Thermal Decomposition of Tobaccos

VII: Influence of Atmosphere on the Formation of Gas Phase Constituents*

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INTRODUCTION

The thermal degradation behavior of tobacco is both qualitatively and quantitatively different when the samples are thermally decomposed in either air or an inert gas (2, 3). In helium, tobacco undergoes a 32% weight change between 150° and 350° C and an 18% weight change between 350° and 550° C. The derivative thermogravimetric curve (DTG) contains rate of weight loss maxima at 75°, 210°, 250°, 400° and 650° C. The maxima at 210° and 400° C are not well defined but are characteristic of tobacco. By contrast, the thermal degradation of tobacco in the presence of air has a 36% weight loss between 150° and 350° C and a 34% weight loss between 350° and 500° C (2). The DTG curve contains five maxima at 75°, 210°, 275°, 430° and 650° C, with the two major maxima being at 275° C and 430° C (2, 3).

Although the influence of atmosphere on the weight loss of tobacco has been defined, there is little information on the influence of the atmosphere on the formation of the major gas phase constituents. Data on the formation of both CO and CO₂ have shown that they are formed within a well defined temperature range and correspond to the thermal analysis data (1). Therefore, other gas phase constituents should also have well defined temperatures of formation. By determining the profiles for several additional low molecular weight gases in both air and helium, it should be possible to define the influence of an oxidizing atmosphere on the thermal decomposition of tobacco with respect to the formation of these gas phase constituents.

Baker and Kilburn have shown that the alkanes and oxides of carbon are formed in well defined regions of a burning cigarette (4). The purpose of the present communication is to provide additional evidence on the temperature of formation of the alkanes, alkenes, aldehydes, ketones and other gas phase components which

aid in defining the thermolytic processes occurring in a burning cigarette. To obtain this objective the formation profiles for methane, ethane, ethene, propane, propene, isoprene, formaldehyde, acetaldehyde, acetone, 2-butanone, benzene, and toluene have been determined from the thermal decomposition of tobacco in oxidizing and non-oxidizing atmospheres.

EXPERIMENTAL

University of Kentucky 1R1 reference tobacco was used for this study. The apparatus and the conditions employed for the thermal decomposition of tobacco have been previously described (3). To prevent condensation of the pyrolysis products in the gas sampling assembly the apparatus was modified so that the 1/16 in transfer line from the differential thermal analysis (DTA) unit to the gas sample valve, the 50 ml sample loop, and the transfer line from gas sampling valve to the gas chromatograph could be heated at 130° C.

The tobacco samples were thermally decomposed in both air and helium. For the analysis of the gas phase constituents, a 6 ft. × 1/4 in. column packed with 110–110 mesh Porapak Q was used. Gas chromatographic conditions were: injector, 200° C; detector, 250° C; column, initial 70° C for 7 min, 8°/min to 220° C; detector, FID. These conditions allowed for the separation of methane, ethene, ethane, propane, propene, butane, methanol, formaldehyde, acetaldehyde, acetone, isoprene, 2-butanone, benzene, and toluene.

The gases were identified by comparison of the retention time of the unknown peaks to the retention of known gases and were further substantiated by previously reported data on the gas phase constituents in cigarette smoke (5, 6). To obtain the formation profiles for each pyrolysis product, gas samples were collected and analyzed at a minimum of 20 different temperatures which required a minimum of eight thermal analysis runs. Additional runs were required to clearly establish the temperatures of maximum formation of some of these gases. By plotting the chromatographic peak heights of these components vs. temperature it has been possible to obtain profiles for the major gas phase constituents formed during thermal decomposition of tobacco. All gas components are reported as relative recorder response since the purpose of this study was to determine the temperatures for their optimum formation.

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Figure 1. Formation profiles of methane from the thermal degradation of 1R1 tobacco.

Figure 2. Formation profiles of ethene from the thermal degradation of 1R1 tobacco.

RESULTS AND DISCUSSION

1. Alkanes and Alkenes

Methane is the predominant hydrocarbon in the gas phase of cigarette smoke and, as expected, is one of the predominant gas phase hydrocarbons formed during the dynamic thermal degradation of tobacco (Fig. 1). Thermal degradation of tobacco in helium gives a methane profile having a temperature of maximum formation at approximately 500° C. This temperature of maximum formation corresponds to the maximum exhibited by the effluent gas detection (EGD) curve obtained from the 1R1 tobacco (3). Little weight loss occurs at this temperature indicating that methane is one of the major products formed at this temperature. A small quantity of methane is formed at temperatures below 350° C, and in comparison with CO and CO₂ it is one of the minor products formed during the temperatures of major weight loss of the tobacco. However, the presence of methane below 250° C indicates that radical reactions occur at these temperatures. The thermal decomposition of tobacco in air has a

Figure 3. Formation profiles of ethane from the thermal degradation of 1R1 tobacco.

significant influence on methane formation (Fig. 1). The temperatures of maxima formation coincide with the rate of weight change maxima at 300° and 420° C in the derivative thermogravimetric (DTG) curve. The role of oxygen for enhancing methane formation at 300° C most likely is due to its property of being a radical initiator (7). This premise is further supported by differential thermal analysis (DTA) data which show that the weight loss at this temperature is accompanied by a large exotherm. This exotherm is at least 100 times larger than that observed at the same temperature in helium (8). Therefore, the radical and exothermic reactions are large enough to enhance the formation of methane and other pyrolysis products.

The maximum for methane formation in air at 420° C corresponds to the rate of weight loss maximum exhibited by DTG which is at the ignition temperature of the tobacco (2). Even though tobacco is thermally decomposed in excess oxygen, the methyl radical intermediates are reacting with atomic hydrogen or abstracting hydrogen from other tobacco components to form methane rather than being completely destroyed by reacting with oxygen or other gas phase intermediates. The formation profiles for ethene and ethane are shown in Figures 2 and 3, respectively. In helium these gases have one formation maximum at 500° C and are formed in trace quantities below 400° C. This is analogous to the temperature of formation of methane suggesting that these hydrocarbons have the same thermal requirements for formation. An oxidizing atmosphere has a dramatic influence on their formation since both profiles contain two maxima which correspond to the rate of weight loss maxima of the DTG curves (2). The low temperature maximum (300° C) gives further evidence that oxygen enhances the radical reactions occurring at this temperature. Of particular interest is the enhanced formation of both C_2H_4 and C_2H_6 at 420° C in the presence of air, which is converse to the profiles obtained for methane. Even though the temperatures for maximum formation for these products are the same (420° C) it is obvious that oxygen can effect either an increase or decrease in the formation levels of the hydrocarbons. This also is evident for propene formation (Fig. 4) since its profile is quite similar to those of CH_4 , C_2H_4 and C_2H_6 and, like methane, it is formed in lower quantities in air than in helium.

The profiles in Figure 5 are a composite of propane, methanol and methyl chloride (5). Even though this profile contains at least these three components it gives valuable information. Except for the maximum at 250° C the profile obtained in helium is qualitatively similar to the other hydrocarbons. Since the other hydrocarbons do not have formation maxima at these temperatures this maximum (250° C) is most likely due to the presence of only methanol or methyl chloride. In comparison with helium, air enhances the formation of these components (250°–350° C) but air reduces their formation at higher temperatures. The profiles of the hydrocarbons containing four or more carbon atoms also exhibit maxima that are characteristic hydrocarbons.

Figure 4. Formation profiles of propene from the thermal degradation of 1R1 tobacco.

Figure 5. Formation profiles of propane from the thermal degradation of 1R1 tobacco.

However, the chromatographic peaks for the butanes and the pentanes, contain other components and will not be presented until a more complete separation has been achieved.

The hydrocarbons appear to have common temperatures for optimum formation which occur between 450° and 525° C. In helium, they are formed during a minimum weight loss transition. This indicates that the processes leading to their formation are not predominant during the major region of weight change. In an oxidizing atmosphere hydrocarbon formation is enhanced between 275° and 325° C, which indicates that they can be formed at these temperatures in a burning cigarette. These data agree in part with those reported by Baker and Kilburn (4) who found that maximum concentrations of methane, ethane, ethene, and other low molecular weight hydrocarbons are found in the burning cigarette at approximately 200° C. Therefore, the data indicate that oxygen may be responsible for their formation, even though the oxygen content at this temperature in a burning cigarette is between 0.2 and 0.5 percent (4).

2. Isoprene

The formation profiles presented in Figure 6 show that in helium isoprene has two temperatures for maximum

Figure 6. Formation profiles of isoprene from the thermal degradation of 1R1 tobacco.

formation. The maximum at 380° C is due primarily to the decomposition of the cyclohexane-soluble isoprenoids, whereas the maximum at 475° C is due to the more polar isoprenoids (9). This shows that there are at least two temperature regions involved in isoprene formation which suggests isoprene has two types of thermally labile precursors. In air, the level of isoprene formed has been reduced in comparison to that in helium. The maximum at 300° C again shows that air enhances the formation of the non-oxygen containing hydrocarbons at this temperature. However, the low level of isoprene formed at 420° C indicates there is an antagonistic effect of oxygen on isoprene formation. This is expected since this unsaturated hydrocarbon or its precursors should be more susceptible to air oxidation at this temperature.

3. Aliphatic Aldehydes and Ketones

In an inert atmosphere formaldehyde is formed as low as 200° C (Fig. 7). This is expected since the formaldehyde precursors, such as glucose, fructose, and sucrose, begin to decompose at this temperature (10, 11). In the non-oxidizing atmosphere there is little formation of CH₂O above 400° C, which indicates that decomposition of the carbonaceous residue does not contribute significantly to CH₂O formation.

In comparison with helium, air effects a twofold increase of formaldehyde formation at 265° C. However, the most striking difference between the profiles is the CH₂O maximum at 420° C which again corresponds to the DTG rate of weight change maximum. In comparison with the CH₂O formed in helium this is over a 30fold increase. Therefore, in air formaldehyde is formed in significant quantities at both 265° and 420° C.

Acetaldehyde (Fig. 8) has formation profiles that are similar to formaldehyde. This is expected since acetal-

Figure 7. Formation profiles of formaldehyde from the thermal degradation of 1R1 tobacco.

dehyde and formaldehyde have common precursors (10, 11). However, acetaldehyde is formed in slightly larger quantities than formaldehyde. Air effects a threefold increase in the level of acetaldehyde formed at 290° C, and there is no maximum present at 420° C. The absence of this maximum indicates that, in air, it is not formed in large quantities during the major weight loss of tobacco (350°–500° C). If it were formed in substantial quantities there should have been evidence of a maximum even if it were being destroyed by reacting with O₂ or other smoke components. It should be noted that acetaldehyde is one of the few examples of the gas phase constituents in which the formation profile contains no maximum at 420° C.

In helium, the formation profile of acetone (Fig. 9) is different from the profiles of either CH₂O or C₂H₄O since its maximum formation is at 450° C. Although acetone is the major component (12, 13) the profiles contain at least four other components which have not been resolved by gas chromatographic analysis and include acrolein, propionaldehyde, furan and propionitrile. Since the carbohydrates are major precursors for acetone, acrolein, propionaldehyde and furan (12, 13) one would expect them to have similar formation profiles. However, the profile is not as simple as those of either CH₃CHO or CH₂O and indicates that the reactions leading to the formation of acetone, furan, etc., are quite complex. Although the gas phase aldehydes and ketones have common precursors these data show that higher temperatures are required for optimum formation of acetone. Acetone is formed at temperatures as low as 200° C, however, it is formed in lower levels than either CH₂O or CH₃CHO, which is in agreement with published data (13). In air it is formed between 200° and 340° C and the maximum at 240° C represents a 20fold increase in its formation. The temperature for maximum formation also coincides with those for both CH₂O and C₂H₄O. The absence of a sharp maximum at 420° C shows that oxygen has little influence on the level of acetone formed at these temperatures.

The profiles for 2-butanone (Fig. 10) are qualitatively similar to those of acetone. In helium, the major portion of 2-butanone is formed between 250° and 500° C even though it is formed as low as 200° C. Air effects a fivefold increase in the level of 2-butanone formed at 285° C. The formation maximum at 420° C gives evidence that 2-butanone is formed during the major weight loss even though its level is no greater than that formed in helium at the same temperature.

The profiles for the low molecular weight aldehydes and ketones have shown that in helium the temperatures for optimum formation of the aldehydes are quite different from the two ketones, acetone and 2-butanone. Although sugars and cellulose are common precursors for these compounds (10), it is evident that their formation requires quite different thermal environments. Air enhances the formation of both aldehydes and ketones between 200° and 300° C, and the temperatures for maximum formation are approximately the same.

Figure 8. Formation profiles of acetaldehyde from the thermal degradation of 1R1 tobacco.

Figure 9. Formation profiles of acetone from the thermal degradation of 1R1 tobacco.

Figure 10. Formation profiles of 2-butanone from the thermal degradation of 1R1 tobacco.

Therefore, one can predict that the majority of the acetaldehyde and formaldehyde found in the gas phase cigarette smoke can be formed at temperatures below 350° C, whereas acetone and 2-butanone can be formed between 200° and 500° C.

4. Aromatic Hydrocarbons

In helium, the formation profile for benzene (Figure 11) shows that it is formed primarily above 400° C, yet it is formed as low as 200° C and, therefore, it has a wide temperature range for formation. Benzene contains an additional maximum at 570° C which is unique since no other known profile of a gas phase constituent has a maximum at this temperature. Formation profiles for benzene from other modified tobaccos indicate that this maximum is not an artifact and the major portion of benzene is formed at this temperature (9). As compared with helium, air effects at least a 10fold increase of benzene formation at 285° C in helium. The temperature for maximum formation again coincides with the rate of weight loss maximum exhibited by DTG (2). The increased formation of benzene at lower temperatures is coincident with increased levels of the unsaturated hydrocarbons. These increases may be caused by the thermal cracking of molecules containing the benzene moiety or even at this low temperature may be a result of enhancement of benzene pyrosynthesis by O₂. Air

Figure 11. Formation profiles of benzene from the thermal degradation of 1R1 tobacco.

also effects an increase in benzene formation at 450° C but does not decrease its temperature for maximum formation. These data provide additional evidence that oxygen plays an important role in enhancing the formation of the gas phase hydrocarbons.

In helium, the formation profile for toluene (Fig. 12) shows that it has two areas for maximum formation. The maximum at 240° C indicates that it may be formed as a result of thermal cracking of larger molecules containing the toluene moiety. The maximum at 450° C is identical to those for benzene and the alkanes. Air does not have as large an influence on its formation as it does for benzene or the other hydrocarbons.

Figure 12. Formation profiles of toluene from the thermal degradation of 1R1 tobacco.

It does, however, effect an overall increase of toluene formation especially between 300° and 400° C.

The present results substantiate the premise that the gas phase constituents have well defined temperatures of formation. It is evident that in helium, 450° C is the temperature for optimum formation of the saturated, unsaturated and aromatic hydrocarbons even though little weight loss occurs at this temperature. This suggests that the carbonaceous tobacco residue thermally decomposes via radical fragmentation involving homolytic bond scission, which partially explains the hydrocarbon formation at these temperatures. It must be noted that larger quantities of hydrocarbons will be formed during single temperature (static) pyrolysis (ca. 800° C) than during the dynamic thermal decomposition. This presumably occurs because static pyrolysis involves generation of low molecular weight products from the thermal degradation of the tobacco substrate and from thermal reactions that occur in the gas phase. Therefore, in the present investigation we have determined primarily the contribution of only the tobacco substrate to the formation of the gas phase constituents.

Also we have established that air enhances the formation of the aforementioned gas phase constituents mainly between 200° and 300° C. This seems significant because even though the air has little influence on the total weight loss of tobacco between 150° and 350° C it has a large influence on the levels of gas phase products that are formed. From these data the maximum concentrations of the hydrocarbons found in a burning cigarette at 200° C (4) most likely are the result of oxygen catalysis rather than being formed under non-oxidizing conditions.

SUMMARY

Formation profiles have been obtained for methane, ethane, ethene, propane, propene, butanes, butenes, isoprene, formaldehyde, acetaldehyde, acetone, 2-butanone, benzene, and toluene from the thermal decomposition of tobacco in the presence of helium and air. These data show that in helium the temperatures for optimum formation of gas phase constituents were: hydrocarbons, 450° C; aldehydes, 300° C; ketones, 450° C; isoprene, 380° and 475° C; and aromatic hydrocarbons, 450° C. Air enhances the formation of these gas phase constituents at 280° C and in most cases at 420° C, the latter temperature is an area of major weight loss of tobacco. Each formation maximum corresponds to a rate of weight loss maximum exhibited by derivative thermogravimetry. The results also show that it is possible to use effluent gas analysis to define the thermal behavior of tobacco in terms of the formation of the gas phase constituents which provide a means to elicit the processes that occur during the thermal decomposition of tobacco.

ZUSAMMENFASSUNG

Bei der thermischen Zersetzung von Tabak in Helium und Luft wurden Entstehungsprofile für Methan, Äthan, Äthen, Propan, Propen, Butan, Buten, Isopren, Formaldehyd, Acetaldehyd, Aceton, 2-Butanon, Benzol und Toluol erhalten. In Helium zeigen sich für die Inhaltsstoffe der Gasphase Bildungsmaxima bei folgenden Temperaturen: Kohlenwasserstoffe, 450° C; Aldehyde, 300° C; Ketone, 450° C; Isopren, 380° C und 475° C; aromatische Kohlenwasserstoffe, 450° C. Luft verstärkt die Bildung dieser Gasphasenbestandteile bei 280° C und in den meisten Fällen bei 420° C. Bei der letztgenannten Temperatur ist ein größerer Gewichtsverlust des Tabaks zu beobachten. Jedes Bildungsmaximum entspricht einer durch Thermogravimetrie dargestellten, maximalen Gewichtsverlustrate. Die Ergebnisse zeigen auch, daß es durch die Analyse des austretenden Gases möglich ist, das thermische Verhalten des Tabaks aufgrund der Bildung der Gasphasenbestandteile zu bestimmen, welche es ermöglichen, die während der thermischen Zersetzung des Tabaks stattfindenden Vorgänge aufzuklären.

RÉSUMÉ

De la décomposition thermique du tabac en présence d'hélium et d'air, on a obtenu des courbes de formation pour les composés suivants: méthane, éthane, éthène, propane, propène, butanes, butènes, isoprène, formaldéhyde, acétaldéhyde, acétone, 2-butanone, benzène et toluène. Dans l'hélium, les températures de formation maximale des constituants de la phase gazeuse sont les suivantes: 450° C pour les hydrocarbures, 300° C pour les aldéhydes, 450° C pour les cétones, 380° C et 475° C pour l'isoprène, et 450° C pour les hydrocarbures aromatiques. L'air accélère la formation de ces constituants de la phase gazeuse à 280° C et dans la plupart des cas à 420° C. Cette dernière température est dans une zone de grande perte de poids du tabac. L'on peut montrer par thermogravimétrie que chaque formation maximale correspond à un taux maximal de perte en poids. Les résultats démontrent également qu'il est possible d'utiliser l'analyse par effluent gazeux pour définir le comportement thermique du tabac en termes de formation des constituants de la phase gazeuse. Ceci procure un moyen de déterminer les processus se déroulant au cours de la décomposition thermique du tabac.

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