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KINETIC MECHANISM OF THE THERMAL DECOMPOSITION OF TOBACCO*

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ABSTRACT

Equations have been derived to describe the chemical kinetic factors that affect the rate of formation of products when a mixture of solid components (tobacco) decomposes on heating. Using these equations, a computer model of tobacco pyrolysis has been constructed which can calculate the gas formation rate/temperature profile from a given set of reaction parameters. By comparing the predictions of the model with experimental results at heating rates between 0.8 and 25 deg C s^{-1}, a generalised kinetic mechanism for the thermal decomposition of tobacco has been developed. For carbon monoxide and other low molecular weight gases, the mechanism is an independent formation of each gas from one solid tobacco component in each temperature region. Pyrolysis of some individual tobacco components in other studies suggests that each gas is actually produced from many components in each temperature region. This more complex mechanism is kinetically equivalent to the deduced mechanism of independent formation from one component.

The region in which a given decomposition reaction takes place moves to higher temperatures as the heating rate increases. The amounts of gases formed over any temperature region from 200 to 900 °C can be calculated for a given heating rate using the mechanism and the kinetic constants. The present results imply that 75–90% of the carbon monoxide produced by tobacco decomposition at temperatures up to 900 °C during a puff on a cigarette corresponds to that formed in the "low temperature region" (200–450 °C) defined for pyrolysis experiments at the lower heating rates of 1–10 deg C s^{-1}.

INTRODUCTION

Inside a burning cigarette, the oxides of carbon are formed by both combustion and thermal decomposition of the tobacco[1–3]. Tobacco combustion occurs at

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temperatures as low as 200 °C, when the combustion rate is controlled jointly by both chemical kinetic and oxygen mass transfer processes[4]. As the temperature is increased, mass transfer of oxygen in the gas phase becomes increasingly important, and it is dominant in determining the overall reaction rate at temperatures above 400 °C. In contrast, the carbon oxides that are formed by tobacco decomposition are produced at a rate which is determined entirely by that of the chemical kinetics, over the range 150–1000 °C. The rate of mass transfer of the products between the reactant surface and the gas phase is very rapid compared with the rate of the chemical decomposition of tobacco.

Thus, chemical kinetics determine the rate of production of carbon monoxide and dioxide from tobacco decomposition. Various aspects of the general mechanism of the formation of gases by the thermal decomposition of tobacco are not known. In particular, when a product is formed from a given tobacco component in a given temperature region, the product could be formed independently from the component, or in competition with other products. In the present study, a computer model is presented which describes the kinetic factors that affect the formation rate of products, when a mixture of solid components (tobacco) decomposes on heating. Predictions from the model are compared with experimental results on tobacco pyrolysis at different heating rates, in order to define a generalised kinetic mechanism.

GENERAL APPROACH

Tobacco consists of many independent solid components, each of which can decompose into several products. The observed product formation rate/temperature profiles of the gases from tobacco decomposition often consist of several peaks, each peak in a specific temperature region[4–8]. In a given temperature region, the products can arise from one of several alternative possible mechanisms, for example

(a) each observed product is formed from a different tobacco component,

(b) more than one of the products are formed competitively from the same component.

Included in case (a) would be the situation in which different fractions of the component decompose independently into products, e.g. a polymer that can undergo depolymerisation and side group splitting.

The general type of mechanism of tobacco decomposition that actually occurs can be elucidated with the aid of a pyrolysis model. The procedure is an extension of a suggestion made by Flynn and Wall[9] in 1966, and more recently by Ozawa[10], for the analysis of thermogravimetric data from a complex decomposition. The method is based on the fact that increasing the heating rate applied to a mixture of decomposing solids affects the gas formation rate/temperature profiles differently for the two mechanisms (a) and (b) above. The method contains the inherent assumption that the kinetic mechanisms for the formation of gases do not change with heating rate. The work of Tiller and Gentry[11] on the effects of heating rate on the differential thermal analysis of tobacco suggests that this is a reasonable assumption for the bulk de-

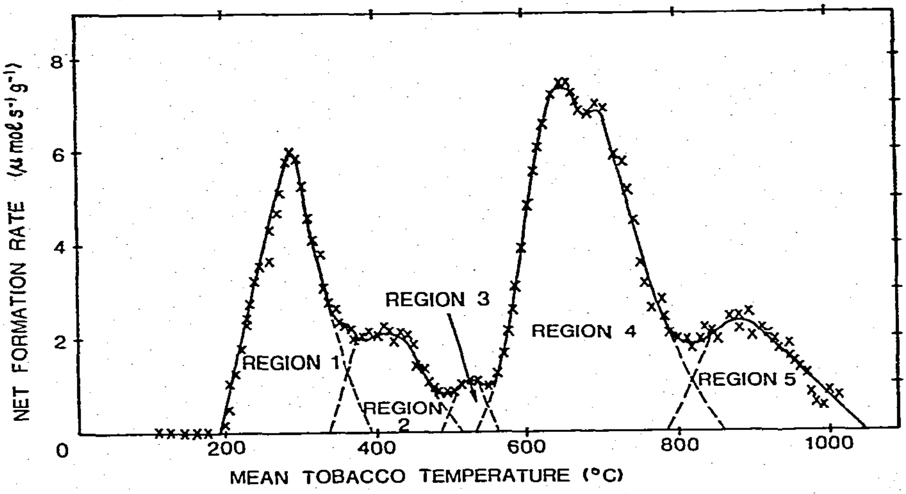


Fig. 1. Deconvolution of carbon monoxide formation profile. Tobacco pyrolysed in argon at a heating rate of 1.3 deg C s^{-1}.

TABLE 1

MECHANISM I: KINETIC PARAMETERS FOR INDEPENDENT FORMATION OF CARBON MONOXIDE AND CARBON DIOXIDE

Component	*Approximate temperature range (°C) of decomposition at 1.3 deg C s^{-1}*	*Temperature region*	*Reaction*	*Formation parameters**				
				n	*A*	*E*	*F*	*r*
S_1	175–420	1	$S_1 \rightarrow CO$	1.00	2.20×10^3	13.1	524	0.980
S_2	350–510	2	$S_2 \rightarrow CO$	1.00	8.23×10^5	23.7	190	0.941
S_3	480–570	3	$S_3 \rightarrow CO$	1.00	8.38×10^{14}	59.2	45.9	0.998
S_4	525–825	4	$S_4 \rightarrow CO$	1.25	7.55×10^5	35.6	813	0.987
S_5	760–1040	5	$S_5 \rightarrow CO$	1.00	7.33×10^5	41.0	295	0.962
S_6	150–400	1	$S_6 \rightarrow CO_2$	1.00	1.41×10^3	12.2	2230	0.972
S_7	320–570	2	$S_7 \rightarrow CO_2$	1.50	2.06×10^6	28.7	393	0.977
S_8	510–720	4	$S_8 \rightarrow CO_2$	1.25	2.30×10^8	42.8	233	0.957

* Defined in nomenclature section.

composition reactions of tobacco, for heating rates in the range 0.1–100 deg C s^{-1}. The procedure is as follows.

(i) Tobacco is pyrolysed at a predetermined heating rate and the observed formation rate/temperature profile for a given product is deconvoluted by hand into different production regions. For example, the profile for carbon monoxide production at a heating rate of 1.3 deg C s^{-1} can be deconvoluted into five temperature regions (Fig. 1).

(ii) A mechanism for the formation of the gas in each temperature region is assumed, and kinetic parameters are calculated from the data in each region, as described previously[12]. As an example, the kinetic parameters calculated from the data in Fig. 1, assuming that carbon monoxide is formed independently in each temperature region from a given tobacco component, are shown in the first half of Table 1. As discussed previously[12], these kinetic parameters are regarded simply as empirical parameters which describe the decomposition of tobacco components into carbon monoxide; they are not assumed to have the same significance as is given to them for homogeneous reactions.

(iii) The kinetic parameters calculated in (ii) are inserted into the pyrolysis model program and the program predicts the formation rate/temperature profiles for a series of heating rate regimes.

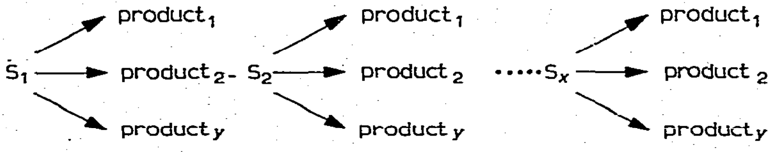
(iv) The formation rate/temperature profiles are determined experimentally at the heating rates used in (iii), and the predicted and experimental profiles are compared.

(v) The mechanism adopted is that which gives the best agreement between the predicted and experimental profiles for all the heating rates.

The experimental procedure and computer calculation of the experimental results were similar to those described previously[4], except that the furnace used was smaller (6 mm i.d.) and smaller quantities of tobacco were pyrolysed (about 0.3 g). A flue-cured Virginia tobacco was used throughout this study.

DESCRIPTION OF THE PYROLYSIS MODEL

The computer model enables the rate of formation of gases to be calculated when a mixture of independent solid components is heated. In the model, the tobacco consists of a mixture of x independent components S_1, S_2 . . . S_x. Each component can decompose by y competitive reactions to give a total of y products.



Previous work[12] has shown that the formation rates of gases from the thermal decomposition of tobacco are described very well, albeit empirically, by the Arrhenius relationship used in homogeneous reactions, viz.

$$\text{Rate} = (F - F_T)^n A e^{-E/RT} \tag{1}$$

where the symbols are defined in the nomenclature section.

By extending previous treatments[9, 13], it can be shown that the formation rate of product i from solid component j at a linear heating rate θ_q is given by eqn. (2) when the reaction order $n_j = 1$, and by eqn. (3) when $n_j \neq 1$.

$$R_{ji} = A_{ji} \exp(-E_{ji}/RT) C \exp(-B) \tag{2}$$

$$R_{ji} = A_{ji} \exp(-E_{ji}/RT) \{C^{1-n_j} + (n_j - 1)B\}^{n_j/1-n_j} \tag{3}$$

$$\text{where C} = \sum_{i=1}^{i=y} (F_{ji} b_{ji}) \tag{4}$$

$$\mathrm{B} = \sum_{i=1}^{i=y} \left[(A_{ji}/\theta_q) \int_{T_0}^{T} \exp\left(-\, E_{ji}/RT\right) \mathrm{d}T \right] \tag{5}$$

and T_0 is the temperature at which the linear heating rate θ_q commences.

In order to accommodate non-linear heating rate regimes, linear portions are superimposed onto the real temperature/time relationship so that eqns. (2) and (3) can be used.

The integral in eqn. (5) cannot be expressed by a simple analytical expression. Various approximations have been proposed for calculating the integral, e.g. refs. 9, 14–22, although these approximations can be inaccurate[17, 20]. In the present model, the integral has been expressed in terms of exponential integrals, $E_1(\phi)$ and $E_1(\phi_0)$.

$$\int_{T_0}^{T} \mathrm{e}^{-E/RT}\, \mathrm{d}T = \frac{E}{R} \left\{ \frac{\mathrm{e}^{-\phi}}{\phi} - \frac{\mathrm{e}^{-\phi_0}}{\phi_0} \left[E_1(\phi_1) - E_1(\phi_0) \right] \right\} \tag{6}$$

The exponential integrals are given by[23]

$$E_1(\phi) = \int_{\phi}^{\infty} \frac{\mathrm{e}^{-\lambda}}{\lambda}\, \mathrm{d}\lambda \qquad (|\arg \lambda| < \pi) \tag{7}$$

and have been evaluated by a computer subroutine based on a Chebyshev series expansion[24].

The following information is input to the model:

(a) the total number of components in the tobacco, x;

(b) the total number of competitive decomposition reactions of each tobacco component, y;

(c) the number of different linear heating rate regimes over the pyrolysis, z, together with their values (θ_q, $q = 1,2 \ldots z$), and the temperatures over which they apply;

(d) a list of reaction orders for the decomposition of each tobacco component, n_j ($j = 1,2 \ldots x$);

(e) a list of concentration proportionality constants for each decomposition reaction of each tobacco component, b_{ji} ($j = 1,2 \ldots x$; $i = 1,2 \ldots y$);

(f) an array of kinetic parameters for each decomposition reaction of each tobacco component, A_{ji}, E_{ji}, F_{ji} ($j = 1,2 \ldots x$; $i = 1,2 \ldots y$).

The rates of formation of each product from each tobacco component are calculated at 10 °C intervals, using eqns. (2)–(7), together with the total amounts of products formed during each temperature interval. As each heating rate regime is reached in the model, the value of C in eqns. (2) and (3) is adjusted to account for the

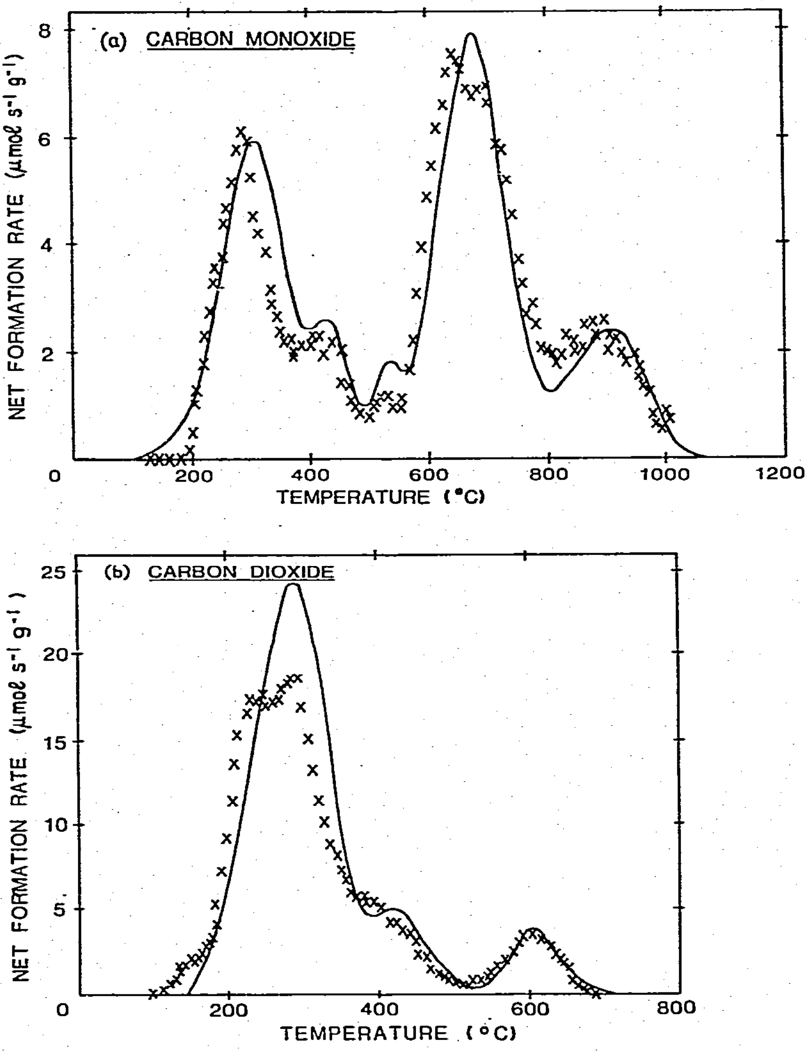


Fig. 2. Mechanism I: comparison of predicted and experimental formation profiles at heating rate of 1.3 deg C s^{-1}. —, Predicted from model; ×, experimental points.

amounts of products formed at lower temperatures. At each temperature, the total formation rate for each product *i* from all the tobacco components is given by

$$R_i = \sum_{j=1}^{j=x} (R_{ji}) \tag{8}$$

RESULTS AND DISCUSSION

Following the general approach to the elucidation of the general kinetic mechanism of tobacco decomposition, outlined above, the formation of carbon monoxide and carbon dioxide are considered in the present paper. The two extreme types of mechanism are analysed for given sets of data at different heating rates and that mechanism giving the most consistent predictions of the experimental results is taken as being the best mechanism.

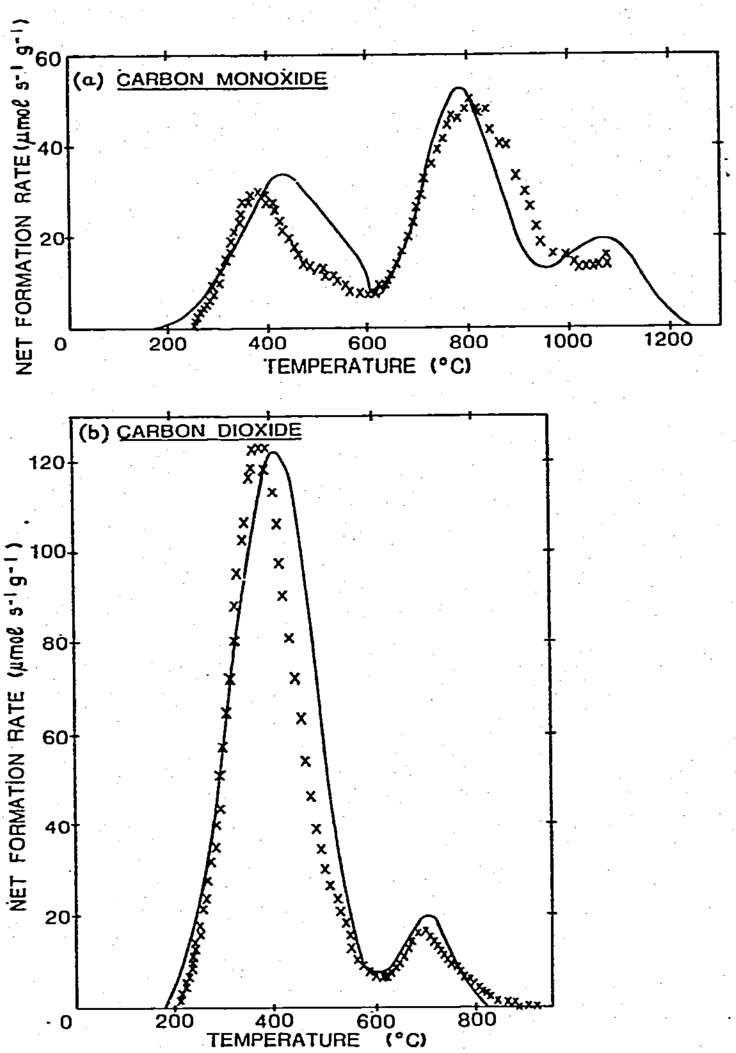


Fig. 3. Mechanism I: comparison of predicted and experimental formation profiles at heating rate of 14 deg C s^{-1}. —, Predicted from model; ×, experimental points.

Mechanism I: independent formation from different components

In mechanism I, both carbon monoxide and carbon dioxide are formed independently from specific tobacco components. The profile in Fig. 1 can be deconvoluted into five formation regions for carbon monoxide, and it is assumed that each formation region is due to the decomposition of one component. The carbon dioxide profile [Fig. 2(b)] can be deconvoluted into three formation regions. Thus in mechanism 1, the tobacco is considered to contain a total of eight solid components of which five decompose into carbon monoxide only and three decompose into carbon dioxide only. The kinetic parameters obtained from the experimental profiles at a heating rate of 1.3 deg C s^{-1}, calculated as described previously[12], are given in Table 1.

If these kinetic parameters are inserted into the pyrolysis model, the predicted profiles at a heating rate of 1.3 deg C s^{-1} should coincide exactly with the experimental profiles. Although the coincidence is good (Fig. 2), it is not exact, presumably because the assumed mechanism is over-simplified. In a given temperature region, it is assumed that carbon monoxide or carbon dioxide is formed from one tobacco component only. Burton[25] and other studies[26, 27] have shown that both oxides of carbon can be formed by thermal decomposition from many of the components of tobacco: starch, celluloses, sugars, amino acids, esters etc. Thus the mechanism is an approximation to the real situation. However, the inclusion of more components in the mechanism does not significantly improve the agreement between the predicted and experimental profiles.

Using the kinetic parameters given in Table 1, the carbon monoxide and dioxide formation profiles predicted from the model have been compared with the experimental profiles at a variety of heating rates between 0.8 and 25 deg C s^{-1}. In general, the agreement between predicted and experimental profiles is good, e.g. Fig. 3 (heating rate 14 deg C s^{-1}). Consequently, this mechanism can predict experimental profiles for carbon monoxide and carbon dioxide formation with reasonable precision, over a thirty-fold increase in heating rate.

TABLE 2

MECHANISM II: KINETIC PARAMETERS FOR COMPETITIVE FORMATION OF CARBON MONOXIDE AND CARBON DIOXIDE

Component	*Approximate temperature range (°C) of decomposition at 1.3 deg C s⁻¹*	*Temperature region*	*Reaction*	*Formation parameters**				
				n	*A*	*E*	*F*	*r*
S_A	150–420	1	$S_A \rightarrow CO$	1.00	1.54×10^4	16.6	524	0.966
			$S_A \rightarrow CO_2$	1.00	4.78×10^2	11.4	2230	0.973
S_B	320–570	2	$S_B \rightarrow CO$	1.50	3.63×10^4	24.8	190	0.985
			$S_B \rightarrow CO_2$	1.50	1.72×10^7	32.4	393	0.978
S_C	480–570	3	$S_C \rightarrow CO$	1.00	8.38×10^{14}	59.2	45.9	0.998
S_D	510–825	4	$S_D \rightarrow CO$	3.00	1.96×10^{14}	90.0	813	0.961
			$S_D \rightarrow CO_2$	3.00	11.3	38.3	233	0.941
S_E	760–1040	5	$S_E \rightarrow CO$	1.00	7.33×10^5	41.0	295	0.962

* Defined in nomenclature section.

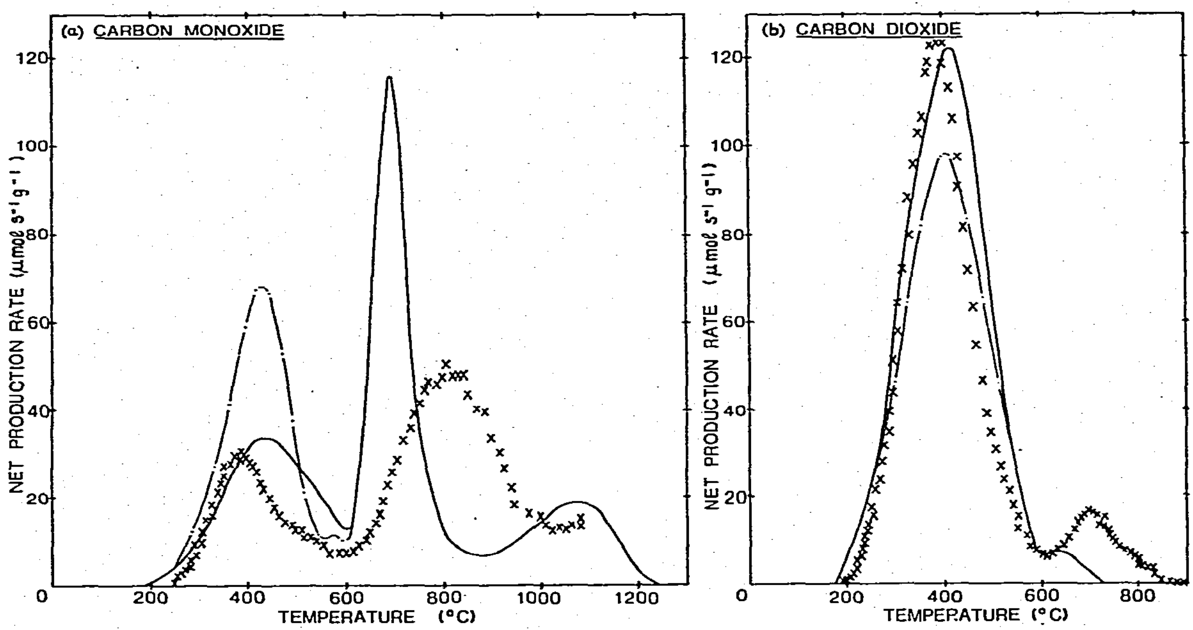


Fig. 4. Mechanisms II and III: comparison of predicted and experimental formation profiles at heating rate of 14 deg C s^{-1}. —·—, Predicted from model, Mechanism II; —, predicted from model, Mechanism III; ×, experimental points.

Mechanisms II and III: competitive formation from the same component

In mechanism II, carbon monoxide and dioxide are assumed to be produced competitively from the same component in all the temperature regions where both gases are formed. Thus the tobacco is assumed to consist of five components in mechanism II, of which three decompose into both carbon monoxide and carbon dioxide, and two decompose into one product only. The kinetic parameters for the gas production, calculated from the experimental profiles at a heating rate of 1.3 deg C s^{-1}, are given in Table 2. Using these parameters in the model, the predicted profiles at a variety of heating rates for carbon monoxide in particular are substantially different from the experimental profiles (e.g. Fig. 4). Consequently, the predictions of mechanism II are incorrect, confirming that mechanism I is a better description of the reaction.

Various mechanisms intermediate between I and II are possible. For example, mechanism III in which the carbon oxides are formed competitively in the high temperature region (510–825°C) and independently in all other temperature regions. The predictions from the model with this mechanism are also depicted in Fig. 4, and, again, the predicted profiles are substantially different from the experimental profiles in the high temperature region.

From considerations of the predictions of the above mechanisms and other (unreported) permutations, it is apparent that carbon monoxide and dioxide behave as if they were each formed independently from different components in each temperature region. Similar studies, in which hydrogen and low molecular weight hydrocarbons were considered, indicate that these products also behave as if they were each

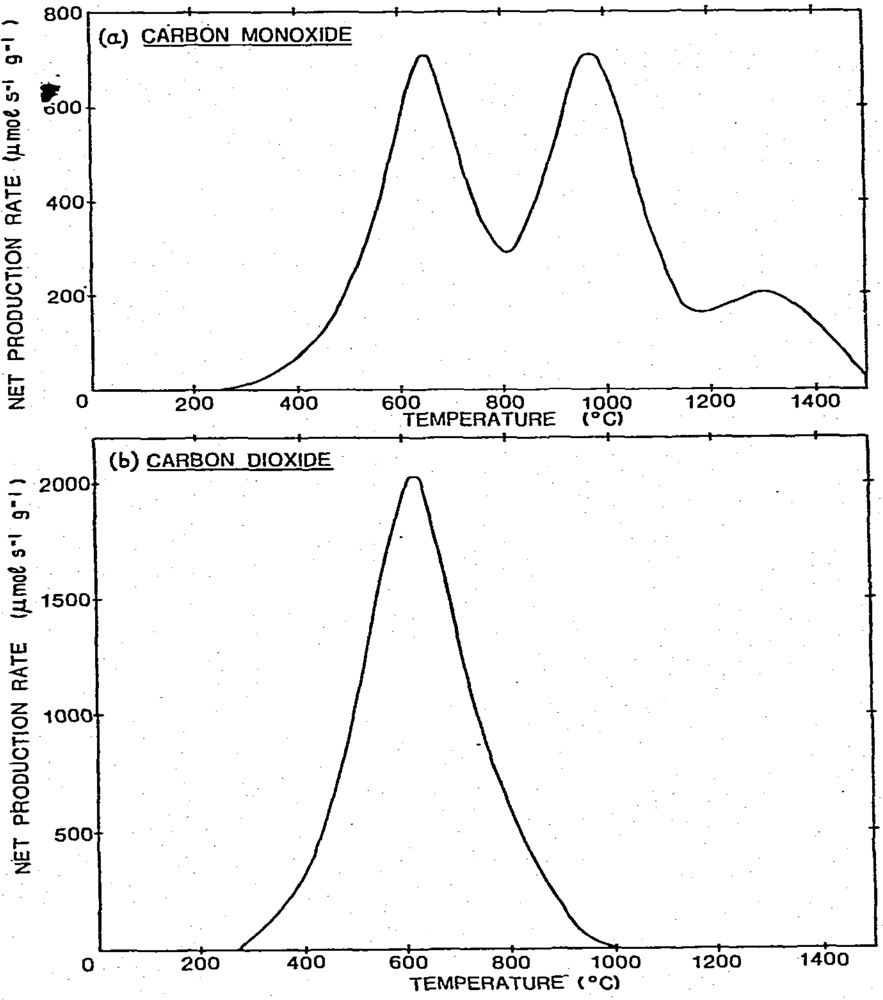


Fig. 5. Predicted formation profile at a heating rate of 200 deg C s^{-1} (mechanism I).

formed independently from different components in each temperature region. As pointed out above, each gas is actually produced in small amounts from many components in each temperature region. Consequently, the accumulation of a specific gas production from many components in a given temperature region would be expected to approximate to independent formation from one component, as the model has shown.

IMPLICATIONS INSIDE A BURNING CIGARETTE

Typical heating rates at various positions in the combustion coal of a cigarette during the smoulder period are 5–20 deg C s^{-1}; during a puff they are 100–600 deg C s^{-1}, while during the lighting puff they can approach 1000 deg C s^{-1} at the tip of the coal[28]. Using the mechanism developed for carbon monoxide and dioxide formation, together with the pyrolysis model, the formation profiles at these high heating rates can be predicted, e.g. Fig. 5.

TABLE 3

TOTAL QUANTITIES OF CARBON MONOXIDE AND DIOXIDE PRODUCED AS A FUNCTION OF HEATING RATE*

Heating rate (deg C s^{-1})	*Total quantity of gas (μmole g^{-1}) produced up to 900°C*	
	Carbon monoxide	*Carbon dioxide*
0.8	1,790	2,860
1.3	1,730	2,860
5.2	1,620	2,860
14.2	1,560	2,860
25.4	1,470	2,860
100	1,120	2,860
200	973	2,860
500	813	2,580
1000	653	2,070

* Predicted from mechanism I.

As the heating rate increases, the peaks move towards higher temperatures and the two main carbon monoxide peaks become less resolvable. Inside the coal during a puff, the majority of the solid phase is below 900°C (ref. 25). The most typical heating rates during a puff are between 200 and 500 deg C s^{-1}, and at these heating rates (Fig. 5) the majority of the carbon monoxide "high temperature" region (i.e. region 4 of Fig. 1) occurs above 900°C. Thus, during a puff, sufficiently high temperatures are not reached for the "high temperature" thermal decomposition carbon monoxide to be completely evolved. At the low heating rate of 1.3 deg C s^{-1}, the "low temperature" carbon monoxide is that formed in the first major peak, i.e. that formed up to 500°C (Fig. 1), which is 730 μmole g^{-1}. The total amounts of carbon monoxide formed over the decomposition up to 900°C are given in Table 3 as a function of heating rate. Clearly, during a puff (200–500 deg C s^{-1}), 75–90% of the total carbon monoxide formed by thermal decomposition of tobacco is "low temperature" carbon monoxide, providing the kinetic mechanisms for the formation of gases do not change with heating rate.

Studies[1, 2] in which a cigarette is smoked in an atmosphere of nitrogen and oxygen-18 have shown that both oxides of carbon are produced in comparable amounts from both decomposition and combustion of the tobacco, during a puff. The present results imply that the decomposition carbon monoxide is that produced in the "low temperature" region of low heating rate pyrolysis experiments. The carbon monoxide produced in this region is from the decomposition of starch, cellulose, sugars, amino acids and esters[25–27].

NOMENCLATURE

A	Arrhenius pre-exponential constant (units of s^{-1} μmole^{1-n} g^{n-1} for an *n*th order reaction)

B	function of reaction parameters, defined by eqn. (5)
C	Summation of all products formed over the whole pyrolysis, equal to $\sum_{i=1}^{i=y} (F_{ji})$ (units of μmole g^{-1})
E	activation energy (cal mole^{-1})
$E_1(\phi)$	exponential integral, defined in eqn. (7)
F	total amount of products formed from a solid component over a given temperature region (μmole g^{-1})
F_T	amount of products formed from a solid component up to temperature T (μmole g^{-1})
F_{ji}	the quantity of product i formed from tobacco component j over the whole pyrolysis (μmole g^{-1})
R	universal gas constant, 1.987 cal mole^{-1} K^{-1}
R_{ji}	the rate of formation of product i from tobacco component j (μmole s^{-1} g^{-1}, i.e. per g of *total* tobacco weight)
S_j	representation of tobacco component j
T	temperature (K)
b_{ji}	concentration proportionality constant for product i formed from tobacco component j. In all the calculations for the present paper, all values of b_{ji} were set equal to unity
e or exp	exponential operator
n	reaction order
r	correlation coefficient for a linear regression of $\ln[\text{Rate}/(F - F_T)^n]$ against $1/T$
t	time(s)
x	number of independent components in the tobacco mixture
y	total number of competitive decomposition reactions of a tobacco component and total number of products formed
z	number of linear heating rate regimes over the whole pyrolysis
θ	heating rate, dT/dt (deg C s^{-1} or K s^{-1})
ϕ	equal to E/RT

Subscripts

i	product number ($i = 1,2 \ldots y$)
j	tobacco component number ($j = 1,2 \ldots x$)
0	initial
q	linear heating rate number ($q = 1,2 \ldots z$)

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