Model Pyrolysis - The Study of Cellulose*

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INTRODUCTION

Relating smoke products to smoke precursors when burning any naturally occurring plant material is an ambiguous task, at best. To facilitate interpretation of results a simple, model pyrolysis system was studied using cellulose as the smoke precursor and monitoring benzo(a)pyrene [B(a)P] as the smoke product. Cellulose was ideally suited because its structure and stereochemistry are known; because it was available in pure form; and because it is nonvolatile, it necessarily must decompose on heating thereby contributing to the products of combustion. In addition, cellulose is found abundantly in plants and constitutes more than 16% of the dry weight of tobacco.

ISOTHERMAL PYROLYSIS EXPERIMENTS

Procedure

Pyrolysis was carried out in a vertically mounted Vycor® glass tube (2"×15") containing Berl saddles which covered a thermocouple at the tube's center. Carrier gas (nitrogen, unless otherwise specified) was introduced at the top of the tube, and pyrolyzate was collected at the lower end of the tube on either Cambridge filter pads or in cold traps. Usually a carrier gas flow rate of 85 ml per minute was used while heating was controlled by a 220 volt electric furnace. The substance to be pyrolyzed was introduced at the top of the tube through a powder funnel (under carrier gas) at the rate of 5 grams per 30 minutes.

The pyrolyzate was dissolved in reagent grade acetone and evaporated to dryness on a steam bath, and the residues were dissolved in small volumes of benzene-methanol (4:1). Aliquots were chromatographed on acetylated paper using ethylene glycol monomethyl ether as the developing solvent. The details of the paper chromatographic procedure and subsequent fluorimetric analysis of B(a)P have been published (1). The results of analyses are given as nanograms (ng) of B(a)P formed per gram of cellulose (or other material) pyrolyzed.

Results and Discussion

B(a)P Yield vs. Temperature The results of the isothermal pyrolysis of cellulose at various temperatures are given in Table 1. In general, the yield of B(a)P increased with temperature. The yield below 600° C was relatively small, between 600° C and 750° C varied only slightly, and above 750° C increased very sharply. These results suggested two independent processes for forming B(a)P; one operating below 650° C and the other taking effect above 750° C.

TABLE 1 Isothermal pyrolysis of cellulose: Temperature vs. B(a)P yield

Pyrolysis temperature (°C)	B(a)P yield (ng/g cellulose)
350	0
450	60
500	<100
550	<1,000
600	5,000
650	20,000
700	16,000
750	16,000
775	53,500
800	76,000
850	100,000
880	142,000

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B(a)P Yield vs. Oxygen Concentration When nitrogen was replaced with atmospheres containing oxygen, an unexpected increase in the B(a)P yield resulted (Table 2). This experiment suggests that any attempt to increase the amount of oxygen in an oxygen-deficient pyrolysis zone will not decrease the amount of B(a)P formed there.

TABLE 2

Isothermal pyrolysis of cellulose: Effect of oxygen

Pyrolysis temperature (°C)	Carrier gas	B(a)P yield (ng/g cellulose)
700	Nitrogen	16,000
700	Nitrogen: oxygen (80:20)	15,000
850	Nitrogen	100,000
850	Nitrogen: oxygen (90:10)	114,000
850	Nitrogen: oxygen (80:20)	144,000

TABLE 3

**Isothermal pyrolysis of cellulose at 850° C in nitrogen:
Effect of metals**

Metallic sponge	B(a)P yield (ng/g cellulose)
None	100,000
Copper (Chore Girl*)	124,000
Stainless steel (Kurly Kate*)	900
Iron (steel wool)	270

* Trade name

TABLE 4

Isothermal pyrolysis of cellulose with 10% additive at 850° C in nitrogen

Additive	B(a)P yield (ng/g cellulose)
None	92,000
Tungsten powder	95,000
Alumina	80,000
Ceric ammonium nitrate	65,000
Aluminum t-butoxide	62,000
Cupric chloride	59,000
Aluminum hydroxide	56,000
Zinc peroxide	50,000
Cupric acetate	44,000
Aluminum nitrate	34,000
Vanadium pentoxide	30,000
Cupric oxide	30,000
Sodium nitrate	24,000
Cupric nitrate	23,000
Nickel acetate	14,000
Iron powder	13,000
Ferrous oxalate	10,000
Nickel powder	7,600
Nickel oxalate	6,000
Cobalt powder	4,800
Ferric oxide	3,500
Ferrocene	350

B(a)P Yield vs. Additives (at 850° C) To learn the effect of high-surface-area metals on the pyrolysis of cellulose, the packing in the tube was partially replaced by a metallic sponge (scouring pad), see Figure 1. Cellulose, in contact with these sponges, was pyrolyzed (Table 3). Because nearly complete inhibition of B(a)P formation by the iron sponges was noted, a series of pyrolyses were performed in which the cellulose was mixed with one-tenth its weight of various inorganic materials. The results are listed in Table 4.

FIGURE 1

Isothermal pyrolysis apparatus

The conclusions drawn from these isothermal studies were: compounds of the metallic elements were more effective than were the metals themselves; in a salt, the anion exerted some effect with nitrate being the more effective in decreasing B(a)P yield; and of the metallic elements; iron, cobalt, and nickel were the only ones tried which showed any effectiveness. In the case of iron compounds,

decreased B(a)P yields resulted with all valance states of the metal. In addition, the degree of physical mixing of the inorganic compound with the cellulose appeared unimportant.

The anion and the cation in these salts exerted their effects independently which permitted the calculation of a numerical factor for each anion and cation. Multiplication of these factors by 92,000 (the control value for cellulose) gave a "predicted" value for the B(a)P yield which closely approximated the observed value (Table 5). Note that the factor for aluminium, being greater than one, implies that aluminium has a tendency to increase B(a)P formation.

It was apparent that B(a)P was not the only product whose yield was reduced, because the total pyrolyzate which formed abundantly from cellulose at 850° C was absent in the cellulose-plus-iron experiments. The paper chromatograms in which B(a)P was separated, normally had many fluorescent zones attributed to other polycyclic compounds; the chromatograms of the cellulose-steel wool pyrolyzate had only one faint fluorescent zone which was identified as anthracene.

It was thought that this effect of iron might be occurring only in the absence of oxygen. This was not the case as both iron oxide and steel wool were capable of decreasing B(a)P yield both in air and in nitrogen (Table 6). The effect of water on this cellulose-iron reaction is shown in Table 7. Evidently the presence of water prevented the iron from inhibiting the B(a)P formation.

Finally, the effect of iron at various pyrolysis temperatures was studied. The resulting B(a)P yields are compared with those obtained from cellulose alone in Figure 2. From this we have concluded that this effect of iron begins at about 600° C, as the difference between the B(a)P yields with and without the iron decreased at the lower temperatures until at temperatures below 600° C they were about the same.

TABLE 5
Anion and cation factors for B(a)P yield
Predicted B(a)P yield = 92,000 (f_a) (f_c)

Anion	Factor, F_a	Cation	Factor, F_c
Metal	1.00	Aluminum	2.19
Acetate	0.79	Tungsten	1.03
Oxalate	0.68	Copper	1.00
Chloride	0.64	Sodium	0.93
Oxide	0.37	Vanadium	0.88
Nitrate	0.28	Iron	0.10
		Nickel	0.09
		Cobalt	0.05

TABLE 6
Isothermal pyrolysis at 850° C: Effect of iron

Material pyrolyzed	B(a)P yield (ng/g cellulose)	
	Nitrogen carrier	Air carrier
Cellulose	92,000	144,000
Cellulose with 10% iron oxide	3,500	5,000
Cellulose over steel wool	300	7,000

TABLE 7
Isothermal pyrolysis at 850° C in nitrogen:
Effect of iron plus water

Material pyrolyzed over steel wool	B(a)P yield (ng/g cellulose)
Cellulose	300
Cellulose:water (6:3)	44,300
Cellulose:water (6:4)	76,000

GRADUATED HEATING EXPERIMENTS

The large amount of B(a)P formed in the isothermal pyrolysis experiments was surprising; and, as noted, much lower B(a)P yields were observed at temperatures below 600° C. Therefore, this low-temperature, low-efficiency, B(a)P-forming process was studied. The type of experiment chosen was one in which the cellulose was heated from room temperature to 850° C during a period of several minutes with the pyrolyzate being collected during successive temperature intervals.

Procedure

The same apparatus was used except that the material to be heated was placed in the Vycor® glass tube on top of the porcelain packing. After adjusting the carrier gas flow (normally 85 ml per minute) the apparatus was allowed to heat up. In general, 22 minutes was required to bring the apparatus from 30° C to 850° C. The pyrolyzate was collected on Cambridge pads which were changed during the experiment, usually at intervals of 100° C.

FIGURE 2

Isothermal pyrolysis: B(a)P yield vs. temperature

The temperature of the material being pyrolyzed was higher than the recorded temperature, because the apparatus was not in thermal equilibrium while heating and because the heating elements in the furnace were at a much higher temperature than that recorded by the thermocouple. The magnitude of this error was estimated by measuring the temperature at the inner wall of the tube with a separate thermocouple. It was found that the temperature difference between the wall of the tube and the thermocouple could be as great as 100° C, depending on the temperature and the heating rate.

As B(a)P yields below 350° C were negligible, it was felt that the total yield of B(a)P collected from 350° C to 850° C was the most significant figure. Therefore, yields of B(a)P collected in the individual temperature ranges are given only when they are of special interest.

Results and Discussion

Effect of Flow Rate As seen in Table 8 increased carrier gas flow rate caused an increase in B(a)P yield; however, the total yields were much lower than those encountered in the isothermal pyrolysis experiments.

TABLE 8

Graduated heating of cellulose in nitrogen:
Flow rate vs. B(a)P yield

Carrier gas flow rate (ml/min.)	Total yield of B(a)P 350–850° C (ng/g cellulose)
85	560
285	810
500	1,340
1,050	1,080

TABLE 9

Graduated heating in nitrogen:
Effect of iron additives

Compound pyrolyzed	Total B(a)P yield 350–850° C (ng/g cellulose)
Cellulose (control)	560
Cellulose + 10% iron oxide	570
Cellulose + 10% iron powder	850
CMC (control)	370
CMC Ferrous Salt	410
Cellulose (control)	550
Cellulose + 10% ferricinium chloride	18
Cellulose + 2% ferricinium chloride	325

isothermal pyrolysis experiments.

It appeared that the graduated heating caused a very different type of B(a)P formation reaction to take place which did not involve volatile, gaseous intermediates; for increased flow would certainly reduce B(a)P yield, if volatiles were involved. These B(a)P precursors appeared to be nonvolatile being formed from the solid state decomposition of cellulose.

The destruction of B(a)P at the low flow rate (85 ml/min.) was demonstrated by heating cellulose plus added B(a)P. Only 38% of the added hydrocarbon was recovered in the pyrolyzate. When the volatility of B(a)P was decreased further by adsorption on charcoal, none was recovered.

Graduated Heating Experiments with Iron Additives Mixtures of cellulose plus iron and cellulose plus iron oxide were heated to 850° C. The B(a)P yields (Table 9) were not reduced below the control value; in fact, the yield with iron powder was somewhat greater.

Graduated Heating in Different Carrier Atmospheres The substitution of other gases for the nitrogen carrier gas was explored. The gases used were air, carbon dioxide, hydrogen, nitric oxide, and propylene. An attempt was made to include steam as one of the carrier gases. This was done by heating cellulose from 30° C to 850° C with a nitrogen gas flow of 85 ml per minute while water was added to the pyrolysis tube from a dropping funnel at a rate of about 1 ml per minute throughout the reaction. Results are given in Table 10.

TABLE 10

Graduated heating of cellulose in various atmospheres

Carrier gas (85 ml/min.)	B(a)P yield in temperature ranges °C (ng/g cellulose)					
	350-450	450-550	550-650	650-750	750-850	Total
Nitrogen	210	160	90	50	50	560
Air	300	180	100	90	60	730
Hydrogen	250	300	210	50	55	865
Nitric oxide	30	none	none	none	none	30
Propene	400	1,100	26,000	95,000	—	—
Carbon dioxide	290	410	110	70	100	980
Water (1 ml/min.)	none	980	1,660	370	300	3,310

When air was used, the total B(a)P yield was somewhat higher than it was in nitrogen. This result was the same as that observed with air in the isothermal pyrolyses and again suggests the futility of trying to reduce the yield of B(a)P by supplying additional oxygen to the pyrolysis.

Carbon dioxide and hydrogen nearly doubled the B(a)P yield with the maximum being in the 450° C to 550° C range. Water caused a sixfold increase in B(a)P yield. No acceptable hypothesis for explaining these increases is evident.

Propylene was used as a carrier gas because in pyrolyses in the 100° C to 400° C range it is reported (2) to act as an inhibitor, similar to nitric oxide. We observed, however, enormous yields of B(a)P which must have come from pyrolysis of the propylene itself.

When nitric oxide was used as a carrier gas, B(a)P formation was barely detectable (30 ng/g of cellulose). Because nitric oxide is a well-known inhibitor of free radical processes, there is reason to propose that a similar process occurred in this cellulose pyrolysis with nitric oxide.

To establish the mechanism of the effect of nitrate additives, cellulose mixed with sodium nitrite (a substance known *not* to evolve NO) was heated from 30° C to 850° C, as was cellulose mixed with MM-1* (a mixture we found to evolve oxides of nitrogen sharply at 425° C). With sodium nitrite a slight decrease in B(a)P yield was observed, but with MM-1 there was a decrease in total B(a)P yield of 39% (Table 11).

The amounts of B(a)P collected in the various temperature ranges showed that the decrease when using MM-1 was due mainly to a decreased formation of B(a)P in the 350° C to 450° C range. It was evident that the additive was preventing the formation of B(a)P only in the temperature range in which the additive decomposed.

Free-Radical Nature of the Low Temperature Reaction These experiments with nitric oxide made it appear that this low-temperature process involved a free-radical mechanism. The experiments with propylene to be described next reinforced this conclusion.

Propylene, when pyrolyzed isothermally at 550° C, yielded no detectable amount of B(a)P although at higher temperatures it gave abundant yields of B(a)P. When propylene was passed over cellulose while the temperature was raised from room temperature to 700° C, the

TABLE 11

**Graduated heating of cellulose in nitrogen:
Effect of nitrogen oxides**

Temperature ranges, °C	B(a)P yield (ng/g cellulose)		
	Cellulose (control)	Cellulose + 10% NaNO ₂	Cellulose + 10% MM-1*
350-450	210	170	60
450-550	160	110	140
550-650	90	60	100
650-750	50	40	30
750-850	50	56	10
TOTAL	560	436	340

* KNO₂ : KNO₃ : Cr₂O₃ : Fe₂O₃ = 6.38:2.52:7.6:12.0 (3)

propylene was converted to B(a)P at temperatures as low as 400° C. The data are given in Table 12. A probable explanation was that the cellulose decomposed in the 350° C to 450° C range with the formation of radicals, which were capable of initiating the reaction of propylene. In the absence

TABLE 12

Graduated heating experiments: Effect of propylene

Material pyrolyzed	Carrier gas	B(a)P formed (ng)			
		350-450	450-550	550-650	650-700
5 g cellulose	Nitrogen	1,065	800	450	250
Nothing	Propylene	none	none	24,200	79,000
5 g cellulose	Propylene	2,000	2,700	23,500	119,000

of cellulose this low temperature initiation was not possible; however, at much higher temperatures the propylene decomposed by thermal cleavage. Thus, the induced reaction of propylene by decomposing cellulose gave evidence of the production of radicals capable of initiating the conversion of propylene to B(a)P.

Experiments on Substances Other than Cellulose

The experiments reported thus far were all carried out with cellulose; however, in an earlier experiment the carboxymethylcellulose control sample gave 370 ng/g of B(a)P compared with 570 ng/g of B(a)P from cellulose. Thus, it appeared that the amount of B(a)P formed from two quite similar carbohydrates could vary considerably.

Cellulose was taken as the basic molecule, and the following structural changes were studied: the stereochemistry of the C₁-C₄ glycoside link, the nature of the substituent on C₅, and the molecular weight. The results are arranged in tabular form in Table 13. In the high polymers, the C₁-C₄ stereochemistry affected B(a)P yield. With the exception of glucuronic acid, all the

TABLE 13

Graduated heating experiments, 350°-850° C: Carbohydrate structure vs. B(a)P yield

Monomer		Dimer		Polymer	
Compound	B(a)P (ng/g)	Compound	B(a)P (ng/g)	Compound	B(a)P (ng/g)
β-D-glucose	220	Cellobiose	120	Cellulose	550
		Sucrose	130		
		Maltose	138	Amylose	143
				Soluble starch	80
Xylose	175			Xylan	500
Glucuronic acid	56			NO ₂ -oxidized cellulose	103

monosaccharides (β-glucose, dextrose and xylose) gave the same yield of B(a)P within the limits of error of the experiment. Likewise, all of the disaccharides (cellobiose, maltose, and sucrose) gave a constant yield.

Another regularity was the effect of converting the C₆-hydroxymethylene group to carboxyl. In both the polymer and monomer this change caused an 80% decrease in B(a)P yield. It was found in later experiments with pectic substances and with other nitrogen dioxide-oxidized

TABLE 14

Graduated heating experiments, 350°-850° C in nitrogen: Effect of physical form

Physical form	B(a)P yield (ng/g)	
	From cellulose	From NO ₂ -oxidized cellulose
Powder	550	103
Paper	418	—
Gauze	268	53

materials that this was quite general. Table 14 illustrates that a change in physical form affected the yield of B(a)P from the chemically altered cellulose to about the same extent that it did the control.

CONCLUSIONS

These experiments have led to the conclusion that large quantities of B(a)P can be formed by high temperature (850° C) isothermal pyrolysis of cellulose through a very efficient gaseous reaction route. In this reaction the B(a)P yield decreased in the presence of iron, cobalt, and nickel while the yield *increased* with increasing temperatures and with the introduction of oxygen into the system.

In contrast, the graduated heating experiments demonstrated that B(a)P was formed from cellulose at temperatures as low as 450° C. This reaction was inefficient with respect to B(a)P yield and was unaffected by the presence of metals. The B(a)P precursors were hypothesized to be nonvolatile, being formed via a solid state decomposition of cellulose and involving the generation of free radicals. This reaction was inhibited by the presence of nitric oxide or salts generating nitric oxide. Additionally, oxidation of the cellulose molecule at the C₆ position produced a decreased B(a)P yield.

One final point of interest relates to the quantity of B(a)P reportedly present in cigaret smoke (4). If, for example, one considers the filtration efficiency of cut tobacco filler per unit length of cigaret rod and the amount of the cigaret consumed during static burning, the reported yield of B(a)P is about 130 to 150 ng per gram of tobacco smoked in the normal way. The yield of B(a)P from the isothermal pyrolysis of cellulose at 880° C (approximately the coal temperature of a cigaret) was 1,000 times greater than that reported from a burning cigaret. Obviously, conclusions drawn from studies conducted under experimental conditions similar to isothermal pyrolysis at 850° C should not be extrapolated to the pyrolytic conditions which exist in a burning cigaret.

SUMMARY

The purpose of this study was to learn how cellulose pyrolysis was affected by changes in atmospheres, by varied pyrolysis temperatures, by the addition of inorganic materials, and by chemical modifications of the cellulose molecule.

These studies have led to the hypothesis that cellulose can pyrolyze by two different modes to form B(a)P. Large quantities of B(a)P can be formed by high temperature (850° C) isothermal pyrolysis of cellulose via a very efficient gaseous reaction route. In this reaction the B(a)P yield decreased in the presence of iron, cobalt, and nickel while the yield *increased* with increasing temperatures and with the introduction of oxygen into the system.

In contrast, graduated heating experiments demonstrated that B(a)P began to form at 450° C. This reaction was inefficient with respect to B(a)P yield and was unaffected by the presence of metals. The B(a)P precursors were hypothesized to be nonvolatile, being formed via a solid state decomposition of cellulose and involving the generation of free radicals. This reaction was inhibited by the presence of nitric oxide or salts generating nitric oxide. Additionally, oxidation of the cellulose molecule at the C₆ position produced a decreased B(a)P yield.

ZUSAMMENFASSUNG

Die Pyrolyse von Cellulose wurde in Abhängigkeit von einer Veränderung der Luftzusammensetzung, von unterschiedlichen Temperaturen, vom Zusatz anorganischer Stoffe und von chemischen Veränderungen des Cellulosemoleküls untersucht.

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Aus den Untersuchungen wurde die Hypothese abgeleitet, daß die Pyrolyse von Cellulose und die mit ihr verbundene Bildung von Benz(a)pyren auf zwei verschiedenen Wegen verlaufen kann. Große Mengen von Benz(a)pyren können bei isothermer Pyrolyse von Cellulose bei hohen Temperaturen (850° C) durch eine sehr wirksame Gasphasenreaktion entstehen. Bei dieser Reaktion verminderte sich die Benzpyrenausbeute in Gegenwart von Eisen, Kobalt und Nickel, während die Ausbeute bei Erhöhung der Temperaturen und bei Zuführung von Sauerstoff anstieg.

Im Gegensatz zu diesen Befunden ging aus Versuchen mit einer stufenweise durchgeführten Erhöhung der Temperatur hervor, daß sich Benz(a)pyren bei 450° C zu bilden beginnt. Diese Reaktion ergab keine sehr hohe Benzpyrenausbeute und wurde durch die Gegenwart von Metallen

nicht beeinträchtigt. Es wird vermutet, daß die B(a)P-Vorläufer schwer flüchtig sind und beim Abbau der Cellulose aus dem festen Aggregatzustand unter Bildung freier Radikale entstehen. Diese Reaktion wurde in Gegenwart von Stickoxiden oder von Salzen, aus denen diese Oxide gebildet werden, gehemmt. Außerdem führte die Oxydation des Cellulosemoleküls in C₆-Stellung zu einer geringeren Ausbeute an Benz(a)pyren.

RÉSUMÉ

La présente étude se propose d'élucider les effets qu'ont sur la pyrolyse de la cellulose les modifications d'atmosphères, les diverses températures de pyrolyse, l'addition de matières inorganiques et les modifications chimiques de la molécule de cellulose.

Ces études ont conduit à l'hypothèse que la cellulose peut se pyrolyser suivant deux modes différents pour former du B(a)P. De grandes quantités de B(a)P peuvent être formées par une pyrolyse isothermique de la cellulose à haute température (850°) suivant une voie de réaction gazeuse très efficace. Dans cette réaction, le rendement en B(a)P décroît en présence de Fe, Co et Ni, alors qu'il croît pour des températures croissantes et avec l'introduction de O₂ dans le système.

A l'opposé, des expériences de chauffage graduel ont démontré que le B(a)P commence à se former à 450° C. Cette réaction a un mauvais rendement en B(a)P et n'est pas affectée par la présence de métaux. On suppose que les précurseurs du B(a)P ne sont pas volatils, prenant naissance via une décomposition de la cellulose à l'état solide et comportant la production de radicaux libres. La réaction est inhibée par la présence de NO₂ ou de sels engendrant du NO₂. De plus, l'oxydation de la molécule de cellulose sur la position C₆ abaisse le rendement en B(a)P.

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