang *et al.*⁹ studied the typical pyrolysis mechanism of phenylalanine in tobacco. To study the possibility of phenethyl carbonate used as flavour additives in tobacco products, diphenethyl carbonate was specifically synthesized first. The pyrolysis behaviour of diphenethyl carbonate and the thermal degradation products were investigated by pyrolysis-gas chromatography/mass spectroscopy. The pyrolysis temperatures were 300, 500 and 700 °C for simulating the temperatures of cigarette burning. The thermal degradation mechanism of diphenethyl carbonate was discussed.

EXPERIMENTAL

Diphenethyl carbonate preparation: Diphenethyl carbonate was prepared by the transesterification of dimethyl carbonate and phenethyl alcohol with potassium carbonate as a catalyst (Fig. 1)¹⁰. All reagents used were of AR grade.

A stirred mixture of phenethyl alcohol (4.0 g), dimethyl carbonate (10 mL) and potassium carbonate (5.5 g) was heated at 85 °C, in a round-bottomed flask fitted with a reflux condenser for 48 h. The excess of dimethyl carbonate was removed by distillation. phenethyl alcohol (5.0 g) was added to the residue and the mixture heated to 120 °C. In order to ensure removal of methanol in time, the reaction performed under distillation condition. After 8 h, the mixture was cooled to room temperature. Potassium carbonate was filtered off and washed with dichloromethane (50 mL × 3 mL). The solvent was removed under reduced pressure. Progress of the reaction was monitored by thin layer chromatography (TLC). On completion of the reaction, the residue was separated on silica gel column chromatography to give product as white solid.

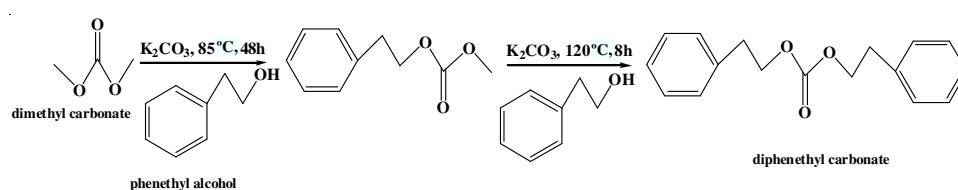


Fig. 1. General synthetic procedure for diphenethyl carbonate

TLC and silica gel column chromatography: TLC was carried out using silica gel GF254 (Merck) as stationary, petroleum ether: ethyl acetate (5:1, v/v) as mobile phase. Silica gel column chromatography was carried out using a glass column (6 cm × 100 cm i.d.) filled with silica gel (0.03-0.06 mm, Qingdao ocean chemistry factory, China), eluted with petroleum ether: ethyl acetate (15:1, v/v), checked by TLC.

Structure identification: IR spectra was recorded with a EQUIVOX55 infrared spectrometer, the sample was analyzed as KBr micropellets. ¹H NMR spectra data

were recorded on an AVANCE III 400 Hz spectrometer with CDCl_3 as solvent and TMS as internal reference standard.

Pyrolysis-gas chromatography/mass spectrometry: Pyrolysis-gas chromatography/mass spectroscopy analysis was tested on a combined system of a GC6890/5973 GC/MS (Agilent Corporation, USA) and CDS5200 pyrolyzer (CDS corporation, USA). Pyrolysis temperature was set up at 300, 500 and 700 °C, respectively, heating time 20 s. GC/MS qualitative analysis was conducted with HP-5MS capillary column (30 m \times 0.25 mm i.d. \times 0.25 μm d.f); column temperature programmed from 60 °C for 1 min, then raised to 280 °C at a rate of 150 °C/min; carrier gas helium; flow rate 10 mL/min; injector temperature 280 °C; volume injected 1 μL ; MS condition: ionization energy 70 eV; ion source temperature 230 °C; mass scan range 35-500 amu. Data analyses were performed with a HP Chem. Station G1034 (version 3.00) to match the NIST98 Mass Spectra Library by comparison.

RESULTS AND DISCUSSION

Sample preparation: The procedure of the synthesis according to this study was shown in Fig. 1. Some techniques such as IR, ^1H NMR were adopted to identify the structure of the diphenethyl carbonate (Table-1). The yield of diphenethyl carbonate was 72.3 %.

TABLE-1
IR, ^1H NMR IDENTIFICATION OF THE SYNTHESIZED DIPHENETHYL CARBONATE

IR (KBr, ν_{max} , cm^{-1} micropollets)	^1H NMR δ (in CDCl_3)
1730 (C=O)	2.96-2.99 (4H, t, 2Ph- CH_2)
1720 (C-O-C)	4.31-4.35 (4H, t, $\text{CH}_2\text{-O-CO-O-CH}_2$)
701, 754 (mono-substituted Ph)	7.21-7.33 (10H, m, 10Ph-H)
1405 (CH ₂)	—

Study of pyrolysis products of diphenethyl carbonate: The decomposition compounds were identified by mass spectra after separated by GC. The total ion chromatographic curve was shown in Fig. 2. It was shown that less pyrolysis products at 300 and 500 °C. Although the array of pyrolysis products were relative complex, a similar range of the main components were observed at 700 °C. The major compounds found as a result of pyrolysis of diphenethyl carbonate were listed in Table-2.

The relative content variations of phenethyl alcohol and 2-phenethyl- β -phenylpropionate were shown in Fig. 3. With the increase of temperature, the relative content of phenethyl alcohol increased continuously, but decreased sharply in case of 2-phenethyl- β -phenylpropionate.

The pyrolysis of diphenethyl carbonate produced 2.55 % phenethyl alcohol at 300 °C, 11.89 % at 500 °C and 32.21 % at 700 °C. Among pyrolysis products, phenethyl alcohol was the compound we expected, other compounds were decomposition compounds or rearrangement compounds during high temperature condition. The result indicated pyrolysis of diphenethyl carbonate at high temperature was better

TABLE-2
MAIN PYROLYSIS PRODUCTS OF DIPHENETHYL
CARBONATE AT DIFFERENT TEMPERATURES

Retention time (min)	Pyrolysis product	m.w.	Area (%)		
			300 °C	500 °C	700 °C
3.77	Toluene	92	–	–	4.40
4.87	Ethylbenzene	106	–	–	1.31
5.21	Styrene	104	0.21	9.14	22.45
10.07	Phenylethyl alcohol	122	2.55	11.89	32.21
16.34	Acetic acid, 2-phenylethyl ester	152	1.57	1.55	2.67
20.52	Bibenzyl	182	–	0.01	1.69
33.63	2-Phenethyl- β -phenylpropionate	254	90.69	73.58	27.77

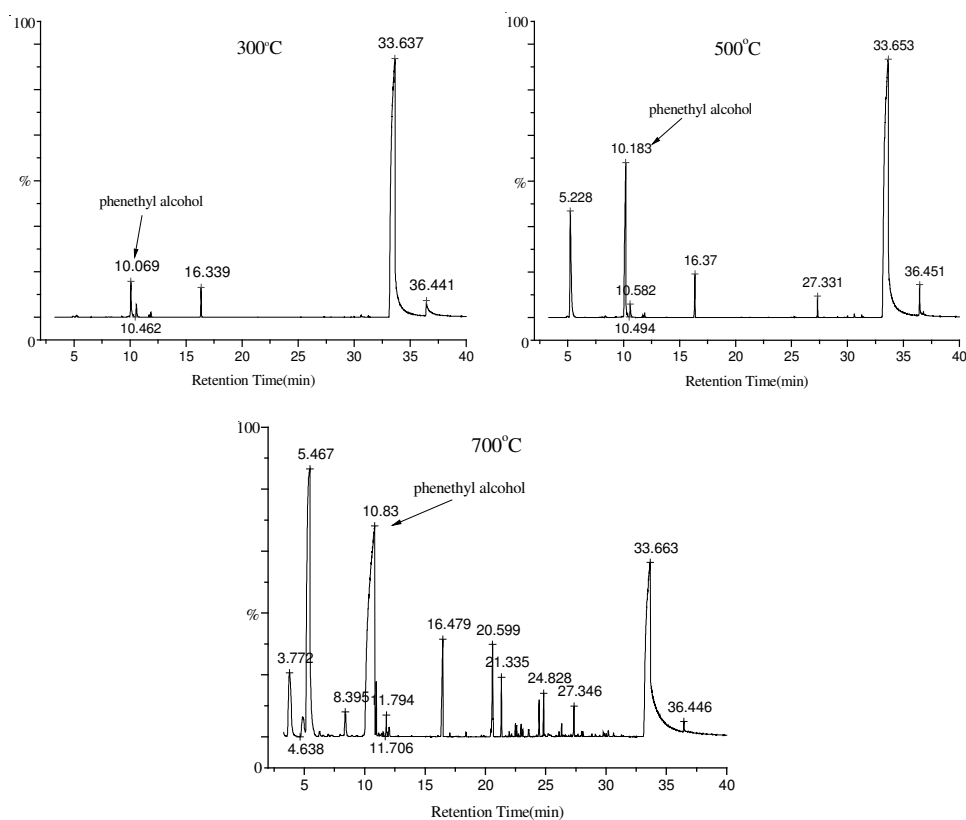


Fig. 2. Total ion chromatograms (TIC) of the pyrolysates of diphenethyl carbonate at 300, 500 and 700 °C

than at low temperature, because there was a significant amount of phenethyl alcohol occurred. Phenethyl alcohol was the main products at 700 °C. The pyrolysis-gas chromatography/mass spectroscopy indicated that the flavour precursor release characteristic flavour during high temperature treatment.

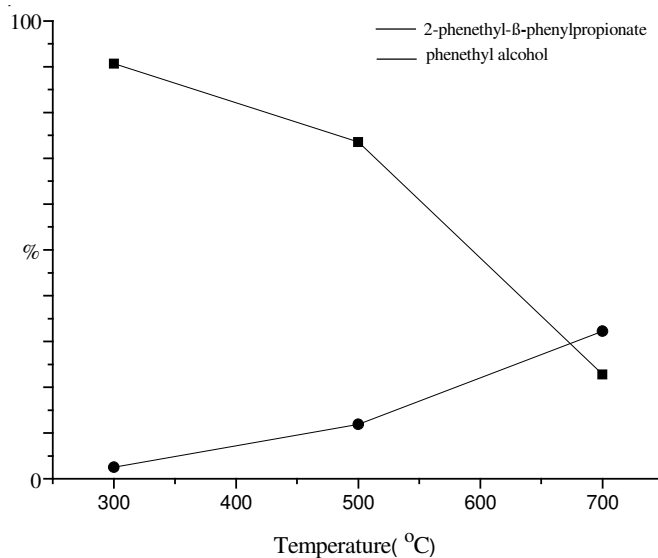


Fig. 3. Relative contents of phenethyl alcohol and 2-phenethyl-β-phenylpropionate at different temperatures

Pyrolysis mechanism of diphenethyl carbonate: The cleavage of C-O single bonds and C-C single bonds occurred probably during the initial thermal degradation stage of diphenethyl carbonate, because the benzene ring and C=O double bond possessed the high thermal stability. That no carbonate ester was detected in pyrolysis products indicated that the cleavage of at least one of the two C-O single bonds of ester group occurred.

There are two kinds of C-O single bond of diphenethyl carbonate, the one is C-O single bond of ester group and the other is C-O single bond of phenylethyloxy group. Cleavage of them could give different kinds of radicals (Fig. 4).

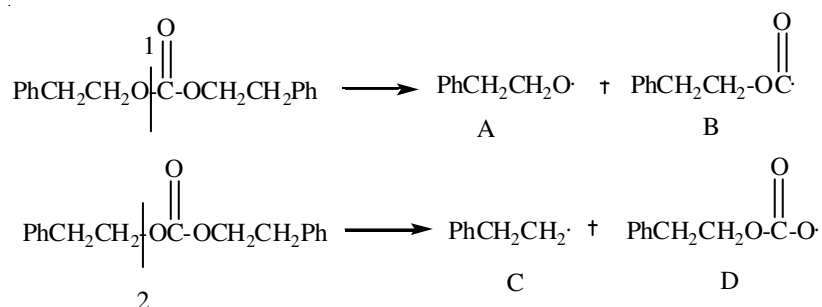


Fig. 4. Species of radicals

The reactions for the formation of the major pyrolysis products of diphenethyl carbonate could be described in Fig. 5.

At 300 °C, the relative content of 2-phenethyl- β -phenylpropionate reached to 90.69 % among pyrolysis products. The radical B and C could recombine to form 2-phenethyl- β -phenylpropionate and the radical A and D could also be further degraded to form the radical C and B, respectively. Hence, the amounts of the radical B and C were very high at this temperature, the content of 2-phenethyl- β -phenylpropionate was certainly high. From this result, it is speculated that not only the cleavage of two kinds of the C-O single bonds occurred, but also the cleavage of the C-O single bonds was predominant, in other words, the cleavage of the C-C single bonds rarely occurred. The pyrolysis of diphenethyl carbonate also produced 2.55 % phenylethyl alcohol.

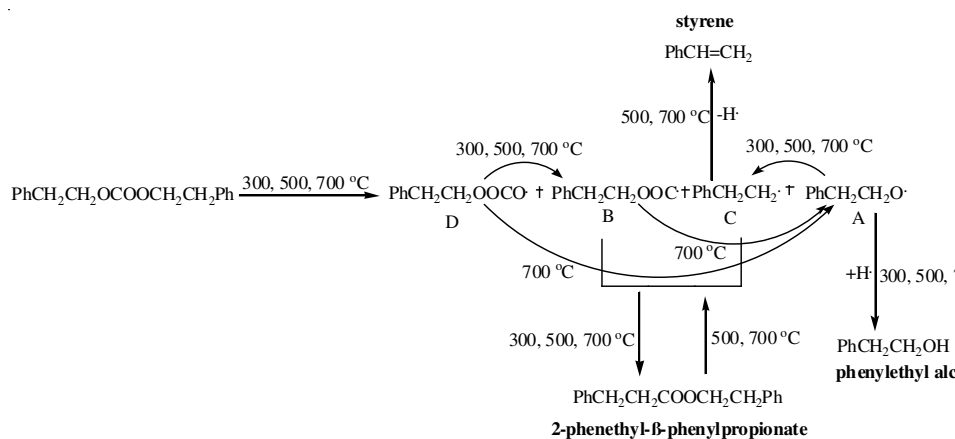


Fig. 5. Pyrolysis mechanisms of diphenethyl carbonate at different temperatures

At 500 °C, the relative content of 2-phenethyl- β -phenylpropionate decreased to 73.58 % because of its thermal instability causing the re-decomposition. However, 2-phenethyl- β -phenylpropionate was still the main pyrolysis product and the species of pyrolysis components at 500 °C were similar to those at 300 °C. At this time, less the radical A transformed into the radical C and the more phenylethyl alcohol formed. The decomposition of 2-phenethyl- β -phenylpropionate produced the radical B and C, so the trend of evolution of styrene from the radical C also increased. Thus, it could be concluded that the pyrolysis behaviour at 500 °C was analogous to that proposed for the thermal decomposition at 300 °C of diphenethyl carbonate.

At 700 °C, the relative content of 2-phenethyl- β -phenylpropionate sharply reduced to 27.77 %, to further verify its thermal instability. Similar to at 500 °C, the further decomposition of 2-phenethyl- β -phenylpropionate produced a large number of the radical C which formed more styrene. The content of the radical A transformed into the radical C decreased significantly, the trend of evolution of phenylethyl alcohol enhanced obviously. The radical B and D could also transform into the radical A and phenylethyl alcohol was the most in all products at this temperature.

The majority of pyrolysis products were still phenylethyl alcohol, 2-phenethyl- β -phenylpropionate and styrene. All of these facts implied that the pyrolysis mechanism of diphenethyl carbonate not altered at 700 °C.

Conclusion

A flavour precursor of diphenethyl carbonate was synthesized by the transesterification of dimethyl carbonate and phenethyl alcohol with potassium carbonate as a catalyst. The pyrolysis mechanism of diphenethyl carbonate was discussed by pyrolysis-gas chromatography/mass spectroscopy analysis. Result from pyrolysis-gas chromatography/mass spectroscopy suggested that the amount of phenethyl alcohol increased rapidly with the increase of temperature, but the amount of 2-phenethyl- β -phenylpropionate decreased sharply. Phenethyl alcohol was the main product at high temperature. It indicated that the flavour precursors release characteristic flavour during high temperature treatment. The typical thermal degradation mechanism of diphenethyl carbonate included the cleavage of the C-O single bonds of ester group and phenylethoxy group and the recombination of radicals at three temperatures.

ACKNOWLEDGEMENTS

This work was completed in National Synchrotron Radiation Laboratory of China. The authors thank to National Natural Science Foundation of China (No. 20405013) for the financial support.

REFERENCES

1. A.G. Kallianos, F.A. Shelburne, R.E. Means, R.K. Stevens, R.E. Lax and J.D. Mold, *Biochem. J.*, **87**, 596 (1963).
2. T.V. Van Auken, H.J. Grubbs and W.R. Johnson, Smoking Tobacco Compositions, US Patent 4177339 (1979).
3. W.S. Schlotzhauer and O.T. Chortyk, *J. Anal. Appl. Pyrol.*, **12**, 193 (1987).
4. R.W. Jenkins Jr. and D.D. McRae, *Recent Adv. Tob. Sci.*, **22**, 337 (1996).
5. S.J. Stotesbury, H.A. Digard, L.J. Willoughby and A. Couch, *Beitr. Tabakforsch. Int.*, **18**, 147 (1999).
6. S.J. Stotesbury, L.J. Willoughby and A. Couch, *Beitr. Tabakforsch. Int.*, **19**, 55 (2000).
7. W. Xie, J. Tang, X.H. Gu, C.-R. Luo, G.-Y. Wang, *J. Anal. Appl. Pyrol.*, **78**, 180 (2007).
8. W.-C. Xie, X.-H. Gu, Z.-C. Tan, J. Tang, G.-Y. Wang, C.-R. Luo and L.-X. Sun, *J. Thermal Anal. Calorim.*, **87**, 505 (2007).
9. S. Wang, B. Liu and Q. Su, *J. Anal. Appl. Pyrol.*, **71**, 393 (2004).
10. M. Selva, C.A. Marques and P. Tundo, *J. Chem. Soc. Perkin Trans I*, 1889 (1995).